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A Study on the Adsorption of Benzotriazole on Copper in Hydrochloric Acid Using the Inflection Point of the Isotherm

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Abstract. This paper is a contribution to correlate benzotriazole (BTA) adsorption films on copper with BTA concentration in bulk solution with hydrochloric (HCl) acid. Three HCl concentrations were tested, 0.001, 0.005, and 0.01 M. Twelve BTA concentrations, from 1×10^{-5} to 1×10^{-1} M, were added to the HCl acid solution at four temperatures from 298 to 328 K. Commercial copper was used. Gravimetric measurements were performed after 3 h experimentation. The Frumkin isotherm gave the best fit to the experimental results. This result was based on the inflection point approach of the isotherm.

Keywords: copper, hydrochloric acid, benzotriazole, Frumkin and Damaskin-Parsons adsorption isotherms

1. Introduction

Pickling in dilute hydrochloric (HCl) and sulfuric (H_2SO_4) acids is the most common method for removing oxides formed on the surface of copper-based materials during mill processing and fabrication operations. Other chemical cleaning methods can be used, depending on the desired finish (Davis, 2001).

Tarnishing of copper alloys after pickling or degreasing operations is accelerated when the metal is inadequately dried or the final rinse solution is contaminated with the cleaning solution. Significant resistance to tarnishing after cleaning can also be obtained by incorporating inhibitors. Benzotriazole (BTA) is an effective corrosion inhibitor for copper in aqueous chloride solutions (Poling, 1970; Tromans and Li, 2002; Mansfeld et al., 1971). Two mechanisms have been proposed: the adsorption of single BTA molecules on the copper surface; and the formation of a protective polymeric film involving the complex ions Cu(I) and $(Cu^+BTA^-)_n$, (Lewis, 1981; Dugdale and Cotton,

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1963; Papapanayiotou et al., 1998). Nevertheless, despite the widespread use of BTA no consensus has been reached on its mechanism. There is also a lack of agreement regarding the orientation of BTA on the copper surface. Some authors propose a flat orientation on the surface and bonding through the lone-pair nitrogen orbital, with lone nitrogen atoms bonded to two copper atoms (Cotton and Scholes, 1967; Rubim et al., 1983; Tromans and Sun, 1991; Vogt et al., 1997). It has also been claimed that BTA does not lie flat on the surface, but that the nitrogen lone-pair orbital bonds to the copper surface atoms (Fang et al., 1986). An angle orientation not far from the horizontal and not vertically on the copper surface has also been proposed (Törnkvist, et al., 1989).

The aim of this paper is to study the copper adsorption mechanism of BTA in HCl acid solutions. The results are discussed using the interaction term (f) parameter, the configurational term (χ) parameter, and both f and χ parameters. Special attention is paid to studying the properties of the isotherms using the inflection point parameter.

2. Experimental

The commercial copper used had the following chemical composition (by weight %): 0.019 P, <0.001 Fe, <0.001 As, <0.001 Mn, <0.002 Sb, <0.001 Al, 0.009 Sn, 0.003 Ni, 0.015 Pb, <0.005 Ag, <0.001 Bi, <0.001 S, <0.005 C, the balance being Cu. The copper was phosphorus-reduced and had a low residual phosphorus content, Type C12000 (ASTM B-224 Standard).

The specimens, 5 cm × 5 cm, were mechanically cut from a sheet 1.0 mm thick. The calculated exposed specimen surface area was 52 cm^2. The specimens were dry hand-polished with emery paper down to grade 600, degreased with acetone, rubbed with cotton wool soaked in ethanol, dried at room temperature, weighed to determine initial mass, and tested immediately.

Three HCl acid concentrations were tested: 0.001, 0.005, and 0.01 M. Twelve BTA ($C_6H_4N_3H$) concentrations were tested: 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 10, 50, and 100×10^{-3} M. Commercial BTA compound and HCl acid were used (Merck analytical grade chemicals).

