Physical Chemistry 2018, 8(1): 1-12
DOI: 10.5923/j.pc.20180801.01

Role of Anion in the Electrochemical Dissolution of Copper and Its Inhibition by Diethyl Dithiocarbamate in Neutral Aqueous Solutions

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Abstract Electrochemical dissolution of copper in 0.5M aqueous solution of $NaNO_3$, Na_2SO_4, NaCl or NaI in absence and presence of different concentrations of diethyl dithiocarbamate (DEDTC) has been studied using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and cyclic voltametry techniques. In absence of DEDTC, the results indicated that oxidation of copper greatly depends on the kind of anion of the electrolyte. In $NaNO_3$ and Na_2SO_4 solutions, oxidation of copper takes place through a two-electron transfer step Cu → Cu(II), however in NaCl and NaI solutions, oxidation of copper occurs through two consecutive one-electron transfer steps Cu → Cu(I) and Cu (I) → Cu(II). These results were discussed on the basis that the mechanism of oxidation of copper depends on the adsorbability of the anion of the electrolyte at the Cu/solution interface which affects each of the potential of zero charge (PZC) and the surface charge of the metal. In presence of DEDTC, the results indicated that its inhibition efficiency for corrosion of copper decreases in the electrolytes containing adsorbable anions due to the competitive adsorption between the anion of the electrolyte and that of DEDTC. Theoretical fitting of the Langmuir isotherm and the Kinetic-thermodynamic model for the adsorption of DEDTC on the copper surface in the four examined electrolytes are tested to clarify the nature of adsorption. The results showed that the value of the standard free energy change of adsorption (ΔG^o_{ads}) for the tested four electrolytes equal (-35.55 to -39.70 kj/mol.) indicating that the adsorption process of DEDTC on the copper surface is comprehensive (chemical and physical adsorption).

Keywords Copper, Corrosion, Inhibitors, Diethyl Dithiocarbamate

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1. Introduction

Copper and its alloys have a wide range of applications in industry and seawater systems, such as shipbuilding, heat exchange systems, water pipelines and seawater desalination owing to the excellent properties such as mechanical workability, thermal and electrical conductivity. However copper and its alloys have good resistance, they suffer different forms of corrosion depending on the service environment, particularly in the presence of chloride ions. Therefore, the protection of copper and its alloys against corrosion has attracted the attention of many scientists [1-7].

The use of organic inhibitors is one of the most efficient approaches for protecting copper against corrosion [8-13]. There are numerous reports points out the importance of heteroatoms such as N, O, S and P in organic compounds to give good corrosion inhibition of copper. The efficiency ofsulfur-containing compounds for corrosion inhibition of copper in a variety of media has been reported [14-17]. Benzotriazole is one of the most efficient organic inhibitors for the corrosion of copper in neutral-chloride media [18]. In addition, amines, azoles derivatives and mercapto-organic compounds are also potentially effective copper corrosion inhibitors [19-24]. Dithiocarbamates were shown as good inhibitors for the corrosion of copper in neutral chloride media; its inhibition was attributed to the formation of an insoluble Cu (II)-chelate film [25-27]. Adsorption of ammonium pyrolidine dithiocarbamate (PDTC) on copper surface was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy measurements and surface analysis. The electrochemical results indicated that PDTC adsorbs rabidly on copper surface and act as mixed type inhibitor. Surface analysis confirmed the adsorption of PDTC on copper and the formation of Cu-PDTC complexes through the sulfur atom. XPS results showed that PDTC bonds with cuprous species indicating the formation of Cu(I)-PDTC complex.

Dithiocarbamate compounds has been considered as fungicides which have low or moderate toxicity i.e it is not have acute hazard [28, 29]. Also, dithiocarbamate extensively used as agriculture biocide (pesticide), used

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before planting for elimination of soil pathogens, weeds and nematodes and used after planting as herbicide [30].

It is well known that the electrochemical dissolution of metals in aqueous solutions is greatly affected by the kind of ions of the electrolyte. In our previous recent work [31] we studied the co-operative effect of chloride ions and some natural extract in retarding corrosion of steel in neutral media. Effect of lupine and damsisa extracts on the corrosion of steel in 0.5M Na_2SO_4 solution free from and containing 0.01M or 0.1M NaCl were examined by potentiodynamic and EIS techniques. Increasing chloride ion concentration in the solution led to increase of the inhibition efficiency of the extracts and this behavior was explained on the basis of co-operative mechanism of adsorption.

In this work we studied the electrochemical dissolution of copper in 0.5M solutions of $NaNO_3$, Na_2SO_4, NaCl and NaI in absence and presence of different concentrations of sodium diethyl dithiocarbamate in order to explore the role of the anion of the electrolyte in the mechanism of electrochemical dissolution of copper and its inhibition.

2. Experimental Methods

2.1. Chemicals and Materials

An electrochemical measurement takes place in a three electrode cell with Copper as a working electrode that had the chemical composition Cu 99.5% and Ca 0.5%. A cylinder of copper was fixed in a rod of poly tetrafluoroethylene (PTFE) (Teflon) by an epoxy resin in such a way that only one side of constant surface area (0.2827 cm^2) left uncovered and in contact with the solution. Copper wire was enclosed in a glass tube which acted as a holder as well as insulator. Graphite sheet was used as auxiliary electrode and saturated calomel electrode (SCE) as reference electrode. Before each experiment, the working electrode was polished with a series of emery papers of different grit sizes (120-1200). After polishing, the working electrode was washed with double distilled water and dried at room temperature. All the measurements were done under unstirred conditions at 30.0±0.2 °C in solutions open to the atmosphere. For each experiment 50 mL of electrolyte was used. All chemicals were purchased from Sigma-Aldrich Co.

2.2. Electrochemical Measurements

The polished electrode cleaned as mentioned before and introduced in the electrochemical cell that was filled by 50 mL of the tested solution. The cell was thermostated for 20 minutes before starting the experiment. The open circuit potential of working electrode result from the formation of electrical double layer at metal/solution interface was followed as a function of time for 15 min, until steady state potential at which the variation of potential is 1.0 mV/ min. is established to ensure reliable measurements.

Electrochemical impedance measurements were achieved by connecting the electrochemical cell to Gill AC impedance instrument. The Gill AC instrument was controlled by personal computer, for data logging and data analysis. The frequency range studied was $0.1 \leq f \leq 1.0 \times 10^4$ Hz. Amplitude of 10.0 mV peak to peak was used for alternating current signal for all impedance spectroscopy measurements with respect the open circuit potential. Five data points were taken for each decade of frequency or for each change in frequency by ten multiplications. Gill AC serial number 604 sequencer software used for all the electrochemical measurements. The software Zsimpwin was used for analysis the impedance spectra of Nyquist plots using the suitable equivalent circuit model that well fit Nyquist plots with small error.

