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Prediction of Isotherm Concerning Dual Competitive and Enhancing Action of Chloride Ion on Benzotriazol Adsorption on Heterogeneous Steel Surface

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Adsorption of benzotriazol on steel surface from hydrochloric acid solutions was studied indicating decrease of corrosion inhibition effectiveness and surface coverage as hydrochloric acid concentration increases. Considering competitive action of chloride ions with benzotriazol molecules for adsorption on steel, Jaroniec adsorption isotherm for adsorption of two components of different molecular sizes on heterogeneous solids is not applicable to our results except at high benzotriazol concentrations and could not explain experimental behaviours. An adsorption isotherm concerning enhancing and competitive action of chloride ion on benzotriazol adsorption is predicted, which is applicable to and explains experimental results.

Key Words: Corrosion, Benzotriazol adsorption isotherm, Steel surface.

INTRODUCTION

Benzotriazol (BTA) and its derivatives are largely employed as efficient corrosion inhibitors for copper and its alloys[1–4] and for steel[5, 6]. In acidic media, BTA as most of the organic effective inhibitors containing nitrogen as hetero atoms in their structure are capable of forming coordinate covalent bond with metals owing to their free electron pairs and thus acting as inhibitors by surface coverage. Also organic compounds with π-bond exhibit good inhititive properties due to interaction of π-bond orbital with metal surface[5, 7–9].

The electrochemical study of the effect of some BTA derivatives as inhibitors of corrosion of steel in 0.1 M hydrochloric acid solution[5] indicates that the inhibition was under anodic control and it is due to adsorption of inhibitor on steel surface. The results were explained in the light of corrosion mechanism of iron and steel in hydrochloric acid solutions[10] which are represented by the following equations:

On anodic sites:

$$Fe + Cl^- \rightleftharpoons (FeCl^-)_{ads} \tag{1}$$

$$(FeCl^-)_{ads} \rightleftharpoons (FeCl)_{ads} + e^- \tag{2}$$

$$(FeCl)_{ads} \rightleftharpoons FeCl^+ + e^- \tag{3}$$

$$FeCl^+ \rightleftharpoons Fe^{2+} + Cl^- \tag{4}$$

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On cathodic sites:

$$Fe + H^+ \rightleftharpoons (FeH^+)_{ads} \quad (5)$$

$$(FeH^+)_{ads} + e^- \rightleftharpoons (FeH)_{ads} \quad (6)$$

$$(FeH)_{ads} + e^- + H^+ \rightleftharpoons Fe + H_2 \quad (7)$$

Considering that in acidic solutions imine group is protonated to form positive organic molecule[11, 12], for example,

$$BTA + H^+ \rightleftharpoons (HBTA^+)$$

Bereket *et al.*[5] refer to that protonated molecule as (org^+) and explain the inhibition mechanism as follows:

1. Physical adsorption of the org^+ ion may take place due to electrostatic interaction with $(FeCl^-)_{ads}$ species in step (1) eqn. (1) as:

$$(FeCl^-)_{ads} + org^+ \rightleftharpoons (FeCl^-)_{ads} - org^+ \quad (8)$$

2. Chemisorption of neutral molecule with metal surface occurs following deprotonation of the protonated ions as:

$$(FeCl^-)_{ads} - org^+ \rightleftharpoons (Fe\text{-}org{\cdot}mol)_{ads} + Cl^- + H^+ \quad (9)$$

So, the rest of the corrosion steps 2–7 cannot proceed.

Our work is aimed to study the effect of hydrochloric acid concentration on the adsorption of BTA on heterogeneous steel surface by measuring its surface coverage to estimate the suitable adsorption isotherm which can be applicable to the results and explain the effect of chloride ion concentration in concordance with the mechanism of corrosion and inhibition process[5, 10].

EXPERIMENTAL

All chemicals used were of analytical grade and the conductivity water of grade (410^{-6} ohm^{-1} cm^{-1}) was used in the preparation of test solutions and in washing specimens and glass equipments.

Test solutions were prepared as:

1. A set of pure hydrochloric acid solutions with concentrations (C_2) equal to 1, 1.5, 2, 2.25, 2.5, 2.75 and 3 M were prepared.
2. Another set of inhibited acid solutions with (BTA) of concentrations (C_1) equal to 10, 12, 14, 16, 18, 20×10^{-3} M were prepared from each of the pure acid concentrations.

