

Accepted Manuscript

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Manuscript number: **PCCC-2606-1515**

To appear in: Progresss in Color, Colorants and Coatings

Received: 12 June 2026

Final Revised: 1 August 2026

Accepted: 2 August 2026

Please cite this article as:

Dana Nurzhanova, Aikorkem Tlektes, Ruben Vardanyan, Nikolay Akatyev, Protective Performance of Bromocresol Purple Dye for Aluminum in 1.0 M HCl: Experimental and Theoretical Investigation, Prog. Color, Colorants, Coat., 20 (2027) XX-XXX.

DOI: 10.30509/pccc.2026.167817.1515

This is a PDF file of the unedited manuscript that has been accepted for publication. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form

**Protective Performance of Bromocresol Purple Dye for Aluminum in 1.0 M HCl:****Experimental and Theoretical Investigation**

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**Abstract**

Bromocresol purple (BCP) was investigated as a corrosion inhibitor for D16T aluminum alloy in 1.0 M HCl using experimental and quantum-chemical methods. It was found that the inhibition efficiency increased with inhibitor concentration and temperature, reaching 93.16% at  $0.30 \text{ g} \cdot \text{dm}^{-3}$  and 313 K. Adsorption was best described by the Langmuir model ( $R^2 > 0.996$ ), while the Frumkin model indicated weak lateral interactions between adsorbed species. The negative  $\Delta G^0_{ads}$  values ( $-24.83$  to  $-29.58 \text{ kJ} \cdot \text{mol}^{-1}$ ), together with positive  $\Delta H^0_{ads}$  and  $\Delta S^0_{ads}$ , demonstrated spontaneous, endothermic, and temperature-favored adsorption. Polarization measurements revealed a decrease in  $j_{corr}$  from  $1.16 \cdot 10^{-4}$  to  $1.48 \cdot 10^{-5} \text{ A} \cdot \text{cm}^{-2}$ , confirming mixed-type inhibition, while the contact angle increased from  $53.57^\circ$  to  $93.96^\circ$ . UV–Vis and FTIR analyses confirmed interfacial retention of BCP and the involvement of oxygen-containing groups and the conjugated  $\pi$ -system in adsorption. Quantum-chemical calculations at the DFT/B3LYP/6-311G(d,p) level showed that the quinonoid form had a lower HOMO–LUMO gap (7.30 vs. 9.51 eV), higher softness ( $0.274$  vs.  $0.210 \text{ eV}^{-1}$ ), and higher electrophilicity (5.31 vs. 3.37 eV) than the lactone form, indicating enhanced charge-transfer capability. The results support a mixed physisorption–chemisorption mechanism leading to the formation of a compact

protective layer that limits access of aggressive species to active dissolution sites.

**Keywords:** D16T alloy; Metal protection; Organic inhibitors; Quantum chemical calculations; Sulfophthalein dyes.

## 1. Introduction

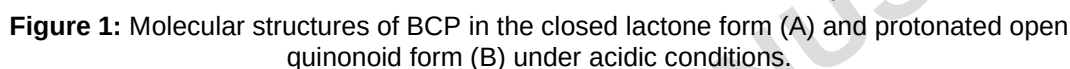
Acidic treatment of aluminum alloys is widely encountered during surface cleaning, pickling, and related technological operations; however, such media can significantly disturb the naturally formed oxide layer that normally provides aluminum with corrosion resistance. This problem is especially important for multicomponent alloys such as D16T, whose Cu-, Mg-, Mn-, Fe-, and Si-containing intermetallic phases may create local electrochemical heterogeneity and accelerate dissolution in chloride-containing acid solutions. Therefore, inhibition of aluminum alloy corrosion in hydrochloric acid requires compounds that can rapidly adsorb at active interfacial sites and limit access of aggressive  $H^+$  and  $Cl^-$  species to the alloy surface [1].

Organic inhibitors remain attractive for this purpose because their protective effect can be tuned through molecular structure. Adsorption is usually controlled by the availability of electron-rich atoms, polar groups, aromatic fragments, and conjugated systems capable of interacting with the metal/solution interface [2, 3]. For aluminum in strongly acidic media, this interaction is complicated by the simultaneous presence of oxide/hydroxide residues, adsorbed chloride ions, protonated inhibitor species, and surface defects. As a result, the inhibition efficiency is governed not only by the number of adsorption centers but also by molecular form, charge distribution, planarity, and the

ability to form a compact interfacial layer.

Organic dyes represent a particularly interesting class of corrosion inhibitors because their structures combine extended  $\pi$ -systems, heteroatom-containing groups, and acid-base-responsive fragments. Previous studies have shown that various dyes, including azine, thiazine, triazole, xanthene, coumarin, azo, and indicator-type compounds, can decrease metal corrosion in acidic media through adsorption-controlled mechanisms [4-15]. An additional advantage is that spectroscopic methods can directly monitor changes in solution-phase behavior, chromophore stability, and depletion of free molecules from the bulk phase during metal exposure. This makes dyes useful not only as inhibitors but also as molecular probes for adsorption processes at corroding surfaces.

Bromocresol purple (BCP) is a water-soluble sulfophthalein dye that contains phenolic hydroxyl groups, a sulfonate fragment, brominated aromatic rings, and an extended conjugated system (Figure 1). In recent years, BCP has attracted increasing interest as a functional chromophore and interfacial material in diverse analytical, sensing, and smart-material applications owing to its pronounced halochromic response and suitability for incorporation into polymeric and hybrid systems. BCP-based materials have been employed as electropolymerized sensing interfaces for the voltametric determination of pharmaceutical and biologically relevant compounds [16], incorporated into porous cellulose-based labels for real-time monitoring of food freshness [17], integrated into multifunctional nanofiber membranes combining particulate filtration with rapid colorimetric ammonia detection [18], and applied in pH-responsive analytical platforms for nanoPET determination in environmental and food-related samples [19]. These recent developments demonstrate the broad environment-responsive and interfacial



Depending on the acidity of the medium, BCP may exist in a closed lactone form (LF) or an open quinonoid form (QF). This structural transformation is especially relevant for corrosion inhibition because opening of the lactone ring alters molecular planarity and charge distribution, as well as accessibility of oxygen-containing adsorption centers [20]. The quinonoid form is expected to interact more effectively with the aluminum alloy surface due to stronger electronic delocalization and a more favorable arrangement of adsorption-active fragments.

Although BCP is well known as an analytical indicator, its behavior as a corrosion inhibitor for aluminum alloys in hydrochloric acid has not been sufficiently clarified. In particular, the relationship between its acid-induced molecular form, adsorption thermodynamics, electrochemical response, surface wettability, spectroscopic changes, and quantum-chemical descriptors remains insufficiently understood. Therefore, the present work investigates BCP as an inhibitor for D16T aluminum alloy in 1.0 M HCl

using gravimetric, adsorption, activation, electrochemical, contact-angle, UV–Vis, FTIR, and quantum-chemical approaches. Weight-loss measurements were used to evaluate the effects of concentration, immersion time, and temperature, while adsorption and thermodynamic analyses characterized interfacial adsorption behavior. Electrochemical and contact-angle measurements assessed corrosion suppression and changes in surface wettability, whereas UV-Vis and FTIR spectroscopy examined inhibitor retention and functional-group participation in surface interaction. Quantum-chemical calculations comparing the lactone and quinonoid forms of BCP were performed to identify the structural and electronic features governing adsorption. This integrated approach relates the inhibition performance of BCP to its adsorption behavior, interfacial film formation, and molecular electronic properties.

## **2. Experimental**

### **2.1. Reagents and solvents**

All reagents used in this study were of analytical-grade, purchased from certified suppliers, and used without further purification. The corrosive solutions were prepared by diluting the required amount of concentrated HCl (37%) with double-distilled water (DDW).

### **2.2. Metal preparation**

D16T aluminum alloy specimens were used for the corrosion experiments. The nominal composition of the alloy was as follows (wt.%): Al 92.7, Cu 4.6, Mg 1.6, Mn 0.6, Fe 0.19, Si 0.17, and Zn 0.07. Rectangular coupons with dimensions of 25.0 × 30.0 × 3.0

mm were cut from industrial alloy sheets. Before each experiment, the specimens were mechanically abraded using successive grades of emery paper ranging from 250 to 1200 grit to obtain a reproducible surface finish. The polished samples were then treated for 10 s in an alkaline solution containing  $40 \text{ g}\cdot\text{dm}^{-3}$  NaOH. Immediately after alkaline treatment, the specimens were thoroughly rinsed with DDW, ethanol, and acetone, dried in an air stream, and stored in a desiccator with silica gel until further use.

## 2.3. Methods

### 2.3.1. Weight loss (gravimetric) method

Gravimetric measurements were carried out to determine the corrosion rate (CR), inhibition efficiency (IE), and degree of surface coverage ( $\theta$ ). After preliminary surface preparation and initial weighing, the alloy specimens were immersed for 10 s in an alkaline solution containing  $40 \text{ g}\cdot\text{dm}^{-3}$  NaOH in DDW to remove the native oxide film. The coupons were then immediately rinsed with DDW and transferred into open 150 mL glass beakers containing 100 mL of the corrosive solution in the absence or presence of the inhibitor. After the immersion period, the specimens were withdrawn from the test solutions, and corrosion products were removed by treating each coupon with a 1:1 nitric acid solution for 5 min at room temperature [21]. The cleaned samples were subsequently washed with running water and DDW, rinsed with ethanol and acetone, dried, and reweighed. All weight measurements were performed using an Ohaus Adventurer Pro AV264 analytical balance with a precision of  $\pm 0.1 \text{ mg}$ .

The corrosion rate ( $\text{CR mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ), inhibition efficiency ( $\text{IE}_{\text{wt}}\%$ ), and degree of surface coverage ( $\theta$ ) were calculated according to equations 1-3, respectively:

$$CR(mg \cdot m^{-2} \cdot h^{-1}) = \frac{\Delta m}{S \cdot \tau} \quad (1)$$

$$IE_{wl}(\%) = \frac{CR_0 - CR_i}{CR_0} \cdot 100 \quad (2)$$

$$\theta = \frac{IE_{wl}(\%)}{100} \quad (3)$$

where  $\Delta m$  is the weight loss of the coupon (mg),  $\tau$  is the immersion period (h),  $S$  is the specimen surface area ( $m^2$ ),  $CR_0$  is the corrosion rate of the D16T aluminum alloy without the inhibitor, and  $CR_i$  is the corrosion rate of the D16T aluminum alloy in the presence of the inhibitor.

### 2.3.2. Calculation of activation parameters

The activation energy was determined using the logarithmic form of the Arrhenius equation as follows (Eq. 4):

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (4)$$

where  $A$  is the Arrhenius pre-exponential factor,  $T$  is absolute temperature (K), and  $R$  is universal gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ). The plots of  $\log CR$  versus  $1/2.303RT$  yield straight lines with slopes equal to  $-E_a$  and intercepts equal to  $\log A$ . The activation enthalpy ( $\Delta H^*$ ,  $\text{kJ} \cdot \text{mol}^{-1}$ ) and activation entropy ( $\Delta S^*$ ,  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) were obtained from the slope  $-\Delta H^*/2.303R$  and intercept  $[\log R/Nh + (\Delta S^*/2.303R)]$ , respectively, of the plot of  $\log CR/T$  versus  $1/T$  in accordance with the following alternative form of Arrhenius equation 5:

$$\log \frac{CR}{T} = \frac{-\Delta H^*}{2.303R} \left( \frac{1}{T} \right) + \left[ \log \frac{R}{N_A h} + \left( \frac{\Delta S^*}{2.303R} \right) \right] \quad (5)$$

where  $h$  is Planck's constant,  $N_A$  is Avogadro's number,  $CR$  is the corrosion rate,  $T$  is absolute temperature, and  $R$  is the universal gas constant [22].