Potentiodynamic polarization technique was used to determine cathodic and anodic polarization curves of copper in different tested aqueous solutions by sweeping the applied overpotentials starting with -250 mV (for cathodic polarization) reaching to rest potential (E_{rest}) then continuing the anodic polarization by applying +250 mV above the rest potential. All electrode potentials were measured with respect to the saturated calomel electrode (SCE).

3. Results and Discussion

3.1. Effect of Anion on the Electrochemical Dissolution of Copper

The mechanism of the electrochemical dissolution of copper in Cl^- media has been extensively studied in the literature [25-27, 32-38], and proposed that copper dissolution involves first electronic transfer corresponds to the oxidation of copper to cuprous chloride species followed by a chemical step producing $CuCl_2^-$.

$$Cu + Cl^- \longrightarrow CuCl + e^- \quad (1)$$

$$CuCl + Cl^- \longrightarrow CuCl_2^- \quad (2)$$

The above steps are followed by a mixed kinetic process producing bivalent copper species [37, 38]. Until now there is consensus that copper electrochemical dissolution takes place through the above mechanism. In order to throw more light on the mechanism of electrochemical dissolution of copper in neutral electrolyte solutions, we investigated the electrochemical behaviour of copper in 0.5M solutions of the electrolytes $NaNO_3$, Na_2SO_4, NaCl and NaI respectively.

3.1.1. Potentiodynamic Polarization Results

Figure 1 shows the polarization curves of copper in 0.5M solutions of $NaNO_3$, Na_2SO_4, NaCl and NaI. The cathodic curve of copper in NaCl shows limiting current indicating that the reduction process is the diffusion controlled reduction of oxygen. However, the cathodic polarization curves in the other electrolytes show Tafel behavior and the reduction process is mainly the reduction of water. The anodic polarization curves of copper in each of $NaNO_3$ and Na_2SO_4 show a characteristic Tafel behavior indicating that the oxidation of copper takes place through one step controlled by charge transfer. The anodic polarization curve of copper in NaCl shows an inflection at -0.125 V (vs. SCE), this inflection was reported previously in a recent work [39] and mainly corresponds to the second electron oxidation step of copper [Cu (I) $\rightarrow$ Cu (II)]. The anodic polarization curve of copper in NaI shows a two steps oxidation process. Figure 1 shows also that the corrosion potential (E_{corr}) of copper is greatly affected by kind of electrolyte and shifts to more negative values with increasing the adsorbability of the anion of the electrolyte from NO^{3-} to I^- in the order:

$$NO_3^- < SO_4^{2-} < Cl^- < I^-$$

The above results can be discussed on the basis that adsorption of anions of the electrolyte at the Cu/solution interface creates a negative charge on the diffuse double layer of copper which enhance the uptake of the cuprous cation from the metal surface to the solution side. This is the case of the electrochemical dissolution of copper in NaCl and NaI solutions, where the oxidation takes place at more negative potentials and through two consecutive steps, Cu $\rightarrow$ Cu (I) and Cu (I) $\rightarrow$ Cu (II). However, in presence of the non-or weak adsorbable anions such as NO_3^- or SO_4^{2-} the electrochemical dissolution of copper becomes more difficult and takes place at less negative potentials through a single two electron transfer step Cu $\rightarrow$ Cu(II). To confirm this proposal the potential of zero charge (PZC) of copper in the four electrolytes has been measured and also the cyclic voltamogram has been investigated.

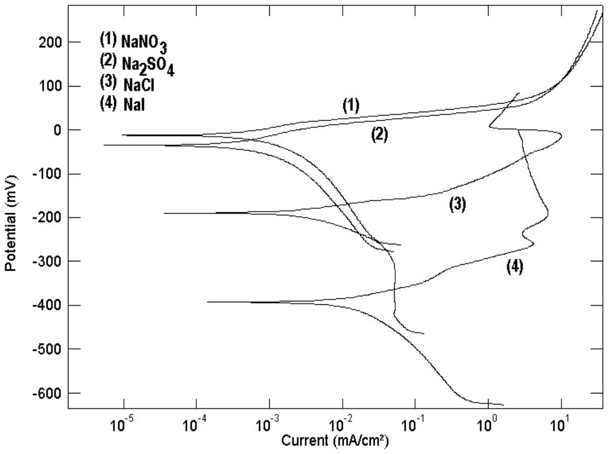

Figure 1. Potentiodynamic polarization curves of copper in 0.5 M aqueous solution of $NaNO_3$, Na_2SO_4, NaCl and NaI

3.1.2. Potential of Zero Charge (E_{PZC}) Results

The potential of zero charge (E_{PZC}) and the surface charge (Φ) of copper in 0.5M solutions of the electrolytes $NaNO_3$, Na_2SO_4, NaCl and NaI were determined using the electrochemical impedance spectroscopy (EIS) technique. The impedance measurements were performed at certain cathodic and anodic overpotentials around E_{rest} of copper and values of the charge transfer resistance (R_{ct}) and electrical double layer capacity (Q_{dl}) are estimated by fitting the Nyquist plots to the equivalent circuit in figure 2.

The variation of R_{ct} and Q_{dl} of copper with potential in the four electrolytes are shown in figures (3-6). R_{ct} had a maximum and there was a parabola with minimum Q_{dl} at the same potential of E_{PZC}. The surface charge of copper (Φ) was defined by the difference between the corrosion potential and E_{PZC} [40, 41]. Table (1) shows the values of each of E_{corr}, E_{PZC} and Φ for copper in the four studied electrolytes. The data in the table indicates that each of E_{corr} and E_{PZC} shifts to more negative potential with increasing the adsorbability of the anion of the electrolyte from NO_3^- to I^-. The surface charge of copper has a positive value in each of the non- or weak adsorbable anions NO_3^- and SO_4^{2-} and has a negative value for the strong adsorbable anions Cl^- and I^-.