Weight loss corrosion test[13–15]

Specimens of low carbon steel in the form of discs of 5 cm^2 cross-sectional area, were isolated from test solution except one of its circular surface for exposure to test solution after polishing by metallurgical emery papers (120–800), water washing, acetone washing and drying.

The specimen was immersed in 500 cm^3 of test solution at 25°C, stirred before and during exposure time (120 min) with pure argon (Globale Product, France). The specimen was washed with hot conductivitiy water during brushing by a hard plastic brush, then washing water was added to the test solution. All or part of the test solution was titrated with standard 0.01 N $K_2Cr_2O_7$ solution for determination of weight loss or dissolved iron[16].

Corrosion rate was determined as weight loss per unit time per unit area[14] if corrosion rate in pure acid is W_1 and in inhibited acid is W_2. So, inhibition effectiveness (F) is determined as:

$$F = [(W_1 - W_2)/W_1] \times 100$$

$$\text{Surface coverage } \theta = 1 - (W_2/W_1)$$

N.B.: The use of large volume of test solution (500 cm^3) for small area specimn (5 cm^2) was done to be sure that there was no significant change in both BTA and hydrochloric acid concentration after exposure, *i.e.*, equilibrium concentration ≅ initial concentration.

RESULTS AND DISCUSSION

Fig. 1 illustrates the relation between inhibition effectiveness (F) and BTA concentration C_1 mol/L at different values of hydrochloric acid concentration C_2 mol/L. The results indicate that as the acid concentration C_2 increases, the effectiveness F decreases; specially in the range from 2–3 mol/L the decrease in F is very sharp.

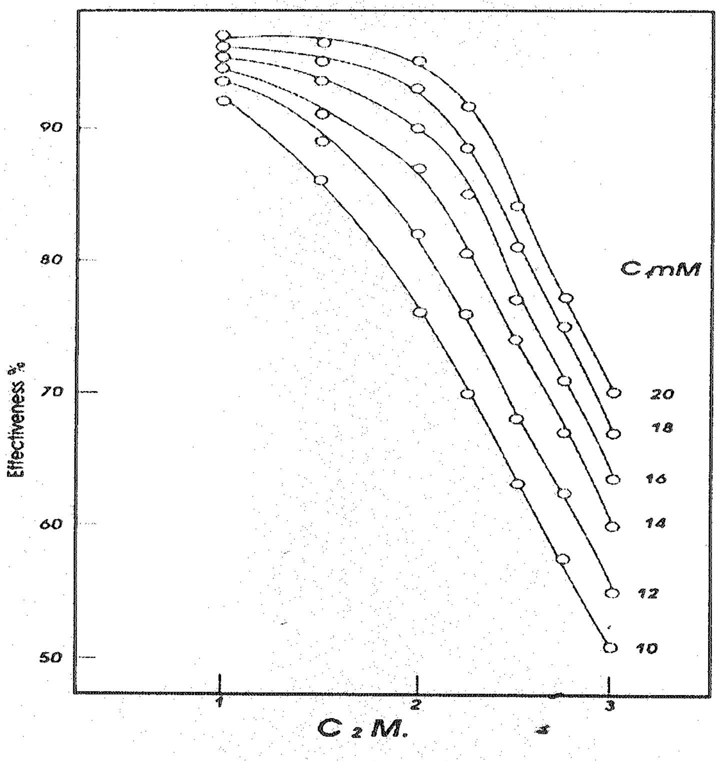

Fig. 1. Relation between effectiveness (F) and (BTA) concentration C_1 M at different HCl concentration C_2 M

From the values of surface coverage θ, we aimed to find the suitable adsorption isotherm which can be applicable to the experimental results in all tested acid and inhibitor concentrations and can explain the decrease of F and θ as hydrochloric acid concentration increases.

In the light of the previously mentioned corrosion and corrosion inhibition mechanism[5, 10], the final image at equilibrium was that part of the metal surface which is covered with chemisorbed BTA molecules and the rest of the surface $(1-\theta)$ is covered with chloride ion (Cl^-) physically adsorbed on the surface [eqn. (1)] with or without ($HBTA^+$) ion physically adsorbed on it [eqn. (8)].

