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The influence of aniline and its derivatives on the corrosion behaviour of copper in acid solution

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Abstract The inhibiting action of aniline and its derivatives on the corrosion of copper in hydrochloric acid has been investigated, with emphasis on the role of substituents. With this purpose five different anilines were selected: aniline, *p*-chloro aniline, *p*-nitro aniline, *p*-methoxy and *p*-methyl aniline. The electrochemical and gravimetric results, obtained in the absence and presence of different concentrations of inhibitors, revealed that aniline reduces the corrosion of copper, with a critical concentration of 10^{-2} M. Furthermore, the interaction energy calculated as ΔG_{ads} gave a value of 4.2 kcal mol⁻¹ indicating physisorption of the organic compound at the copper surface. The results have also shown that substituents, either electron donors ($-\text{CH}_3$, $-\text{OCH}_3$) or, electron acceptors ($-\text{NO}_2$, $-\text{Cl}$) in *para* position, decrease the inhibition action of aniline. A theoretical study using molecular mechanic and ab initio Hartree Fock methods, to model the adsorption of aniline on copper (100) showed results in good agreement with the experimental data. Aniline adsorbs parallel to the copper surface, showing no preference for a specific adsorption site. On the other hand, from

ab initio Hartree Fock calculations, an adsorption energy between 2 kcal/mol and 5 kcal/mol is obtained, which is close to the experimental value, confirming that the adsorption of aniline on the metal substrate is rather weak. In view of these results, the orientation of the aniline molecule with respect to the copper surface is considered to be the dominant effect.

Keywords Copper · Corrosion inhibitors · Modelling

Introduction

Because of the widespread use of copper, the study of its corrosion has become an important issue in industry. Copper has excellent electrical and thermal conductivity and is often used in heating and cooling systems. The presence of corrosion products decreases the heating efficiency of the equipment, making necessary procedures of descaling and cleaning in acid solutions. Additions of certain organic compounds to the cleaning solutions protect the metal from the destructive effect of the acid on such equipments. Among the acid corrosion inhibitors for copper, some nitrogen, sulphur or, oxygen containing compounds reduce copper dissolution due to the chelating action of heterocyclic molecules.

In neutral solution, a whole range of nitrogen containing compounds as corrosion inhibitors for copper is described in the literature. Thus, the effective action of imidazole and its derivatives [1–3], thiazole derivatives [4, 5], 2-hydroxyacetophenone-aroil hydrazone derivatives [6], Schiff bases [7, 8] and recently, *ortho* and *para* substituted anilines [9, 10] have been reported. Among the nitrogen containing compounds, benzotriazole (BTA) is one of the most effective inhibitors for copper corrosion in several corrosive environments [11–13].

The effect of molecular structure on the inhibitor efficiency has been a subject of interest in the corrosion of metals, since the introduction of proper substituents to the non-substituted inhibitor improves the protective characteristic of the organic compound. [14–21].

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Considering this, there have been some recent efforts in the literature in trying to explain inhibition using tools of theoretical chemistry, like quantum chemical calculations. In these studies, the effect of substituents in related molecules, e.g. anilines, aliphatic amines, amides, benzotriazoles on the inhibitive efficiencies, have been correlated with a number of molecular properties, such as orbital energies, dipole moments, charge densities, heats of formation and ionization potentials [22–26]. In most of this work, a clear effect of substituents in the inhibiting efficiency is reported and suggested that the smaller the difference of the inhibitor's E_{LUMO} and the metal surface's E_{HOMO} , the more easily the inhibitor accepts electrons from the metal. However, there is some controversy in the literature concerning this point and some authors have reported that there is no direct correlation between efficiency of inhibitor compounds and individual molecular parameters [27]. This controversy might be the result of the great variety of molecular structures examined as corrosion inhibitors, in particular of the size of the non-substituted compounds and also, of the number of active sites for their adsorption. Further, the position of substituents with respect to the expected interaction site in the molecule is considered to be relevant since steric effects could become more important than electronic effects of substituents. To clarify this point, it is necessary to consider inhibitor molecules of small size and with a minimum of interaction sites. To approach this goal, the objective of the present work was to find a correlation between parameters related to the electronic structure of *para*-substituted aniline molecules and their ability to inhibit the corrosion processes. The nitrogen atom of the aniline molecule is expected to be the only potential active site to interact with the metal surface, and substituents on the benzenic unit can modify the electron density on the nitrogen atom. To avoid steric effects of substituents, we have chosen molecules with groups on the *para* position only.