### 2.3.3. Adsorption and thermodynamics

Adsorption isotherm analysis provides valuable information on the interaction between corrosion inhibitor molecules and the metal surface. It allows the adsorption mode, surface coverage behavior, and thermodynamic characteristics of the inhibitor-metal interface to be evaluated. Several adsorption models, including Langmuir, Temkin, Frumkin, Freundlich, Flory-Huggins, El-Awady, and Dubinin-Radushkevich, are commonly used to describe inhibitor adsorption in corrosive media [23]. Each model is based on specific assumptions regarding surface homogeneity, monolayer formation, lateral interactions between adsorbed species, and the distribution of adsorption energy. Therefore, comparison of different isotherms makes it possible to obtain a more complete understanding of the adsorption mechanism rather than relying on a single model. In the present study, the experimental surface coverage values obtained for BCP on the D16T aluminum alloy in 1.0 M HCl were fitted using all the above adsorption models to determine the most appropriate description of the adsorption process and to estimate the corresponding adsorption parameters in accordance with equations 6-12:

#### *Langmuir adsorption isotherm*

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{abs}} + C_{inh} \quad (6)$$

**Temkin adsorption isotherm**

$$\theta = \ln C_{inh} + K_{ads} \quad (7)$$

**Freundlich adsorption isotherm**

$$\log \theta = \log K_{abs} + \frac{1}{n} \log C_{inh} \quad (8)$$

where  $n$  is a dimensionless constant indicating the intensity of the adsorption process.

**Flory-Huggins adsorption isotherm**

$$\log \frac{\theta}{C_{inh}} = b \log(1-\theta) + \log K_{abs} \quad (9)$$

where  $b$  is the parameter representing the interaction between the adsorbate and the adsorbent.

**Frumkin adsorption isotherm**

$$\log \left[ C_{inh} \left( \frac{\theta}{1-\theta} \right) \right] = 2\alpha\theta + 2.303 \log K_{ads} \quad (10)$$

where  $\alpha$  is the interaction parameter that quantifies the interactions between adsorbed molecules on the surface.

**El-Awady adsorption isotherm**

$$\log \left( \frac{\theta}{1-\theta} \right) = y \log C_{inh} + \log K \quad (11)$$

$$K_{ads} = K^{\frac{1}{y}}$$

where  $y$  is a parameter representing the number of active sites occupied by one molecule of the inhibitor on the metal surface.

**Dubinin–Radushkevich adsorption isotherm** [24]:

$$\ln \theta = \ln \theta_{\max} - \beta \delta^2 \quad (12)$$

where  $\theta_{\max}$  is the maximum surface coverage,  $\delta$  is Polanyi potential, and  $\beta$  is the Dubinin–Radushkevich constant related to the mean adsorption energy. The Polanyi potential is related to the inhibitor concentration by the following equation 13:

$$\delta = RT \ln \left( 1 + \frac{1}{C_{inh}} \right) \quad (13)$$

where  $R$  is the universal gas constant and  $T$  is the absolute temperature. The constant  $\beta$  is used to estimate the mean adsorption energy ( $E$ ) which represents the mean energy required to transfer one mole of inhibitor from the bulk solution toward the metal surface. The value of  $E$  was calculated with the following equation 14:

$$E = \frac{1}{\sqrt{2\beta}} \quad (14)$$

$E$  provides information about the physicochemical characteristics of the adsorption process. If the value of  $E$  is  $<8 \text{ kJ}\cdot\text{mol}^{-1}$ , this indicates physical adsorption, and if its value is  $>8 \text{ kJ}\cdot\text{mol}^{-1}$ , this indicates that the adsorption occurs *via* a chemical process.

The  $K_{ads}$  values obtained from the isotherms were used to calculate the Gibbs free energy according to the known relationship (Eq. 15) [25]:

$$\Delta G_{ads}^0 = -RT \ln(1000K_{ads}) \quad (15)$$

where  $\Delta G_{ads}^0$  is the Gibbs free energy of adsorption,  $R$  is the universal gas constant,  $T$  is the system's thermodynamic temperature, and  $1000 \text{ g}\cdot\text{dm}^{-3}$  is the approximate concentration of water. The heat of adsorption ( $Q_{ads}$ ) of the inhibitor on the metal surface was calculated from the temperature dependence of surface coverage using the following equation (Eq. 16):

$$Q_{ads} = 2.303R \left( \log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right) \cdot \left( \frac{T_1 \cdot T_2}{T_2 - T_1} \right) \quad (16)$$

#### 2.3.4. Electrochemical measurements

Electrochemical measurements were performed using an Autolab PGSTAT101 Metrohm potentiostat/galvanostat controlled by NOVA 2.1.8 software. The experiments were carried out in a conventional three-electrode electrochemical cell containing 100 mL of 1.0 M HCl solution in the absence or presence of BCP. A pretreated D16T aluminum alloy specimen was used as the working electrode (WE), an Ag/AgCl electrode in 3 M KCl served as the reference electrode (RE), and a platinum electrode was employed as the counter electrode (CE). Before polarization measurements, the WE was immersed in the test solution for 30 min to allow stabilization of the open circuit potential (OCP). Potentiodynamic polarization curves were recorded in the potential range from  $-0.50$  to

+0.50 V relative to the OCP at a scan rate of 0.01 V·s<sup>-1</sup>, with a potential step of 0.01 V.

The corrosion potential ( $E_{corr}$ ) and corrosion current density ( $j_{corr}$ ) were determined by extrapolation of the anodic and cathodic Tafel slopes. Equation 17 was used to obtain the inhibition efficiency ( $IE_j$ , %) through the corrosion current density:

$$IE_j (\%) = \frac{j_{corr}^0 - j_{corr}^{inh}}{j_{corr}^0} \cdot 100 \quad (17)$$

where  $j_{corr}^0$  and  $j_{corr}^{inh}$  are the corrosion current densities determined by extrapolating the Tafel slopes in the absence and presence of the inhibitor, respectively, A·cm<sup>-2</sup>. Using equation 18, the inhibition efficiency through the polarization resistance ( $IE_R\%$ ) was determined:

$$IE_R (\%) = \frac{R_p^{inh} - R_p^0}{R_p^{inh}} \cdot 100 \quad (18)$$

where  $R_p^{inh}$  and  $R_p^0$  represent the polarization resistances in the presence and absence of the inhibitor, respectively,  $\Omega$  [26].

### 2.3.5. Contact angle measurement

The wettability of the alloy surface was evaluated by measuring the static water contact angle using an Ossila Contact Angle Goniometer equipped with Ossila software, version 4.2.0. Water droplets were carefully deposited onto the alloy surface using a micro-syringe fitted with a 0.4 mm diameter needle. Images of the droplets were recorded with a high-resolution video camera and analyzed using the corresponding software. For each sample, the reported contact angle was calculated as the mean of at least three measurements performed at different locations on the surface to ensure reproducibility

and account for possible surface heterogeneity.

### 2.3.6. Quantum-chemical calculations

Quantum-chemical calculations are widely used in corrosion-inhibitor studies to correlate molecular electronic structure and reactivity with adsorption behavior at metal interfaces [27, 28]. Quantum-chemical calculations were performed to rationalize the adsorption ability of BCP and to identify the molecular features responsible for its corrosion inhibition performance toward D16T aluminum alloy in 1.0 M HCl. The calculations considered both the closed lactone form (BCP-LF) and the open quinonoid form (BCP-QF), because the acid-induced structural transformation of BCP may substantially influence its electronic properties and adsorption behavior.

All quantum chemical calculations were performed on a desktop PC with Windows 11, a 12<sup>th</sup> generation Intel(R) Core (TM) i7-12700H processor (2.30 GHz) and 16GB of RAM, using GAMESS software [29]. The molecular geometries of both forms were fully optimized without symmetry constraints using the semi-empirical PM3 method, the Hartree-Fock (HF) method with the 6-31G(d) basis set, and density functional theory at the B3LYP/6-311G(d,p) level. The use of different theoretical levels allowed comparison of the stability of the observed structure-property trends and separation of general electronic effects from method-dependent numerical differences. The  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  energies were extracted directly from the molecular orbital energies of the optimized BCP structures at each computational level and subsequently used to calculate the HOMO-LUMO energy gap ( $\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) and the related global quantum-chemical reactivity descriptors.

In accordance with the Koopmans' theorem [30], the HOMO energy is related to ionization potential (IP) while the LUMO energy is related to electron affinity (EA) (Eqs. 19 and 20):

$$IP = -E_{HOMO} \quad (19)$$

$$EA = -E_{LUMO} \quad (20)$$

Electronegativity ( $\chi$ ) and global hardness ( $\eta$ ) were evaluated based on the finite difference approximation as linear combinations of the calculated IP and EA (Eqs. 21 and 22):

$$\chi = \frac{IP + EA}{2} \quad (21)$$

$$\eta = \frac{IP - EA}{2} \quad (22)$$

The global softness ( $\sigma$ ) is the reciprocal of the global hardness (Eq. 23):

$$\sigma = \frac{1}{\eta} \quad (23)$$

The global electrophilicity index ( $\omega$ ) describes the stabilization of a molecule after the acquisition of an additional number of electrons (Eq. 24).

$$\omega = \frac{\chi^2}{2\eta} \quad (24)$$

The nucleophilicity index ( $\varepsilon$ ) is the reciprocal of the global electrophilicity index (Eq. 25):

$$\varepsilon = \frac{1}{\omega} \quad (25)$$

The back-donation energy ( $\Delta E_{b-d}$ ) was also evaluated to estimate the ability of the

inhibitor–metal system to stabilize through back electron donation from the metal surface to the inhibitor molecule (Eq. 26):

$$\Delta E_{b-d} = -\frac{\eta}{4} \quad (26)$$

The fraction of transferred electrons ( $\Delta N$ ) was calculated to estimate the direction and extent of electron transfer between the inhibitor molecule and the aluminum surface (Eq. 27):

$$\Delta N = \frac{\varphi_{Al} - \chi_{inhibitor}}{2(\eta_{Al} - \eta_{inhibitor})} \quad (27)$$

For the Al(111) surface, a theoretical aluminum work function ( $\varphi_{Al} = 4.26$  eV) was used instead of  $\chi_{Al}$ , and the global hardness was used as  $\eta_{Al} = 0$  [31]. In this case, the equation 27 can be rewritten as (Eq. 28):

$$\Delta N = \frac{\varphi_{Al} - \chi_{inhibitor}}{2\eta_{inhibitor}} \quad (28)$$

The metal–inhibitor interaction energy ( $\Delta\psi$ ), which is also derived from electronegativity and global hardness parameters, was calculated according to the following equation (Eq. 29) [32]:

$$\Delta\psi = \frac{(\varphi_{Al} - \chi_{inhibitor})^2}{4(\eta_{Al} + \eta_{inhibitor})} \quad (29)$$

which can be rewritten as (Eq. 30):

$$\Delta\psi = \frac{(\varphi_{Al} - \chi_{inhibitor})^2}{4\eta_{inhibitor}} \quad (30)$$

Electron-donating ( $\omega^-$ ) and electron-accepting power ( $\omega^+$ ) representing the ability of a chemical species to donate or accept electrons, respectively (Eqs. 31 and 32), were

calculated as proposed by Gazquez *et al.* [33]:

$$\omega^- = \frac{(3IP + EA)^2}{16(IP - EA)} \quad (31)$$

$$\omega^+ = \frac{(IP + 3EA)^2}{16(IP - EA)} \quad (32)$$

These parameters indicate, respectively, the ability of a molecule to donate and accept a small fractional amount of electronic charge. Furthermore, Chattaraj *et al.* recently proposed the concept of net electrophilicity ( $\Delta\omega^\pm$ ), which evaluates and compares the electrophilicity of a molecule relative to its own nucleophilicity [34]. The following equation was used to calculate this parameter (Eq. 33):

$$\Delta\omega^\pm = \omega^+ - (-\omega^-) = \omega^+ + \omega^- \quad (33)$$

Within the density functional theory, the chemical potential ( $\mu$ ) is defined as the negative of electronegativity ( $\chi$ ) (Eq. 34):

$$\mu = -\chi \quad (34)$$

Chemical potentials for electrodonating ( $\mu^-$ ) and electroaccepting ( $\mu^+$ ) processes were calculated as follows (Eq. 35):

$$\mu^- = -\frac{1}{4}(3I + A) \quad (35)$$

$$\mu^+ = -\frac{1}{4}(I + 3A) \quad (36)$$

The total negative charge (TNC) and the TNC/*n* ratio were also used as quantum-chemical descriptors reflecting the electron-donating capacity of inhibitor molecules,

particularly at their primary adsorption-active centers. Here,  $n$  denotes the total number of atoms in the molecule [35].

