

# SYNERGISTIC INFLUENCE OF BENZOATE IONS ON INHIBITION OF CORROSION OF MILD STEEL IN 0.5M SULPHURIC ACID BY BENZOTRIAZOLE

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**Abstract** The influence of benzoate anions on the corrosion inhibition effect of benzotriazole (BTA) for mild steel in sulfuric acid has been investigated. The investigation was carried out by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The addition of benzoate ions greatly enhances the inhibition efficiency of BTA in a synergistic manner. This effect has been attributed to co-adsorption of benzoate and protonated benzotriazole ions. While inhibition property of BTA has been attributed to adsorption of the molecules on the metal surface, through interaction of lone pair electrons on nitrogen atoms or  $\pi$  electrons of the aromatic ring, followed by polymeric complex formation. In acid solution, in presence of benzoate anions, protonated BTA molecules are adsorbed mostly by columbic attractions on the surface partially covered with benzoate anions

**Key Words** Benzoate Ions, Benzotriazole, Corrosion Inhibition, Synergistic Effect

**چکیده** اثر تزايد آنیونهای بنزوات بر روی بازدارندگی خوردگی بنزوتریازول (BTA) بر فولاد در محیط سولفوریک اسید بررسی شده است. تحقیقات با استفاده از روشهای بیناب نگاری امپدانس و پلاریزاسیون پتانسیودینامیک انجام گردیده است. اضافه نمودن بنزوات به مقدار قابل ملاحظه ای میزان بازدارندگی BTA را افزایش میدهد که به اثر تزايد مشهور است. علت این امر به جذب همزمان یونهای بنزوات و نمونه پروتونه شده بنزوتریازول نسبت داده شده است. در غیاب بنزوات، بنزوتریازول از طریق جفت الکترونهاي روی اتم نیتروژن و همچنین الکترونهاي  $\pi$  حلقه آروماتیک جذب شده و با تشکیل کمپلکسهای پلیمری بر روی سطح باعث تقلیل سرعت خوردگی می شوند در حالیکه در حضور بنزوات، بنزوتریازول پروتونه شده به وسیله نیروهای الکترواستاتیک بر روی سطح فلزی جذب میشود که قبلا یونهای بنزوات توسط پدیده "جذب ویژه" جذب شده بودند.

## 1. INTRODUCTION

The application of organic compounds, as corrosion inhibitors is one of the most important methods of

prevention of metallic corrosion [1-2]. Benzotriazole (BTA) and its derivatives have been used successfully for protection of copper and its alloys as well as iron and steel in both neutral and acidic media [3-

8]. The general belief is that BTA forms a protective film of polymeric complexes chemically bonded to the metal or metal oxide surface [5,9].

It has been known for sometimes that the inhibition effect of organic compounds can be improved by addition of a secondary compound [10-13]. This effect, which is known as synergism, is an enhanced inhibition effect and can be related to either interactions between two inhibitor molecules or between the inhibitor and one of the ions present in the aqueous media. As regard to BTA inhibition, Soute et al. have observed the synergistic effect of potassium ethyl xanthate on corrosion inhibition of copper by BTA and concluded that this selective composition appear to be one of the best of its type for preventing localized corrosion of copper [13]. Villamill et.al. have studied the synergistic effect of sodium dodecyl sulphate (SDS) on the inhibition effect of BTA for corrosion of copper and stainless steel (AISI Type 304) in aqueous sulphuric acid [14]. They have concluded that BTA and SDS molecules adsorbed on the copper surface simultaneously as ion pairs. This work is concerned with the effect of BTA and (BTA + Sodium benzoate) mixture on mild steel corrosion in sulphuric acid media. The electrochemical impedance spectroscopy (EIS) and Tafel polarization techniques were employed.

## 2. EXPERIMENTAL DETAILS

Electrochemical experiments were conducted in a three-electrode cell with a volume of 250 ml. The mild steel with the following composition were obtained commercially (C % 0.01, Si % 0.35, P% 0.018, Cr %0.04 , Ni % 0.017, Mo % 0.03, Cu %0.02, W % 0.02, Ti %0.001, Fe, bulk). Analytical grade reagents and double-distilled water were used to prepare the solutions.

For Tafel polarization and A.C. impedance studies mild steel specimens embedded in resin with an exposed cross sectional area of 1 cm<sup>2</sup>, were used as the working electrode. The specimens were polished with a sequence of emery papers of various grades (320-1200) washed with detergent solution, rinsed with ethanol and double distilled water and finally dried by warm air. These cleaned specimens were kept in desiccators until the time of experiment. A large area platinum and a

standard calomel electrode (SCE) were employed as counter and reference electrodes respectively. Thus all potentials reported are referred to SCE. The experimental temperature was constant at 25 °C .

