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Corrosion Inhibition Potential and Adsorption Behaviour of Bromophenol Blue and Thymol Blue Dyes on Mild Steel in Acidic Medium

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Inhibition of steel corrosion in HCl solutions by Bromophenol blue (BPB) and Thymol blue (TB) was studied via absorbance difference measurements at 303 and 313K. The percentage inhibition efficiencies ($\%I_E$) were found to increase while corrosion rates decrease with increasing concentration in the order: 0.001M TB [37.8% (0.58×10^{-4} Add)] < 0.001MBPB [40.0 % (0.59×10^{-4} Add)]. The values of inhibition efficiencies obtained from this study show that BPB and TB inhibit steel corrosion in HCl solutions to some an appreciable extent. Inhibition of steel corrosion by BPB and TB obeyed Langmuir adsorption isotherm. From the activation energy, (Ea ≈ 6.85 $kJmol^{-1}$ for BPB and Ea ≈ 6.32$kJmol^{-1}$for TB) values obtained from the study, physisorption mechanism has been proposed for the inhibitors. Synergism parameter evaluated is found to be greater than unity for all concentrations of BPB and TB indicating that the enhanced inhibition efficiency of the inhibitors caused by addition of bromide ion is only due to synergism.

Keywords: Steel Corrosion, Bromophenol Blue, Thymol Blue, Absorbance difference, Physisorption

1. INTRODUCTION

Corrosion of materials depresses the economy of any nation because huge amounts of scarce funds are used in combating it. Corrosion inhibition of metals/alloys such as steel has received considerable attention over the years because of the dominant role of steel in most industries. The oil and gas, the beverage and the metallurgical industries sink huge sum of money to protect their machine parts from corrosion. The need to research into the field of corrosion inhibition of steel is therefore very important.

Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially [1-3]. Different kinds of dyes are known viz. heterocyclic dyes (e.g. safranine T, methylene blue); xanthene dyes (e.g. eosin, thymol blue, phenolphthalein, phenol red) ; anthraquinone dyes (e.g. alixarin red S) and azo dyes (e.g. methyl red, congo red, methyl orange). Of all the dyes, azo dyes are a class of compounds that are strongly coloured. They can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. Because of their colour, azo compounds are of tremendous importance as dyes. Infact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts [4]. Structural features in organic compounds that lead to colour are >C = C<, -N = O, -N = N-, aromatic rings, >C = O and –NO_2. Most importantly, azo (-N = N-) and nitro (-N = O) groups invariably confer colour while the other groups do so under certain circumstances. Dyes have been used to give multi-colour effects to anodized aluminium [5-10]. Cyanine dyes have been reported as efficient corrosion inhibitors on metal corrodent systems [11]. Green S and erythrosine dyes have been studied as potential inhibitors for mild steel corrosion in HCl [12]. A survey of the literature also reveals that the corrosion on aluminium in amine solutions by some dyes has been reported [13-20]. Preliminary experiments in our laboratories in an earlier study have shown, however, that some azo dyes (metanil yellow, naphthol blue black and solochrome dark blue) actually inhibit the corrosion of mild steel in HCl medium [21]. Some other studies by other research groups and from our laboratories recently reported also show that some organic dyes are quite effective in retarding the corrosion of mild steel and aluminium in acidic or basic environments [22-36].

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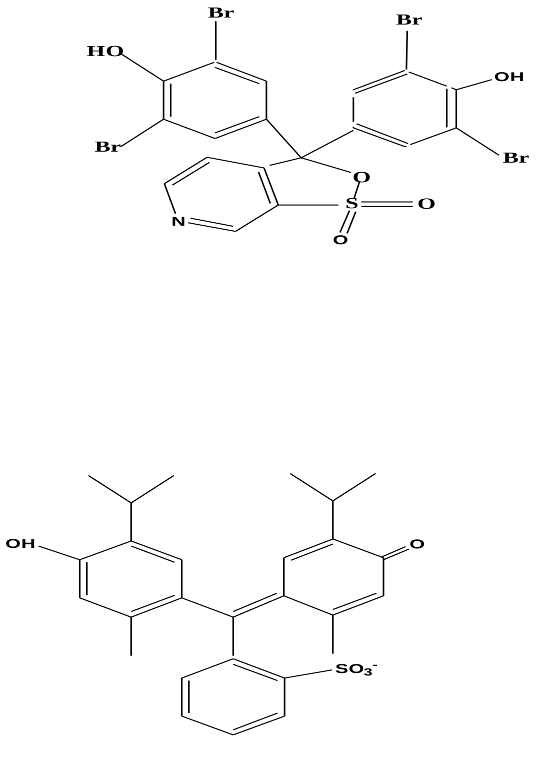