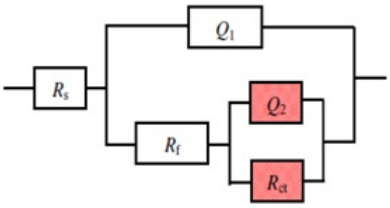

Figure 2. The equivalent circuit model used to fit the EIS experiment

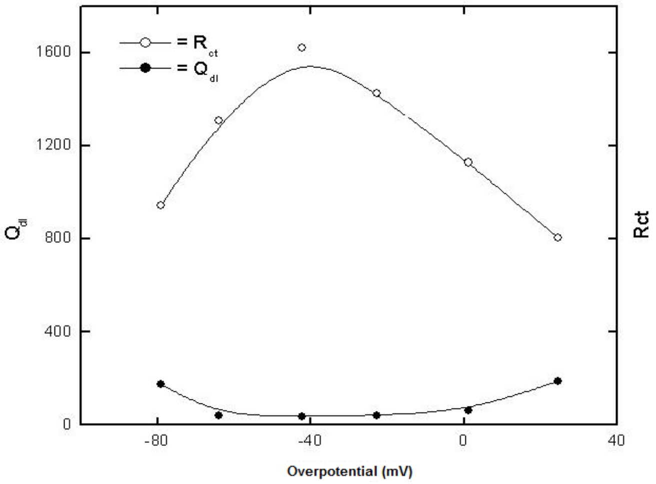

Figure 3. Variation of each of Q_{dl} and R_{ct} with potential of copper in 0.5 M aqueous solution of $NaNO_3$

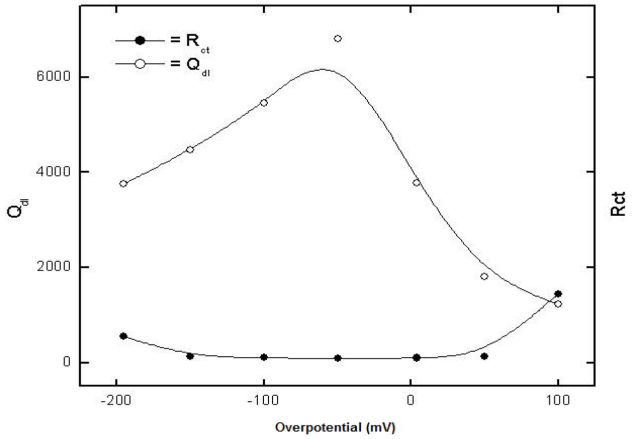

Figure 4. Variation of each of Q_{dl} and R_{ct} with potential of copper in 0.5 M aqueous solution of Na_2SO_4

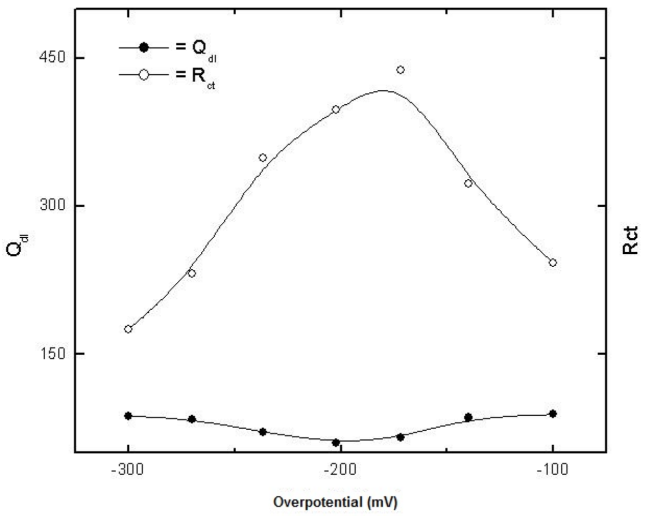

Figure 5. Variation of each of Q_{dl} and R_{ct} with potential of copper in 0.5M aqueous solution of NaCl

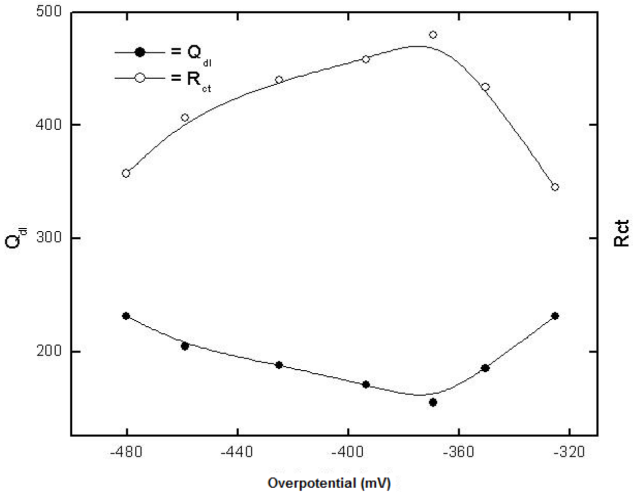

Figure 6. Variation of each of Q_{dl} and R_{ct} with potential of copper in 0.5 M aqueous solution of NaI

Table 1. Values of E_{corr}, E_{PZC} and Φ for copper in 0.5 M aqueous solution of $NaNO_3$, Na_2SO_4, NaCl and NaI

Electrolyte	E_{corr} (mV vs. SCE)	E_{PZC} (mV vs. SCE)	Φ (mV)
$NaNO_3$	- 1.0	-45	44.0
Na_2SO_4	- 11.6	-50	38.4
NaCl	-189.3	-171	-18.3
NaI	-391.0	-370	-21.0

3.1.3. Cyclic Voltametric Results

Several authors [26, 42, 43] studied the cyclic voltametry of copper in artificial seawater as well as in seawater. They reported that the cyclic voltamogram of copper contains two anodic peaks related to the copper oxidation to Cu (I) and Cu (II). Figures (7, 8) show the cyclic voltamograms of copper in the four studied electrolytes. It is clear that the cyclic voltamograms of copper in each of $NaNO_3$ and Na_2SO_4 contain only one peak at 0.280 and at 0.270 volt (vs. SCE). However, the cyclic voltamogram of copper in each of NaCl and NaI contain two anodic peaks; for copper in NaCl the two peaks located at 0.110 and 0.250 while for copper in NaI the two peaks located at - 0.200 and 0.260 volt (vs. SCE). The above results show a good agreement with the potentiodynamic polarization and potential of zero charge results and give support to the proposal stating that the adsorption of the anions at copper/solution interface enhance the uptake of the cuprous ion making preoxidation of copper at more negative potential and the mechanism of electrochemical dissolution of copper goes through two consecutive one electron transfer steps. A further support to the above results is given in figure 9 which shows the cyclic voltamogram of copper in 0.5M Na_2SO_4+0.05M NaI. It can be seen that addition of the strong adsorbable I^- ion to SO_4^{2-} anions leads to the appearance of two anodic peaks at -0.25 and 0.10 volt (vs. SCE) in the cyclic voltamogram of copper in addition to the original peak in presence of Na_2SO_4 only at 0.270 volt (vs. SCE).