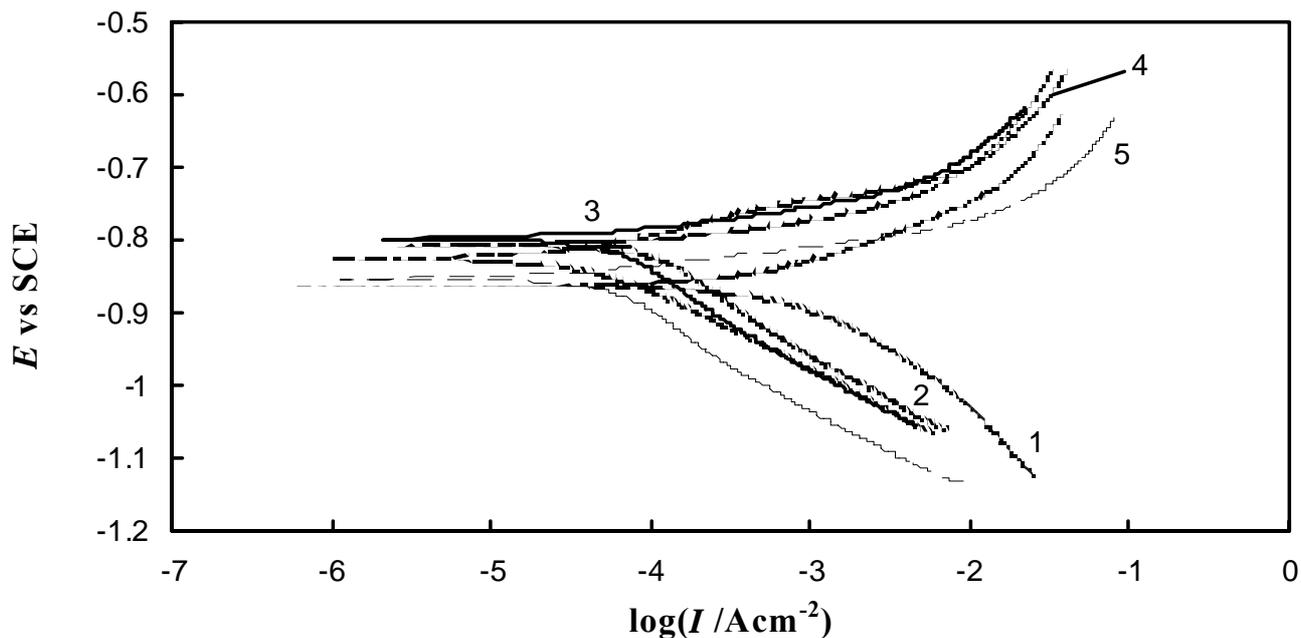
The polarization and A.C. impedance experiments were carried out by an EG&G Potentiostat consisting of a model PARC, M273A potentiostat, using 352M software for polarization and a model SI 1255 Frequency Response Analyzer (FRA), with M398 software for impedance measurements. Tafel polarization sweep was conducted in the potential range -0.25 to +0.25 volt versus open circuit potential (O.C.P.) at a scan rate of 1 mV/s. Inhibition efficiencies were determined from corrosion currents calculated by Tafel extrapolation method and by fitting the curves to the polarization equations. Impedance measurements were carried out over a frequency range of 100 kHz to 0.01HZ with five points per decade. A sine wave with 5-mV amplitude was used to perturb the system. The impedance spectra were analyzed in terms of equivalent circuit by Z-View Software.

## 3. RESULTS AND DISCUSSIONS

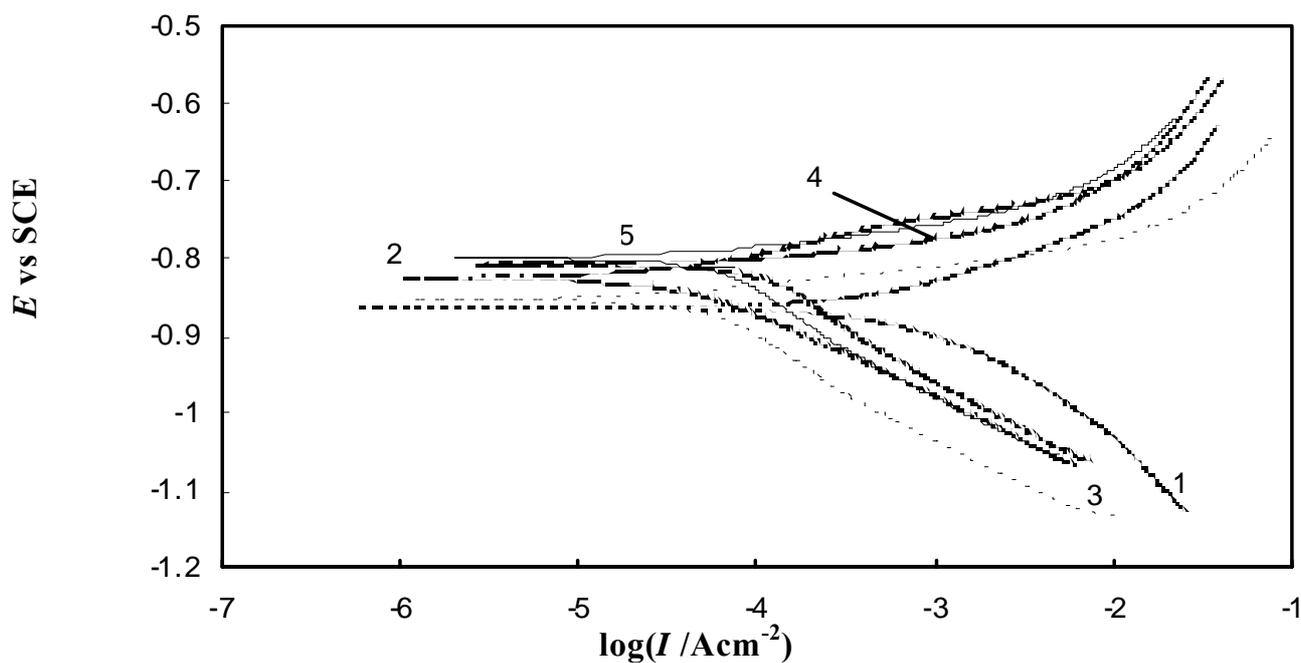
**Tafel Polarization** Figures 1 and 2 represent current density potentials plots for various concentrations of BTA alone and in combination with 200 ppm benzoate anions respectively. Data obtained from these plot through Tafel extrapolation method, are summarized in Table 1. The relative inhibition efficiencies  $\eta_{\%p}$  [15] were calculated by:

