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Corrosion Inhibition Mechanism Concerning Adsorption of Sulfate, Hydrogen Sulfate Anions and Benzotriazol from Sulfuric Acid Solutions on Heterogeneous Steel Surface

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The adsorption of benzotriazol on heterogeneous steel surface from H_2SO_4 solutions of different concentrations was studied by its corrosion inhibition effectiveness. A mechanism of corrosion and corrosion inhibition of carbon steel by benzotriazol illustrate the dual effect of enhancing and competitive influences of sulfate and hydrogen sulfate anions with benzotriazol for adsorption on steel surface. Ismaeel adsorption isotherm for adsorption of multicomponent with different molecular sizes and action on heterogeneous surface is applicable to experimental results at all H_2SO_4 and benzotriazol concentrations. It gives values of adsorption free energy change (ΔG) and heterogeneity parameter (m), which agree with inhibition mechanism and explain the decrease of surface coverage (θ) with benzotriazol as acid concentration increase.

Key Words: Corrosion, Inhibition, Heterogeneous surface, Steel, Adsorption.

INTRODUCTION

The adsorption of benzotriazol (BTA) and its derivatives from acid solutions on steel surface was studied[1-5] by its action as corrosion inhibitors for steel in these solutions acting by surface coverage through its physical or chemical adsorption by forming coordinate covalent bond with metal surface. This behaviour is due to its nitrogen free electron pairs and also its bonds orbitals interaction with metal surface[1,6-8].

Bareket *et al.*[1] studied some of benzotriazol derivatives as corrosion inhibitors of steel in hydrochloric acid solution, in the light of corrosion mechanism[9] which consider the physical adsorption of Cl^- on metal surface anodic sites as a first step of corrosion mechanism:

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

This lead to formation of Fe^{2+}, Cl^- and $2e^-$ transfer to act on the cathodic sites.

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Bareket *et al.*[1] give corrosion inhibition mechanism by considering benzotriazol (BTA) to be protonated in acid medium through the imide group to give positive organic molecule[1,5,10,11].

$$BTA + H^+ \rightarrow (HBTA)^+ \qquad (2)$$

which physically adsorbed by electrostatic interaction with the Cl^- previously adsorbed on steel surface as:

$$(FeCl^-)_{phy.ads}\ (HBTA)^+ \rightleftharpoons (FeCl^-)_{phy.ads}\ (HBTA)^+_{phy.ads} \qquad (3)$$

The neutral BTA molecules were chemically adsorbed on steel surface prior to $(HBTA)^+$ deprotonation:

$$(FeCl^-)_{phy.ads} - (HBTA^+)_{phy.ads} \rightarrow (Fe\text{–}BTA)_{chem.ads} + Cl^- + H^+ \qquad (4)$$

This lead to stop the corrosion mechanism at its first step indicated by eqn. 1.

Ismaeel[5] reported the effect of Cl^- concentration on surface coverage per cent of steel surface by BTA from HCl solutions using weight-loss method[5,13-16] which show a decrease of surface coverage percent as Cl^- concentration increase which contradict with the increase of spontaneity showed by Jaronice[12] adsorption isotherm of 2 components with different molecular sizes on heterogeneous solid surface.

$$\log \theta - r \log (1-\theta) = m \log k + m \log c_2 + m \log c_1 \qquad (5)$$

where θ is surface coverage with BTA, m is heterogeneity parameter, k adsorption equilibrium constant, r is size ratio of BTA to Cl^-, C_1 is concentration of BTA M/L and C_2 is concentration of Cl^-, it was found that Jaronice isotherm was not applicable to experimental results at all Cl^- and BTA concentrations.

Ismaeel[5] predicted an isotherm concerning the dual competitive and enhancing influences of Cl^- with BTA Q molecules for adsorption on steel surface and thus it is represented by eqn. 6:

$$\theta/(1-\theta) = r/mC_2k^{C_1C_2rm} \qquad (6)$$

θ, r, m, k, C_1 and C_2 has the same significance as in Jaronice adsorption isotherm. Eqn. 6 in the logarithemic form is:

$$\log\theta/(1-\theta) = \log r/mC_2 + C_1C_2r\ m \log k \qquad (7)$$

plot of log θ/(1–θ) *vs.* C_1 give straight line with slope = C_2 rm and intercept = (log r/mC_2).
where (log r/mC_2) represents the competitive action of Cl^- and C_1 C_2 r m represent the enhancing part of the isotherm. This study show values of adsorption free energy change ΔG, adsorption equilibrium constant k and heterogeneity parameter (m) which explain the experimental results and solve problem of its contradiction with other isotherms.