Experimental details

The electrochemical measurements were performed at 293 K in a three-electrode cell with a separate compartment for the reference electrode connected with the main compartment via a Luggin capillary. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum wire exposing a geometrical surface area of 7 cm². The counter electrode was also separated from the working electrode in order to avoid any contamination from the aniline oxidation processes taking place at this electrode during the cathodic scan. The working electrode was a polycrystalline high-purity copper rod (99.999% Cu) of 1 cm of thickness, embedded in epoxy resin mould, with a cross section of about 1 cm² exposed to the solution. Prior to the electrochemical measurements, the working electrode was polished with emery paper (1,200 grit size), rinsed with acetone and distilled water and immersed in

the electrolyte. Reagent grade chemicals and double-distilled water were used to prepare the solutions. The base electrolyte was 0.1 M HCl. Aniline and aniline derivatives concentration varied between 10⁻⁵ M and 10⁻² M. Aniline and derivatives were obtained from Aldrich and used as provided.

Potentiodynamic polarization measurements were carried out with an AUTOLAB potentiostat. The inhibition efficiency (IE%) was calculated using the corrosion current density values in the absence and presence of the inhibitor, applying the following relation:

$$IE = \left(\frac{i_{\text{corr}}^{\circ} - i_{\text{corr}}^{\text{inh}}}{i_{\text{corr}}^{\circ}} \right) \quad (1)$$

where i_{corr}° and $i_{\text{corr}}^{\text{inh}}$ are the uninhibited and inhibited corrosion current densities respectively, determined by extrapolation of Tafel lines.

The copper specimens used for the weight loss measurements were 20×10×0.9 mm. The copper samples were degreased in acetone and washed thoroughly with double distilled water and then dried. Experimental data is the result of the average of three-independent measurements at 293 K.

Theoretical calculations

The nature of the interaction inhibitor-copper surface in acid media is rather complicated. Several variables should be considered to obtain a realistic representation of the inhibition process, such as concentration of the organic compound, surface morphology, orientation of the inhibitor molecule, effect of the pH, presence of chloride ions on the surface, solvent effect, to name a few. Considering this, the simultaneous study of these variables on such a process makes the interpretation, at a molecular level, very difficult without a complete knowledge of the features of the inhibition process. As mentioned previously, some efforts were made, in trying, to explain the inhibition using tools of the theoretical chemistry, like quantum chemical types. However, all these studies are based on a simplified description of the process of inhibition, where electronic properties of the organic molecule are correlated with experimental properties of the inhibitor-substrate system [27–29]. A good starting point to begin a theoretical study of the system is to focus on the inhibitor-substrate interaction. In addition, simplification with regard to the number of variables involved is of vital importance for a better understanding of the system. With this in mind we explore an idealized copper surface such as the Cu (100) plane without defects interacting with the aniline molecule in the absence of all external interferences. This is a very simplistic model of the system, but we believe that it is a good starting point. So at this first stage, the modus operandi of the theoretical study was to employ the molecular mechanic method to explore the inhibitor-copper surface interaction in two aspects: orientation

and the involved energy. Then, the use of more sophisticated methods, such as the quantum chemical ones, would allow us to improve the description of the orientation and of the energy of the inhibitor-surface system. This was the strategy used in the present work. So molecular mechanic calculations were made to obtain configurations of minimum energy that served as starting point to the quantum chemical calculations.