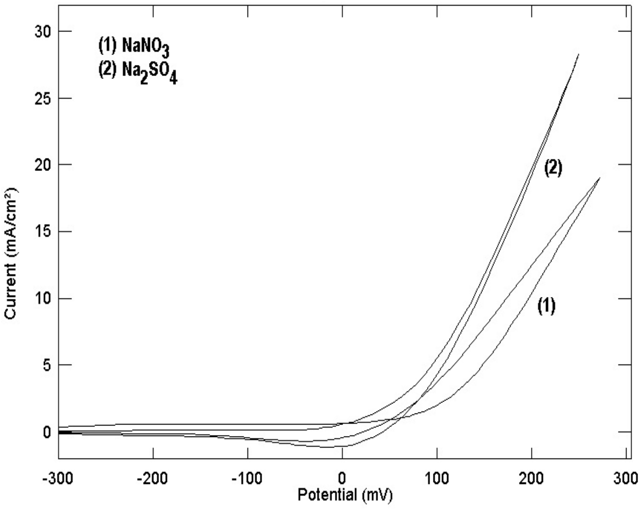

Figure 7. Cyclic voltamogram for copper in 0.5 M aqueous solution of $NaNO_3$ and Na_2SO_4

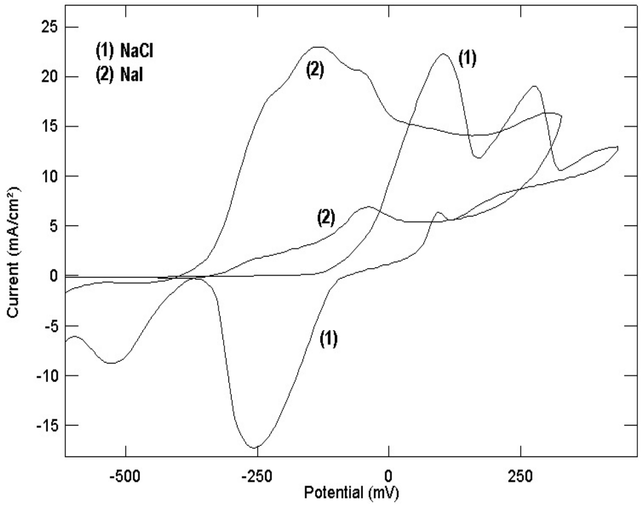

Figure 8. Cyclic voltamogram for copper in 0.5 M aqueous solution of NaCl and NaI

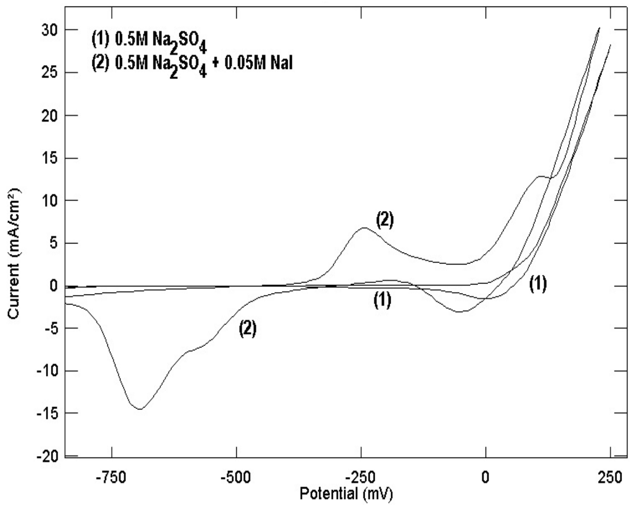

Figure 9. Cyclic voltamogram for copper in aqueous solution of 0.5M Na_2SO_4 and 0.5M Na_2SO_4 + 0.05M NaI

3.2. Effect of Anion on the Inhibition of the Corrosion of Copper by Diethyl Dithiocarbamate (DEDTC)

Dithiocarbamates, the half amides of dithiocarbonic acids, are a class of monoanionic 1, 1-dithio ligands. The structure of dithiocarbamate group represented by the valence bond formalism is shown in Fig (10). The thioureide form (c) results from the delocalization of nitrogen lone pair [44].

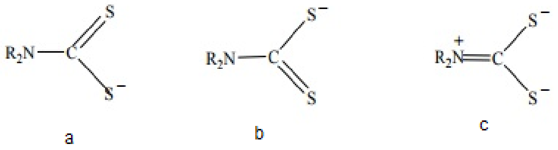

Figure 10. Resonance forms of dithiocarbamates

Dithiocarbamates can function as unidentate, bidentate chelating as well as bidentate bridging ligands [44-46] as given in Fig. (11).

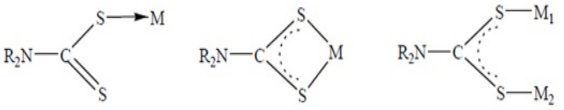

Figure 11. Modes of bonding of the dithiocarbamates

They are capable of stabilizing transition metals in a wide oxidation states, and act as non- sterically demanding ancillary ligands. The major advantage of using the small bite angle of dithiocarbamato moiety as a stabilizing chelating agent is its unique property to remain intact under a variety of conditions. In addition, they are able to stabilize different stereochemical structures, unusual mixed oxidation states such as Cu(I)/Cu(II). The dithiocarbamates form four-membered chelate rings with sulphur donor atoms. Therefore, special interest in the study of metal dithiocarbamates complexes was aroused because of the striking structural features shown them and also because of its diversified applications [45-48]. Among these complexes are the stable monomeric and dimeric dithiocarbamate complexes of copper in both +1 and +2 oxidation states [46-48]. Accordingly, the inhibition of the dissolution of copper in aqueous solutions in the presence of diethyl dithiocarbamate could be referred to the formation of insoluble monomeric $[Cu(DEDTC)_2]$ and/or dimeric $[Cu(DEDTC)_2]_2$ as well as mixed valence copper complexes dimeric $[Cu(DEDTC)Cl]_2$/ monomeric [Cu(DEDTC)].

Results in the first part of this work indicated that kind of electrolyte greatly affect both the rate and the mechanism of the electrochemical dissolution of copper in aqueous solutions. The role of the anion in the inhibition of the corrosion of copper by DEDTC will be studied in this part.

