

Experimental and Theoretical Studies of Media Effects on Copper Corrosion in Acidic Environments Containing 2-Amino-5-mercapto-1,3,4-thiadiazole

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Corrosion behaviour of copper metal in acid solutions (HCl, H₂SO₄ and H₃PO₄) containing 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) was investigated experimentally and theoretically *via* gravimetric, potentiodynamic and quantum electrochemical approaches. Similar behavior was observed for H₂SO₄ and H₃PO₄ media, and related to the nature of anions at metal/solution interface. With regard to HCl, however, the rate of corrosion was determined to be low at initial stages, but high later on using an auto-catalyzing mechanism. In the presence of AMT, the experimental studies revealed that this molecule was a good anodic-type inhibitor causing substantial changes in corrosion potential. Moreover, its adsorption obeys the Langmuir isotherm. The values of ΔG_{ads} were determined and correlated to the inhibitor powers. Finally, the influence of media (anions) on metal corrosion was also investigated from molecular point of view by calculations of the copper-anions interaction using density functional theory.

Keywords: Copper corrosion inhibitors, Media effect, Autocatalysis, Specific adsorption, Molecular electrochemistry

INTRODUCTION

Because of its excellent conductivity, good mechanical workability, and relatively low cost and reactivity, copper is one of the most important materials used widely in different industries, especially in heating and cooling systems [1-3]. Scale and corrosion products produced during the work of systems, have some negative effects on their heat-exchange performance. Thus acid washing is periodically carried out to de-scale and clean these systems. The degradation of base metal in pickling solutions is an undesirable reaction which should be diminished practically during the process. This can be achieved effectively by the application of some specific organic compounds known as corrosion inhibitors [4]. Among

these compounds, 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) is a potential inhibitor reported for corrosion prevention of mild steel, bronze and copper in acid and neutral media [5-8].

As far as the corrosion of copper metal in acidic environments is concerned, it is remarkable to note that the phenomenon is not a simple oxidative process, resulting from direct proton reduction on metal surface; this process is thermodynamically impossible since the standard reduction potential of the proton is mainly negative compared with that of cupric or cuprous species present at metal/solution interface [9]. The degradation mechanism, however, is more complex and is mainly based on direct interaction of the corroding metal atoms with aggressive anions (*e.g.*, Cl⁻¹) present at interface [2,10]. As for oxidizing media, the result of interaction is the formation of an oxide layer on the metal

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surface (Cu_2O) and consecutive dissolution of the layer according to Mattson-Bockris mechanism [11].

The type of acid and its effect on inhibitory performance of compounds are among interesting subjects less investigated systematically so far [12-13]. In this respect, we have recently hypothesized that the effect can be investigated theoretically via direct interactional studies of the media components with corroding metal atoms, using quantum electrochemical calculations based on density functional theory (DFT) [14]. From empirical point of view, however, to the best of our knowledge, no serious study has been reported [15]. Thus the present work is an attempt to investigate the role of media experimentally as well as theoretically.

EXPERIMENTAL

2-Amino-5-mercapto-1,3,4-thiadiazole (AMT) was available for synthesis, purchased from Merck KGaA Co. The aggressive media studied here were 0.5 M HCl, H_2SO_4 , and H_3PO_4 solutions prepared from AnalaR materials and de-ionized water. The coupons applied were copper plates ($20 \times 10 \times 3$ mm) cut from commercially available pure sheets with the following composition (%wt.): Cu (99.9867), Ni (0.0036), Fe (0.0029), Co (0.0021), Zn (0.0009), Cr (0.0007), S (0.0004), and other impurities in trace.

Weight-loss experiments were carried out at room temperature according to the procedure described elsewhere [16]. For electrochemical studies, a conventional three-electrode set-up was used; Pt foil (2.5 cm^2), Ag/AgCl (3 M KCl) with Lugging salt-bridge-capillary and copper plate (1 cm^2 ; $10 \times 10 \times 3$ mm) mounted in epoxy resin as auxiliary, reference and working electrodes, respectively. In these experiments, the surface of copper electrodes was abraded mechanically by successive silicon carbide emery papers # 220, 400 and 600, degreased with ethanol and redistilled water, dipped in 7 M HNO_3 solution for 30 s [1], rinsed again and finally dried by hot air. The electrochemical measurements were carried out potentiodynamically (1 mV s^{-1}) under aerated conditions (purged by oxygen for 15 min), using an AUTOLAB/PGSTAT30 instrument and GPES software (ECO CHEMIE). The steady state potential was read after 30 min. All experiments were duplicated and the mean values were reported.