The aim of our research was to study the effect of HSO_4^- and SO_4^{2-} concentrations on the adsorption of BTA on carbon steel surface at different H_2SO_4 and BTA concentrations at 25ºC and to find inhibition mechanism and its interpretation by suitable adsorption isotherm.

EXPERIMENTAL

All chemicals used were of analytical grade and water of conductivity grade (4×10^{-6} ohm^{-1} cm^{-1}) was used in preparing test solutions and in washing specimens and glass equipments. 88 Test solutions were prepared as: (i) a set of aqueous sulfuric acid solutions with concentrations (C_2M) equal 0.5, 0.6, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6 and 1.7 M/L and (ii) another set of H_2SO_4 solutions contains BTA of concentrations (C_1M) equal 6, 8, 10, 12, 14, 16, 18 and 20 × 10^{-3} M/L were prepared from each of the H_2SO_4 solutions of set (1).

Weight loss corrosion test[5,13-15]

Following the same technique as reported by Ismaeel[5], A large volume test solution of 500 cm^3 for small area specimen of 5 cm^2 is used to ensure that there was no significant change in both BTA and sulfuric acid concentrations during exposure time 2 h, *i.e.* equilibrium ≈ initial concentration. Corrosion rate was determined as weight loss per unit time per unit area[14].

If corrosion rate of carbon steel in sulfuric acid solution was W_1 and in inhibited acid with BTA was W_2, so:

The BTA inhibition effectiveness F, where

$$F = [(W_1 - W_2)/W_1] \times 100 \qquad (8)$$

and the surface coverage fraction (θ) with (BTA):

$$\theta = 1 - (W_2/W_1) \qquad (9)$$

RESULTS AND DISCUSSION

The experimental results are represented in Fig. 1, which show the relations between surface coverage θ, BTA concentration (C_1M) and H_2SO_4 concentration (C_2M), the results illustrate: (i) the increase of surface coverage with increase of BTA conc. (C_1M) line a > b > c > d > ...., (ii) the decrease of surface coverage with the increase of H_2SO_4 concentration (C_2M), which was very sharp over 0.8 M H_2SO_4, these results indicate the effect of H_2SO_4 concentration on the adsorption of BTA on steel surface, the following corrosion and corrosion inhibition mechanism with BTA was predicted.

(i) In H_2O and H_2SO_4 the ionization takes place in 2 steps as[17]:

$$H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^- ....., Ka_1 = 1 \qquad (10)$$

$$H_2O + HSO_4^- \rightleftharpoons H_3O^+ + SO_4^{2-} ....., Ka_2 = 0.013 \qquad (11)$$

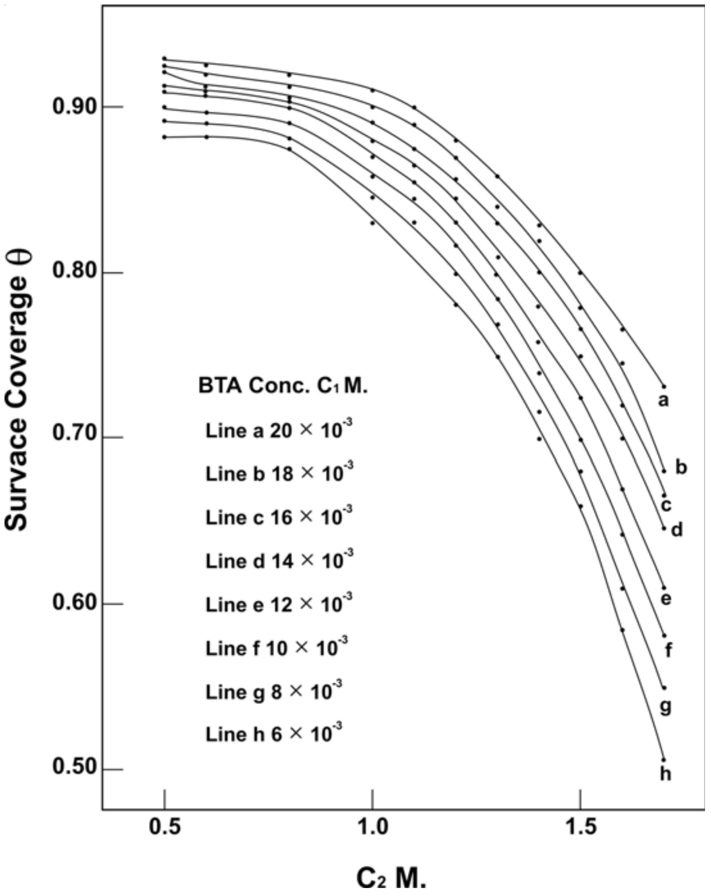
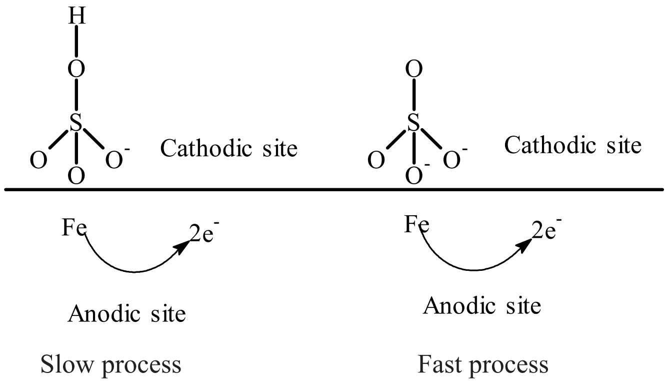