3.2.1. Potentiodynamic Polarization Results

Figures (12, 13) show the polarization curves of copper in 0.5M solutions of $NaNO_3$, Na_2SO_4, NaCl and NaI containing different concentrations of DETDC, the graphs show that it behaves as mixed type inhibitor. Qafsaoui et al [27] reported that pyrollidine dithiocarbamate adsorbed rabidly on copper surface, showed mixed inhibition effect and form complex through the sulfur atom. As seen in figure (12), the anodic polarization curves of copper in $NaNO_3$ and Na_2SO_4 in absence of DEDTC contain one oxidation process corresponds to Cu ➔ Cu (II). On adding DEDTC to the electrolyte solutions, the corrosion potential of copper shifts to more negative values and oxidation of copper takes place trough two consecutive one-electron transfer steps. This behaviour can be discussed on the same basis which reported in the first part of this work. DEDTC anion contains nitrogen and sulfur atoms and also has a negative charge, therefore it is a very strong adsorbable anion and its adsorption at Cu/solution interface creates a negative charge in the diffuse double layer, this enhance the uptake of the cuprous ion from the copper surface to the solution forming [Cu (I)-DEDTC] complex. Formation of the dithiocarbamate complex with cuprous ion has been confirmed previously using the XPS technique [29]. Figure (12) shows also that increasing the concentration of DEDTC in the solution leads to a shift of the potential of the first oxidation step to more negative values, however the potential of the second oxidation step [Cu (I)-DEDTC] ➔ $[Cu\ (II)\text{-}(DEDTC)_2]$ is constant and independent on the amount of DEDTC. This phenomenon can be interpreted on the basis that, increasing the concentration of DEDCT leads to increasing the value of the negative charge on the diffuse double layer at the metal/solution interface causing more enhancement of the uptake of the cuprous ion from the metal surface to the solution side. Kendig et al [49] attributed the corrosion inhibition of Cu-containing alloy AA2024 by diethyl dithiocarbamate to the formation of an insoluble Cu (II)-chelate film.

Figure (13a) shows the polarization curves of copper in 0.5M NaCl containing different concentration of DEDTC, the anodic curves show a similar behaviour to that obtained in $NaNO_3$ and Na_2SO_4, however, the two oxidation steps of copper in NaCl are characterized by current minima which can probably attributed to the competitive adsorption between the very strong adsorbable DEDTC anion and the Cl^- ion which leads to the displacement of some Cl^- ions in the diffuse double layer by DEDTC anions [50]. In this case the two oxidation steps of copper mainly produce the mixed complexes [Cu (I)-Cl-DEDTC]$^{-1}$ and [Cu (II)-Cl-DEDTC], it seems that these mixed complexes are chemically reactive because they contain the labile chloride ions causing the appearance of the minima of the current.

Figure (13b) shows the polarization curves of copper in 0.5M NaI solution in absence and presence of different concentrations of DETDC. The anodic polarization curves contain two oxidation steps Cu → Cu (I) and Cu (I) → Cu (II) and addition of DEDTC has no effect on the corrosion potential of copper. This behavior can be discussed on the basis that I^- ion is a strong adsorbable anion and prevent the adsorption of the DEDTC anion at the Cu/solution interface.

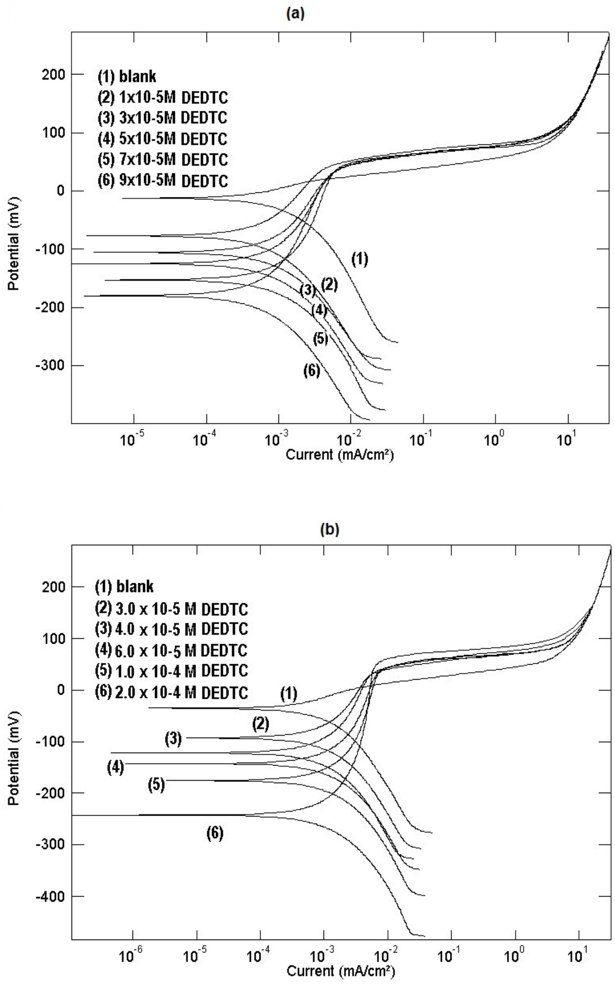

Figure 12. Potentiodynamic polarization curves of copper in 0.5 M aqueous solution of a) $NaNO_3$ b) Na_2SO_4 in absence and presence of different concentrations of DEDTC

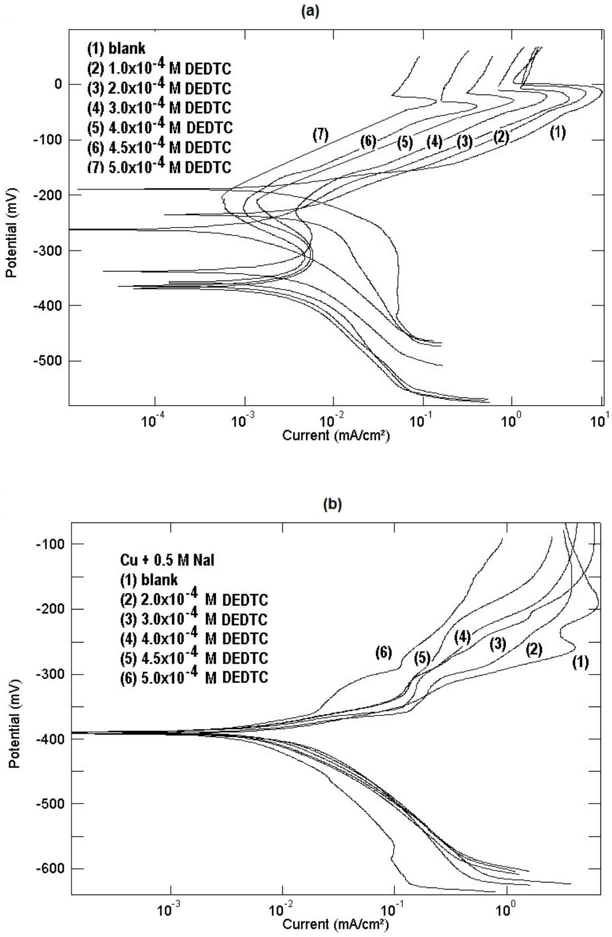

Figure 13. Potentiodynamic polarization curves of copper in 0.5 M aqueous solution of a) NaCl b) NaI in absence and presence of different concentrations of DEDTC