$$\eta_{\%p} = \frac{I_0 - I}{I_0} \times 100 \quad (1)$$

$I_0$  and  $I$  are corrosion currents, with and without inhibitor respectively. Table 1 shows that the effect of addition of benzoate anions, on the inhibition efficiencies of BTA is pronounced in all concentrations. Furthermore, it appears that the mixture, BTA and sodium benzoate affect the anodic polarization curves more than cathodic curves. The inhibition property of BTA alone has been attributed to the adsorption of molecules on the metal surface, through interaction of lone pair



**Figure 1.** Polarization plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of BTA: 1 – blank, 2 – 100 ppm, 3 – 200 ppm, 4 – 300 ppm and 5 – 400 ppm.



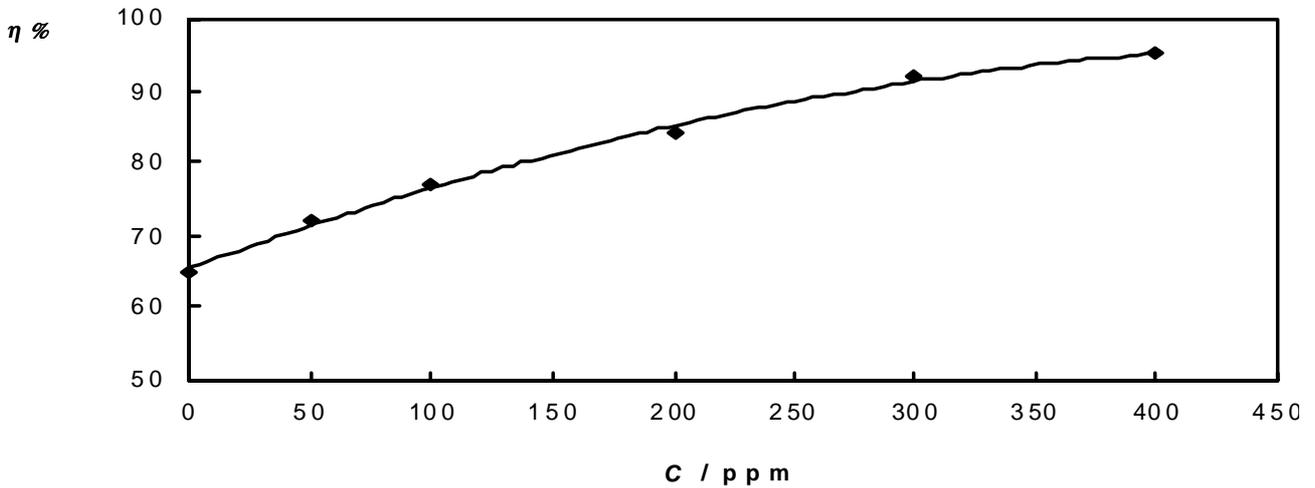
**Figure 2.** Polarization plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in presence of different concentrations of BTA and constant concentration of sodium benzoate: 1 – blank, 2 – 100 ppm, 3 – 200ppm, 4 – 300 ppm and 5 – 400 ppm.

electrons on nitrogen atoms or by the  $\pi$  electrons of the aromatic rings, followed by the formation of

polymeric complexes involving metal atoms or ions [5-6]. In acidic solutions, however, BTA

**TABLE 1. Tafel Polarization Parameters for Corrosion of Mild Steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> with Different Concentrations of BTA in Presence and Absence of Benzoate.**