500 mL volume of the HCl acid solution were tested in a glass vessel in the presence and absence of BTA. The temperature was maintained at 298, 308, 318, and 328 K during the experiments by immersing the glass vessel in a thermostatically-controlled water bath. At the end of the experiments, each of 3 h duration, gravimetric experiments were performed after removal of the corrosion products using a 10% H_2SO_4 aqueous solution for 3 min at room temperature (ASTM G-1 Standard). An electronic analytical balance with a precision of $\pm 0.1 \times 10^{-3}$ g was used. All the experiments were performed in triplicate in a single cell, i.e. the gravimetric corrosion rate is listed as the average value of three specimens studied under identical experimental conditions. The reproducibility of the experimental gravimetric results was higher than 95%. Experimental procedure is in agreement with described elsewhere (Polo et al., 2003).

3. Results and Discussion

In order to study the adsorption of BTA on copper electrode surfaces, the properties of the isotherm equations from Eqs. (1) and (2) (shape, trend of slopes along the curve, and existence of inflection points) were analyzed as the characteristics that differentiate one adsorption equation from another (Frumkin, 1925; Damaskin et al., 1971):

$$kc = \left(\frac{\theta}{1-\theta}\right)\exp(-f\theta) \tag{1}$$

$$kc = \frac{\theta}{(1-\theta)^{\chi}}\exp(-f\theta) \tag{2}$$

The meaning of the parameters in the Eqs. (1) and (2) are as fallow: k is the equilibrium binding constant of the adsorption reaction:

$$\mathrm{Cu} + \mathrm{BTA} \leftrightarrow \mathrm{Cu(BTA)_{ads}} \leftrightarrow \mathrm{Cu^{n+}} + \mathrm{ne^-} + \mathrm{BTA} \tag{3}$$

given by $k = (\frac{1}{55.5})[\exp(-\frac{\Delta G^0_{\mathrm{ads}}}{RT})]$, the value 55.5 is the water concentration in the solution expressed in M, R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature, and $\Delta G^0_{\mathrm{ads}}$ is the adsorption energy; $\mathrm{Cu(BTA)_{ads}}$ is a reaction intermediate; f is the interaction term parameter ($f > 0$ lateral attraction interactions between the adsorbed BTA molecules, and $f < 0$ lateral repulsion interactions between the adsorbed BTA molecules); c is the inhibitor concentration; χ is the number of water molecules replaced by one molecule of organic inhibitor (also referred to as the size ratio parameter):

$$\mathrm{BTA_{aqu}} + \chi \mathrm{H_2O_{ads}} \leftrightarrow \mathrm{BTA_{ads}} + \chi \mathrm{H_2O_{aqu}} \tag{4}$$

where $\mathrm{BTA_{aqu}}$ is the inhibitor in the aqueous phase and $\chi \mathrm{H_2O_{ads}}$ is the number of water molecules adsorbed on the copper surface, χ is assumed to be independent of the coverage or charge on the electrode, and, finally, θ is given by the expression:

$$\theta = \frac{\text{CORROSION}_{\text{abs}} - \text{CORROSION}_{\text{pre}}}{\text{CORROSION}_{\text{abs}}} \qquad (5)$$

where $\text{CORROSION}_{\text{abs}}$ and $\text{CORROSION}_{\text{pre}}$ are the copper corrosion rate in the absence and presence of inhibitor, respectively. It should be noted that the IE (inhibition efficiency), as a %, is related with θ by the expression: $\text{IE} = \theta \times 100$. Equation (5) is valid on the assumption that: (i) the adsorption sites on the copper surface are homogeneous, (ii) a mono-layer inhibitor adsorption is formed, and (iii) corrosion is uniform and no localized attack takes place.