All quantum-chemical calculations were carried out for the aqueous phase, and the solvent ( $\text{H}_2\text{O}$ ) was incorporated via the COnductor-like Screening Model (COSMO) [36]. Visualization of the optimized molecular structures, frontier molecular orbitals, and molecular electrostatic potential maps was performed using Jmol software [37].

### **3. Results and Discussion**

#### **3.1. Weight loss assay**

The gravimetric assessment was carried out to quantify the corrosion behavior of D16T aluminum alloy in 1.0 M HCl and to evaluate the protective effect of BCP under different experimental conditions. The corresponding corrosion parameters are summarized in Table 1, and the observed variations with inhibitor concentration and temperature are illustrated in Figure 2.

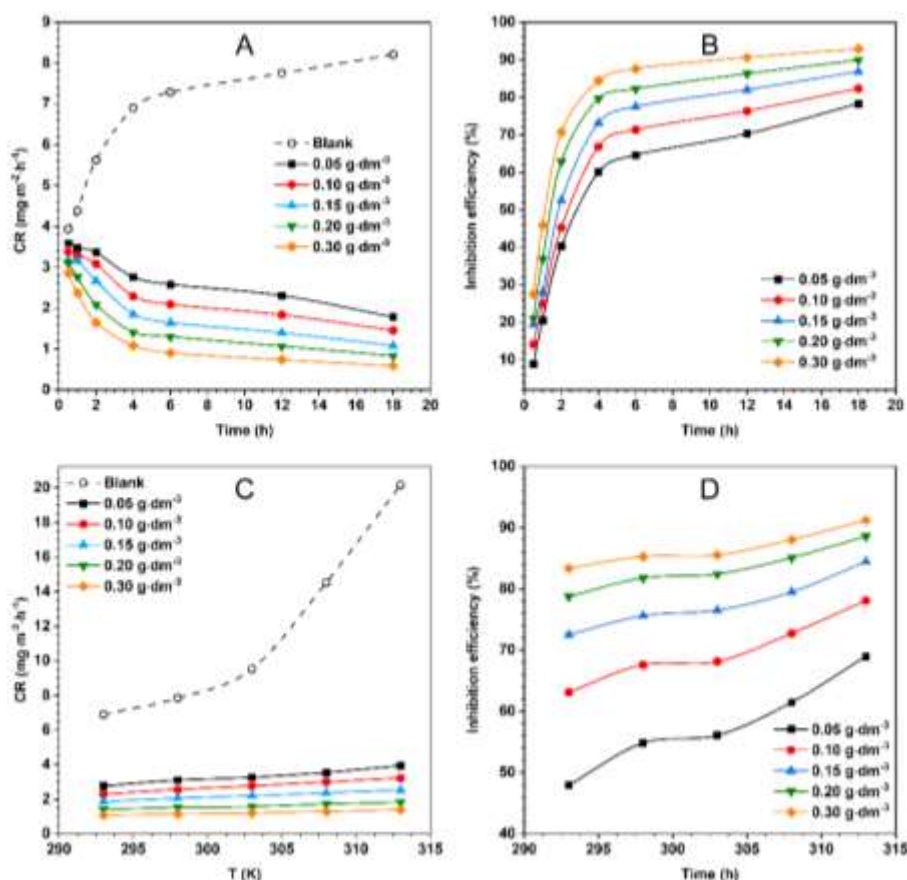


**Figure 2:** Effect of BCP concentration on corrosion rate (CR) and inhibition efficiency (IE) of aluminum in 1.0 M HCl: (A,B) influence of immersion time; (C,D) influence of temperature.

**Table 1:** Corrosion parameters obtained from weight-loss measurements for D16T aluminum alloy in 1.0 M HCl in the absence and presence of BCP at different concentrations and temperatures after 4 h immersion.

| Inhibitor concentration, $\text{g} \cdot \text{dm}^{-3}$ | CR, $\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ | IE <sub>wt</sub> % | $\theta$ |
|----------------------------------------------------------|--------------------------------------------------------|--------------------|----------|
| 293 K                                                    |                                                        |                    |          |
| Blank                                                    | 6.90                                                   | -                  | -        |
| 0.05                                                     | 2.76                                                   | 60.01              | 0.6001   |
| 0.10                                                     | 2.29                                                   | 66.67              | 0.6667   |
| 0.15                                                     | 1.85                                                   | 73.14              | 0.7314   |
| 0.20                                                     | 1.41                                                   | 79.60              | 0.7960   |
| 0.30                                                     | 1.08                                                   | 83.84              | 0.8384   |
| 298 K                                                    |                                                        |                    |          |
| Blank                                                    | 7.84                                                   | -                  | -        |
| 0.05                                                     | 3.10                                                   | 60.45              | 0.6045   |
| 0.10                                                     | 2.56                                                   | 67.36              | 0.6736   |
| 0.15                                                     | 2.05                                                   | 73.81              | 0.7381   |
| 0.20                                                     | 1.52                                                   | 80.67              | 0.8067   |
| 0.30                                                     | 1.14                                                   | 85.42              | 0.8542   |
| 303K                                                     |                                                        |                    |          |
| Blank                                                    | 9.53                                                   | -                  | -        |
| 0.05                                                     | 3.26                                                   | 65.83              | 0.6583   |
| 0.10                                                     | 2.77                                                   | 70.93              | 0.7093   |

|       |       |       |        |
|-------|-------|-------|--------|
| 0.15  | 2.20  | 76.90 | 0.7690 |
| 0.20  | 1.57  | 83.52 | 0.8352 |
| 0.30  | 1.20  | 87.41 | 0.8741 |
| 308 K |       |       |        |
| Blank | 14.53 | -     | -      |
| 0.05  | 3.54  | 75.62 | 0.7562 |
| 0.10  | 3.00  | 79.37 | 0.7937 |
| 0.15  | 2.36  | 83.77 | 0.8377 |
| 0.20  | 1.72  | 88.16 | 0.8816 |
| 0.30  | 1.28  | 91.19 | 0.9119 |
| 313K  |       |       |        |
| Blank | 20.18 | -     | -      |
| 0.05  | 3.94  | 80.49 | 0.8049 |
| 0.10  | 3.22  | 84.04 | 0.8404 |
| 0.15  | 2.53  | 87.46 | 0.8746 |
| 0.20  | 1.82  | 90.98 | 0.9098 |
| 0.30  | 1.38  | 93.16 | 0.9316 |

The observed trend indicates that the corrosion rate (CR) of the D16T aluminum alloy decreases significantly with increasing inhibitor concentration, while the inhibition efficiency (IE) correspondingly increases. In the uninhibited solution, the alloy exhibits a relatively high corrosion rate, reflecting the aggressive nature of the hydrochloric acid medium and the instability of the native oxide film. Upon the addition of BCP, the corrosion rate declines markedly, even at low concentrations, indicating the effective adsorption of inhibitor molecules onto the metal surface.

The time-dependent behavior presented in Figure 2(A,B) shows that the corrosion rate decreases with immersion time in the presence of the inhibitor, whereas the inhibition efficiency increases and gradually approaches a steady value. This behavior indicates gradual occupation of active surface sites by BCP species and progressive development of an interfacial barrier. At longer immersion times, the relatively stable IE values indicate the persistence and stability of this protective layer. The concentration-dependent results further confirm this behavior. At 293 K, the inhibition efficiency increases from 60.01% at 0.05 g·dm<sup>-3</sup> to about 83.84% at 0.3 g·dm<sup>-3</sup>. A similar trend is

observed at higher temperatures, with IE values reaching up to ~93% at 313 K. This systematic increase in efficiency with concentration indicates that the adsorption process follows a surface coverage mechanism, where higher inhibitor concentrations promote the formation of a more compact and continuous film on the D16T aluminum alloy surface.

The effect of temperature, as shown in Figure 2(C,D) and Table 1, reveals that the corrosion rate increases with temperature in both inhibited and uninhibited systems, which is typical for acid corrosion processes. However, in the presence of BCP the inhibition efficiency also increases with temperature. For example, at a concentration of  $0.3 \text{ g}\cdot\text{dm}^{-3}$ , the IE increases from 83.84% at 293 K to 93.16% at 313 K. This behavior suggests that the adsorption of the inhibitor is enhanced at higher temperatures and may involve a significant chemisorption contribution.

The simultaneous increase in inhibition efficiency with both concentration and temperature indicates that the adsorption of BCP on the D16T aluminum alloy surface is not purely physical but likely involves a combined physical–chemical adsorption pathway with a dominant chemisorption component at elevated temperatures. The enhanced efficiency at higher temperatures can be attributed to stronger interactions between the inhibitor molecules and the metal surface, possibly involving charge transfer between the  $\pi$ -electron system and the vacant orbitals of aluminum.

The gravimetric results show that BCP effectively suppresses the dissolution of the D16T aluminum alloy in 1.0 M HCl. Its protective performance is controlled by inhibitor concentration and temperature, while the observed trends support the presence of a stable adsorbed interfacial layer formed through a mixed adsorption pathway.

### 3.2. Activation parameters

The temperature dependence of the corrosion process was further examined using the Arrhenius and transition-state approaches in order to evaluate the kinetic and activation parameters associated with BCP adsorption and inhibition. The corresponding linear plots are presented in Figure 3.

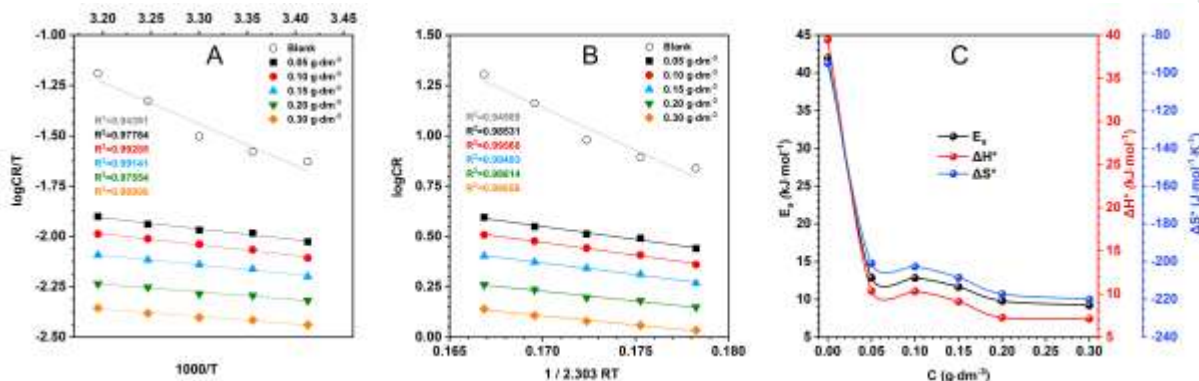


**Figure 3:** Transition-state plots (A), Arrhenius plots (B), and concentration-dependent variation of activation energy ( $E_a$ ), activation enthalpy ( $\Delta H^*$ ) and activation entropy ( $\Delta S^*$ ) (C) for D16T aluminum alloy in 1.0 M HCl in the absence and presence of BCP after 4 h immersion.

The Arrhenius plots of log CR/T versus 1000/T and the transition-state plots of log CR versus 1/2.303RT showed good linearity, confirming that the corrosion process follows temperature-activated kinetics within the investigated temperature range. The correlation coefficients were generally high for both models, indicating that the calculated activation parameters are reliable for discussing the effect of BCP on the metal dissolution process.

In the uninhibited acid solution, the activation energy was 41.99 kJ·mol<sup>-1</sup>, whereas the addition of BCP caused a marked decrease in  $E_a$  to 12.88 kJ·mol<sup>-1</sup> even at the lowest inhibitor concentration. With a further increase in inhibitor concentration,  $E_a$  gradually decreased to 9.20 kJ·mol<sup>-1</sup>. This pronounced reduction indicates that the corrosion process in the inhibited medium proceeds through a different interfacial pathway

compared with the blank solution. An increase in  $E_a$  is often associated with predominantly physical adsorption, where the adsorbed layer acts mainly as a physical barrier for metal dissolution [38]. In contrast, the observed decrease in  $E_a$  suggests that BCP does not simply block the surface by weak electrostatic adsorption; rather, it participates in the formation of a more strongly interacting adsorbed layer that modifies the metal/solution interface and facilitates a lower-energy corrosion pathway under protected conditions [39].