Fig. 1. Relation between surface coverage (θ) and H_2SO_4 conc. C_2M at different values of BTA conc. C_1M at 25ºC

where HSO_4^- and SO_4^{2-} has regular tetrahedral[18] structure as given in diagrams (a) and (b), respectively:



For HSO_4^-, 1 negative charge was spread equally over the 3 oxygen atoms, *i.e.*, at any instant 1 negative charge was presented on one of the 3 oxygen atoms and for SO_4^{2-} the 2 negative charges were spread equally over the 4 oxygen atoms, *i.e.*, at any instant 2 negative charges were presented on any 2 of the 4 oxygen atoms.

(ii) Considering that adsorption on metal surface is a replacement processes of H_2O adsorbed in inner helmholtz plan (IHP) by contact adsorption of the anions[19] HSO_4^- and SO_4^{2-} which diffused from outer helmholtz plan (OHP) to (IHP) and physically adsorbed on steel anodic sites with its negative oxygen atoms in the triangle base towards the surface to continue the corrosion mechanism by pushing or releasing 2 electrons from (Fe) anodic sites to the nearest cathodic site, *i.e.*, in converting Fe to Fe^{2+} also anion was released to solution bulk. But SO_4^{2-} with its 2 negative charges was more efficient than HSO_4^- with 1 negative charge in pushing or releasing the 2 electrons, so corrosion reaction of SO_4^{2-} (eqn. 13a) was more faster than that of HSO_4^- (eqn. 12a).

In eqns. 12b and 13b the inhibition mechanism was indicated as:

$$Fe + HSO_4^- \rightarrow Fe(HSO_4^-)_{ph.ad} \xrightarrow{\text{slow}} Fe^{2+} + HSO_4^- + 2e^- \qquad (12a)$$

$$Fe(HSO_4^-)_{ph.ad} + (HBTA^+) \rightarrow Fe(HSO_4^-)_{ph.ad} - (HBTA^+)_{ph.ad} \rightarrow Fe(BTA)_{ch.ad} + HSO_4^- + H^+ \qquad (12b)$$

Eqn. 12 Represent corrosion-corrosion inhibition mechanism of HSO_4^- with benzotriazol

$$Fe + SO_4^{2-} \rightarrow (Fe(SO_4^{2-})_{ph.ad} \xrightarrow{\text{very fast}} Fe^{2+} + SO_4^{2-} + 2e^- \qquad (13a)$$

$$Fe(SO_4^{2-})_{ph.ad} + (HBTA^+) \rightarrow Fe(SO_4^{2-})_{ph.ad} - (HBTA^+)_{ph.ad} \rightarrow Fe(BTA)_{chem.ad} + SO_4^{2-} + H^+ \qquad (13b)$$

Eqn. 13 Represent corrosion-corrosion inhibition mechanism of SO_4^{2-} with benzotriazol

(1) These equations in its upper corrosion branches indicate that SO_4^{2-} with its 2 negative charges strongly adsorbed on metal surface are more efficient in pushing or releasing the 2 electrons from Fe atom in anodic sites in eqn. 13 than that of weaker adsorption HSO_4^- with only 1 negative charge in eqn. 13, so that corrosion process in eqn. 13 was faster than that in eqn. 12.