The best fit for a given theoretical isotherm is obtained when there is minimal difference between the experimental and calculated values. The expression used to optimize this difference is the objective function (F):

$$F = \sum_{i=1}^{p} w_i \left[c_{\exp_i} - c_{\text{cal}_i}(k, f, \chi)\right]^2 \qquad (6)$$

where the i subscript represents one value in a set of p concentrations of the BTA inhibitor ($1 \leq i \leq p$), c has been defined above (Eqs. (1) and (2): $c_{\exp}$ and c_{cal} are the inhibitor concentrations experimental and calculated, respectively), and w_i denotes the weight associated with the i-th experimental value. The next step is to choose the adequate parameters k, f, and/or χ to ensure that Eq. (6) has the minimum value.

The weights appearing in Eq. (6), which are all unity in the "unweighted" or unity-weighted situations, should ideally be defined by the inverse variance of the individual measurements.

The isotherms in Eqs. (1) and (2) are of the form:

$$kc = g(\theta, \chi)\exp(-f\theta) \qquad (7)$$

where $g(\theta, \chi)$ is the configurational term parameter (as pointed out above) that depends essentially on the physical model and assumptions underlying the derivation of the isotherm.

By considering Eq. (7), then Eq. (6) can be written as:

$$F(f, k) = \sum_{i=1}^{p} w_i \left[c_{\exp_i} - \left(\frac{1}{k}\right) g\left(\theta_{\exp_i}, \chi\right) \exp\left(-f\theta_{\exp_i}\right)\right]^2 \qquad (8)$$

Integer values for χ, for instance ranging from 1 to 5, were considered in this study.

Fitting has been carried out using the Levenberg-Marquardt (LM) algorithm to minimize F. The LM algorithm is robust, converges in many situations, is fast in computing time, and is a compromise between the Gauss-Newton method and the steepest descent method (Bastidas et al., 2001).

The Langmuir slope, $\frac{d\log(c)}{d\theta} = \frac{1}{\ln(10)}[\frac{1}{(1-\theta)\theta}]$, of the Langmuir equation: $kc = \frac{\theta}{1-\theta}$, shows that, for a given value of θ, the slope takes a constant value, regardless of the value of k. The term $(1-\theta)\theta$ is a parabolic function with a maximum at $\theta = 0.50$. Thus, the criterion for identifying Langmurian behavior in a θ versus $\log(c)$ plot lies in the characteristic slopes of the curves.

Figure 1 shows the slope of the Frumkin equation, $\frac{d\log(c)}{d\theta} = \frac{1}{\ln(10)}[\frac{1}{(1-\theta)\theta} - f]$, as a function of θ for copper immersed in 0.001, 0.005, and 0.01 M HCl acid solutions in the presence of BTA compound, at 298, 308, 318, and 328 K. A cubic spline polynomial

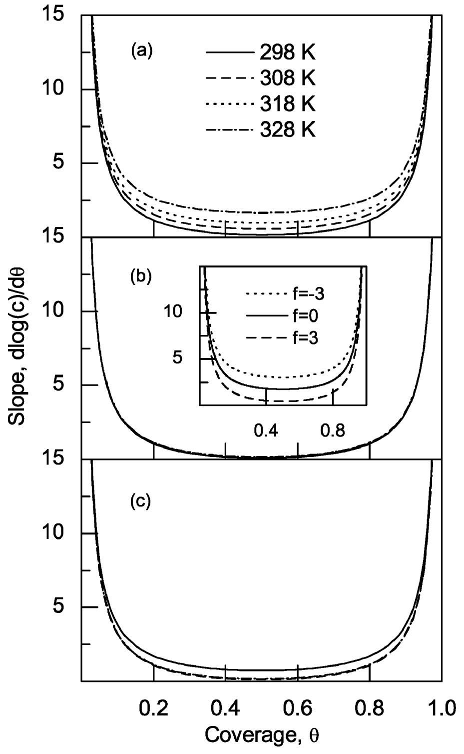

Figure 1. Slope versus coverage for copper in (a) 0.001, (b) 0.005, and (c) 0.01 M HCl acid solutions at 298–328 K in the presence of BTA and for different values of f (inset) using the Frumkin equation.

algorithm:

$$\mathrm{A}\left[\log(c)\right]^3 + \mathrm{B}\left[\log(c)\right]^2 + \mathrm{C}[\log(c)] + \mathrm{D} \qquad (9)$$

where A, B, C, and D are constants, was used to interpolate the adsorption data in the unmeasured BTA concentration domain between each pair of experimental data and to obtain the derivative, $\frac{d\log(c)}{d\theta}$, for a continuous function.