3.2.2. Electrochemical Impedance Spectroscopy (EIS) Results

Figures (14-17) show the Nyquist plots of copper in 0.5M solutions of each of $NaNO_3$, Na_2SO_4, NaCl and NaI in absence and presence of different concentrations of sodium diethyl dithiocarbamate. Most of the Nyquist plots contain two capacitive semicircles. The capacitive semicircle at low frequency corresponds to the double layer capacity and charge transfer resistance, while the capacitive semicircle at high frequency is attributed to the corrosion products formed during the corrosion process [43]. All impedance spectra were analyzed by fitting the experimental data to the equivalent circuit model shown in figure 2. The inhibition efficiency (%P) of DEDTC was calculated from the impedance measurements using the relation [51].

$$\%P = [(R_{ct} - R^{o}_{ct})/R_{ct}] \qquad (3)$$

Where R_{ct} and R^{o}_{ct} are the charge transfer resistance in presence and absence of DEDTC respectively. The electrochemical impedance parameters of copper in 0.5M solutions of the four examined electrolytes in presence and absence of different concentrations of DEDTC are shown in tables (2-5). The data indicated that in presence of DEDTC the values of R_{ct} and %P increase with increasing the concentration of DEDTC indicating decreasing corrosion rate of copper, however the values of Q_{dl} decreases due to adsorption of diethyl dithiocarbamate anions at the Cu/solution interface. Figure 18 shows variation of the protection efficiency of DEDTC with its logarithmic concentration for the corrosion of copper in the four examined electrolytes. It can be seen that the inhibition efficiency of DEDTC in the four electrolytes increases in the order:

$$I^- < Cl^- < SO_4^{2-} < NO_3^-$$

It is clear that the order of the increase of the inhibition efficiency of DEDTC for the corrosion of copper in the four electrolytes is the reverse to the adsorbability of the anions of the electrolytes. This means that adsorption of the anion of the electrolyte retards adsorption of DEDTC anion at the metal/solution interface (competitive adsorption) and then decreases its inhibition efficiency.

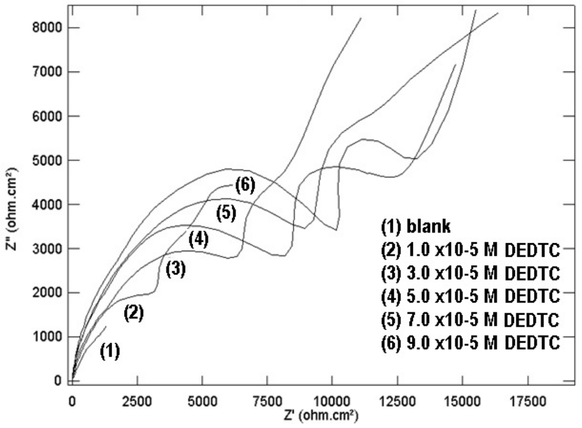

Figure 14. Nyquist plots of copper in 0.5 M aqueous solution of $NaNO_3$ in absence and presence of different concentrations of DEDTC

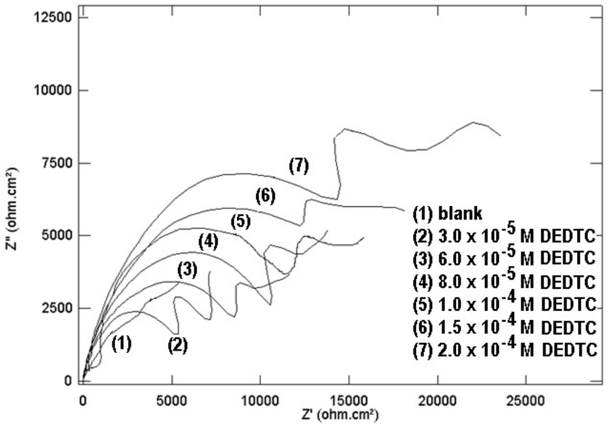

Figure 15. Nyquist plots of copper in 0.5 M aqueous solution of Na_2SO_4 in absence and presence of different concentrations of DEDTC

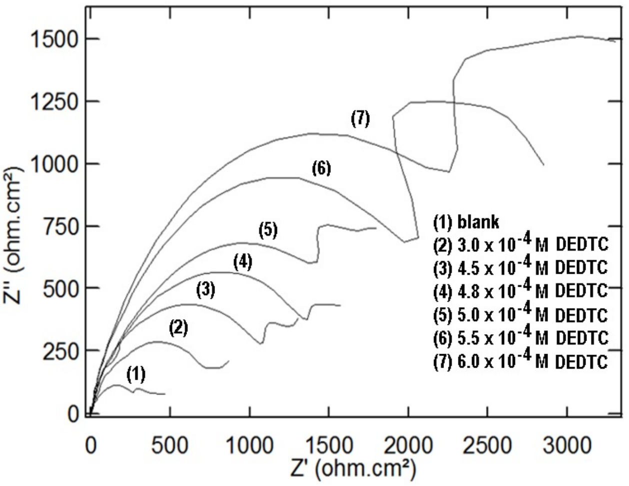

Figure 16. Nyquist plots of copper in 0.5 M aqueous solution of NaCl in absence and presence of different concentrations of DEDTC

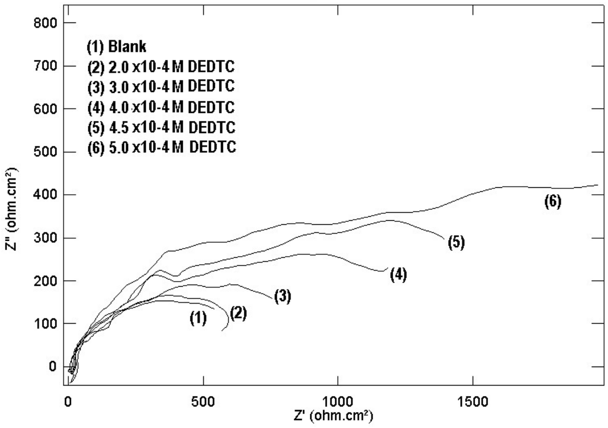

Figure 17. Nyquist plots of copper in 0.5 M aqueous solution of NaI in absence and presence of different concentrations of DEDTC