(2) In eqn. 12 and 13 in its lower corrosion inhibition branches it is observed that (a) ($HBTA^+$) was physically adsorbed due to electrostatic attraction with HSO_4^- or SO_4^{2-} previously adsorbed on metal surface. This adsorption has the time to occur on HSO_4^- as indicated in eqn. 12b because of its slow corrosion reaction, this physical adsorption was followed by chemisorptions of neutral BTA molecule prior to $HBTA^+$ deprotonation[1,5,9].

(b) The adsorption of $HBTA^+$ on SO_4^{2-} was difficult to occur because corrosion reaction (13a) was faster and SO_4^{2-} was released from the surface with Fe^{2+} ion. Before $HBTA^+$ could be adsorbed on it as indicated by eqn. 13 in its supposed inhibition branches.

(3) So $HBTA^+$ was more pronounced because SO_4^{2-} was found in small quantity as $Ka_2 = 0.013$ only and its competitive and corrosive actions appeared to be effective at high H_2SO_4 concentrations (C_2M) which explain the decrease of surface coverage (θ) at this concentrations.

Applying Ismaeel adsorption isotherm[5]

$$\log\theta/(1-\theta) = \log r/mc_2 + C_1\, C_2^{\backslash}\, mr \log k \qquad (14a)$$

where θ is fraction of metal surface covered by BTA molecules and 1–θ was the reminder surface, m was the heterogeneity parameter, k is adsorption equilibrium constant and r is the size ratio between BTA and that of the triangle area of the 3 oxygen atom in HSO_4^-, or SO_4^{2-} tetrahedral structure, which calculated (from its structures, bond lengths and bond angles)[5,17,18] to be (r = 1.6741), in the adsorption competitive part of the isotherm

$$\log\left(r/mc_2\right), \text{ where } C_2 = [HSO_4^-] + [SO_4^{2-}] \qquad (14b)$$

and in the adsorption enhancing part of the isotherm $C^{\backslash}_2$

$$\text{where } \quad C_2^{\backslash} = \left[HSO_4^-\right] = C_2 \times 0.987 \qquad (14c)$$

and C_1 was benzotriazol concentration.

Fig. 2 represent Ismaeel adsorption isotherm at 25ºC by plotting $\log\left[\theta/\left(1-\theta\right)\right]$ *vs.* C_1 at different H_2SO_4 concentrations C_2M.

From the slope of the lines and its intercept with $\log\left[\theta/\left(1-\theta\right)\right]$ axis, the value of m, log k and adsorption free energy change ΔG where ΔG = -2.303 log k were determined and represented in Fig. 3, which represents relations between (C_2), (m), (log k) and ΔG.

Fig. 3 shows that: (i) values of ΔG ranged from (-43.367 KJ/mol) at C_2 = 1.7 M to (-211.458 KJ/mol) at C_2 = 0.5 M, this values were more negative than -40 KJ/mol, indicating spontaneous chemisorption[5] and was in agreement with the predicted (corrosion-corrosion inhibition) mechanism in eqns. 12 and 13. These values of ΔG explain experimental decrease of surface coverage as H_2SO_4 concentration increases, (ii) the values of heterogenity parameter (m) which decreased from (m = 0.579) at C_2 = 0.5 m, H_2SO_4 to (m = 0.375) at C_2 = 0.8 M, H_2SO_4, this was explained to be due to the disappearance of one of the adsorbed species on metal surface which was water replaced by HSO_4^- and/or BTA molecules[19]. At concentration more than 0.8 M H_2SO_4, the heterogenity parameter (m) increased to reach (m = 1.303) at (C_2 = 1.7 M) due to increase of types of adsorbed species by SO_4^{2-} at high H_2SO_4 concentrations, also m increased due to the effect of corrosion processes