RESULTS AND DISCUSSION

Using weight-loss experiments, we determined the extent of degradation (ΔW) at different time intervals (t) and calculated the rate of corrosion (CR) according the following formula:

$$\text{CR} = \Delta W / At \quad (1)$$

where A is the exact value of the surface area of coupons applied in experiments. The results are illustrated in Figs. 1 and 2. As it can be seen from these figures, the behaviors are

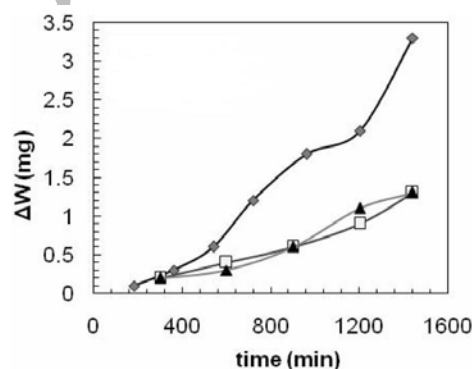


Fig. 1. Variation of weight-loss (ΔW) as a function of exposure time; determined for copper specimens in acid solutions (0.5 M) at room temperature: (◆) HCl, (□) H_2SO_4 and (▲) H_3PO_4 .

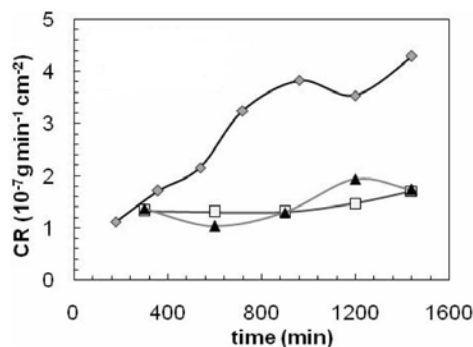


Fig. 2. Variation of corrosion rate with time; calculated for copper specimens in acid media (0.5 M) at room temperature: (◆) HCl, (□) H_2SO_4 and (▲) H_3PO_4 .

approximately similar with regard to H₂SO₄ and H₃PO₄ but different regarding HCl medium. In the latter case, *i.e.*, in the presence of chloride anions, the corrosion process was accelerative. These observations may be related to oxidative/non-oxidative capacity of the acids [17] or justified more precisely by the nature of counter-anions present at metal/solution interface and hence their characteristic interactions with corroding metal atoms. This assumption is scrutinized in the theoretical section of this work.

By weight-loss measurements, we also determined the rate of corrosion in the presence (CRⁱ) and absence (CR^b) of AMT and calculated the percent of inhibition efficiency, IE (%), using the following equation:

$$IE(\%) = \frac{CR^b - CR^i}{CR^b} \times 100 \quad (2)$$

The results are summarized in Table 1 and depicted in Fig. 3 as a function of inhibitor concentration. As it can be seen, not only the inhibitory power of AMT increases with concentration and approaches 100% but the performance also depends on the type of acid and decreases as follows:

$$H_3PO_4 > H_2SO_4 > HCl \quad (3)$$

In this respect, it is worth to note from thermodynamical point of view that the type of media has obviously a direct influence on inhibitor activity at metal/solution interface so that it affects the quality of adsorption and hence the inhibitor performance. This seems to be due to the thermodynamic origin of relation 3. To calculate the stability accompanying the inhibitor adsorption, we applied the most common adsorption isotherms, *i.e.*, Langmuir, Temkin, Frumkin, *etc.*, [5,12-13,18-20] to data of Table 1. The best correlations were observed for Langmuir model (see figure and Eq. 4) which is interpretable on the basis of the hypothesis of single inhibitor adsorption and the formation of a polymeric film thereafter [21-22]. The same model has been witnessed elsewhere for the adsorption of this molecule on iron surface [5].

$$C/\theta = C + 1/K_{ads} \quad (4)$$

where K_{ads} is related to ΔG_{ads} according to the formula below:

Table 1. Inhibition Efficiency Data (%) of AMT as Corrosion Inhibitor of Copper in Acidic Media (0.5 M), Obtained from Mass-Loss Experiments (t = 24 h)