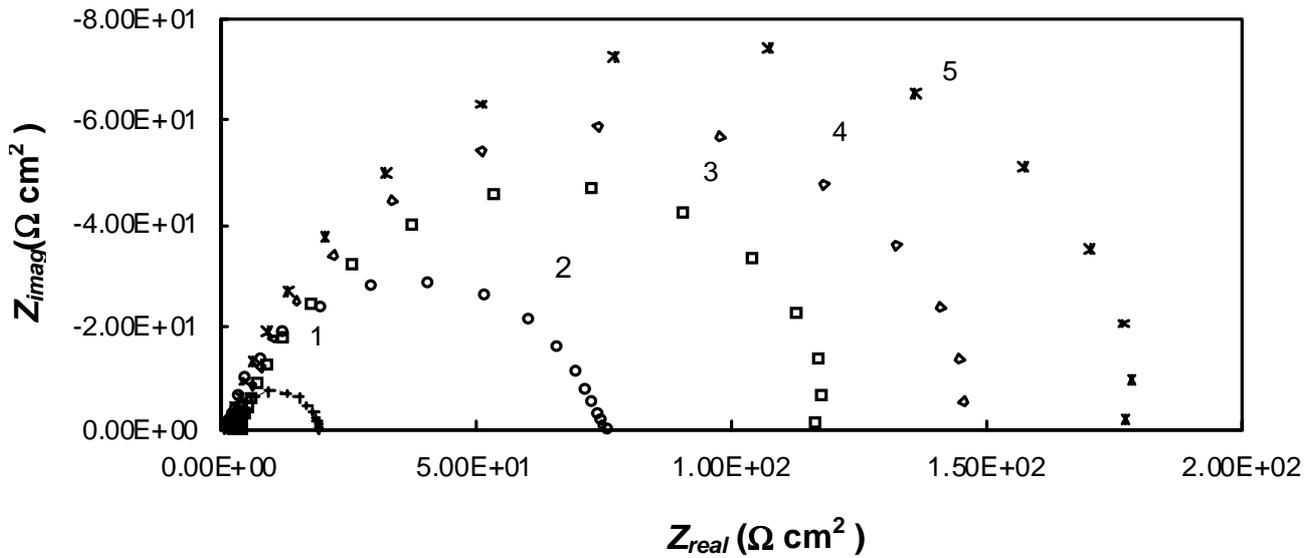
BTA (PPM)	Benzoate (PPM)	Current density (μA/ cm <sup>2</sup> )	β <sub>a</sub> (mv/decade)	β <sub>c</sub> (mv/decade)	η <sub>p</sub> %
-	-	567	110	125	-
-	200	540	93.26	126	-
100	-	180	42	132	68
100	200	157	33	126	72
200	-	135	39.4	131	76
200	200	85	32.7	126	85
300	-	115.5	36.52	128	79.6
300	200	40	30.51	132	92
400	-	97	32.67	131	83
400	200	37	33.92	125	93



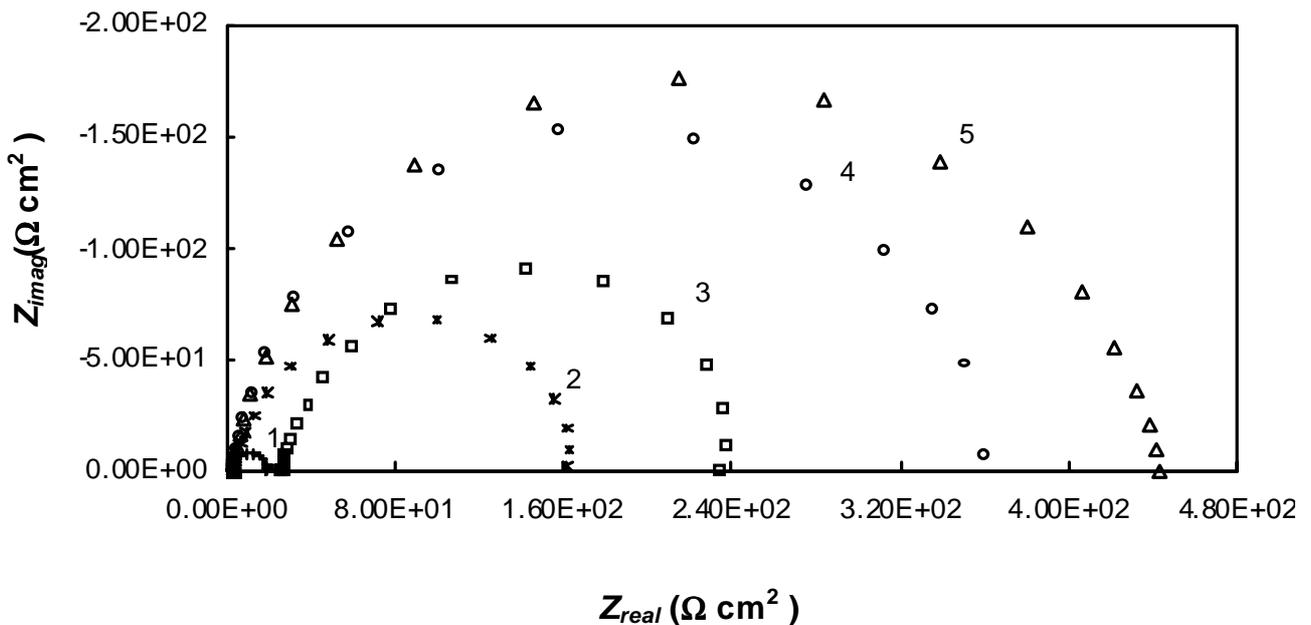
**Figure 3.** The variation of the inhibition efficiency versus different concentrations of benzoate and constant concentration of BTA (200ppm).

molecules are mostly protonated [14,16] and at the open circuit potential ( $E_{OC}$ ) the surface charge of

iron is positive [1], thus in acid solution, in presence of an anion such as benzoate, it is



**Figure 4.** Nyquist plots for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentration of BTA: 1 – blank, 2 – 100 ppm, 3 – 200 ppm, 4 – 300 ppm and 5 - 400ppm.