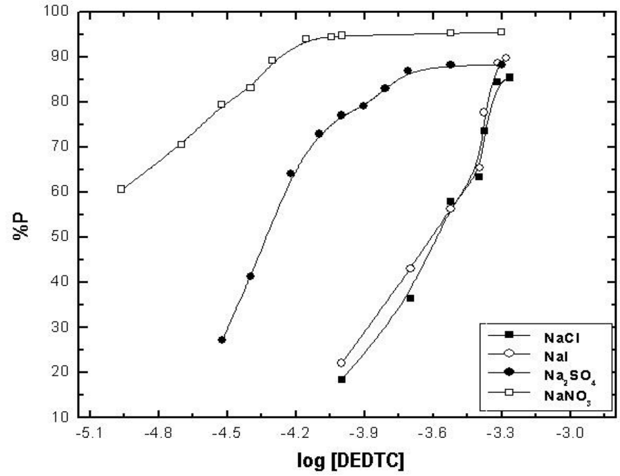

Figure 18. Variation of %P with the logarithmic concentration of DEDTC. for copper in 0.5 M aqueous solution of the four examine electrolytes in absence and presence of different concentrations of DEDTC

Table 2. The electrochemical impedance parameters of copper in 0.5 M aqueous solution of $NaNO_3$ in presence of different concentrations of DEDTC

[DEDTC] mol. L^{-1}	Impedance parameters						
	R_s Ohm.cm^2	Q_{dl} μF/cm^2	N	R_2 Ohm.cm^2	C_{dl} μF/cm^2	R_{ct} Ohm.cm^2	% inh
0.0	3.07	64.14	0.66	3.28	61.11	823.01	0.00
1.0x10^{-5}	3.15	58.25	0.65	4.12	57.31	2258.13	63.57
2.0x10^{-5}	3.22	44.62	0.70	5.20	41.20	2791.72	70.52
3.0x10^{-5}	3.35	38.71	0.86	7.09	35.61	4008.77	79.47
4.0x10^{-5}	3.50	32.84	0.69	11.24	31.85	4858.32	83.06
5.0x10^{-5}	3.17	29.45	0.56	13. 08	28.29	7655.81	89.25
7.0x10^{-5}	3. 61	26.44	0.82	14.25	24.24	13558.48	93. 93
9.0x10^{-5}	3.43	24.23	0.79	15.21	22.38	14855.61	94.46
1.0x10^{-4}	3.51	21.25	0.96	15.54	20.10	15587.12	94.72
3.0x10^{-4}	4.41	19.35	0.88	16.12	18.61	17326.53	95.25
5.0x10^{-4}	4.51	18.66	0.66	15.01	16.05	17930.50	95.41

Table 3. The electrochemical impedance parameters of copper in 0.5 M aqueous solution of Na_2SO_4 in presence of different concentrations of DEDTC

[DEDTC] mol. L^{-1}	Impedance parameters						
	Rs Ohm.cm^2	Q_{dl}	N	R_f	C_f	R_{ct} Ohm.cm^2	% inh
0.0	6.2	265	0.85	6.30	38.4	3281	0.00
3.0x10^{-5}	4.2	242	0.87	6.52	31.2	4512	27.28
4.0x10^{-5}	4.6	196	0.66	6.98	29.1	5590	41.31
6.0x10^{-5}	1.0	149	0.67	8.41	23.0	9120	64.02
8.0x10^{-5}	9.9	136	0.63	9.35	17.3	12120	72.93
1.0x10^{-4}	5.2	135	0.66	9.94	15.8	14310	77.07
1.2x10^{-4}	5.4	122	0.66	7.80	13.5	15658	79.05
1.5x10^{-4}	4.6	116	0.81	8.81	9.2	19265	82.97
2.0x10^{-4}	6.6	101	0.80	11.09	1.1	24960	86.86
3.0x10^{-4}	6.8	99	0.88	11.58	0.8	27820	88.21
5.0x10^{-4}	5.7	92	0.77	12.10	0.6	27880	88.23

Table 4. The electrochemical impedance parameters of copper in 0.5 M aqueous solution of NaCl presence of different concentrations of DEDTC

[DEDTC] mol. L^{-1}	Impedance parameters						
	R_s Ohm.cm^2	Q_{dl} μF/cm^2	N	C_{dl} μF/cm^2	R_2 Ohm.cm^2	R_{ct} Ohm.cm^2	% inh
0.00	2.12	93.49	0.62	62.24	1.89	370	0.00
1.0x10^{-4}	3.07	87.54	0.5713	51.54	2.10	452	18.43
2.0x10^{-4}	3.18	72.51	0.6164	44.64	2.90	582	36.43
3.0x10^{-4}	3.29	64.80	0.8994	41.62	3.10	880	57.95
4.0x10^{-4}	2.39	59.94	0.555	36.55	3.41	1012	63.44
4.2x10^{-4}	3.06	42.25	0.5578	31.20	4.41	1401	73.59
4.8x10^{-4}	3.41	30.79	0.62	25.40	4.51	2378	84.44
5.0x10^{-4}	3.44	21.51	0.5933	23.20	5.52	2790	86.74

Table 5. The electrochemical impedance parameters of copper in 0.5 M aqueous solution of NaI in presence of different concentrations of DEDTC

Conc, mol. L^{-1}	Impedance parameters						
	Rs Ohm.cm^2	Q_{dl} µF/cm^2	n	C_{dl} µF/cm^2	R_2 Ohm.cm^2	R_{ct} Ohm.cm^2	% inh
0.0	2.22	181.51	0.76	121.12	5.01	460.00	0.00
1.0 x10^{-4}	2.24	168.32	0.77	102.03	6.22	590.60	22.12
2.0 x10^{-4}	2.41	144.51	0.85	92.33	10.40	809.43	43.17
3.0 x10^{-4}	2.14	126.04	0.66	84.87	14.21	1053.11	56.32
4.0 x10^{-4}	2.35	121.21	0.78	75.10	15.71	1329.48	65.41
4.2 x10^{-4}	2.57	110.02	0.88	68.2	17.84	2062.78	77.70
4.8 x10^{-4}	2.66	105.22	0.66	62.3	18.77	3824.50	84.57
5.0 x10^{-4}	2.11	101.71	0.75	50.21	18.42	4010.35	85.29