Inhibitor concentration (M)	HCl	H ₂ SO ₄	H ₃ PO ₄
Blank	-	-	-
10 ⁻⁴	33.08	57.84	83.65
5 × 10 ⁻⁴	60.00	75.49	91.35
10 ⁻³	66.15	84.31	92.31
5 × 10 ⁻³	90.00	91.96	93.27
10 ⁻²	93.85	96.08	96.15

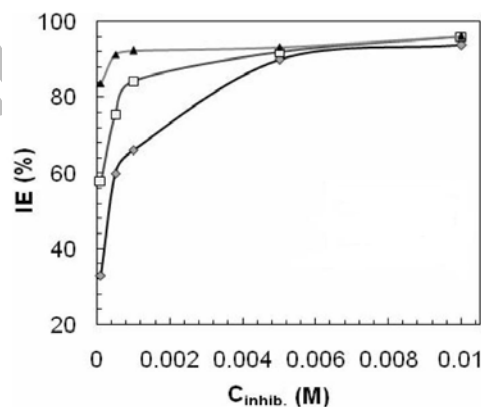


Fig. 3. Percent of inhibition efficiency, IE (%), as a function of inhibitor concentration; determined for AMT molecule as a corrosion inhibitor of copper in acidic media (0.5 M) at room temperature (t = 24 h): (◆) HCl, (□) H₂SO₄ and (▲) H₃PO₄.

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}) \quad (5)$$

Here, C, θ, K_{ads} and ΔG_{ads} denote the inhibitor concentration, surface coverage (estimated by IE data; see Table 1), adsorption equilibrium constant and free energy, respectively. The values of K_{ads} are 3.33 × 10³, 10⁴ and 2 × 10⁴ M⁻¹ determined for HCl, H₂SO₄ and H₃PO₄ solutions, respectively. The values of ΔG_{ads} were also calculated as -30.05, -32.77 and -34.49 kJ mol⁻¹, indicating the strong spontaneous adsorption

of the inhibitor compound in these media [18]. On the basis of these investigations, we can deduce that the AMT adsorption is more favourable in H_3PO_4 than in H_2SO_4 and subsequently HCl as shown in relation 3.

The particular behaviour of copper dissolution in HCl media was also confirmed by the electrochemical studies as depicted in Fig. 5. This figure also shows a shift in corrosion potential (E_{corr}) for sulphuric and phosphoric acid solutions to the positive (noble) values which is interpretable according to the formation of oxide layer in oxidizing environments [21]. Furthermore, there is a hump in proximity of E_{corr} in cathodic region. This is justified by the oxygen reduction reaction and/or copper ion re-deposition on electrode surface producing extra current densities [23]. Regarding HCl, the hump is less clear compared with the two other media and disappears totally in de-aerated HCl solutions [24]. The intensity and shape of the hump are obviously related to the activity of the reducing species present at the interface affected by the type of media. To be brief, the similarities/dissimilarities observed here are in accord with those of weight-loss experiments.

The electrochemical behaviour of the copper electrodes were also investigated in the presence of AMT molecules, illustrated in Fig. 6 and summarized in Tables 2 through 4. As it can be seen, there are some displacements in E_{corr} which could be due to the formation of a sticky-yellowish film on copper surface; *i.e.* the product of copper with AMT compounds. This layer may be also responsible for the strong protection of copper specimens in acidic environments. The shifts in E_{corr} in the presence of AMT seem to be a direct result of the more complex interactions between protonated form of the inhibitors inside electrical double layer, counter anions of media, and corroding metal atoms at metal/solution interface, introduced previously as ion-pair hypothesis in the field of corrosion inhibition science [14]. These complex forces are also responsible for the dissimilarities observed in the graphs of H_3PO_4 and H_2SO_4 media in the presence of AMT compounds (see Figs. 6). Furthermore, the extent of displacement seen for E_{corr} is obviously related to the thickness and tenacity of the protective film forming in different acidic environments. By comparing the graphs plotted in Figs. 5 and 6, we can conclude that the presence of AMT inhibitors causes a polarization, mostly in anodic branch of the plots, and reduces the metal dissolution accordingly.