Molecular Structures of Bromophenol Blue and Thymol Blue

This investigation is carried out using a relatively new technique ‘Absorbance difference’ technique to study the corrosion inhibition potential of Bromophenol blue (BPB) and thymol blue (TB) dyes at 303K and 313K respectively. This paper forms part of an extensive data base on the inhibition profiles of dyes for corrosion of different metals and alloys in various aggressive environments

2. EXPERIMENTAL

2.1.Materials preparation

The steel bars used for this study and of purity 99.7% were obtained from Mubi in Adamawa state of Nigeria. Each of these bars was 8.0 x 10^{-2} mm thick. They were mechanically press cut into 5cm x 4cm (area of 20 cm^2) and were used without further polishing. They were however degreased in ethanol, dried in propanone and stored in moisture free – desiccators before corrosion studies commenced.

The Bromophenol blue, BPB and Thymol blue, TB dyes (BDH grades) used as inhibitors were used as sourced without further purification. A concentration range of $10^{-4} – 10^{-3}$M for Bromophenol blue and Thymol blue dyes were prepared and used for the study. A concentration range of 0.1 – 0.5M HCl solutions was also prepared and used as corrodent.

2.2. Absorbance Difference Measurements

Five 250mL beakers labeled A, B, C, D and E containing 0.1, 0.2, 0.3, 0.4, 0.5M HCl solutions were placed in a thermostated water bath maintained at 303 and 313K. Absorbance (A_0) of each of these solutions was taken at a wave length of 510 nm using UV/Visible spectrophotometer (Jenway, 6405 model). The steel bars were then dipped into each of the beakers containing different concentrations of HCl with the aid of clips. These bars were retrieved at 24hr intervals progressively for 168hours (7 days). The absorbance difference (A_1) of these solutions was again taken at a wavelength of 510nm. The difference between A_0 and A_1 was recorded as the absorbance difference of the corrodent in each case. Further measurements were also performed after dipping each steel bar into inhibitor + 0.5M HCl mixtures contained in beakers and maintained at 303K and 313K and a wavelength of 510 nm. Each of the reported readings is an average of seven experimental readings recorded to the nearest 0.0001 on a Jenway 6405 UV/Visible spectrophotometer. The difference in absorbance recorded for a period of 168 hours was recorded as the total absorbance difference.

The inhibition efficiency ($\%I_E$) of Bromophenol blue (BPB) and Thymol blue (TB) was calculated using the formula

$$\% I_E = \frac{A_o - A_1}{A_o} x100\% \qquad (1)$$

where A_0 and A_1 are absorbance for steel in the absence and presence of the inhibitors in HCl solution at 303K and 313K and 380 nm [38].

The surface coverage (Θ) at each concentration of the inhibitors was determined using the expression [21, 38

$$\Theta = \left[1 - \left(\frac{A_1}{A_0}\right)\right] \quad (2)$$

Corrosion rates (ρ) of steel in different concentrations of HCl, BPB, and TB have been determined for 168 hourly period from the absorbance difference measurements using the relation;

$$\text{Corrosion rate (Add)} = \Delta A/\mathbf{dat} \quad (3)$$

where ΔA is the absorbance difference, **d** is the density of steel, **a** is the area of steel bar and **t** is the time of exposure (hours) [38].