3.2.3. Application of Adsorption Isotherms

Langmuir isotherm and Kinetic-thermodynamic model [52] were used to fit the corrosion data of copper in the four studied electrolytes in presence of different concentrations of DEDTC. Langmuir isotherm is given by:

$$(\theta/ 1-\theta) = K\ C \qquad (4)$$

Where K is the adsorption equilibrium constant or the binding constant which represent the interaction of the inhibitor with the metal surface and C is the concentration of the inhibitor. Kinetic-thermodynamic model is given by:

$$\text{Log}\ (\theta/ (1-\theta) = \log K` + y \log C \qquad (5)$$

Where y is the number of inhibitor molecules occupying one active site of the metal surface. The binding constant K is given by:

$$K= K^{`(1/y)} \qquad (6)$$

Figures (19, 20) show applications of each of Langmuir isotherm and Kinetic-thermodynamic model to the data of inhibition of the corrosion of copper by DEDTC in the four examined electrolytes using impedance technique. The linear fitting parameters of the data are depicted in table 6. It is clear that Langmuir and Kinetic-thermodynamic model were found to be applicable to fit the data of adsorption of dithiocarbamate anion on the copper surface. The data in the table indicates that there is a fairly agreement between the values of the binding constant K obtained using Langmuir isotherm and Kinetic-thermodynamic model. Since, the efficiency of a given inhibitor was essentially a function of the magnitude of its binding constant K, large value of K indicate better and stronger interaction, whereas small values of K mean the interaction between the inhibitor molecule and the metal is weaker. Hence, according to the numerical values of K in table 6, the order of the increase of the inhibition efficiency of DEDTC in the four tested electrolytes is given as follows:

$$NaI < NaCl < Na_2SO_4 < NaNO_3$$

These results give a good support to that obtained from the electrochemical measurements. The values of the number of active sites occupied by a single inhibitor molecule (1/y) were nearly equal to one. This means that the adsorbed dithiocarbamate anion occupies only one active site of the copper surface.

The binding constant of DEDTC molecules and copper surface (K) is related to the standared free energy of adsorption (ΔG^o_{ads}) according to the following equation [53].

$$K = 1/C_{solvent} \exp(-\Delta G^o_{ads}/ RT) \qquad (7)$$

Where R is the universal gas constant, T is the absolute temperature, $C_{solvent}$ is the molar concentration of solvent which is water and equal 55.5 mol/L.

Substitute of the values of the binding constant K which obtained by Langmuir isotherm in equation 7 gives the values of ΔG^o_{ads} for the adsorption of DEDTC on the copper surface in the four examined electrolytes (table 6). The results show that the values of ΔG^o_{ads} are between (-35.55 to -39.70 kj/mol.) indicating the adsoprption of DEDTC at the copper surface is comprehensive (chemical and physical adorption).

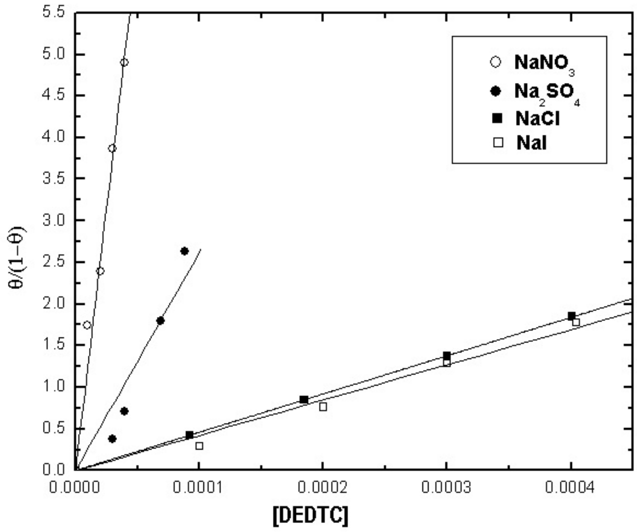

Figure 19. Langmuir adsorption isotherm of copper in 0.5 M aqueous solution of $NaNO_3$, Na_2SO_4, NaCl and NaI in presence of different concentrations of DEDTC

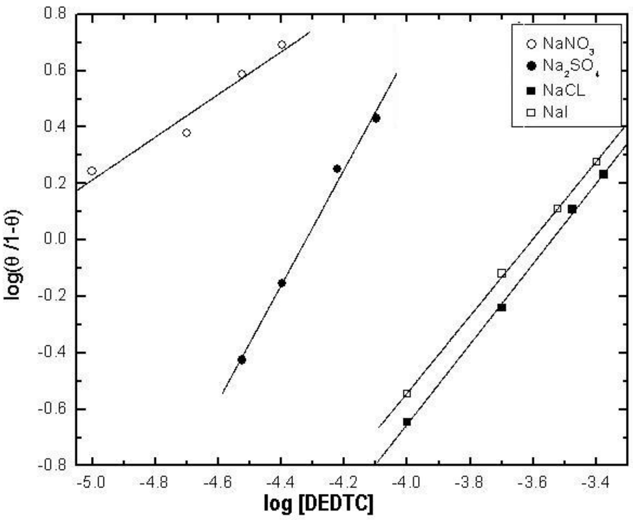

Figure 20. Kinetic-thermodynamic model for copper in 0.5 M aqueous solution of $NaNO_3$, Na_2SO_4, NaCl and NaI in presence of different concentrations of DEDTC

Table 6. The linear fitting parameters of Langmuir isotherm and Kinetic-thermodynamic model for copper in 0.5 M aqueous solution of $NaNO_3$, Na_2SO_4, NaCl and NaI

Electrolyte	Calculated parameters			
	Langmuir		Kinetic-thermodynamic	
	K	- ΔG^o_{ads} (kj/mol.)	K	1/y
$NaNO_3$	125849.21	39.70	117255.3	1.32
Na_2SO_4	26239.20	35.75	27685.33	0.71
NaCl	24600.84	35.59	27360.87	0.71
NaI	24233.49	35.55	26711.66	0.73

4. Conclusions

The results of this study show that:

1- The electrochemical dissolution of copper in aqueous solutions greatly depends on the kind of anion. Oxidation of copper takes place through a two-electron transfer step Cu → Cu(II) in electrolytes contain non- or weak adsorbable anions, however oxidation goes through two consecutive one electron transfer steps Cu → Cu(I) and Cu(I) → Cu(II) in electrolytes contain anions strongly adsorbed at metal/solution interface.

2- Diethyl dithiocarbamate act as mixed type inhibitor in the four studied electrolytes and its inhibition efficiency depends on the kind of the electrolyte, its inhibition efficiency in electrolytes contain strong adsorbable anions is lower than that contain weak or non-adsorbable anions due to the competitive adsorption between the anions of the electrolytes and that of DEDTC at metal-solution interface.

3- Both Langmuir isotherm and Kinetic-thermodynamic model are applicable to fit the experimental data of adsorption of DEDTC on the copper surface in the four examined electrolytes. The results showed that the value of the standard free energy change of adsorption (ΔG^o_{ads}) equal (-35.55 to -39.73 kj/mol.) indicating that the adsorption process of DEDTC on the copper surface is comprehensive (chemical and physical adsorption).

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