We consider that Cl^- has competitive action with BTA for adsorption on metal surface and applying Jaroniec[17] isothermfor multi-adsorption from dilute aqueous solution for two components 1 and 2 with different sizes r_1 and r_2 on heterogeneous solid, the isotherm eqation is:

$$[a_1/(a_2)^{r_{12}}] = [k\ C_1/(C_2)^{r_{12}}]^m$$

and in the logarithmic form,

$$\log a_1 - r_{12} \log a_2 = m \log K - mr_{12} \log C_2 + m \log C_1$$

where r_{12} is the molecular size ratio of components (1) and (2) = r_1/r_2, and a_1 and a_2 are the amounts adsorbed of components (1) and (2) at concentrations C_1 and C_2, respectively, m is the heterogeneity parameter which is related to molecular sizes of adsorbate and specific relation between adsorbate and topography of the solid surface and K is the adsorption equilibrium constant. By considering BTA as component (1) and amount adsorbed a_1 represented by θ and chloride ion as component (2) with amount adsorbed a_2 represented by $(1-\theta)$, the ratio r_{12} = size of BTA/size of Cl^- was calculated from BTA molecular structure, bond lengths and bond angle[18] and from the chloride ion size[19] the ratio $r_{12} = 2.03$. The isotherm equation becomes

$$\log \theta - r_{12} \log (1-\theta) = m \log K - mr_{12} \log C_2 + m \log C_1$$

Plot of $[\log \theta - r_{12} \log (1-\theta)]$ *vs.* $\log C_1$ gives a straight line of slope m and intercept with y-axis = $(m \log k - mr_{12} \log C_2)$, from which one can calculate log K and adsorption free energy change ΔG, where $\Delta G = -2.303\ RT \log K$ and heterogeneity parameter (m) for each chloride ion concentration C_2. Jaroniec isotherm[17] is not applicable to our results except at BTA concentration from 14×10^{-3} to 20×10^{-3} M. Fig. 2 in this range values of log K, G and m *vs.* acid concentration C_2 are illustrated in Fig. 3. This result indicates that:

1. ΔG values are negative indicating spontaneous adsorption process but the values are in the range from −14.614 kJ/M at 1 M HCl to −17.693 kJ/M at 3 M HCl, which is less than 42 kJ/M, indicating weak physical adsorption[20–22] while the corrosion inhibition mechanism[5, 10] shows final strong chemisorption of neutral organic molecule; this also is in contradiction with observed high effectiveness F and surface coverage in Fig. 1 specially at low hydrochloric acid concentration.
2. The increase of log k from 2.56 at $C_2 = 1$ M to 3.0993 at $C_2 = 3$ M is the reverse of the expected decrease according to the decrease of F and by increasing C_2 (Fig. 1).

So it was illustrated that Jaroniec isotherm[17] is not our goal; accordingly we had to predict a new isotherm, which can be applicable and concord with the results. From the corrosion inhibition mechanism it is clear that the role of chloride ion is not only competing with BTA for adsorption on metal surface but also enhancing

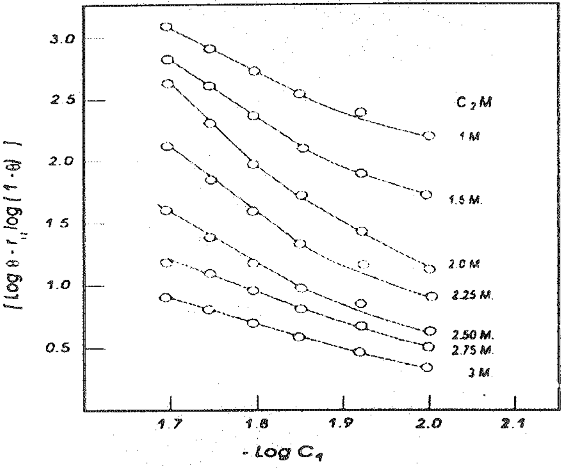

Fig. 2. Jaroniec adsorption isotherm representing the relation between [log $\theta - r_{12}$ log $(1 - \theta)$] *vs.* log C_1 for adsorption of BTA of concentration C_1 M at different concentrations of chloride ion C_2 M