The same trend was observed for the activation enthalpy. The blank solution exhibited a  $\Delta H^*$  value of  $39.48 \text{ kJ}\cdot\text{mol}^{-1}$ , whereas the inhibited systems showed much lower values, decreasing from  $10.36$  to  $7.12 \text{ kJ}\cdot\text{mol}^{-1}$  with increasing BCP concentration. The positive values of  $\Delta H^*$  in all cases indicate that the dissolution process remains endothermic and requires energy input to reach the activated state [40]. However, the substantial decrease in  $\Delta H^*$  after inhibitor addition confirms that the energetic nature of the activated complex changes in the presence of BCP. The close relationship between  $E_a$  and  $\Delta H^*$  is expected because these parameters are thermodynamically related, and their parallel decrease therefore provides consistent evidence that inhibitor adsorption alters the activation barrier to metal dissolution [41].

The entropy of activation provides additional information on the degree of order in the activated state. For the blank solution,  $\Delta S^*$  was  $-94.90 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , indicating that the activated complex is more ordered than the initial state [42]. In the presence of BCP,  $\Delta S^*$  became considerably more negative, reaching  $-220.00 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  at the highest concentration. This trend suggests that the formation of the activated complex in inhibited solutions is accompanied by a greater increase in order. Such behavior is

consistent with the development of an organized adsorbed layer at the metal/solution interface, where BCP molecules become oriented and immobilized on active corrosion sites through interactions involving heteroatoms, aromatic  $\pi$ -systems and charged/polar functional groups.

The simultaneous decrease in  $E_a$  and  $\Delta H^*$ , together with the increasingly negative  $\Delta S^*$ , indicates that BCP inhibits corrosion not only by simple surface coverage but also by modifying the interfacial reaction pathway [43]. The inhibitor molecules appear to form a compact and relatively ordered protective film, which limits the access of aggressive chloride ions and hydrogen ions to the metal surface. The decrease in activation energy and enthalpy supports the contribution of stronger adsorptive interactions, while the negative entropy values point to the formation of a more structured inhibitor–metal interfacial layer. Therefore, the inhibition mechanism can be described as mixed adsorption with a significant chemisorptive contribution, accompanied by the formation of an ordered protective film that reduces the effective rate of metal dissolution in 1.0 M HCl [44].

A particularly important observation is that the activation parameters change sharply even at low inhibitor concentrations and then vary more gradually at higher concentrations. This suggests that the most active corrosion sites are occupied preferentially at the initial stage of inhibitor addition, while further increases in concentration mainly improve the compactness and continuity of the adsorbed layer. This interpretation agrees well with the concentration-dependent decrease in corrosion rate and supports the formation of a protective adsorption film as the dominant factor governing the anticorrosion performance of BCP.

### 3.3. Adsorption and thermodynamics

To provide further insight into the adsorption behavior of BCP on the D16T aluminum alloy surface in 1.0 M HCl, the experimental surface coverage data were fitted using several adsorption models. The corresponding linear plots are presented in Figure 4, while the calculated adsorption and thermodynamic parameters are summarized in Table 2.

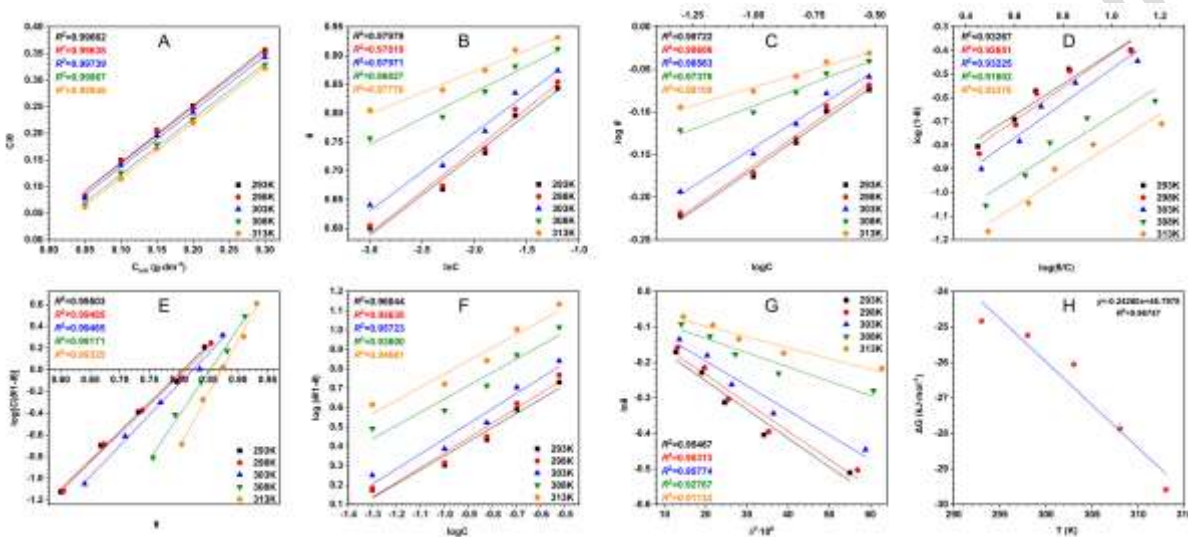


**Figure 4:** Adsorption isotherms of BCP on the D16T aluminum alloy surface in 1.0 M HCl solution for 4 h immersion: (A) Langmuir, (B) Temkin, (C) Freundlich, (D) Flory-Huggins, (E) Frumkin, (F), El-Awady, (G) Dubinin-Radushkevich, and temperature dependence of Gibbs free energy of adsorption (H).

**Table 2:** Adsorption and thermodynamic parameters for BCP adsorption on D16T aluminum alloy in 1.0 M HCl, derived from different adsorption models.

| Isotherm   | T, K | Slope   | Intercept | R <sup>2</sup> | K <sub>ads</sub> ,<br>10 <sup>-3</sup> ·dm <sup>-3</sup> ·g <sup>-1</sup> | ΔG <sup>0</sup> <sub>ads</sub> ,<br>kJ·mol <sup>-1</sup> | Isotherm<br>property |
|------------|------|---------|-----------|----------------|---------------------------------------------------------------------------|----------------------------------------------------------|----------------------|
| Langmuir   | 293  | 1.07160 | 0.03757   | 0.99662        | 26.62                                                                     | -24.83                                                   | -                    |
|            | 298  | 1.05533 | 0.03785   | 0.99638        | 26.42                                                                     | -25.23                                                   | -                    |
|            | 303  | 1.04406 | 0.03230   | 0.99739        | 30.96                                                                     | -26.05                                                   | -                    |
|            | 308  | 1.04077 | 0.01888   | 0.99867        | 52.97                                                                     | -27.86                                                   | -                    |
|            | 313  | 1.03972 | 0.01161   | 0.99946        | 86.13                                                                     | -29.58                                                   | -                    |
| Temkin     | 293  | 0.14060 | 1.00919   | 0.97979        | 1.009                                                                     | -16.85                                                   | -                    |
|            | 298  | 0.14455 | 1.02478   | 0.97819        | 1.025                                                                     | -17.18                                                   | -                    |
|            | 303  | 0.13594 | 1.03775   | 0.97971        | 1.038                                                                     | -17.50                                                   | -                    |
|            | 308  | 0.09079 | 1.01795   | 0.96827        | 1.018                                                                     | -17.74                                                   | -                    |
|            | 313  | 0.07384 | 1.02006   | 0.97776        | 1.020                                                                     | -18.03                                                   | -                    |
|            |      |         |           |                |                                                                           |                                                          | <b>n</b>             |
| Freundlich | 293  | 0.19729 | 0.03031   | 0.98722        | 0.982                                                                     | -16.79                                                   | 5.07                 |
|            | 298  | 0.20076 | 0.03777   | 0.98606        | 1.091                                                                     | -17.33                                                   | 4.98                 |

|                          |     |                       |          |         |                                  |                                                                                            |                                                           |
|--------------------------|-----|-----------------------|----------|---------|----------------------------------|--------------------------------------------------------------------------------------------|-----------------------------------------------------------|
|                          | 303 | 0.18124               | 0.03889  | 0.98563 | 1.094                            | -17.63                                                                                     | 5.52                                                      |
|                          | 308 | 0.10943               | 0.01646  | 0.97376 | 1.039                            | -17.79                                                                                     | 9.14                                                      |
|                          | 313 | 0.08530               | 0.01419  | 0.98109 | 1.033                            | -18.06                                                                                     | 11.72                                                     |
|                          |     |                       |          |         |                                  |                                                                                            | <b>b</b>                                                  |
| Flory-Huggins            | 293 | 0.65751               | -1.06736 | 0.93267 | 0.0856                           | -10.84                                                                                     | 0.658                                                     |
|                          | 298 | 0.70269               | -1.11898 | 0.92651 | 0.0760                           | -10.73                                                                                     | 0.703                                                     |
|                          | 303 | 0.72766               | -1.20631 | 0.93225 | 0.0622                           | -10.41                                                                                     | 0.728                                                     |
|                          | 308 | 0.64638               | -1.32505 | 0.91602 | 0.0473                           | -9.88                                                                                      | 0.646                                                     |
|                          | 313 | 0.65208               | -1.46136 | 0.93376 | 0.0346                           | -9.22                                                                                      | 0.652                                                     |
|                          |     |                       |          |         |                                  |                                                                                            | <b><math>\alpha</math></b>                                |
| Frumkin                  | 293 | 0.18812               | 0.80711  | 0.99503 | 2.24                             | -18.80                                                                                     | 0.094                                                     |
|                          | 298 | 0.18927               | 0.81149  | 0.99485 | 2.25                             | -19.13                                                                                     | 0.095                                                     |
|                          | 303 | 0.17643               | 0.82348  | 0.99465 | 2.28                             | -19.48                                                                                     | 0.088                                                     |
|                          | 308 | 0.12462               | 0.85293  | 0.99171 | 2.35                             | -19.88                                                                                     | 0.062                                                     |
|                          | 313 | 0.10140               | 0.87265  | 0.99325 | 2.39                             | -20.25                                                                                     | 0.051                                                     |
|                          |     |                       |          |         |                                  |                                                                                            | <b><math>1/y</math></b>                                   |
| El-Awady                 | 293 | 0.72819               | 1.08044  | 0.96044 | 33.05                            | -25.35                                                                                     | 2.75                                                      |
|                          | 298 | 0.76602               | 1.13339  | 0.95638 | 35.50                            | -25.96                                                                                     | 2.61                                                      |
|                          | 303 | 0.78011               | 1.21961  | 0.95723 | 42.51                            | -26.85                                                                                     | 2.56                                                      |
|                          | 308 | 0.68815               | 1.33355  | 0.93600 | 62.65                            | -28.29                                                                                     | 2.91                                                      |
|                          | 313 | 0.68340               | 1.45772  | 0.94661 | 83.96                            | -29.51                                                                                     | 2.93                                                      |
|                          |     |                       |          |         | <b><math>\theta_{max}</math></b> | <b><math>\beta, \cdot 10^{-9}</math><br/><math>\text{mol}^2 \cdot \text{J}^{-2}</math></b> | <b>E<br/><math>\text{kJ} \cdot \text{mol}^{-1}</math></b> |
| Dubinin-<br>Radushkevich | 293 | $-8.08 \cdot 10^{-9}$ | -0.08999 | 0.95467 | 0.9139                           | 8.08                                                                                       | 7.87                                                      |
|                          | 298 | $-7.94 \cdot 10^{-9}$ | -0.07566 | 0.95313 | 0.9271                           | 7.94                                                                                       | 7.94                                                      |
|                          | 303 | $-6.96 \cdot 10^{-9}$ | -0.05670 | 0.95774 | 0.9449                           | 6.96                                                                                       | 8.48                                                      |
|                          | 308 | $-4.02 \cdot 10^{-9}$ | -0.05171 | 0.92767 | 0.9496                           | 4.02                                                                                       | 11.15                                                     |
|                          | 313 | $-3.05 \cdot 10^{-9}$ | -0.03663 | 0.91132 | 0.9640                           | 3.05                                                                                       | 12.80                                                     |

Among the examined models, the Langmuir isotherm provided the best description of the adsorption process, with very high linear regression coefficients  $R^2 > 0.996$ . This indicates that BCP molecules form an adsorbed protective layer on the aluminum alloy surface and that the degree of surface coverage increases regularly with inhibitor concentration. The Langmuir slopes were close to unity, suggesting that the adsorption process approximately follows monolayer-type behavior [45]. However, the slight deviation of the slopes from the ideal value also implies that the adsorption is not completely ideal, most likely because of surface heterogeneity, oxide/hydroxide species, and interactions between adsorbed inhibitor molecules. The adsorption equilibrium constant obtained from the Langmuir model increased markedly with temperature, from

26.62 at 293 K to 86.13 at 313 K. This trend shows that the adsorption of BCP becomes more favorable at elevated temperatures. Such behavior is consistent with the experimental inhibition results and indicates that heating does not destroy the inhibitor film; rather, it promotes stronger adsorption and better organization of BCP molecules at the aluminum/acid interface. This may be related to the partial removal of pre-adsorbed water molecules and chloride-containing species, followed by more effective anchoring of BCP through oxygen-containing groups and aromatic  $\pi$ -systems.