Molecular mechanic calculations

Mechanic molecular calculations were carried out using the Insight II, a comprehensive graphic molecular modelling program, to obtain configurations of minimum energy [30]. The Cu (100) surface was modelled using 5,000 atoms of copper in three layers and generated using the solid builder module [30]. The aniline molecule and derivatives were optimized using consistent-valence force field (CVFF), a classical force field often used in organic and biochemistry studies, which gives very good results when compared with more sophisticated methods. [31–33]. The Metropolis procedure [34] was employed to obtain the configuration of minimum energy for each adsorbate-substrate systems using the solid docking module [35]. First, we investigated the configuration of minimum energy for one aniline molecule interacting with the copper surface. Then, we used several aniline molecules interacting with the copper surface. This procedure was repeated for all the aniline systems studied in the present work. The simulation, which begins from a random configuration generated by the program, consists in events. One event is an energy configuration of the interactive system, which can be accepted or rejected using Metropolis algorithms. From all the accepted configurations, the configuration of the minimum energy was selected. To carry out this type of simulation, about 100 events are necessary for a simple system (one aniline molecule in interaction with the surface) and about 10,000 events for a more complex system (several aniline molecules in interaction with the surface).

Quantum chemical calculations

In order to get more quantitative results for the adsorbate-copper surface interaction, and taking into account the results obtained by molecular mechanic calculations, *ab initio* self-consistent Hartree Fock (SCF-HF) calculations were performed. For anilines, hydrogen, carbon, oxygen, nitrogen and chlorine atoms, the D95 basis set have been used [36], in which all electrons were explicitly considered. The optimized geometries for all anilines were found and used to build the aniline-copper systems. The adsorbate-copper surface interaction is described using a cluster model, successfully used to describe this type of interaction [37–39]. The Cu (100) surface was simulated by a cluster of 14 atoms, with a Cu–Cu distance of 2.54 Å, which corresponds to the

Cu–Cu separation in the bulk of the solid. The copper atoms were distributed in three layers: nine Cu atoms in the first layer, four Cu atoms in the second layer and one Cu atom in the third layer, which can be represented as Cu (9:4:1) (Fig. 1). Recently, a similar copper cluster was used to study the interaction of oxygen with Cu (100) surface [40]. The Stuttgart pseudopotential for copper atoms was used [37]. It consists of ten core electrons and 19 active valence electrons. For copper atoms, the D95V basis set was used [41]. To optimize the aniline-surface distance for several orientations, the geometry of the copper cluster and the aniline molecule was maintained rigid. The binding energy of the adsorption process was calculated as

$$E_{\text{ads}} = E(\text{Cu}_{14} - \text{aniline})_{\text{eq}} - E(\text{Cu}_{14} - \text{aniline})_{\infty} \quad (2)$$

where the first term in Eq. 2 represents the energy in the equilibrium position for the copper–aniline system and the second, represents the energy at infinite distance. Since for the last term, the energy of the system was constant from 30 Å, a distance of 50 Å was taken for all the systems; this makes possible to correct for errors originated by the basis set superpositions in the energy of the interacting system. All these calculations were performed using the Gaussian 98 program [42].

Results and discussion

Experimental results

Electrochemical measurements

Anodic and cathodic polarizations of copper were carried out in aerated 0.1 M HCl with various concentra-