The case where lateral attractive interactions between BTA molecules arise ($f > 0$) can be directly identified by observing the slope at intermediate coverage values. The slope of the Frumkin equation is steeper than that of the Langmuir equation, and the deviation is due to a positive f value. For lateral repulsive interactions ($f < 0$) the slope of the Frumkin equation is less steep than that of the Langmuir equation. For the case where $f = 0$, the slope of the Frumkin equation is simplified to the slope of the Langmuir equation. This means that, compared with the Langmuir equation, in the Frumkin equation the slope is modified by a constant value f. This effect is shown graphically in the theoretical inset of Fig. 1, where the slope, $\frac{d\log(c)}{d\theta}$, of the Frumkin equation is plotted as a function of θ.

Figure 1 inset also shows that the Langmuir equation ($f = 0$) exhibits a minimum slope for intermediate coverage. At high or low coverage the slope values are determined by the term $\frac{1}{(1-\theta)\theta}$, which dominates whenever $\frac{1}{(1-\theta)\theta} \gg f$. Thus, f is only able to modify the slope at intermediate coverage values (when $\frac{1}{(1-\theta)\theta} \sim f$) by shifting the Langmuir slope by a constant value of f. This shift can be positive (rising) for $f < 0$ or negative (falling) for $f > 0$ (see Fig. 1 inset). This property is not exclusive to the Frumkin equation, and can be extended to any adsorption isotherms which include the $\exp(-f\theta)$ term, e.g. Hill-de Boer, Parsons, Damaskin-Parsons, and Kastening-Holleck equations (Hill, 1952; De Boer, 1953; Parsons, 1964; Kastening and Holleck, 1965).

The two-parameters (k and f) in the Hill-de Boer, $kc = (\frac{\theta}{1-\theta})\exp(\frac{\theta}{1-\theta})\exp(-f\theta)$, and Parsons, $kc = (\frac{\theta}{1-\theta})\exp[\frac{2-\theta}{(1-\theta)^2}]\exp(-f\theta)$, equations are similar to the Frumkin equation. They produce S curves with distinctive inflection points (θ_{ip}) at 0.33 for Hill-de Boer and at 0.21 for Parsons equations (see Fig. 2(a)). This feature can be appreciated from their derivatives. Figure 2(b) shows the theoretical variation of $\frac{d\log(c)}{d\theta}$ as a function of θ using the Frumkin, Hill-de Boer, and Parsons equations. The minima correspond to the θ_{ip} of the slope (in a θ versus BTA concentration plot), which is characteristic of each equation and independent of the k and f parameters. Finally, the Hill-de Boer and Parsons equations are depressed curves, and the slopes of the isotherms are sensitive to f changes for $\theta \sim \theta_{ip}$.