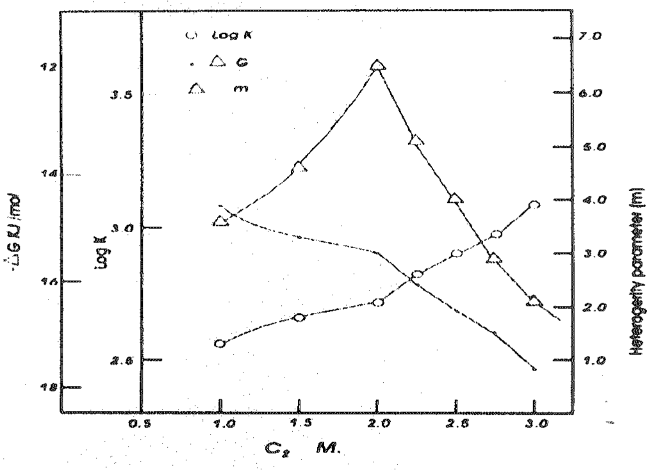

Fig. 3. Values of log K, ΔG and m at different values of chloride ion concentrations C_2

BTA chemisorption process equations (8) and (9), we suggested the following isotherm equation:

$$\theta/(1 - \theta) = (r_{12}/m \cdot C_2)^{C_1C_2r_{12}m}$$

where θ, r_{12}, C_1, C_2, m and K have the same identifications as in Jaroniec isotherm[17]. The term (r_{12}/mC_2) represents the competitive action of chloride ion of concentration C_2 where the term $K^{C_1C_2mr_{12}}$ represents its enhancing action.

The logarithmic form of this iostherm is

$$\log [\theta/(1 - \theta)] = \log (r_{12}/mC_2) + C_2C_2r_{12}m \log k$$

Plot of log $[\theta/(1 - \theta)]$ *vs.* C_1 gives straight lines for all values of C_2 and C_1 (Fig. 4), the slope = $mC_2 r_{12}$ log k and the intercept = log $[r_{12}/(mC_2)]$. By substituting the values of r_{12}, C_2 in the intercept, we calculate m; substituting m in the value of slope we calculate log k = slope/(mr_{12} C_2).

The values and relation between log k, m and G at different values of chloride ion concentrations C_2 are given in Fig. 5 which indicates the following:

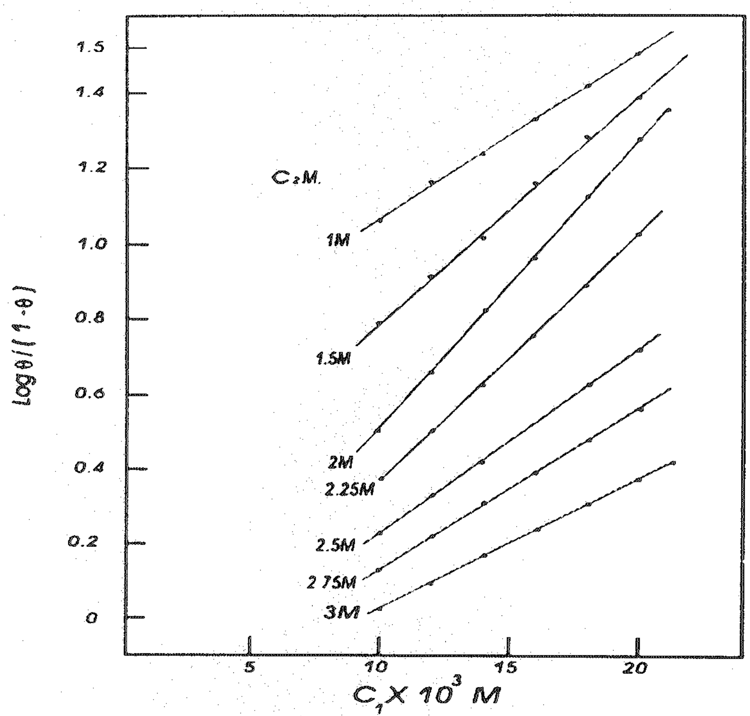

Fig. 4. Predicted adsorption isotherm representing the relation between log θ/(1 – θ) *vs*. BTA concentration C_1 M at different chloride ion concentrations C_2 M

1. The predicted isotherm is applicable to experimental results in all tested chloride ions and BTA concentrations.
2. At high chloride ion concentration from 2.5–3 M, the values of ΔG indicate spontaneous physical adsorption while at low C_2 from 1–2.5 M indicate spontaneous chemisorption[20–22].
3. As chloride ion concentration increases the value of log K decreases which explains and is in agreement with the experimental decrease of (F) and θ with the increase of C_2. The previous results conduct us to suggest the following steps to be added to Bereket *et al.*[5], corrosion inhibition mechanism. Considering that BTA can act as cathodic inhibitor as well as anodic inhibitor:
   (a) Physical adsorption of (BTA) protonated ion ($HBTA^+$) on cathodic sites as

$$Fe_{cath} + (HBTA^+) \rightleftharpoons [Fe(HBTA^+)]_{ads} \qquad (10)$$

   (b) Chemisorption of neutral organic molecules following deprotonization

$$[Fe\ (HBTA^+)]_{ads} \rightleftharpoons [Fe\text{-}(BTA)]_{ads} + H^+ \qquad (11)$$