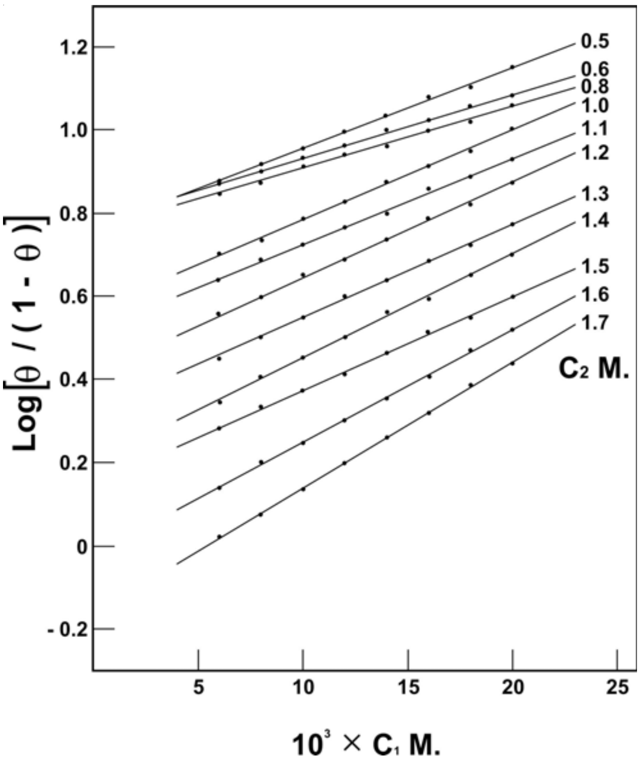


Fig. 2. Ismaeel adsorption isotherm represent the relation between log[θ/(1-θ)] and BTA conc. C_1M at different values of H_2SO_4 conc. C_2M at 25ºC

on the nature of metal surface at this higher H_2SO_4 concentration and (iii) all the previous points give interpretation of the predicted corrosion-corrosion inhibition mechanism with Ismaeel adsorption isotherm[5].

Conclusion

Ismaeel adsorption isotherm was applicable to the experimental results, explain and interpreted the predicted (corrosion-corrosion inhibition) mechanism.

The effect of acid concentration shall be concerned in choosing suitable corrosion inhibitor and acid concentrations, to gain maximum surface coverage (θ) and to avoid loss of efficiency at high acid concentration.

Taking into account the ionization constant of the acid K_a and its effect on the types and concentrations of produced ions and the influences of each type on corrosion and corrosion inhibition mechanism.

Pickling of steel in H_2SO_4 solutions shall be started with mechanical removal of scales instead of using H_2SO_4 of high concentrations, then followed by H_2SO_4 solution of low concentration which need low BTA concentration to gain maximum inhibition effectiveness.

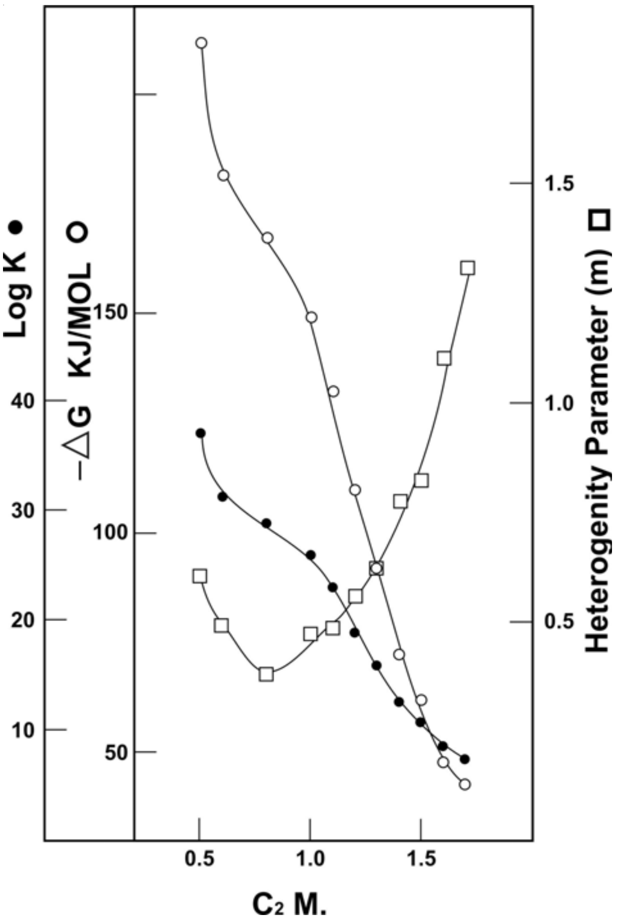


Fig. 3. Values of log K, ΔG and m at different values of H_2SO_4 conc. C_2M at 25ºC

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