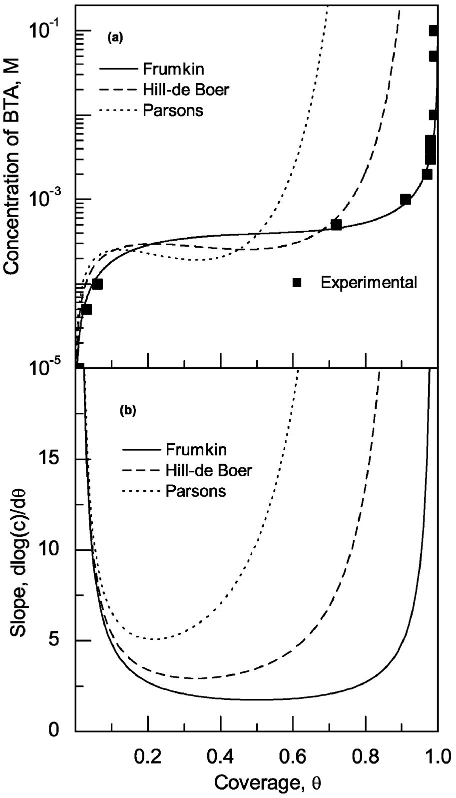

Figure 2. Copper in 0.001 M HCl acid solution in the presence of BTA at 298 K. (a) BTA concentration versus coverage using Frumkin ($f = 3.60$ and $k = 422.21$), Hill-de Boer ($f = 7.58$ and $k = 237.96$), and Parsons ($f = 13.56$ and $k = 1203.57$); (b) theoretical variation of slope versus coverage using Frumkin, Hill-de Boer, and Parsons equations for $f = 0$.

Figure 3 shows θ versus BTA concentration for copper immersed in 0.001 M HCl acid solution at 298 K using the Damaskin-Parsons, $kc = [\frac{\theta}{(1-\theta)^{\chi}}]\exp(-f\theta)$, (Fig. 3(a)) and Kastening-Holleck, $kc = [\frac{\theta}{\chi(1-\theta)^{\chi}}][1 - \theta + \frac{\theta}{\chi}]^{(\chi-1)}\exp(-f\theta)$, (Fig. 3(b)) equations. As can be observed, a poor fit was obtained between the experimental and simulated data except for $\chi = 1$, in which the Damaskin-Parsons and Kastening-Holleck equations coincide with the Frumkin equation. Adsorption equations that contain the χ parameter have the overall effect of depressing an adsorption curve. This is shown for the Damaskin-Parsons equation in the theoretical inset of Fig. 3(a) and for the Kastening-Holleck equation in the theoretical inset of Fig. 3(b).