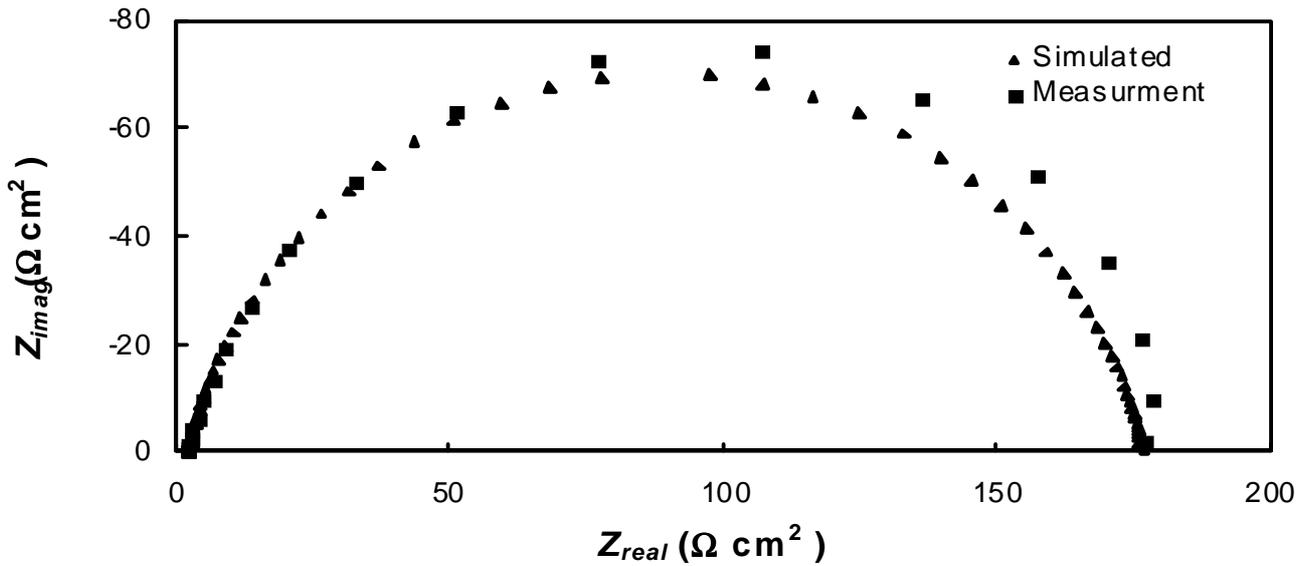


**Figure 5.** Nyquist plots for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentration of BTA and constant concentration of sodium benzoate (200ppm): 1 – blank, 2 – 100 ppm, 3 – 200 ppm, 4 - 300ppm and 5 - 400ppm.

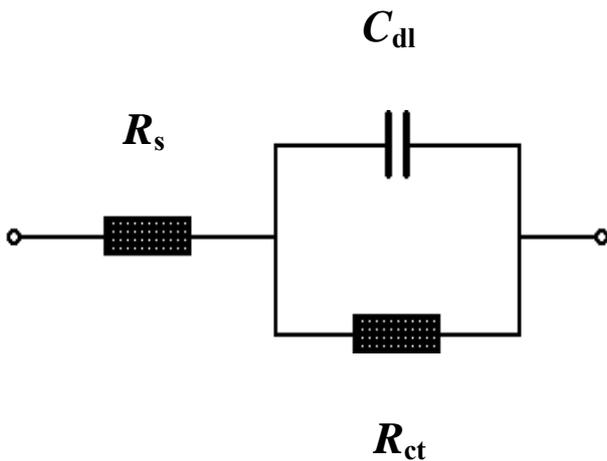
expected that adsorption of BTAH<sup>+</sup> is taken place by the following events: the adsorption of added anions (in this case benzoates) will occurs first through specific adsorption and lowers the metal surface charge, then BTAH<sup>+</sup> ions are adsorbed by

coulbmic attractions as well as electron pair donations on metal surface where anions have already been adsorbed.

Figure 3 represents values of inhibition efficiencies as a function of sodium benzoate concentration, for



**Figure 6.** Impedance spectra of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of 400PPM BTA (measurement) and fitted results using equivalent circuit model, R(RQ), (Simulated).



**Figure.7.** Simplified Ershler - Randles circuit (  $R_s$  electrolyte resistance;  $C_{dl}$  double – layer capacitance;  $R_{ct}$  Charge transfer resistance (Equivalent circuit model [R(RQ)]).

a constant amount of BTA (200 ppm). As it can be seen, the increase in synergistic effect reaches its highest value at about 300 ppm. This can be interpreted according to the followings: as the benzoate ions concentration in solution is increased, the amount of adsorbed anions is also increased causing a shift in metal surface charge to lower values. When the concentration of anions on metallic surface reaches a certain value, further

adsorption will not take place and addition of extra sodium benzoate to the solution will not affect the inhibition efficiencies anymore [4].