The Frumkin isotherm also showed excellent linearity ( $R^2 > 0.99$ ). Its strong applicability confirms that lateral interactions between adsorbed BCP molecules contribute to the adsorption process [46]. The Frumkin interaction parameter ( $\alpha$ ) was positive but relatively small, decreasing from 0.094 to 0.051 with increasing temperature. This suggests weak attractive interactions between adsorbed inhibitor species and indicates that the protective layer becomes more uniformly distributed at higher temperatures. Therefore, the Frumkin model supports the conclusion that BCP adsorption is not purely ideal monolayer adsorption but involves intermolecular interactions within the adsorbed film.

Other models provided additional evidence for the non-ideal character of the adsorption process. The Freundlich and Temkin isotherms gave satisfactory correlation coefficients, indicating surface heterogeneity and variation in adsorption energy with surface coverage. The Dubinin–Radushkevich model yielded moderate adsorption energy values, suggesting contributions from both physical adsorption and stronger inhibitor–surface interactions. However, its comparatively lower linearity indicates that it provides only a supplementary description of BCP adsorption. The better agreement with the

Langmuir and Frumkin models, together with the increase in  $K_{ads}$  and the increasingly negative  $\Delta G^0_{ads}$  values, further indicates that BCP adsorption cannot be attributed solely to simple physical accumulation at the surface.

The values of  $\Delta H^0_{ads}$  and  $\Delta S^0_{ads}$  were determined from the temperature dependence of  $\Delta G^0_{ads}$  using the rearranged Gibbs-Helmholtz equation as follows (Eq. 37):

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \quad (37)$$

The slope and intercept of the  $\Delta G^0_{ads}$  versus T plot were used to determine  $\Delta S^0_{ads}$  and  $\Delta H^0_{ads}$ , respectively (Figure 4H).

The negative Gibbs free energy values calculated from the Langmuir model, ranging from -24.83 to -29.58 kJ·mol<sup>-1</sup>, confirm the spontaneous nature of BCP adsorption on the D16T aluminum alloy surface [47]. The increasingly negative  $\Delta G^0_{ads}$  values with temperature indicate that adsorption becomes thermodynamically more favorable as the temperature rises. These values are more negative than those usually associated with weak physisorption but less negative than those typical for purely chemical adsorption. Therefore, the adsorption of BCP can be interpreted as a mixed process involving electrostatic attraction between inhibitor species and charged surface sites, together with stronger donor–acceptor interactions through oxygen atoms and  $\pi$ -electron systems.

The positive value of  $\Delta H^0_{ads}$ , equal to 46.80 kJ·mol<sup>-1</sup>, indicates that the adsorption of BCP on the D16T aluminum alloy surface is endothermic. This suggests that increasing temperature facilitates adsorption, which is consistent with the rise in  $K_{ads}$  and the more negative  $\Delta G^0_{ads}$  values at elevated temperatures. Such behavior may be associated with the partial desorption of water molecules and aggressive chloride-

containing species from the D16T aluminum alloy surface, followed by stronger interaction of BCP molecules with active adsorption sites [48]. The positive  $\Delta S_{ads}^0$  value of  $242.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  indicates an increase in disorder during adsorption, most likely due to the replacement of ordered water molecules at the metal/solution interface by larger organic inhibitor molecules [49]. Therefore, the positive enthalpy and entropy values support a temperature-assisted adsorption process, in which BCP molecules become more effectively adsorbed and form a more stable protective film at higher temperatures.

Thus, the adsorption analysis demonstrates that BCP spontaneously adsorbs on the D16T aluminum alloy in 1.0 M HCl and forms a protective interfacial film. The Langmuir model supports predominant monolayer-type surface coverage, whereas the Frumkin model reveals lateral interactions between adsorbed species. The thermodynamic parameters indicate a mixed adsorption mechanism, in which initial electrostatic interaction is accompanied by stronger binding through oxygen-containing functional groups and aromatic  $\pi$ -systems. This adsorbed layer limits the access of aggressive chloride and hydrogen ions to the D16T aluminum alloy surface, thereby reducing alloy dissolution in hydrochloric acid.

### 3.4. Heat of adsorption ( $Q_{ads}$ )

To further elucidate the temperature-dependent adsorption behavior of BCP at the metal/solution interface, the heat of adsorption ( $Q_{ads}$ ) was calculated over different temperature intervals. This parameter provides useful information on the thermal response of the adsorbed inhibitor layer and allows assessment of whether the adsorption process becomes more favorable, less stable, or mechanistically altered with increasing

temperature. The calculated ( $Q_{ads}$ ) values are presented in Table 3, while their variation as a function of temperature interval and temperature difference is illustrated in Figure 5.

**Table 3:** Heat of adsorption ( $Q_{ads}$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ) values for BCP on the D16T aluminum alloy surface in 1.0 M HCl over different temperature intervals and inhibitor concentrations.

| Temperature range, K | $T_2-T_1$ , K | Inhibitor concentration, $\text{g}\cdot\text{dm}^{-3}$ |       |       |       |       |
|----------------------|---------------|--------------------------------------------------------|-------|-------|-------|-------|
|                      |               | 0.05                                                   | 0.10  | 0.15  | 0.20  | 0.30  |
| 293/298              | 5             | 2.65                                                   | 3.88  | 4.98  | 9.73  | 12.28 |
| 298/303              | 5             | 23.00                                                  | 25.11 | 25.05 | 29.21 | 25.49 |
| 303/308              | 5             | 86.08                                                  | 70.64 | 68.07 | 59.72 | 61.96 |
| 308/313              | 5             | 45.74                                                  | 50.36 | 48.24 | 48.62 | 43.96 |
| 293/303              | 10            | 12.66                                                  | 14.32 | 14.85 | 19.31 | 18.77 |
| 293/308              | 15            | 36.33                                                  | 32.47 | 32.00 | 32.33 | 32.69 |
| 293/313              | 20            | 38.57                                                  | 36.73 | 35.87 | 36.21 | 35.37 |

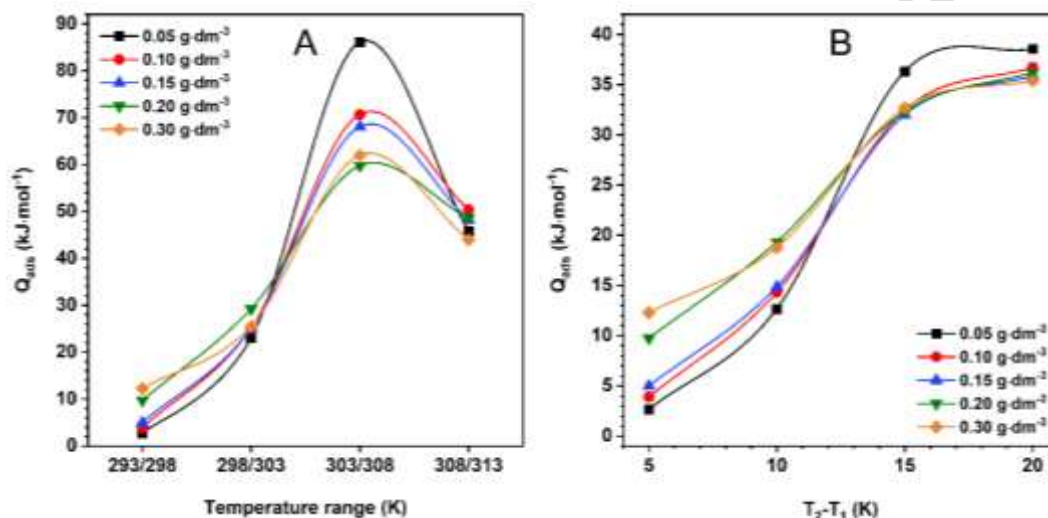


**Figure 5:** Temperature-dependent variation of adsorption heat ( $Q_{ads}$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ) for BCP on D16T aluminum alloy surface in 1.0 M HCl: effect of temperature interval (A) and temperature difference ( $T_2 - T_1$ ) (B).

The  $Q_{ads}$  values were positive for all investigated systems, indicating that the adsorption of BCP on the D16T aluminum alloy surface is endothermic and associated with heat absorption [50]. This suggests that the inhibition process is not limited to simple physical accumulation of molecules at the interface but also involves temperature-assisted rearrangement of the adsorbed layer, replacement of water molecules and aggressive ions, and strengthening of inhibitor–surface interactions.

For the lowest temperature interval, 293–298 K,  $Q_{ads}$  values were relatively small, ranging from 2.65 to 12.28 kJ·mol<sup>-1</sup>, and increased with inhibitor concentration. This behavior indicates that, near room temperature, adsorption is mainly governed by surface coverage and the occupation of the most active corrosion sites. A sharp increase in  $Q_{ads}$  was observed at higher-temperature intervals, especially at 303–308 K, where the maximum values were reached. This temperature range may represent a transition region in which thermal activation promotes molecular mobility, interfacial reorganization and the formation of a more compact protective film. At the highest interval of 308–313 K, the adsorption heat decreased, although it remained relatively high. This decrease suggests that a further temperature increase does not simply enhance adsorption but changes the balance between film strengthening and partial destabilization [51]. In this range, thermal motion may promote some loosening or rearrangement of weakly bound inhibitor molecules, while the protective layer remains present on the alloy surface.

The dependence of  $Q_{ads}$  on the temperature difference ( $T_2 - T_1$ ) shows a general increase from 5 to 15–20 K, followed by a tendency toward stabilization. This indicates that the thermal response of the adsorbed layer becomes more pronounced over broader temperature ranges, but after the formation of a sufficiently compact interfacial film, the additional thermal effect becomes less pronounced.

Therefore, the  $Q_{ads}$  changes demonstrate that the inhibition mechanism of BCP is strongly temperature-dependent. At lower temperatures, adsorption is controlled mainly by surface coverage and physical occupation of active sites. With increasing temperature, especially in the 303–308 K range, stronger inhibitor–surface interactions and structural ordering of the adsorbed film become more important. At still higher temperatures,

partial reorganization or destabilization of the layer occurs. These findings suggest that BCP inhibits D16T aluminum alloy corrosion through a combined physical–chemical adsorption pathway involving initial physical adsorption followed by temperature-assisted strengthening of interfacial interactions and formation of a compact protective film.

### 3.5. UV–visible spectroscopic analysis

UV–visible spectroscopy is widely employed in corrosion inhibition studies to probe the electronic structure and solution behavior of inhibitor molecules. It enables the detection of changes in molecular state, concentration, and chromophore integrity during interaction with metallic surfaces. In particular, comparison of spectra before and after alloy exposure provides valuable insight into adsorption processes and the stability of the inhibitor in aggressive media, thereby supporting the interpretation of inhibition mechanisms. The UV–visible spectra of the BCP solution in 1.0 M HCl before and after immersion of the aluminum specimen are presented in Figure 6.