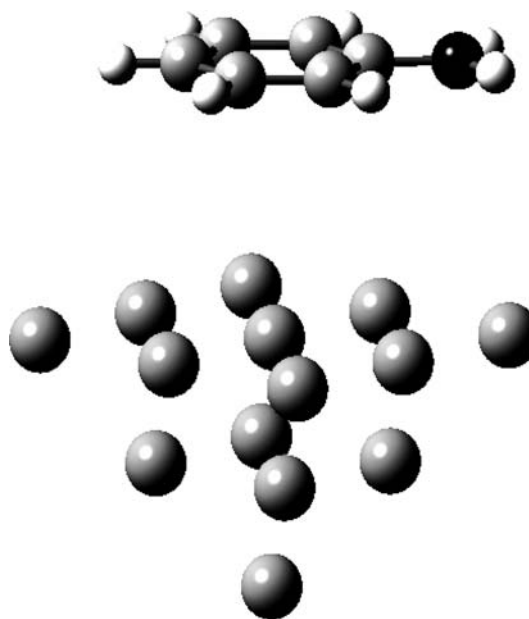


Fig. 1 The cluster model for aniline molecule on copper surface

tions of the inhibitors at 293 K, at a potential scan rate of 0.1 mV s^{-1} . The potential-current density responses of copper in the absence and presence of different concentrations of aniline are presented in Fig. 2. The polarization curves for the substituted anilines are not shown here, since they were relatively similar to that of aniline. The corrosion parameters calculated from the corresponding polarization curves are presented in Table 1. As observed, the corrosion potential of the copper electrode in 0.1 M HCl shifts towards more cathodic values in the presence of aniline and the displacement is higher with increasing the aniline concentration. From Table 1, the shift of the corrosion potential with different concentrations of the *para* substituted anilines is less significant. On the other hand, the variation of the corrosion current density with the inhibitor concentration reveals a critical concentration for aniline. However, for the substituted anilines, the change in the corrosion current density with the inhibitor concentration does not follow a pattern. Also, from the cathodic and anodic Tafel slopes in Table 1, the inhibitors do not seem to influence the electrochemical mechanism of copper corrosion, since the deviation of the anodic and cathodic Tafel slopes does not follow a clear trend.

This could be due to the weak interaction between the inhibitor and the copper surface, as discussed later, which corresponds to a physisorption.

In order to obtain the free energy of adsorption of aniline at copper surface, different adsorption isotherms were considered. However, for the electrochemical data informed here the best correlation between the surface coverage and the inhibitor concentrations was obtained with the Temkin's isotherm [43]. This suggests that adsorption of aniline and its derivatives on the copper surface proceeds to a low extent and consequently, low surface coverage of the inhibitors can be envisaged. According to this isotherm, the relationship between the coverage and inhibitor concentration follows Eq. 3:

$$\Theta = \frac{1}{f} \ln(K_{\text{ads}} C_{\text{inh}}) \quad (3)$$

where θ represents the surface coverage, f is a constant associated with the variation of the adsorption free energy with coverage, K_{ads} is the adsorption equilibrium constant and C_{inh} is the inhibitor concentration. Eq. 3 predicts a linear correlation between Θ and $\ln C_{\text{inh}}$, which can be expressed as follow:

$$\Theta = \frac{1}{f} \ln K_{\text{ads}} + \frac{1}{f} \ln C_{\text{inh}} \quad (4)$$

From Eq. 4, the equilibrium constant of adsorption can be related to the standard free energy of adsorption as follow:

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

The dependence of coverage and inhibitor concentrations for the aniline and its derivatives are represented in Fig. 3. In Fig. 3 the *p*-nitroaniline data is not included, since the coverage values obtained for this inhibitor were negative. The coverage was taken from the percent efficiency of the inhibitor for concentrations between 10^{-5} M and 10^{-2} M , which are also presented in Table 1. Applying Eqs. 4 and 5, to the graphic in Fig 3, $\Delta G_{\text{ads}}^{\circ}$ values between 4 Kcal mol^{-1} and 5 Kcal mol^{-1} were calculated. With respect to the physical meaning of these values, some contradictory interpretations have been reported, which clearly suggests the role of the metal substrate on the type of interaction between the organic molecules and the metallic surface. Thus, $\Delta G_{\text{ads}}^{\circ}$ values greater than $23.9 \text{ Kcal mol}^{-1}$ are reported for chemisorption of thiourea on gold surfaces [44, 45]. On the other hand, a minimum value of $\Delta G_{\text{ads}}^{\circ}$ of $9.31 \text{ Kcal mol}^{-1}$ for chemisorption of thiourea on iron surfaces, is reported [46]. Considering the previous information, the $\Delta G_{\text{ads}}^{\circ}$ values obtained for the aniline-copper system suggest that the organic compound is physisorbed at the metal substrate surface.