### Electrochemical Impedance Spectroscopy (EIS)

Figures 4 and 5 are some of the Nyquist diagrams from A.C. impedance experiments of steel in 0.5M sulfuric acid containing BTA and (BTA + sodium benzoate ) mixture respectively. Figure 6 represents a set of these data, processed by Z- View Software. The square points are the experimental values and the fitted curve (triangles) is plotted in terms of equivalent electrical circuit shown Figure 7. Where  $R_s$  is uncompensated solution resistance,  $R_{ct}$  and  $C_{dl}$  charge transfer resistance and double layer capacitance respectively.

Electrochemical parameters obtained by this procedure are given in Table 2. Charge transfer resistances,  $R_{ct}$ , were calculated from the impedance values at lowest and highest frequencies ( $R_{ct} = R_l - R_h$ ). Double-layer capacitance  $C_{dl}$  were calculated from the frequencies at which the imaginary  $Z_{img}$  is maximum according to the relationship given below [15,17]:

$$C_{dl} = \frac{1}{R_{ct} \cdot \omega_{z_{max}}} \quad (2)$$

**TABLE 2. Impedance Parameters for Corrosion of Mild Steel in 0.5M H<sub>2</sub>SO<sub>4</sub> with Different Concentrations of BTA in Pretence and Absence of Benzoate.**

BTA ( PPM )	Benzoate (PPM)	C <sub>dl</sub> ( μf cm <sup>-2</sup> )	R <sub>ct</sub> ( Ω cm <sup>2</sup> )	η <sub>Rt</sub> %
-	-	217.18	28	-
-	200	220	27	-
100	-	169	81	65
100	200	140	95	71
200	-	156	114	75
200	200	130	155	82
300	-	135	144	80
300	200	120	357	93
400	-	130	168	83
400	200	110	437	94

where  $\omega_{z_{max}}$  equals  $2\pi$  times the frequency at the complex plane plot semicircles apex. The relative inhibitive efficiencies were calculated from the following relation [3]:

$$\eta_{\%Rt} = \frac{Rt_0^{-1} - Rt^{-1}}{Rt_0^{-1}} \times 100 \quad (3)$$

R<sub>t</sub> and R<sub>t0</sub> are charge transfer resistances, with and without addition of inhibitor respectively. From data in Table 2, one can deduce that: 1. Values of, R<sub>ct</sub> increase with increases in BTA concentration while C<sub>dl</sub> decreases. 2. These increase in R<sub>ct</sub> and decrease in C<sub>dl</sub> are more pronounced in the

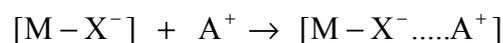
presence of benzoate anions. These can be attributed to the enhanced adsorption of BTA (or BTAH<sup>+</sup>) in the presence of benzoate anions. Thus EIS results confirm those of Tafel polarization.

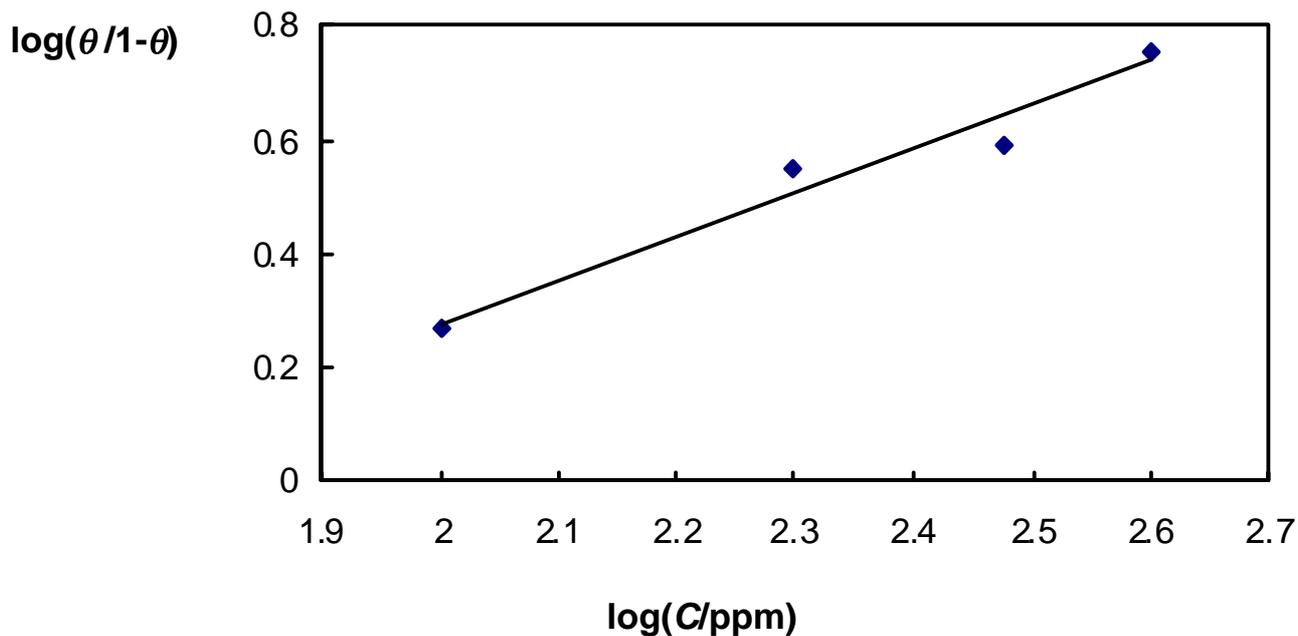
The joint adsorption of anions and cations (BTAH<sup>+</sup>) can occurs by two different ways [11]:

1-The anions are first adsorbed on metal surface:

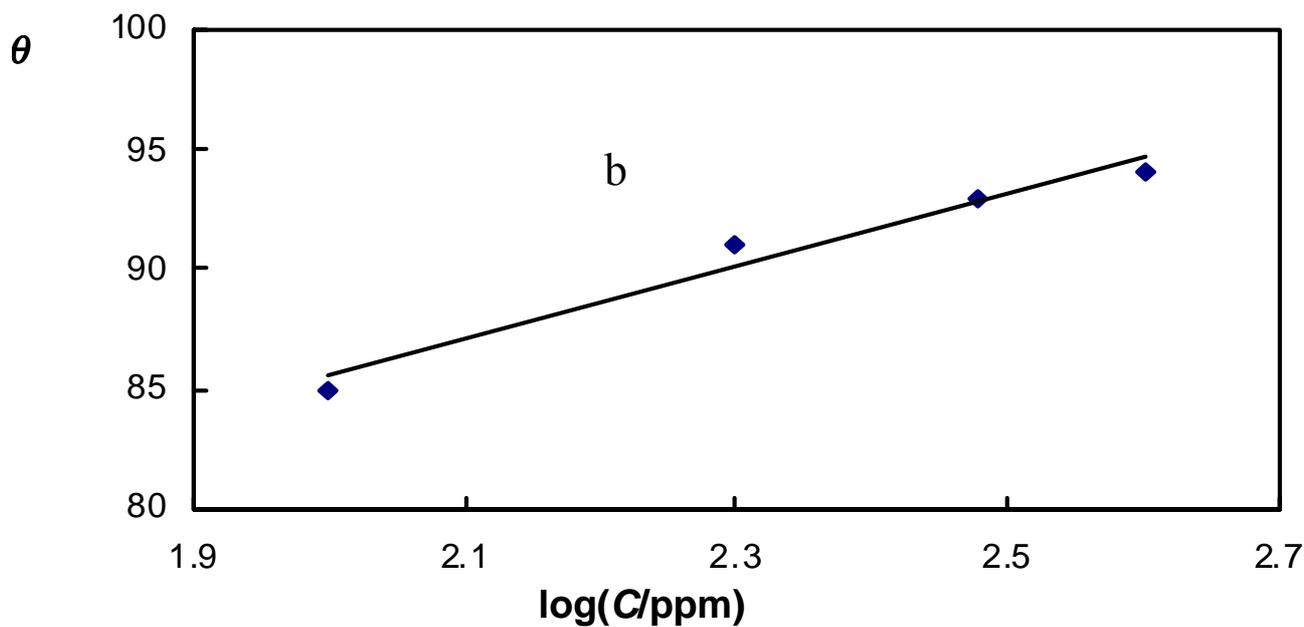


Then cation A<sup>+</sup> is adsorbed on the same site where the X<sup>-</sup> is specifically adsorbed:





**Figure 8a.** Adsorption isotherm for BTA on mild steel in 0.5 M sulfuric acid.



**Figure 8b.** Adsorption isotherm for BTA and constant concentration of sodium benzoate (200PPM) on mild steel in 0.5 M sulfuric acid.

2 - The anion and cation are adsorbed at different sites on the metal surface.

The former is called cooperative adsorption and

the latter is called competitive adsorption [11]. It is not possible to deduce, from our data, the type of joint adsorption taken place here. For the adsorption

of anion and ammonium cation, however, the competitive adsorption has been assumed [18].

Values of surface coverage  $\theta$  have been obtained from the inhibition efficiency and corrosion current  $I_{\text{corr}}$  with different concentrations of BTA alone and in combination with 200 ppm benzoate. The plot of  $\log(\theta / 1 - \theta)$  versus  $\log(C)$  in Figure 8a gives a straight line for BTA alone indicating the occurrence of Langmuir's adsorption isotherm but for BTA combined with benzoate, the plot of  $\theta$  versus  $\log(C)$  in Figure 8b gives a straight line, this confirms that the adsorption obeys Temkin's adsorption isotherm [11-12]. These are in line with our discussions of the results given in Figure 3 and the fourth columns of Tables 1 and 2.

Comparison with the data in Tables 1 and 2 learns that satisfactory agreement is found with the inhibition efficiencies as obtained through polarization and EIS measurements, except for poorly inhibited situations where EIS leads systematically to relatively high values of  $\eta$ . Further, it is observed that the measured double layer capacitance decreases as inhibition is more efficient, i.e., as higher values of  $R_{\text{ct}}$  are measured. This phenomenon is commonly found in cases where adsorption at the metal/electrolyte interface occurs, as solvent molecules become replaced with molecules with far less pronounced dielectric properties [19].