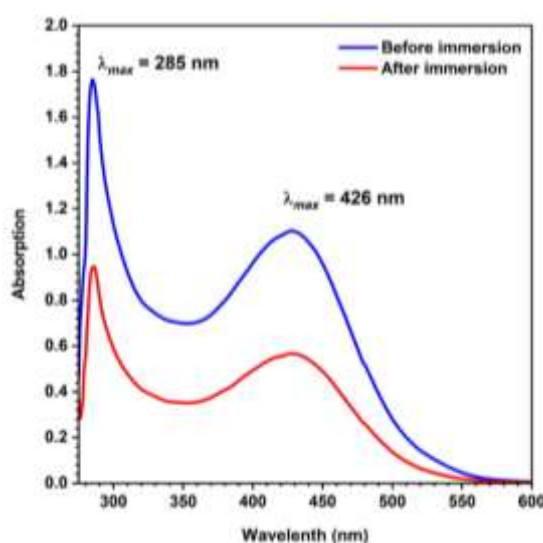


**Figure 6:** UV–visible spectra of BCP in 1.0 M HCl solution before and after 24 h immersion of D16T aluminum alloy coupon.

The initial spectrum of the inhibitor solution exhibits two characteristic absorption maxima at 285 and 426 nm, which can be attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transitions associated with the conjugated chromophore system of the dye. In a strongly acidic medium, bromocresol purple predominantly exists in its quinonoid form, characterized by an extended  $\pi$ -electron system and enhanced charge delocalization, which contributes to its pronounced absorption in the visible region.

After exposure of the D16T aluminum alloy sample to the corrosive medium, the positions of the absorption maxima remain essentially unchanged, indicating that the electronic structure of the chromophore is preserved. However, a significant hypochromic effect is observed across the entire spectral range, with a more pronounced reduction in the long-wavelength region around 426 nm. The absence of bathochromic or hypsochromic shifts suggests that no substantial chemical transformation or degradation of the inhibitor occurs in the solution phase. The observed hypochromic effect can therefore be attributed to a decrease in the concentration of free dye molecules in the bulk solution due to their adsorption onto the D16T aluminum alloy surface. Under acidic conditions, the predominance of the quinonoid form may further promote adsorption owing to its higher planarity and enhanced electron delocalization, which favor stronger interactions with the metal surface. Thus, the UV–Vis spectroscopic results provide clear evidence of adsorption-driven inhibition and agree well with the thermodynamic data, confirming the formation of a stable interfacial protective film through a mixed adsorption mechanism.

### 3.6. FTIR spectroscopic analysis

Fourier-transform infrared (FTIR) spectroscopy is a commonly employed spectroscopic technique in corrosion inhibition studies to identify functional groups involved in adsorption processes and to elucidate the nature of interactions between inhibitor molecules and metal surfaces. Comparative analysis of the spectra of the pure inhibitor and corrosion products formed in its presence allows the identification of changes in vibrational bands, shifts in characteristic frequencies, and the appearance or disappearance of specific absorption features. These variations provide valuable insights into the adsorption mechanism and the possible formation of surface complexes. The FTIR spectra of the pure inhibitor and the corrosion products formed after immersion of the aluminum specimen in 1.0 M HCl are presented in Figure 7.

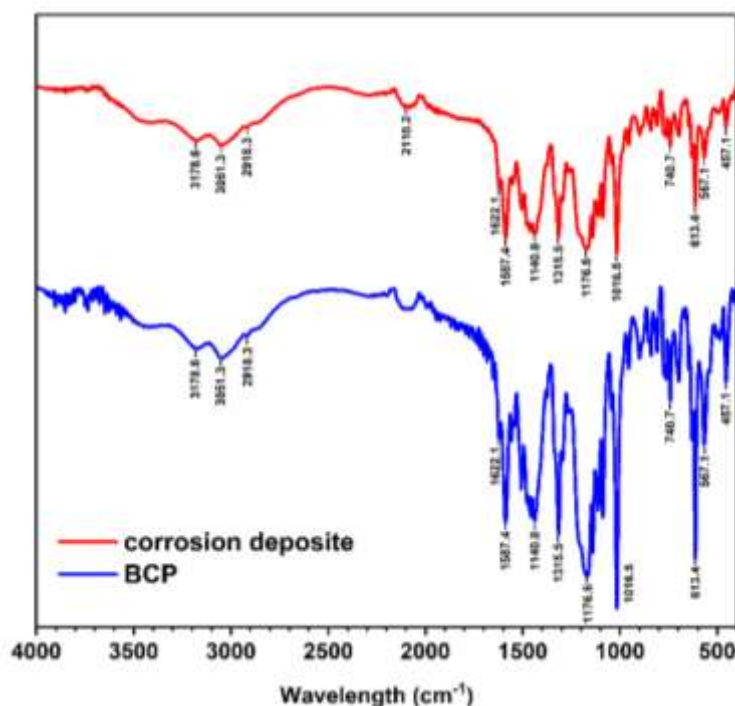


**Figure 7:** FTIR spectra of pure BCP and corrosion products formed on D16T aluminum alloy after immersion in 1.0 M HCl.

The FTIR spectrum of pure BCP exhibits a broad absorption band centered at  $3178.6\text{ cm}^{-1}$ , which is attributed to O–H stretching vibrations associated with phenolic groups and hydrogen bonding [52]. Additional bands observed at  $3051.3$  and  $2918.3\text{ cm}^{-1}$  correspond to aromatic and aliphatic C–H stretching vibrations. In the spectrum of the corrosion deposits, these bands appear at  $3178.6$ ,  $3051.3$ , and  $2918.3\text{ cm}^{-1}$  with slightly reduced intensity, indicating the involvement of hydroxyl groups in adsorption while preserving the overall molecular framework of the inhibitor.

In the fingerprint region, more pronounced changes are observed. The strong band at  $1622.1\text{ cm}^{-1}$ , associated with C=C stretching vibrations of the aromatic ring, remains present but exhibits a decrease in intensity in the corrosion product spectrum, indicating interaction of the  $\pi$ -electron system with the alloy surface. The band at  $1587.4\text{ cm}^{-1}$  shows similar behavior, further supporting the involvement of the aromatic system in adsorption. Significant modifications are also detected in the region of  $1400\text{--}1000\text{ cm}^{-1}$ . The bands at  $1400.8$  and  $1315.5\text{ cm}^{-1}$ , attributed to C–O stretching vibrations, as well as the strong absorption at  $1176.6\text{ cm}^{-1}$  corresponding to S=O stretching of the sulfonate group, exhibit noticeable changes in intensity and slight shifts upon adsorption. In particular, the band at  $1016.5\text{ cm}^{-1}$  becomes less intense in the corrosion deposit spectrum, indicating the participation of sulfonate oxygen atoms in interaction with the metal surface. In the low-frequency region, bands at  $740.7$ ,  $613.4$ ,  $567.1$ , and  $457.1\text{ cm}^{-1}$  are observed in both spectra; however, their relative intensities differ in the corrosion deposits, which may be attributed to the formation of metal–oxygen bonds.

The obtained spectral characteristics indicate that bromocresol purple is adsorbed onto the D16T aluminum alloy surface through multiple active centers, including

phenolic hydroxyl groups, sulfonate functionalities, and the conjugated  $\pi$ -electron system. The absence of significant band disappearance or the emergence of new dominant peaks confirms that the molecular structure of the inhibitor remains largely intact, while the observed intensity changes and minor shifts point to a mixed adsorption mechanism involving both physical adsorption and chemical interaction. These findings are consistent with the UV–visible spectroscopic results, where a pronounced hypochromic effect without significant shifts in absorption maxima was observed. This indicates that the decrease in absorbance is primarily due to the adsorption of inhibitor molecules onto the metal surface rather than their degradation or chemical transformation in solution. Based on the combined spectroscopic evidence, BCP is likely adsorbed on the D16T aluminum alloy surface mainly in its protonated quinonoid form, which is favored in acidic media. The adsorption process is driven by donor–acceptor interactions between oxygen atoms of the inhibitor and the D16T aluminum alloy surface, as well as  $\pi$ -electron interactions, leading to the formation of a less permeable interfacial film responsible for corrosion inhibition.

### 3.7. Electrochemical experiments

The electrochemical behavior of D16T aluminum alloy in 1.0 M HCl in the absence and presence of BCP was investigated using open circuit potential (OCP) monitoring and potentiodynamic polarization measurements. The corresponding OCP–time and Tafel polarization curves are presented in Figure 8. The calculated electrochemical parameters are summarized in Table 4.

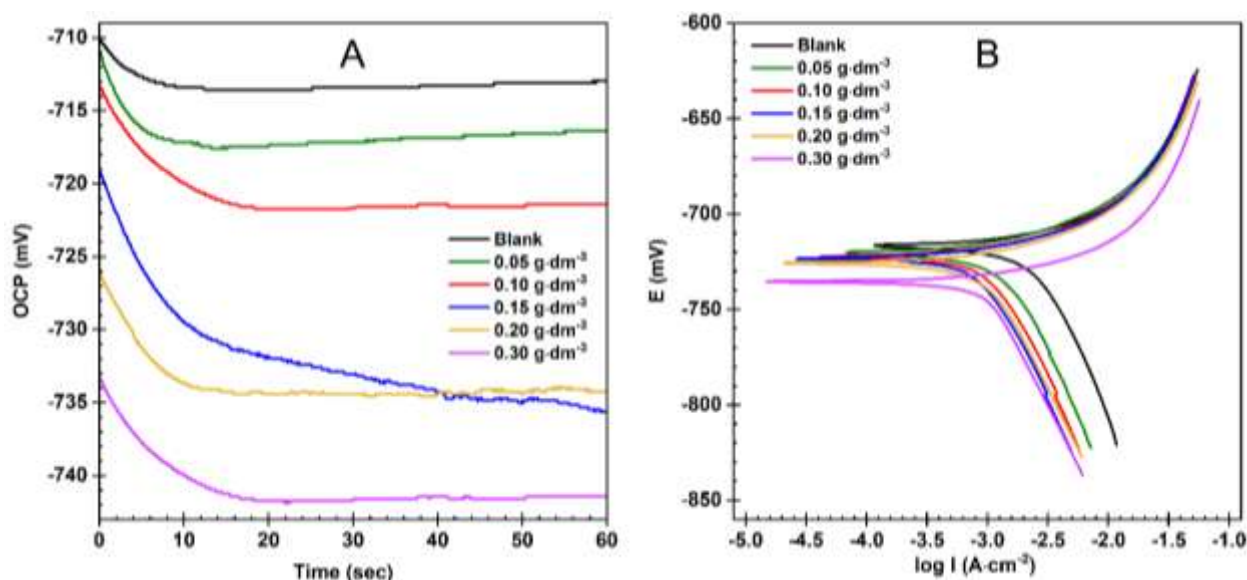


**Figure 8:** OCP - time curves (A) and potentiodynamic polarization curves (B) of D16T aluminum alloy in 1.0 M HCl with and without different concentrations of BCP at room temperature.

**Table 4.** Electrochemical corrosion parameters of D16T aluminum alloy in 1.0 M HCl with and without different concentrations of BCP at room temperature.

| Concentration, g·dm <sup>-3</sup> | -E <sub>corr</sub> , mV | j <sub>corr</sub> , A·cm <sup>-2</sup> | IE <sub>i</sub> , % | b <sub>a</sub>  , mV·dec <sup>-1</sup> | b <sub>c</sub>  , mV·dec <sup>-1</sup> | R <sub>p</sub> , Ω | IE <sub>R</sub> , % |
|-----------------------------------|-------------------------|----------------------------------------|---------------------|----------------------------------------|----------------------------------------|--------------------|---------------------|
| 0.00                              | 716.43                  | 1.16·10 <sup>-4</sup>                  | -                   | 35.2                                   | 132.5                                  | 5.35               | -                   |
| 0.05                              | 719.90                  | 6.89·10 <sup>-5</sup>                  | 40.84               | 33.5                                   | 136.2                                  | 8.68               | 38.25               |
| 0.10                              | 722.58                  | 4.14·10 <sup>-5</sup>                  | 64.43               | 23.2                                   | 118.0                                  | 8.69               | 38.45               |
| 0.15                              | 723.61                  | 2.65·10 <sup>-5</sup>                  | 77.29               | 22.3                                   | 122.8                                  | 8.82               | 39.33               |
| 0.20                              | 725.72                  | 2.08·10 <sup>-5</sup>                  | 82.17               | 25.9                                   | 123.5                                  | 9.56               | 38.25               |
| 0.30                              | 735.47                  | 1.48·10 <sup>-5</sup>                  | 87.27               | 22.5                                   | 128.5                                  | 9.96               | 46.24               |

The OCP curves show that the addition of BCP shifts the corrosion potential of the D16T aluminum alloy toward more negative values compared with the blank solution. This trend becomes more pronounced as the inhibitor concentration increases, indicating modification of the aluminum/acid interface due to the adsorption of BCP molecules. After the initial potential variation, the curves tend to reach relatively stable values, suggesting the gradual establishment of a quasi-steady interfacial state. The more negative OCP values in inhibited solutions may be associated with preferential suppression of the cathodic reaction and the formation of an adsorbed organic layer on

the alloy surface.