Weight loss measurements

From the percent of weight loss of copper with time, obtained in the absence and presence of aniline and its derivatives, aniline inhibits copper corrosion for exposure times longer than 50 h, while the substituted anilines for exposure times longer than 150 h. Although the influence of the anilines is negligible for exposure times up to 20 h, this becomes more significant with increasing exposure time. This indicates that adsorption of aniline proceeds slowly, possibly as a result of the strong adsorption of chloride species. Further, aniline is protonated in acid so it is forming ion pairs with chloride ions. The interaction energies for ion pairing are comparable to the energies involved in aniline adsorption so the driving force for aniline molecules to adsorb on copper are rather small. In addition, composition

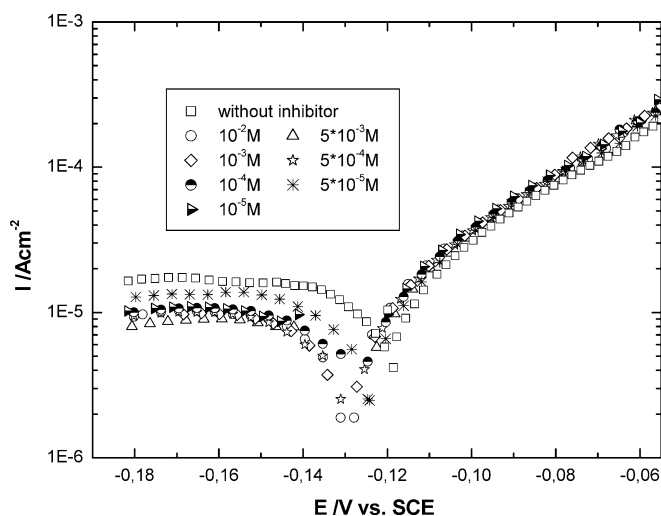


Fig. 2 Polarization curves for copper in 0.1 M HCl in the absence and presence of different concentrations of aniline

Table 1 Electrochemical parameters of copper in 0.1 M HCl without and with different concentrations of *p*-substituted anilines

	Conc (M)	E_{corr} (V)	I_{corr} (A cm ⁻²)	$-b_c$ (mV dec ⁻¹)	b_a (mV dec ⁻¹)	IE (%)
Blank		-0.122	9.37E-06	126	44	
Aniline	10 ⁻⁵	-0.132	7.44E-06	162	69	20.60
	5×10 ⁻⁵	-0.127	7.20E-06	74	42	23.16
	10 ⁻⁴	-0.129	6.77E-06	123	41	27.75
	5×10 ⁻⁴	-0.132	4.92E-06	71	37	47.49
	10 ⁻³	-0.132	4.62E-06	53	35	50.69
	5×10 ⁻³	-0.132	6.76E-06	167	44	27.85
	10 ⁻²	-0.136	5.24E-06	36	42	44.08
4-Chloroaniline	10 ⁻⁵	0.117	6.74E-06	96	41	28.07
	5×10 ⁻⁵	-0.126	6.83E-06	92	52	27.11
	10 ⁻⁴	-0.122	4.92E-06	63	36	47.49
	5×10 ⁻⁴	-0.116	6.08E-06	81	36	35.11
	10 ⁻³	-0.118	5.45E-06	81	35	41.84
	5×10 ⁻³	-0.121	6.18E-06	99	47	34.04
	10 ⁻²	-0.124	4.19E-06	61	39	55.28
4-Methylaniline	10 ⁻⁵	-0.122	4.76E-06	63	33	49.20
	5×10 ⁻⁵	-0.123	5.35E-06	79	46	42.90
	10 ⁻⁴	-0.119	4.74E-06	75	34	49.41
	5×10 ⁻⁴	-0.113	7.05E-06	127	34	24.76
	10 ⁻³	-0.123	5.16E-06	96	41	44.93
	5×10 ⁻³	-0.120	5.04E-06	80	39	46.21
	10 ⁻²	-0.120	4.33E-06	69	36	53.79
4-Nitroaniline	10 ⁻⁵	-0.118	5.29E-06	72	35	43.54
	5×10 ⁻⁵	-0.120	4.79E-06	60	34	48.88
	10 ⁻⁴	-0.116	8.33E-06	124	41	11.10
	5×10 ⁻⁴	-0.120	7.64E-06	140	46	18.46
	10 ⁻³	-0.123	5.61E-06	102	44	40.13
	5×10 ⁻³	-0.111	8.33E-06	156	37	11.10
	10 ⁻²	-0.115	9.71E-06	61	35	-3.63
4-Methoxyaniline	10 ⁻⁵	-0.125	5.77E-06	76	61	38.42
	5×10 ⁻⁵	-0.125	5.77E-06	101	43	38.42
	10 ⁻⁴	-0.124	5.46E-06	84	41	41.73
	5×10 ⁻⁴	-0.125	4.76E-06	72	38	49.20
	10 ⁻³	-0.121	5.16E-06	64	38	44.93
	5×10 ⁻³	-0.121	5.16E-06	89	37	44.93
	10 ⁻²	-0.135	5.16E-06	69	49	44.93

changes in the electrolyte, associated with the aggregation of anilines units, might also be important on the delayed effect of aniline on copper dissolution.