#### 4. CONCLUSIONS

1. The presence of benzoate anions enhances the inhibition efficiency of BTA for corrosion of steel in 0.5 M acid sulfuric to a large extent.
2. The optimum concentration of this inhibitive mixture is 300 ppm BTA plus 200 ppm sodium benzoate.
3. BTA is preferentially adsorbed by the columbic attraction on the surface where the anions have already been chemisorbed.
4. Polarization results indicate that the anodic polarization curves are mostly affected by these inhibitor combination rather than cathodics.
5. The increases in charge transfer resistances and the decrease in double layer capacities, in EIS experiments points to the formation of a stable protective film on the surface of the metal.

#### 5. ACKNOWLEDGMENT

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#### 6. REFERENCE

1. TrabANELLI, G., "Fundamentals and General Aspects of Inhibition Science", *Corrosion-NACE Annual Conference on Inhibitors*, Boston, Mass, Nov. (1989), 133/1-133/25.
2. SASTRI, V. S., "Corrosion Inhibitors", John Wiley and Sons, (1998), 655-670.
3. FOX, P. G., LEWIS, G. and BODEN, P. J., "Some Chemical Aspects of the Corrosion Inhibition of Copper by Benzotriazole", *Corrosion Science*, Vol. 19, (1979), 457-467.
4. MANSFELD, F., SMITH, T. and PARRY, P. E., "Benzotriazole as Corrosion Inhibitors for Copper", *Corrosion -NACE*, Vol. 27, (1971), 289-294.
5. KORPIC, C. J., "Aromatic Triazoles as Corrosion Inhibitors of Copper and Copper Alloys", *Anti-Corrosion Methods and Materials*, March, (1974), 11-13.
6. LEWIS, G., "The Adsorption of Benzotriazole on to Coprous Oxide Surface: An Electrochemical Impedance Study", *Corrosion*, Vol. 34, (1978), 424-428.
7. WU, J. S. and NOBE, K., "Effect of Substituted Benzotriazole on the Electrochemical Behavior of Copper in Sulphuric Acid", *Corrosion -NACE*, Vol. 37, April, (1981), 223-225.
8. RODRIGUEZ, P. R. P., AOKI, I. V., DE ANDREDE, A. H. P., DE OLIVERIA, E. and AGOSTINHO, S. M. L., "Effect of Benzotriazole on Electrochemical and Corrosion Behavior of Type 304 Stainless Steel in 2 M Sulphuric Acid Solution", *British Corrosion J.*, Vol. 31, (1996), 305-308.
9. VOGT, M. R., NICHOLS, R. J., "Benzotriazole Adsorption and Inhibition of Cu (100) Corrosion in HCl", *J. Physical Chemistry B*, Vol. 102, (1998), 5859-5865.
10. FENG, Y., SIOW, K. S., TEO, W. K., TAN, K. L. and HSUH, A. K., "Synergistic Effect Between Sodium Tripolyphosphate and Zinc Sulphate in Corrosion Inhibitor for Copper in Neutral Tap Water", *Corrosion-NACE*, Vol. 53, (1997), 546-555.
11. ARAMAKI, K., HAGIWARA, M. and NISHIHARA, H., "The Synergistic Effect of Anions and the Ammonium Cations on the Inhibition of Iron Corrosion in Acid Solution", *Corrosion Science*, Vol. 27, (1987), 487-497.
12. MURALIDHARAN, S., SEYED AZIM, S., BERCHMANS, L. J. and IYER, S. V. K., "Synergistic Influence of Iodide Ions on the Inhibition of Corrosion of Mild Steel in Sulfuric Acid by N-Hexylamin", *Anti-Corrosion Methods and Material*, Vol. 44, (1997), 30-36.
13. SOUTO, R. M., FOX, V., LAZ, M. M., PEREZ, M. and GONZALEZ, S., "Some Experiments Regarding the Corrosion Inhibition of Copper by Benzotriazole and Potassium Ethyl Xanthate", *J. Electroanalytical*

- Chemistry*, 411, (1996), 161-165.
14. Villamill, R. F. V., Corio, P., Rubin, J. C., Agostinho, S. M. L., "Effect of Sodium Dodecyl Sulfate on Copper Corrosion in Sulfuric Acid Media in the Absence and Presence of Benzotriazole", *J. Electroanalytical Chemistry*, 472, (1999), 112-119.
  15. Sykes, J. M., "25 Years of Progress in Electrochemical Methods", *British Corrosion J.*, Vol. 25, (1990), 175-180.
  16. Aramaki, K. and Nishahara, H., "Relation Between the Adsorption of Anions on Metals or Metallic Oxide and the Hard and Soft Acid and Base Rule", *Corrosion Engineering*, 40, (1991), 733-746.
  17. Hladky, L., Callow, M. and Dawson, J. L., "Corrosion Rates From Impedance Measurements, An Introduction", *British Corrosion J.*, Vol. 15, (1980), 21-25.
  18. Murokawa, T., Naqayra, S. and Hackerman, N., "Coverage of Iron Surface by Organic Compounds and Anions in Acid Solution", *Corrosion Science*, Vol. 7, (1967), 79-89.
  19. Hosseini, M. G., Mertens F. L. S. and Arshadi, M. R., "Synergism and Antagonism in Mild Steel Corrosion Inhibition By Sodium Dodecyl benzenesulfonate and Hexamethylenetetramine", *Corrosion Science*, 45, (2003), 1473-1489.