The potentiodynamic polarization curves confirm the protective effect of BCP. In the uninhibited solution, the corrosion current density was  $1.16 \cdot 10^{-4} \text{ A} \cdot \text{cm}^{-2}$ , whereas the addition of BCP reduced it progressively to  $1.48 \cdot 10^{-5} \text{ A} \cdot \text{cm}^{-2}$  at the highest inhibitor concentration. The corresponding inhibition efficiency increased from 40.84 to 87.27%, demonstrating that BCP effectively suppresses aluminum dissolution in 1.0 M HCl. This improvement can be attributed to increasing surface coverage and the blocking of active corrosion sites by adsorbed inhibitor molecules.

The shift in  $E_{corr}$  in the presence of BCP did not exceed 85 mV relative to the blank solution, indicating that BCP acts as a mixed-type inhibitor suppressing both anodic and cathodic processes. Thus, the inhibitor affects both anodic aluminum dissolution and cathodic hydrogen evolution. However, the negative displacement of the corrosion potential and the more pronounced change in the cathodic branch suggest that the cathodic process is more strongly influenced. This behavior is consistent with the adsorption of protonated BCP species and their ability to hinder hydrogen-ion reduction at the alloy surface.

The polarization resistance increased from  $5.35 \, \Omega$  for the blank solution to  $9.96 \, \Omega$  at the highest BCP concentration. Although the absolute  $R_p$  values remain relatively low because of the high aggressiveness of 1.0 M HCl toward the D16T aluminum alloy, their systematic increase confirms the formation of a more resistive interfacial layer. The inhibition efficiency calculated from  $R_p$  reached 46.24%, further supporting partial suppression of charge-transfer processes at the aluminum/acid interface.

The electrochemical findings follow the same trend as the weight-loss, adsorption,

and activation results, collectively supporting the formation of an effective protective layer on the metal surface. The progressive decrease in  $j_{corr}$  and increase in inhibition efficiency are consistent with the reduction in corrosion rate observed from weight-loss measurements. The mixed-type behavior and increase in  $R_p$  are also consistent with the adsorption-isotherm results, which indicated spontaneous BCP adsorption and increasing  $K_{ads}$  values with temperature. These changes point to the development of a less permeable interfacial film that reduces the transport of  $H^+$  and  $Cl^-$  species toward active dissolution sites.

### 3.8. Contact angle measurement

Contact angle measurements were performed to evaluate the wettability of the D16T aluminum alloy surface and to assess the effect of bromocresol purple on the formation of a protective layer. This method provides insight into the hydrophilic or hydrophobic nature of the surface, which is directly related to corrosion resistance. An increase in contact angle reflects a shift toward lower surface wettability, which is typical of an organic phase retained at the metal/solution interface. The contact angle images and corresponding values for the D16T aluminum alloy surface in the absence and presence of BCP at different concentrations are presented in Figure 9.

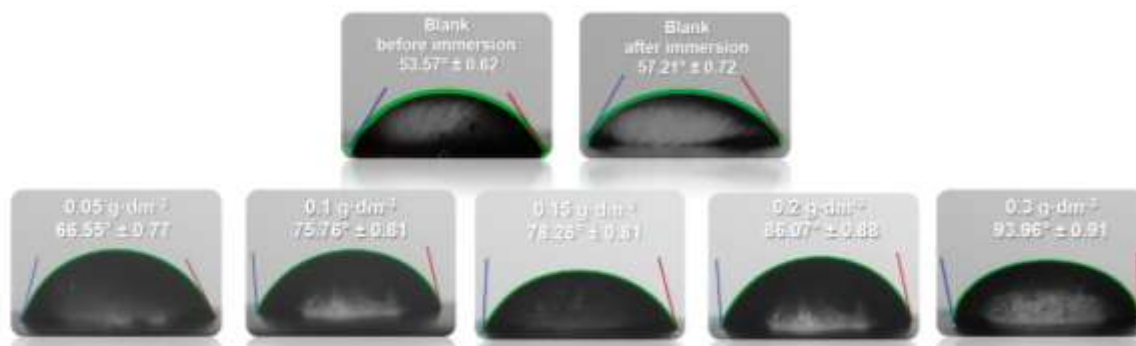


**Figure 9:** Contact angle images of D16T aluminum alloy surface before and after 24 h immersion in 1.0 M HCl in the absence and presence of BCP at different concentrations.

The blank D16T aluminum alloy surface before immersion exhibits a relatively low contact angle of 53.57°, indicating a hydrophilic surface. After immersion in the acidic medium without the inhibitor, the contact angle increases slightly to 57.21°, suggesting minor changes in surface morphology due to corrosion processes. However, the surface remains predominantly hydrophilic. In the presence of BCP, a significant increase in contact angle is observed with increasing inhibitor concentration. At 0.05 g·dm<sup>-3</sup>, the contact angle rises to 66.55°, indicating the initial formation of an adsorbed layer. A further increase to 75.76° and 78.26° is observed at concentrations of 0.1 and 0.15 g·dm<sup>-3</sup>, respectively, reflecting improved surface coverage and enhanced barrier properties. At higher concentrations of 0.2 and 0.3 g·dm<sup>-3</sup>, the contact angle reaches 86.07° and 93.96°, respectively, indicating a transition toward a hydrophobic surface. The progressive increase in contact angle with inhibitor concentration suggests that bromocresol purple molecules adsorb on the D16T aluminum alloy surface, forming a compact and protective film. This film reduces the surface free energy and limits the penetration of water and aggressive ions, thereby enhancing corrosion resistance. The hydrophobic character observed at the highest concentration (0.3 g·dm<sup>-3</sup>) indicates the formation of a dense and well-organized inhibitor layer. These results are consistent with the electrochemical and

spectroscopic findings, confirming that the inhibition mechanism is governed by adsorption. The increase in hydrophobicity supports the formation of a stable protective barrier, which effectively isolates the metal surface from the corrosive environment.

### 3.9. Quantum-chemical calculation results

The optimized structures, electrostatic potential maps and frontier molecular orbital distributions of BCP in the lactone form (BCP-LF) and quinonoid form (BCP-QF), calculated at the PM3, HF/6-31G and DFT/B3LYP/6-311G(d,p) levels in the aqueous phase, are shown in Figure 10.

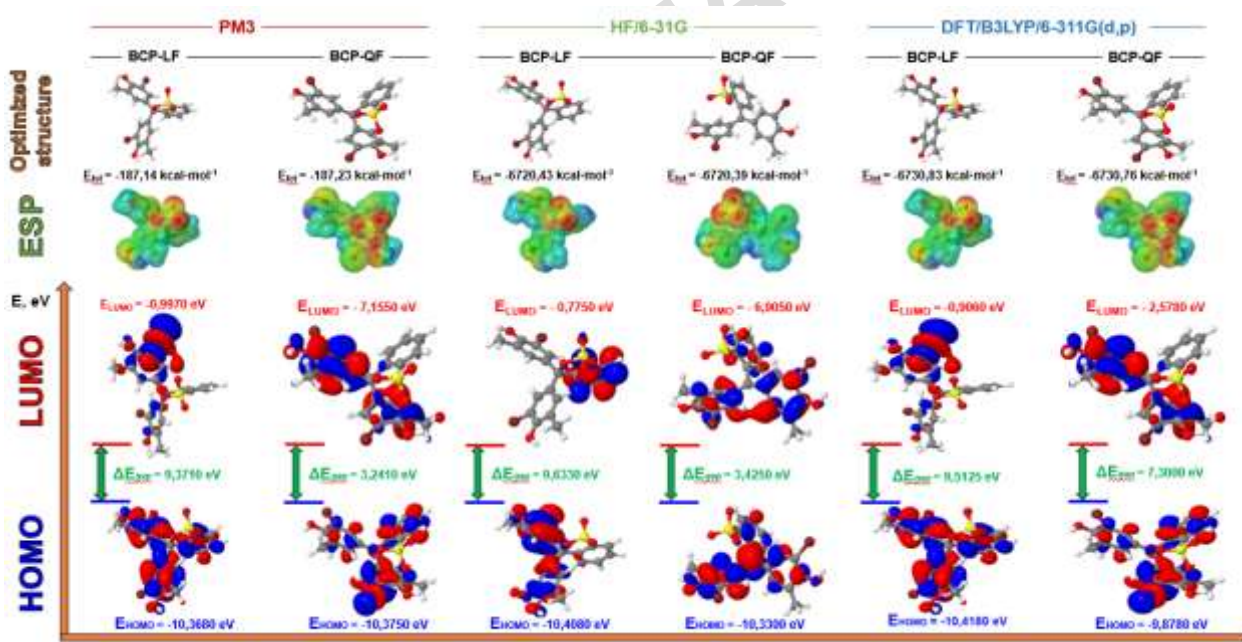


**Figure 10:** Optimized geometries, ESP maps, and frontier molecular orbital distributions of BCP-LF and BCP-QF calculated using PM3, HF/6-31G, and DFT/B3LYP/6-311G(d,p) methods in aqueous phase.

The optimized geometries indicate that BCP-LF retains a more compact and sterically constrained lactone-type structure, whereas BCP-QF exhibits an open molecular framework with extended conjugation. The opening of the lactone moiety may

favor a transition toward a more planar conformation, which is advantageous for corrosion inhibition because a flatter molecular geometry can improve surface contact with aluminum, facilitate  $\pi$  - electron interactions with the metal surface, and promote the formation of a more continuous adsorbed layer. Thus, from a structural perspective, the quinonoid form is expected to interact more effectively with the metal surface than the closed lactone form.

The ESP maps reveal that the most electron-rich regions are mainly localized around oxygen-containing groups, including phenolic oxygen atoms, sulfonate/sulfonyl oxygen atoms and the lactone fragment in BCP-LF. These centers can participate in adsorption through electrostatic interactions, coordination-type interactions, and hydrogen-bonding-like contacts with surface species [53]. For BCP-QF, the redistribution of electron density over the opened quinonoid system and the sulfonate fragment suggests a more delocalized electrostatic pattern, which can enhance multipoint adsorption on the D16T aluminum alloy surface. Therefore, both forms contain active adsorption centers, but BCP-QF provides a broader and more conjugated interaction platform.

The FMO analysis further supports the higher interfacial activity of the quinonoid form. For all three computational approaches, BCP-QF shows a lower HOMO–LUMO energy gap than BCP-LF. In the PM3 calculations, the gap decreases from 9.3710 eV for BCP-LF to 3.2410 eV for BCP-QF, while the HF/6-31G method gives a similar trend, with a decrease from 9.6330 to 3.4250 eV. The DFT/B3LYP/6-311G(d,p) results also confirm the same tendency, although the difference is less pronounced, with the gap decreasing from 9.5125 eV for BCP-LF to 7.3000 eV for BCP-QF. This consistent reduction in  $\Delta E_{gap}$  indicates that the quinonoid form is electronically softer and more

polarizable than the lactone form, which should favor charge-transfer interactions with the D16T aluminum alloy surface.

The spatial distribution of the HOMO and LUMO also differs between the two forms. In BCP-LF, the frontier orbitals are distributed over separated aromatic and heteroatom-containing fragments, reflecting the less extended conjugation of the closed structure. In contrast, BCP-QF demonstrates a more delocalized orbital distribution over the quinonoid framework and aromatic rings. Such delocalization is beneficial for adsorption because it increases the probability of electron donation from occupied orbitals to vacant metal orbitals and back-donation from the metal surface to the antibonding orbitals of the inhibitor. Therefore, BCP-QF can be considered the more electronically favorable form for interaction with the D16T aluminum alloy surface in acidic solution.