Theoretical results

Molecular mechanic calculations

In the first part of this study, we obtained the configuration of minimum energy for one molecule of aniline with the copper surface. The results showed that approaching the aniline molecule to the copper surface, no distortion of its structure results, maintaining a parallel orientation with respect the metal substrate surface. Similar results were obtained with approaching a molecule of the aniline derivatives to the copper surface. In addition, a preference for a diagonal alignment along cell (100) surface symmetry was found. In the second part of this study, we obtained the configuration of minimum energy for several molecules of anilines on the copper surface, revealing the same configuration than that of one inhibitor molecule, i.e. a parallel orientation to the copper surface and a diagonal alignment along cell (100) surface symmetry. In addition to the orientation of the organic molecules on the copper

surface, simulations of such systems showed no specific adsorption sites and no a specific symmetry for the adsorbate face. This indicates the absence of a high repulsive interaction adsorbate-adsorbate, which is possibly associated with the weak adsorbate-surface interaction. As mentioned in the experimental section, the previous results represent a first approach to the theoretical calculations and were the base to the quantum chemical calculations.

Quantum chemical calculations

First, we explored the possibility of correlating the electronic properties of isolated aniline molecules obtained from ab initio SCF-HF with the capacity of inhibition of the organic molecules obtained from the electrochemical experiments data. Table 2 includes the main properties for aniline molecules obtained from ab initio SCF-HF, with the corresponding experimental inhibition efficiencies. Net charges are analysed for the following groups: -NH₂, ring, and substituents (H-, Cl-, CH₃-, CH₃O- and NO₂-). Several authors have tried to correlate the experimental data for corrosion inhibition with quantum chemical data. Correlations between corrosion inhibition efficiency and a number of molec-