3. RESULTS AND DISCUSSION

3.1. Effect of Corrodent Concentration and Temperature on mild steel Corrosion

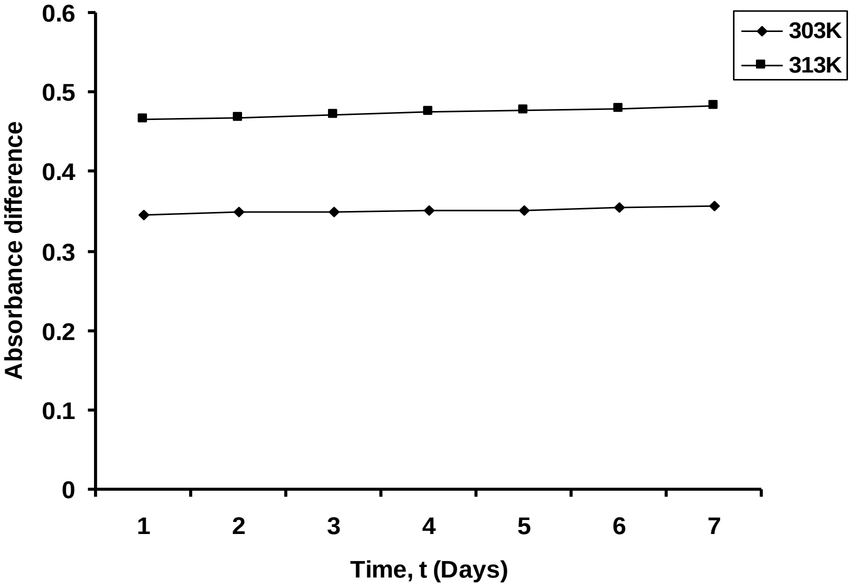

Figure 1. Variation of Absorbance difference (Ad) with Time, t (Days) for Steel Corrosion in 0.50 MHCl at 303K and 313K

Fig. 1 and Table 1 show the variation of absorbance difference and corrosion rates with time, t (days) for steel in HCl at 303 and 313K with BPB and TB. It was observed that absorbance difference/corrosion rate (Abs.dm^2.day^{-1}, Add) of steel increased with increasing concentration of HCl and temperature.

Table 1. Corrosion Parameters for Steel corrosion in 0.50M HCl containing BPB and TB from Absorbance difference measurements

Inhibitor Conc. (M)	Absorbance difference (Ad)		Corrosion rate (Add)		Inhibition Efficiency (%I_E)		Surface coverage (Ө)	
	303K	313K	303K	313K	303K	313K	303K	313K
Blank	0.352	0.472	0.93 x 10^{-4}	1.20 x 10^{-4}	-	-	-	-
BPB								
0.0001	0.245	0.380	0.65 x 10^{-4}	1.10 x 10^{-4}	30.40 (59.91)	19.49 (40.00)	0.30 (0.60)	0.20 (0.40)
0.0003	0.238	0.369	0.63 x 10^{-4}	0.97 x 10^{-4}	32.39 (62.90)	21.82 (41.82)	0.32 (0.63)	0.22 (0.42)
0.0005	0.232	0.337	0.61 x 10^{-4}	0.89 x 10^{-4}	34.09 (66.96)	28.60 (58.42)	0.34 (0.67)	0.29 (0.58)
0.0007	0.228	0.323	0.60 x 10^{-4}	0.85 x 10^{-4}	37.70 (73.49)	31.57 (64.80)	0.37 (0.73)	0.32 (0.65)
0.001	0.212	0.300	0.59 x 10^{-4}	0.78 x 10^{-4}	40.00 (80.19)	36.44 (74.80)	0.40 (0.80)	0.36 (0.75)
TB								
0.0001	0.243	0.388	0.64 x 10^{-4}	1.02 x 10^{-4}	29.80 (58.91)	18.00 (37.10)	0.30 (0.59)	0.19 (0.37)
0.0003	0.241	0.365	0.63 x 10^{-4}	0.96 x 10^{-4}	31.50 (60.81)	22.66 (43.81)	0.31 (0.61)	0.23 (0.44)
0.0005	0.239	0.351	0.62 x 10^{-4}	0.92 x 10^{-4}	32.10 (65.20)	25.64 (50.92)	0.32 (0.65)	0.26 (0.51)
0.0007	0.225	0.341	0.59 x 10^{-4}	0.89 x 10^{-4}	36.10 (71.81)	27.75 (56.20)	0.36 (0.72)	0.28 (0.56)
0.001	0.219	0.335	0.58 x 10^{-4}	0.88 x 10^{-4}	37.78 (75.20)	29.03 (60.00)	0.38 (0.75)	0.29 (0.60)

( ) = Values obtained on addition of 0.06M KBr (halide)

Similar observation has been made by several workers on the corrosion of metals in HCl solution [37 – 40]]. This could be attributed to the fact that rates of chemical reactions generally increase with increasing acid concentration and temperature. It may also be due to an increase in the rate of ionization and diffusion of active ions in the corrosion process. Increase in temperature favors the formation of iron (iii) chloride, $FeCl_3$ with the Cl^- ions which is also corrosive to steel.