The comparison of computational methods shows that the absolute total energies and orbital energies depend strongly on the theoretical level and should not be directly compared across PM3, HF, and DFT. However, the internal trend within each method is meaningful. All three approaches consistently indicate that transformation from BCP-LF to BCP-QF leads to stronger conjugation, redistribution of the electrostatic potential, and a lower HOMO–LUMO gap. PM3 and HF predict a particularly strong decrease in  $\Delta E_{gap}$ , whereas DFT gives a more moderate but still clear reduction. Since DFT includes electron correlation effects more reliably than HF and is generally more suitable for molecular electronic-structure interpretation, the B3LYP/6-311G(d,p) results may be regarded as the most balanced description of the electronic properties.

The quantum-chemical descriptors calculated for the lactone form (BCP-LF) and

the quinonoid form (BCP-QF) of BCP are summarized in Table 5. These parameters provide additional information on the relative electron-donating/electron-accepting ability, molecular softness, electrophilic/nucleophilic character, and charge-transfer tendency of both molecular forms.

**Table 5:** Quantum-chemical descriptors of BCP-LF and BCP-QF calculated using PM3, HF/6-31G and DFT/B3LYP/6-311G(d,p) methods in aqueous phase.

| Descriptors                      | PM3     |         | HF/6-31G |         | DFT/B3LYP/6-311G(d,p) |         |
|----------------------------------|---------|---------|----------|---------|-----------------------|---------|
|                                  | BCP-LF  | BCP-QF  | BCP-LF   | BCP-QF  | BCP-LF                | BCP-QF  |
| I, eV                            | 10.3680 | 10.3750 | 10.4080  | 10.3300 | 10.4180               | 9.8780  |
| A, eV                            | 0.9970  | 7.1550  | 0.7750   | 6.9050  | 0.9060                | 2.5780  |
| $\chi$ , eV                      | 5.6825  | 8.7650  | 5.5915   | 8.6175  | 5.6620                | 6.2280  |
| $\eta$ , eV                      | 4.6855  | 1.6100  | 4.8165   | 1.7125  | 4.7560                | 3.6500  |
| $\sigma$ , eV <sup>-1</sup>      | 0.2134  | 0.6211  | 0.2076   | 0.5839  | 0.2103                | 0.2740  |
| $\omega$ , eV                    | 3.4458  | 23.8588 | 3.2456   | 21.6821 | 3.3703                | 5.3134  |
| $\varepsilon$ , eV <sup>-1</sup> | 0.2902  | 0.0419  | 0.3081   | 0.0461  | 0.2967                | 0.1882  |
| E <sub>b-d</sub> , eV            | -1.1714 | -0.4025 | -1.2041  | -0.4281 | -1.1890               | -0.9125 |
| $\Delta N$                       | -0.1518 | -1.3991 | -0.1382  | -1.2723 | -0.1474               | -0.2696 |
| $\Delta \psi$                    | 0.1080  | 3.1514  | 0.0920   | 2.7719  | 0.1033                | 0.2653  |
| $\omega^-$ , eV                  | 6.8728  | 28.4425 | 6.6434   | 26.2049 | 6.7958                | 8.8837  |
| $\omega^+$ , eV                  | 1.1903  | 19.6775 | 1.0519   | 17.5874 | 1.1338                | 2.6557  |
| $\omega^\pm$ , eV                | 8.0630  | 48.1200 | 7.6953   | 43.7924 | 7.9296                | 11.5393 |
| $\mu$ , eV                       | -5.6825 | -8.7650 | -5.5915  | -8.6175 | -5.6620               | -6.2280 |
| $\mu^-$ , eV                     | -8.0253 | -9.5700 | -7.9998  | -9.4738 | -8.0400               | -8.0530 |
| $\mu^+$ , eV                     | -3.3398 | -7.9600 | -3.1833  | -7.7613 | -3.2840               | -4.4030 |
| TNC                              | -4.7379 | -4.7326 | -5.8732  | -6.1563 | -5.2297               | -5.6194 |
| TNC/n                            | -0.2059 | -0.2151 | -0.2349  | -0.2565 | -0.2615               | -0.2554 |

The ionization potential values indicate that BCP-QF generally requires slightly lower energy for electron removal than BCP-LF, especially at the HF and DFT levels. This suggests that the quinonoid form has a higher tendency to donate electron density to the D16T aluminum alloy surface. At the same time, the electron affinity of BCP-QF is higher than that of BCP-LF for all applied methods, indicating an enhanced ability of the open quinonoid structure to accept electron density from the metal surface. Therefore, BCP-QF can participate more efficiently in donor–acceptor interactions, which are important for adsorption and the stabilization of the inhibitor layer.

The electronegativity and global hardness values further confirm the difference between the two forms. BCP-QF shows lower global hardness and higher softness than BCP-LF, irrespective of the computational method. This means that the quinonoid form is more polarizable and can more easily redistribute electron density during interaction with the metal surface. Such behavior is favorable for corrosion inhibition because softer molecules usually adapt more readily to the electronic environment of the metal/solution interface and form stronger adsorption contacts.

The electrophilicity index and related electron-donating/electron-accepting descriptors also indicate that structural opening considerably changes the reactivity profile of BCP. BCP-QF demonstrates much higher electrophilicity values than BCP-LF, particularly in the PM3 and HF calculations, reflecting the increased ability of the quinonoid form to participate in charge-transfer processes. The increase in both electron-donating and electron-accepting power suggests that BCP-QF may interact with the D16T aluminum alloy surface through a bidirectional charge-transfer mechanism, involving electron donation from oxygen atoms and  $\pi$ -systems to aluminum centers and partial back-donation from the surface to antibonding molecular orbitals [54].

The calculated fraction of transferred electrons also supports the stronger interaction propensity of the quinonoid form. The  $\Delta N$  values are negative for both forms, indicating that the direction and magnitude of charge transfer are affected by the selected theoretical reference parameters for aluminum [55]. Nevertheless, BCP-QF exhibits more negative  $\Delta N$  values than BCP-LF for all methods, suggesting a greater tendency toward charge redistribution upon contact with the metal surface. This is consistent with the more delocalized electronic structure of BCP-QF and its lower resistance to electronic

reorganization.

The total negative charge (TNC) values show that both molecular forms contain electron-rich regions capable of interacting with positively charged or electron-deficient surface sites. The negative charge is mainly associated with oxygen-containing fragments and aromatic systems, which are also visible in the ESP maps. The TNC/*n* values are relatively close for both forms, but the slightly more negative values obtained for BCP-QF at the HF and DFT levels indicate a somewhat higher average availability of electron density per atom. This supports the view that the open quinonoid form provides more favorable adsorption centers for interaction with the D16T aluminum alloy surface.

In general, the PM3, HF/6-31G, and DFT/B3LYP/6-311G(d,p) results give the same qualitative conclusion: transformation from BCP-LF to BCP-QF increases molecular polarizability, improves charge-transfer capability, and enhances the ability of BCP to interact with the D16T aluminum alloy surface. Although the numerical values differ between methods, the trend is consistent and agrees with the ESP and FMO analyses. The quinonoid structure is therefore expected to contribute more strongly to interfacial anchoring under acidic conditions. Its higher softness, stronger electrophilic and nucleophilic reactivity, more pronounced charge redistribution, and electron-rich adsorption centers support the formation of a protective film on aluminum in 1.0 M HCl.

Therefore, the theoretical analysis indicates that both molecular forms can participate in BCP adsorption on aluminum; however, the quinonoid form is predicted to be more favorable for corrosion inhibition in an acidic medium. Opening of the lactone ring leads to a more extended conjugated system, greater electronic delocalization, and an increased ability of the molecule to redistribute electron density during interaction with

the metal surface. The descriptor analysis further confirms that BCP-QF possesses higher softness, a stronger electrophilic and nucleophilic reactivity, and more pronounced charge-transfer capability than BCP-LF. Together with the ESP maps, these results identify oxygen-containing groups and aromatic  $\pi$ -systems as the main adsorption centers. Accordingly, the protective action of BCP in 1.0 M HCl can be associated with the adsorption of its molecular forms, especially the quinonoid form, followed by the formation of a compact inhibitor layer at the aluminum/acid interface.

### 3.10. Proposed adsorption and corrosion inhibition mechanism

Based on the combined gravimetric, adsorption-thermodynamic, electrochemical, spectroscopic, wettability, and quantum-chemical results, a schematic representation of the proposed adsorption and corrosion-inhibition mechanism of BCP at the D16T aluminum alloy-1.0 M HCl interface is presented in Figure 11.

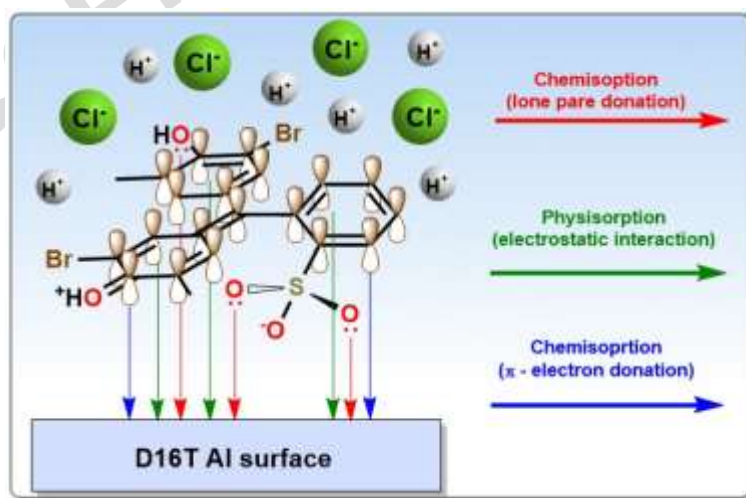


**Figure 11:** Schematic representation of the proposed adsorption and corrosion-inhibition mechanism of BCP-QF at the D16T aluminum alloy/1.0 M HCl interface.

The proposed mechanism involves complementary physisorption and

chemisorption contributions. In a strongly acidic chloride medium, electrostatic interactions can promote the association of protonated and polar BCP species with the heterogeneous, chloride-modified alloy/solution interface, providing a physical contribution to the initial retention of inhibitor species. This interpretation is consistent with the intermediate  $\Delta G_{ads}^0$  values and the non-ideal adsorption behavior revealed by the Langmuir and Frumkin models. At the same time, the increase in  $K_{ads}$  with temperature, the positive  $\Delta H_{ads}^0$ , and the temperature-enhanced inhibition efficiency indicate that the protective action cannot be attributed solely to weak electrostatic accumulation. A chemical contribution is proposed through charge transfer from electron-rich regions of BCP toward electron-deficient interfacial Al sites. Lone-pair donation may occur from oxygen-containing centers, consistent with the electron-rich regions identified by the ESP analysis, while the extended conjugated system can participate in  $\pi$ -electron donation toward interfacial acceptor sites. This pathway is particularly relevant to the quinonoid form, for which the quantum-chemical calculations revealed a lower HOMO–LUMO gap, higher softness, enhanced charge-redistribution ability, and a more delocalized frontier-orbital pattern than those of the closed lactone form. These features support the greater capacity of BCP-QF to participate in interfacial donor–acceptor interactions and establish multiple adsorption contacts with the alloy surface. The resulting interfacial layer therefore arises from the combined action of electrostatic retention and charge-transfer-assisted adsorption rather than from a single interaction mode.

#### 4. Conclusion

Bromocresol purple was found to be an effective corrosion inhibitor for D16T aluminum

alloy in 1.0 M HCl, with its inhibition efficiency increasing with both inhibitor concentration and temperature. Gravimetric, adsorption, and electrochemical measurements consistently demonstrated a marked reduction in alloy dissolution, while polarization results identified BCP as a mixed-type inhibitor with a stronger influence on the cathodic reaction. The adsorption process was spontaneous, became more favorable at elevated temperatures, and was best described by the Langmuir model with weak lateral interactions between adsorbed species. Contact-angle measurements, together with UV–Vis and FTIR analyses, confirmed the formation of a stable adsorbed layer involving oxygen-containing groups and the conjugated  $\pi$ -system without significant disruption of the molecular framework. Quantum-chemical calculations identified the quinonoid form as the more adsorption-active structure because of its lower HOMO–LUMO gap, greater softness, and enhanced charge-transfer capability. The combined experimental and theoretical results support a mixed physical–chemical adsorption mechanism involving electrostatic retention together with charge-transfer-assisted interactions through oxygen lone pairs and the conjugated  $\pi$ -system, leading to the formation of a compact protective layer that limits the access of  $H^+$  and  $Cl^-$  species to active dissolution sites.

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