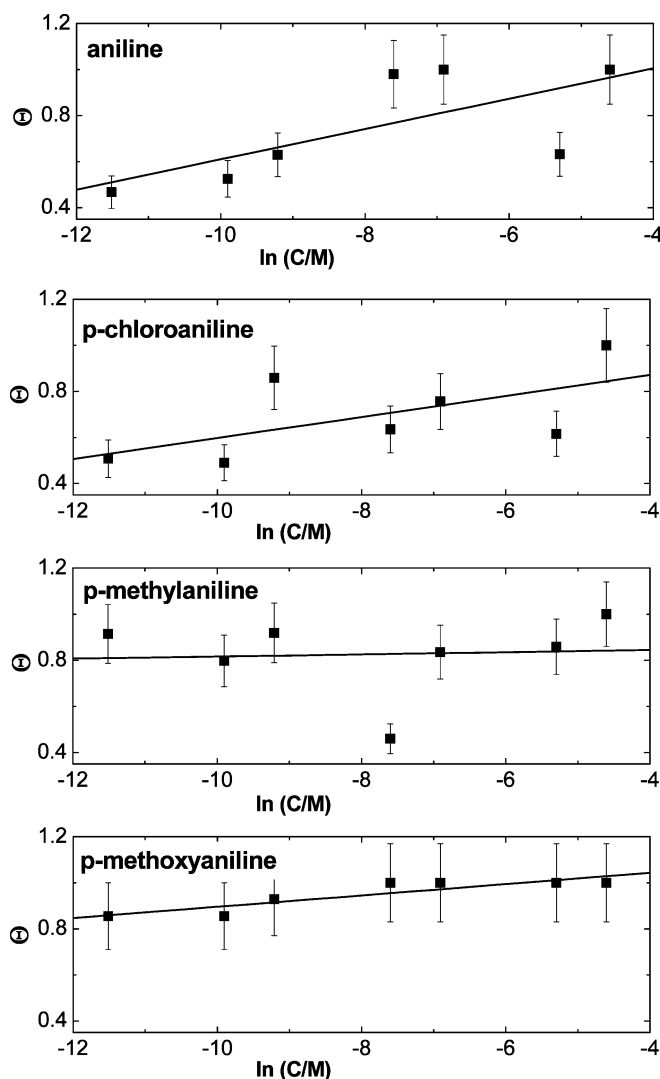


Fig. 3 Adsorption Temkin isotherms for the copper-inhibitor systems

ular properties such as orbital energies, dipole moment, charge density and heat of formation have been carried out [27–29]. From Table 2, no simple correlation can be derived. However, the analysis of these quantum parameters can help us to establish the most relevant properties for aniline molecules. The difference in the net

charge values in Table 2 correlates well with the electron acceptor or electron donor character of substituents. Further, the energy of frontier orbitals reveals clearly the electronic effect of the substituents. In general, the energy of the HOMO (the highest occupied molecular orbital) for aniline is increased by electron donor substituents and is decreased by electron acceptor substituents. In addition, the results suggest that electron donor substituents increase the electrophilic character of aniline. On the other hand, the substituents over the energy of the LUMO (the lowest unoccupied molecular orbital) give rise to an opposite effect so, electron acceptor substituents increase the nucleophilic character of aniline. The ($E_{LUMO}-E_{HOMO}$) gap is associated with another reactivity parameter, the molecular hardness [47]. From Table 2, the hardness is slightly affected by substituents and no clear tendency can be established. The dipole moment values in Table 2, which are related to the hydrophobic character of the molecules, reveal that the hydrophobic character of aniline increases with electron donor substituents and decreases with electron acceptor substituents. With respect to the correlation of the corrosion inhibition efficiency with quantum chemical parameters, the efficiency data for two inhibitor concentrations were considered, 10^{-5} and 10^{-3} M. From the data, for 10^{-5} M aniline in Table 2, electron donor substituents increase the corrosion inhibition efficiency as observed: $H < CH_3O- < CH_3-$, which follow an order with respect to the electron donor character of substituents. Although the previous observation suggests that an increase in the energy of the HOMO could increase the corrosion efficiency, for electron acceptor substituents is not possible to establish a similar tendency. For the data of 10^{-3} M aniline, however, a correlation between the $E_{LUMO}-E_{HOMO}$ values and the corrosion efficiencies is observed, the greater the gap the higher the corrosion efficiency. Similar correlations have been reported in the literature when inhibitors are chemisorbed on the copper surface [26], which is not the case here.

The interaction of aniline molecules with the copper surface for mean quantum chemical calculation using the cluster model showed a weak adsorbate–substrate interaction, with the aniline lying flat onto the copper surface. The same tendency was observed for all the studied systems, which are in good agreement with the

Table 2 Quantum chemical parameters for aniline molecules and inhibition efficiency

Aniline	q(NH ₂)	q(ring)	q(R)	E_{HOMO}	E_{LUMO}	Gap	μ	IE% ^a	IE% ^b
H-	-0.20	-0.01	0.21	-7.80	3.51	11.31	1.43	20.6	50.69
CH ₃ O-	-0.22	0.61	-0.39	-7.03	3.56	10.59	0.08	38.4	44.93
CH ₃ -	-0.21	0.32	-0.11	-7.52	3.49	11.01	1.09	49.2	44.93
Cl-	-0.20	0.32	-0.13	-8.17	3.00	11.17	4.17	28.1	48.84
NO ₂ -	-0.17	0.65	-0.48	-9.11	1.00	10.11	8.18	43.5	40.13

q(R) is the net charge for a specific group R (H, CH₃O, CH₃, Cl or NO₂). E_{HOMO} is the energy of the HOMO in e.V.; E_{LUMO} is the energy of the LUMO in e.V.; Gap is the difference $E_{LUMO}-E_{HOMO}$ in e.V.; μ is the dipole moment in Debye; IE% is the inhibitor efficiency: ^a 10^{-5} M and ^b 10^{-3} M

results obtained from molecular mechanic calculations. Thus, an equilibrium distance of 4.2 Å between the aniline molecule and the copper surface was found. On the other hand, the adsorption energies calculated from Eq. 2 were between 2 kcal mol⁻¹ and 5 kcal mol⁻¹, depending on the particular system, which are in good agreement with those calculated from the Temkin's isotherm. Further, the analysis of the charge density of the system showed that a charge transfer between the aniline molecule and the copper surface does not occur. Therefore, a pure electrostatic interaction between the anilines and the copper surface, describing a physisorption process, is thought to take place.