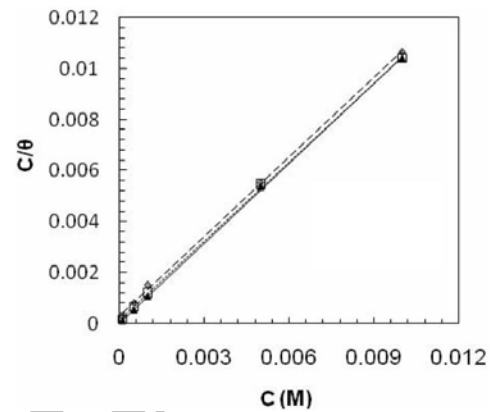


Fig. 4. Langmuir isotherm for adsorption of AMT on copper surface in acid media (0.5 M), determined at room temperature: (◆) HCl, (□) H_2SO_4 and (▲) H_3PO_4 .

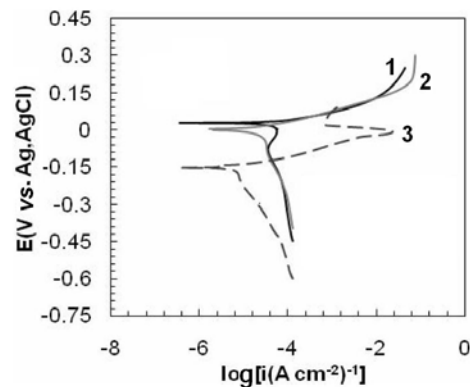


Fig. 5. Tafel plots of copper corrosion in acidic media (0.5 M): 1- H_3PO_4 (top), 2- H_2SO_4 (middle), 3- HCl (down).

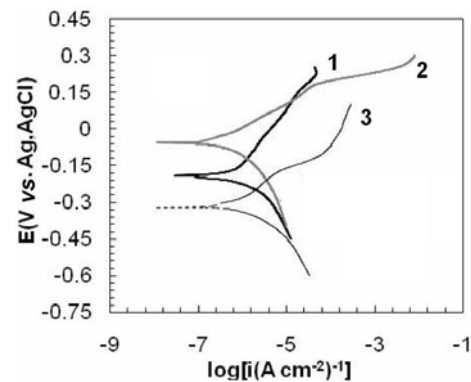


Fig. 6. Tafel plots for copper electrode in acid solutions (0.5 M), in presence of 0.01 M of AMT corrosion inhibitors: 1- H_3PO_4 (middle), 2- H_2SO_4 (top), 3- HCl (down).

Table 2. Corrosion Parameters, Obtained from Tafel Polarization (Potentio-Dynamic) Experiments, for Copper Electrode in HCl Media (0.5 M), in Presence of AMT Inhibitors at Various Concentrations

C_{inhib}	$E_{corr}^{obs. a}$	$E_{corr}^{calc. b}$	β_a	β_c	i_{corr}	R_p	Q_a^c	I.E (%) ^d		
(M)	(mV _{Ag/AgCl})	(mV _{Ag/AgCl})	(mV decade ⁻¹)	(mV decade ⁻¹)	(μ A cm ⁻²)	(k Ω cm ⁻²)	(mC cm ⁻²)	i_{corr}	R_p	Q_a
0	-152	-164	44	-248	5.61	2.89	582.30	0	0	0
10 ⁻⁴	-168	-167	46	-188	4.93	3.25	169.70	12.12	11.08	70.86
5 \times 10 ⁻⁴	-221	-221	84	-157	4.15	5.72	13.63	26.02	49.47	97.66
10 ⁻³	-236	-228	45	-146	2.50	5.97	8.44	55.44	51.59	98.55
5 \times 10 ⁻³	-273	-264	80	-95	0.67	28.14	3.11	88.06	89.73	99.46
10 ⁻²	-322	-316	134	-88	0.61	37.81	0.46	89.13	92.36	99.92

^aCorrespond to the breaking point on polarization curves where the current direction is reversed. ^bCalculated from extrapolation of Tafel (anodic and cathodic) lines. ^cCharges passing under anodic polarization regime ($\eta = 0-150$ mV); interpretable as the extent of corrosion if the anodic reactions (occurring under this circumstance) are limited to the metal oxidation only. ^dInhibition efficiencies determined from i_{corr} (corrosion rate), R_p (polarization resistance) and Q_a (extent of corrosion), respectively.