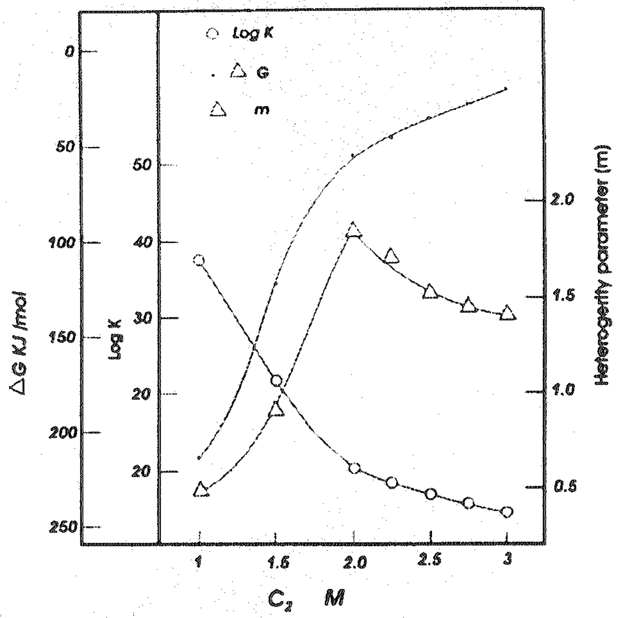

Fig. 5. Values of log K, G and m at different values of chloride ion concentrations C_2

As general results we get the following species adsorbed on metal surface according to the conditions:

	Represented by
1. $(FeCl^-)_{ads}$ physically adsorbed resulting from eqn. (1)	$(1 - \theta)$
2. $(FeCl^-)_{ads}$ $(HBTA^+)$ physically adsorbed resulting from eqn. (8)	θ
3. $[Fe(HBTA^+)]_{ads}$ physically adsorbed resulting from eqn. (10)	
4. $(Fe\text{-}BTA)_{ads}$ by chemisorption resulting from eqns. (9 and 11)	

We concluded that:

At low chloride ion concentrations, the chance for eqn. (8) to proceed is high due to low competitive action of chloride ion. Also the low hydrogen ion concentration and its much smaller size than that of $(HBTA^+)$ give high chance for steps in eqns. (10) and (11) to proceed.

So, most of adsorbed species $[Fe\text{-}(BTA)]_{ads}$ (chemisorption) which explain lower heterogeneity parameter m = 0.48 at 1 M chloride ion concentration and the chemisorption is in agreement with the high value of (log K) and high spontenity of adsorption indicated by ΔG values (Fig. 5).

At high chloride ion concentration C_2 competitive action with $[BTA^+]$. For adsorption on steel surface is high, from other hand negative chloride ions in the solution bulk attract $[HBTA^+]$ and using it in forming Cl^- solvation layer specially in case of lack of H_2O molecules at this high Cl^- concentration leading to decrease of free $[HBTA^+]$ in solution bulk; accordingly its adsorption either on cathodic site (eqn. 10) or physical adsorption on the adsorbed chloride ion (eqn. 8) decreased one can say that at high chloride ion concentration not only there is competitive action between chloride ion and [HBTA$^+$] for adsorption on metal surface but also there is competing of bulk chloride ion and metal surface for attracting [HBTA$^+$], so most of adsorbed species are physically adsorbed $(FeCl^-)_{ads}$ and some of $[Fe(HBTA^+)]_{ads}$; this explains the low value of (log K) at high chloride ion concentration C_2 which is in agreement with the experimental low values of effectiveness (F) and surface coverage (θ) and explain the higher heterogeneity parameter (m = 1.41) than that at 1 M chloride ion concentration (Fig. 5).

At moderate chloride ion concentration at $C_2 = 2$ M, one expects all types of adsorption, which explain the maximum value of heterogeneity parameter m = 1.85 at 2 M chloride ion concentration and moderate values of log K and ΔG (Fig. 5).

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