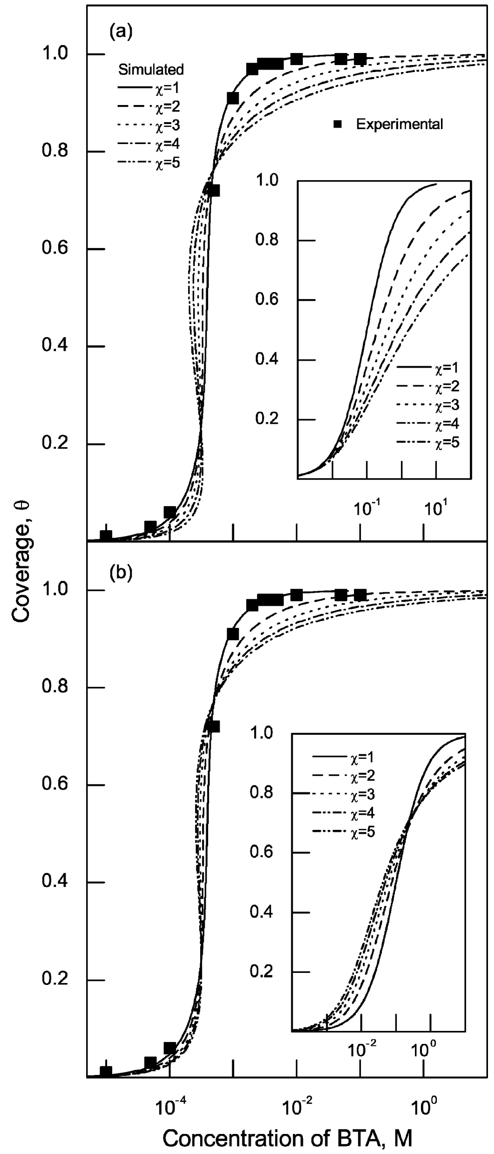

Figure 3. Coverage versus BTA concentration for copper in 0.001 M HCl acid solution at 298 K and for different values of χ (inset, theoretical behavior) using: (a) the Damaskin-Parsons equation for $\chi = 1$ ($f = 3.60$ and $k = 422.21$), $\chi = 2$ ($f = 5.81$ and $k = 329.39$), $\chi = 3$ ($f = 8.02$ and $k = 256.98$), $\chi = 4$ ($f = 10.23$ and $k = 200.49$), and $\chi = 5$ ($f = 12.44$ and $k = 156.41$); and (b) the Kastening-Holleck equation for $\chi = 1$ ($f = 3.60$ and $k = 422.21$), $\chi = 2$ ($f = 5.15$ and $k = 169.21$), $\chi = 3$ ($f = 6.03$ and $k = 96.34$), $\chi = 4$ ($f = 6.61$ and $k = 64.43$), and $\chi = 5$ ($f = 7.03$ and $k = 47.25$).

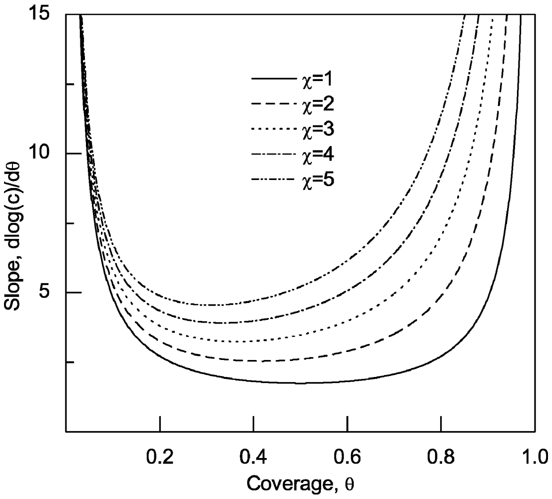

Figure 4. Slope versus coverage for $f = 0$ and different values of χ using the Damaskin-Parsons equation.

The derivative of the Damaskin-Parsons equation,

$$\frac{1}{\ln(10)}\left[\frac{1}{(1-\theta)\theta}+\frac{\chi-1}{1-\theta}-f\right],$$

is identical to the Frumkin slope, apart from the term: $\frac{\chi-1}{1-\theta}$. Figure 4 shows that the contribution of this term increases as the value of θ rises and is responsible for the overall depression of the adsorption equation curve.

The derivative of the Kastening-Holleck equation,

$$\frac{1}{\ln(10)}\left[\frac{1}{(1-\theta)\theta}+\frac{\chi-1}{1-\theta}\right.$$
$$\left.-\frac{(\chi-1)^2}{\chi}\left(1-\theta+\frac{\theta}{\chi}\right)^{-1}-f\right],$$

is identical to the Damaskin-Parsons slope, apart from the term: $-\frac{(\chi-1)^2}{\chi}(1-\theta+\frac{\theta}{\chi})^{-1}$. The latter term is the least important, and affects the low coverage region. The minimum of the slope values in Fig. 4 serves as a criterion for distinguishing between species that adsorb according to the χ parameter and those that adsorb according to the Langmuir and Frumkin equations, which present a constant θ_{ip} at ~0.50. Finally, it should be said that the derivatives of the Flory-Huggins and Dhar-Flory-Huggins equations are identical to the derivative of the Damaskin-Parsons equation, apart from the term f.

From the preceding discussion it is concluded that the Frumkin equation best describes the adsorption of BTA compound on copper electrode surfaces in the presence of 0.001, 0.005, and 0.01 M concentrations of HCl acid. The discussion is now centered on results using the Frumkin equation.

Figure 5 shows θ versus BTA inhibitor concentration for copper in 0.001, 0.005, and 0.01 M concentrations