Table 3. Corrosion Parameters, Obtained from Tafel Polarization (Potentio-Dynamic) Experiments, for Copper Electrode in H₂SO₄ Media (0.5 M), in Presence of AMT Inhibitors at Various Concentrations

C_{inhib}	$E_{corr}^{obs. a}$	$E_{corr}^{calc. b}$	β_a	β_c	i_{corr}	R_p	Q_a^c	I.E (%) ^d		
(M)	(mV _{Ag/AgCl})	(mV _{Ag/AgCl})	(mV decade ⁻¹)	(mV decade ⁻¹)	(μ A cm ⁻²)	(k Ω cm ⁻²)	(mC cm ⁻²)	i_{corr}	R_p	Q_a
0	-4	-11	51	-325	18.46	1.04	376.65	0	0	0
10 ⁻⁴	-265	-262	414	-228	14.91	4.28	1.81	19.23	75.70	99.52
5 \times 10 ⁻⁴	-277	-277	237	-247	8.59	6.11	1.62	53.47	82.98	99.57
10 ⁻³	-193	-193	560	-133	6.36	7.34	0.63	65.55	85.83	99.83
5 \times 10 ⁻³	-190	-189	348	-118	2.49	15.37	0.34	86.51	93.23	99.91
10 ⁻²	-57	-46	105	-143	0.35	75.11	0.28	98.10	98.61	99.92

^aThe values observed for corrosion potential, correspond to the breaking point on polarization curves, where the current direction is reversed. ^bCalculated from extrapolation of Tafel (anodic and cathodic) lines. ^cCharges passed under anodic polarization regime ($\eta = 0-150$ mV); interpretable as the extent of corrosion if the anodic reactions (occurring in this circumstance) are limited only to the metal dissolution (oxidation). ^dInhibition efficiencies determined from i_{corr} (corrosion rate), R_p (polarization resistance) and Q_a (extent of corrosion), respectively.

Concerning the inhibition efficiency data listed in Tables 2 through 4, we also determined these values using Eq. (2) where the CR is replaced by quantities corrosion current density (i_{corr}), polarization resistance (R_p), and the charges passing through anodic polarization of the electrode (Q_a). The latter quantity can be interpreted as the extent of corrosion if the anodic reactions were limited to the metal oxidation only. All the three methods applied here confirmed the results of weight-loss experiments, namely, AMT is a good corrosion

inhibitor for copper degradation in acidic environments and the inhibitor power increases by concentration. The only difference may be related to the rate of corrosion in blank solution. In other words, at initial stages of the phenomenon, both electrochemical and weight-loss experiments indicate the rate of corrosion to be $H_3PO_4 \approx H_2SO_4 > HCl$; however, the inequality sign will be reversed while the process takes place, because of auto-catalyzing nature of the chloride anions in long term.

Table 4. Corrosion Parameters, Obtained from Tafel Polarization (Potentio-Dynamic) Experiments, for Copper Electrode in H₃PO₄ Media (0.5 M), in Presence of AMT Inhibitors at Various Concentrations

C_{inhib}	$E_{\text{corr}}^{\text{obs. a}}$	$E_{\text{corr}}^{\text{calc. b}}$	β_a	β_c	i_{corr}	R_p	Q_a^c	IE (%) ^d		
(M)	(mV _{Ag/AgCl})	(mV _{Ag/AgCl})	(mV decade ⁻¹)	(mV decade ⁻¹)	($\mu\text{A cm}^{-2}$)	($\text{k}\Omega \text{cm}^{-2}$)	(mC cm^{-2})	i_{corr}	R_p	Q_a
0	27	10	35	-347	17.96	0.77	1023.00	0	0	0
10 ⁻⁴	28	30	30	-188	1.65	6.81	1702.00	90.81	88.69	-
5 × 10 ⁻⁴	-5	-4	143	-196	0.77	46.62	0.51	95.71	98.35	99.95
10 ⁻³	57	54	82	-245	0.67	39.82	1.97	96.27	98.07	99.81
5 × 10 ⁻³	-18	-17	84	-218	0.62	42.47	0.67	96.55	98.19	99.93
10 ⁻²	-191	-205	231	-83	0.56	47.34	0.29	96.88	98.37	99.97

^aThe values observed for corrosion potential, correspond to the breaking point on polarization curves, where the current direction is reversed. ^bCalculated from extrapolation of Tafel (anodic and cathodic) lines. ^cCharges passed under anodic polarization regime ($\eta = 0-150$ mV); interpretable as the extent of corrosion if the anodic reactions (occurring in this circumstance) are limited only to the metal dissolution (oxidation). ^dInhibition efficiencies determined from i_{corr} (corrosion rate), R_p (polarization resistance) and Q_a (extent of corrosion), respectively.