General conclusions

The electrochemical measurements of copper in the presence of aniline and its derivatives have shown that these compounds reduce the corrosion rate of copper in acid media in about 50%. The presence of substituents in *para* position in the aniline, whether they are electron acceptors or electron donors, do not affect the capacity of the aniline as an inhibitor of copper corrosion in acid media. Each compound is physisorbed on the copper surface following a Temkin behaviour. This suggests a low surface coverage, associated with the local adsorption of the inhibitor above cathodic sites, possibly copper surface areas free of corrosion products.

The type of adsorption of anilines seems to be related to the environment in which the aniline is dissolved. The Pourbaix diagram and the open circuit potential of the copper electrode in 0.1 M HCl, -0.19 V (SCE) suggest that the electrode surface is covered by CuCl and/or CuCl₂ [48]. The strong affinity between copper and chloride ions might hinder the direct adsorption of aniline on the copper surface. Although the presence of chloride ions at the electrode-solution interface is expected to favour the protonated aniline adsorption (pK = 4.63), because of its positive charge, the chemisorption of chloride species reduces the net negative charge of chloride to interact with aniline. In spite of that physically adsorbed aniline reduces the anodic dissolution of copper in 0.1 M HCl, which was visually observed for exposure times longer than 12 h. Considering the lack of influence of the anilines on the anodic and cathodic Tafel regions, it is unlikely that the local physisorbed inhibitors reduces copper dissolution by affecting the mechanism of copper corrosion in chloride acid solution. It is possible however, that aniline molecules concentrated at the electrodic interface form dimer or, tetramers with time, decreasing copper dissolution by limiting the diffusion of CuCl₂ species away from the Cu surface [49].

The effect of *p*-substituted anilines on the copper corrosion is different to that of *o*-substituted anilines, where efficiencies between 76% and 80% have been reported [9]. Further, for the same substituents, chloro and methyl, a comparison of the electrochemical data for the

o-substituted anilines [9] and the *p*-substituted anilines reported here, reveals differences in the values of the cathodic Tafel slopes. They are about 100 mV/decade greater for the *o*-substituted anilines than for *p*-substituted anilines, suggesting that the position of substituents is relevant to the kinetic of oxygen reduction and therefore, to the inhibiting capacity of the organic compounds. Despite the differences between the *ortho*- and *para*-substituted anilines, their adsorption on copper in hydrochloric acid media are similar, following a Temkin behaviour.

Theoretical calculations on the idealized copper-inhibitor system indicate that the maximum interaction between copper and aniline is achieved for a molecule-orientated parallel to the copper surface. For this configuration, aniline interacts with copper through the aromatic ring and therefore, the substituents in *para* position only affect the charge density of nitrogen atoms, then not playing a significant role in the inhibition capacity of the organic compound. Quantum chemical calculations suggest that there is no charge transfer between aniline and copper surface, indicating that on an idealized copper-inhibitor system aniline is physisorbed. On the other hand, from the inhibition performance of the anilines (Table 1) and the theoretical data in Table 2, no simple correlation to individual molecular parameters can be derived. Similar results have been reported for theoretical calculations on *o*-substituted anilines, where poor correlations between corrosion efficiency and molecular structure were determined [9]. The difficulty in obtaining a direct correlation between quantum chemical parameters and corrosion inhibition efficiency illustrates the complexity of the interactions involved in the corrosion protection by aniline molecules. It seems that the observed corrosion inhibition by aniline molecules is the result of its local adsorption on the copper surface. Along these lines new theoretical studies are in progress.

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