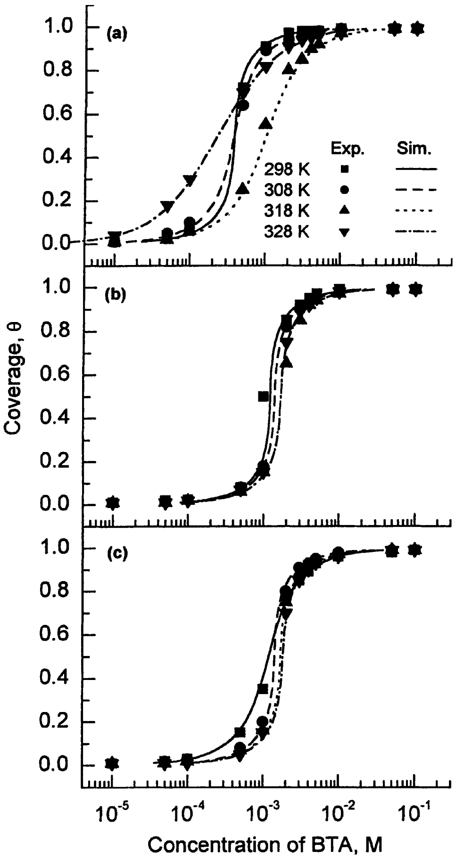

Figure 5. Coverage versus BTA concentration for copper in: (a) 0.001, (b) 0.005, and (c) 0.01 M HCl solution using the Frumkin equation.

Table 1. Lateral interaction parameter (f), adsorption energy (ΔG^0_{ads}) and binding constant (k) for BTA using the Frumkin equation in HCl acid.

Temperature (K)	f	ΔG^0_{ads} (kJ mol^{-1})	k
	0.001 M HCl acid		
298	3.60	−24.9	422
308	2.69	−27.0	676
318	1.75	−26.5	405
328	0.18	−33.5	944
	0.005 M HCl acid		
298	3.81	−21.9	121
308	3.73	−22.3	110
318	3.63	−22.7	96
328	3.63	−23.4	96
	0.01 M HCl acid		
298	2.28	−23.8	271
308	3.73	−22.3	111
318	3.63	−22.7	96
328	3.60	−23.3	91

of HCl acid, and from 298 to 328 K using the Frumkin equation. This figure also shows the simulated data using the Frumkin isotherm. All the curves in Fig. 5 show an *S* shape, as is predicted by the Frumkin equation, defining three regions on the isotherm plot: (i) at low inhibitor concentrations an increase in the inhibitor concentration does not produce an increase in θ; (ii) at intermediate inhibitor concentrations a small increase in the inhibitor concentration causes a high θ (a linear dependence of θ versus log(c)); and (iii) at high inhibitor concentrations θ is independent of the inhibitor concentration. It should be noted that no pitting corrosion was observed on the copper surface after experimentation in the presence and absence of BTA.

Table 1 includes f, ΔG^0_{ads}, and k parameters from Fig. 5. The value of f is different from zero and consequently is another proof that the adsorption mechanism cannot be related with the Langmuir equation model. The f parameter values are positive. The small and positive value of the f parameter indicates a weak attraction between the adsorbed BTA molecules. The negative value of the ΔG^0_{ads} parameter indicates that the reaction proceeds spontaneously for BTA compound and is accompanied by highly efficient adsorption. The high value of the k parameter produces electrical interaction between the double layer existing at the phase boundary and the adsorbing BTA molecules.

The inhibition mechanism of BTA may be explained by the $\text{Cu(BTA)}_{\text{ads}}$ reaction intermediates, see Eq. (3) (Bockris and Drazic, 1962). At first, when there is not enough $\text{Cu(BTA)}_{\text{ads}}$ to cover the copper surface, because the inhibitor concentration is low or because the adsorption rate is slow, metal dissolution takes place at sites on the copper surface free of $\text{Cu(BTA)}_{\text{ads}}$. With a high inhibitor concentration an inhibitor overlayer is formed on the copper which reduces chemical attacks on the metal.

4. Conclusions

The Frumkin equation model best describes the adsorption of BTA compound on copper electrode surfaces in the presence of 0.001, 0.005, and 0.01 M concentrations of HCl acid, and at four temperatures from 298 to 328 K.

The inflection point (θ_{ip}) and the shape of the isotherm plot provide a good approach to discerning between the interaction (f) and substitutional (χ) term parameters in the adsorption process of BTA on copper surface.

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