THEORETICAL STUDY

To reveal the role of media on the characteristic behavior of copper corrosion in acidic environments, one can investigate the phenomenon via direct interactional studies of the corrosive anions with the corroding metal atoms [14]. Briefly, in this approach, the solvent effect was studied applying the modified version of polarized continuum model based on integral equation formalism (IEF-PCM) with dielectric constant of six. The equilibrium structure of the species, in solution part of the interface (metal/solution), was determined using this model and quantum chemical calculations based on standard techniques, *e.g.*, DFT. The details of the method are reported elsewhere [25]. In this work, we applied the B3LYP version of DFT and the geometry optimization and single point calculations were carried out using Gaussian standard 3-21G** and 6-311G** basis sets, respectively [26]. In the case of copper atoms, we utilized extra basis set called LANL2DZ in which the eighteen core electrons of the metallic atoms are substituted with LANL2 pseudo-potential and the other remaining electrons at the valence shells are described by double zeta (DZ) quality basis set [14].

Interaction energy and induced charge to metal surface obtained from these calculations are among the important factors governing the quality of adsorption [27]. The first

factor determines the type of bond and adsorption strength on metal surface. However, the second factor affects the value of residual charge on metal surface (q_M) and hence the extent of adsorbed species at interface. Both of these factors determine the ensemble energy released during the adsorption process. These quantities were calculated for a variety of possible corrosive anions through different adsorption modes, namely, capped, top and scissor forms (Fig. 7 and 8). The results are

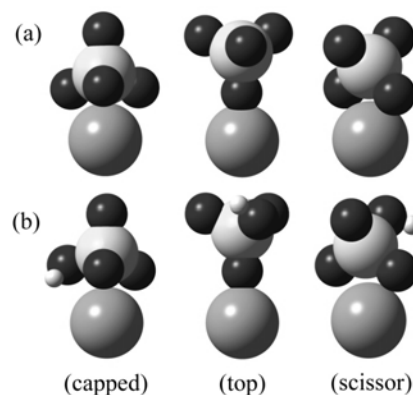


Fig. 7. Three-dimensional structures (ball and tube model with 115% scaled van der Waals radii) of counter anions presence in H₂SO₄ corrosive media, adsorbed on corroding copper atoms: a) Cu(SO₄²⁻) and b) Cu(HSO₄⁻) complexes in capped, top and scissor modes, respectively.

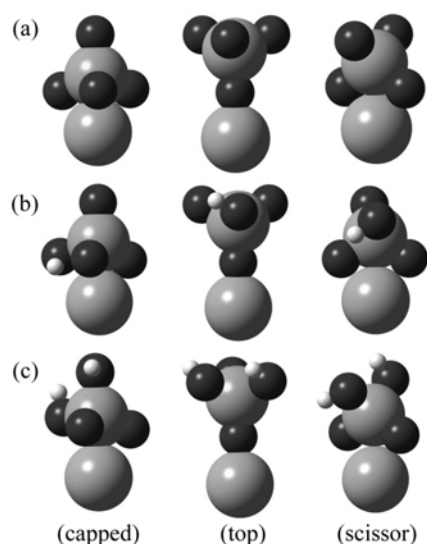


Fig. 8. Three-dimensional structures (ball and tube model with 115% scaled van der Waals radii) of counter anions presence in H_3PO_4 corrosive media, adsorbed on corroding metal atoms: a) $\text{Cu}(\text{PO}_4^{3-})$, b) $\text{Cu}(\text{HPO}_4^{2-})$ and c) $\text{Cu}(\text{H}_2\text{PO}_4^-)$ complexes in capped, top and scissor modes, respectively.

listed in Table 5. Here, we also tabulated the equilibrium distance of the adsorbed species from metal surface and their concentrations in the bulk of solution.

As it can be seen from Table 5, for each corrosive medium, the anions with single negative charge are most abundant. Furthermore, for these mono-valent anions, the following relations are deducible from the interaction energy and induced charge data, respectively:

$$\text{Cl}^- > \text{H}_2\text{PO}_4^- > \text{HSO}_4^- \quad (6)$$

$$\text{Cl}^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^- \quad (7)$$

These relations signify that chloride anions are not only adsorbing more strongly but inducing also greater negative charges to the corroding metal atoms. As for HSO_4^- and H_2PO_4^- , however, there is no definite preference on the basis of these criteria and the effects are competitive and may be cancelled out! This characteristic behaviour calculated for the species at metal/solution interface, seems to be due to the molecular origin of the experimental observations, *i.e.* specific

Table 5. Interaction of Acids' Counter Anions with Corroding Metal (Cu) Atoms through Different Adsorption Modes; See Figs. 7 and 8

Counter anions	Bulk concentration (M) ^a	Equilibrium distance (Å)	Interaction energy (kcal mol ⁻¹) ^b	Induced charges on metal atoms (au)
Cl^-	0.5	2.2	-31.14	-0.317820
HSO_4^-	4.89×10^{-1}	2.6 ^c	-14.04	-0.273759
		1.9 ^d	-19.88	-0.143462
		2.7 ^e	-17.84	-0.249504
SO_4^{2-}	1.15×10^{-2}	2.4 ^c	-44.33	-0.527507
		1.8 ^d	-51.37	-0.307361
		2.6 ^e	-53.09	-0.486178
H_2PO_4^-	3.99×10^{-2}	2.4 ^c	-16.74	-0.220144
		1.9 ^d	-27.08	-0.160477
		2.6 ^e	-21.39	-0.258083
HPO_4^{2-}	2.84×10^{-8}	2.4 ^c	-53.83	-0.557830
		1.8 ^d	-59.80	-0.333676
		2.5 ^e	-62.31	-0.526048
PO_4^{3-}	1.34×10^{-19}	2.2 ^c	-119.03	-0.922728
		1.8 ^d	-129.75	-1.041634
		2.5 ^e	-133.34	-0.862355

^aFor the case of the polyprotic acids, the values of concentrations were calculated from analytical equations formulated classically as a function of pH [28]. The experimental data of pH applied here are 0.38 and 1.05, standing for H_2SO_4 and H_3PO_4 solutions (0.5 M), respectively. ^bDefined as $E_{\text{int}} = E_{\text{complex}} - (E_{\text{anion}} + E_{\text{Cu}})$ and corrected by counterpoise method [14].

^{c, d, e}Standing for capped, top and scissor forms, respectively; see Figs. 7 and 8.

behavior of copper corrosion in HCl but not H₂SO₄ and H₃PO₄ media.

Among the remaining species with more negative charges, sulphate is the one whose concentration is not negligible in the bulk of solution. Unlike HSO₄⁻, the surface concentration of sulphate should be rather low, because of strong electrostatic repulsions operating between these divalent anions at interface [14]. Similar results are deducible for other di- and tri-valent anions.

The other important results obtainable from this table are as follows:

-The longest distance between anionic species and corroding metal atoms is related to the scissor mode while the shortest is due to top one. This result can be simply justified by hindrance effect relating to these modes.

-Although the interactions between corroding metal atoms and species having more negative charges are relatively high, their effects are considered negligible since the species are in tiny quantities.

-For anions having unit charge, the strong adsorption occurs through top mode while others, follow scissor mode.

CONCLUSIONS

-The experimental studies revealed an auto-catalyzing mechanism for copper dissolution in HCl but not in H₂SO₄ or H₃PO₄ media. For these two media, the rate of corrosion was competitive but approximately similar. These observations were totally in agreement with the theoretical results.

-The effect of media on corrosion behavior of a metal can be investigated rigorously *via* the recently developed quantum electrochemical models based on density functional theory.

-Among the various anions present at interface in great abundance, the strongest adsorption and the greatest induced charge to corroding metal atoms are related to chloride ones. In addition, no priority is given to either HSO₄⁻ or H₂PO₄⁻.

-AMT is a good anodic-type inhibitor for acidic environments causing substantial changes in corrosion potential. The adsorption of this molecule obeys the Langmuir isotherm. Furthermore, the values of ΔG_{ads} correlate with the inhibitory powers of the molecule in acidic media.

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