3.2. Effect of Inhibitors (BPB and TB) Concentration on mild steel Corrosion

Fig. 2 shows variation of absorbance difference with time, t (days) for steel corrosion in 0.5M HCl with various concentrations of BPB and TB respectively at 303 and 313K. These graphs reveal that absorbance difference was lowest at 0.001M BPB and TB (highest concentrations of inhibitors studied). This indicates that BPB and TB inhibit corrosion of steel to a little extent, with inhibition increasing with increasing inhibitor concentration at a low temperature.

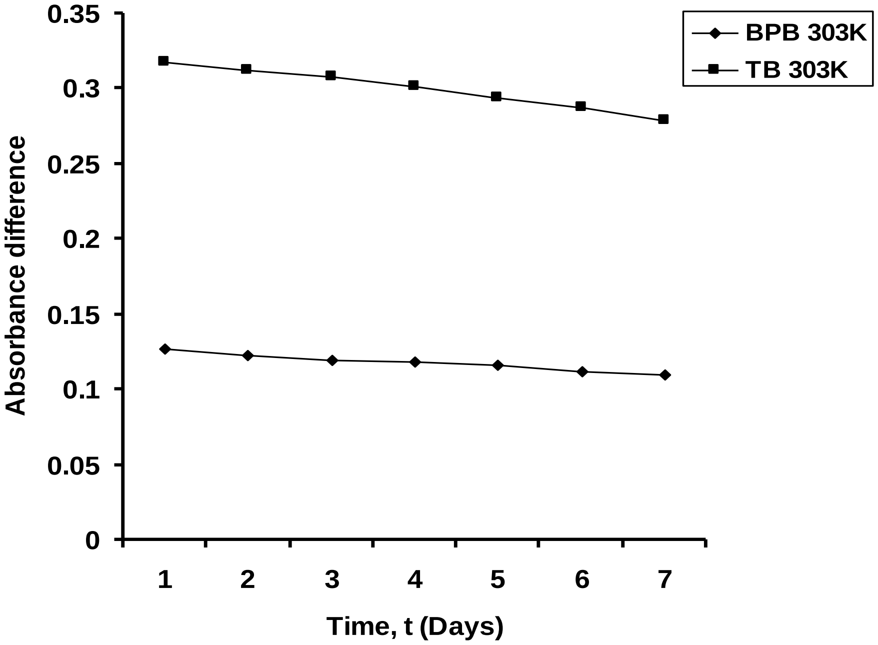

Figure 2. Variation of Absorbance difference (Ad) with Time, t (Days) for Steel Corrosion in 0.50M HCl with 0.001M BPB and TB at 303K

With the addition of the inhibitors (BPB and TB), the inhibition efficiency (%I_E) and the surface coverage were found to increase while corrosion rates decrease with increasing concentration in the order: 0.001M TB [37.8% efficiency and 0.58×10^{-4} Add corrosion rate]< 0.001M BPB [40.0% efficiency and 0.59×10^{-4} Add corrosion rate] but inhibition efficiency decreases with increasing temperature (303 – 313K) (Table 1). This shows that the inhibitors function effectively at lower temperatures which suggest physisorption. This assertion agrees with the findings of Ebenso *et al* [21].

3.3. Adsorption Considerations of the Results

From Table 1 and Figs (3a – b), it is evident for both compounds that the inhibition efficiency (%) and surface coverage (ϴ) increase with inhibitor concentration and decrease with increasing temperature. This further attests to physisorption (physical adsorption) mechanism. At high concentrations, lower surface coverage is observed because very little interactions between the adsorbed species would be expected. The surface coverage data implies that the adsorption of the inhibitors (BPB and TB) at the steel interface may be due to electrostatic force between the adsorbates and the atoms on the metal surface. This assertion confirms to observations earlier published by Ekpe *et al* [41].

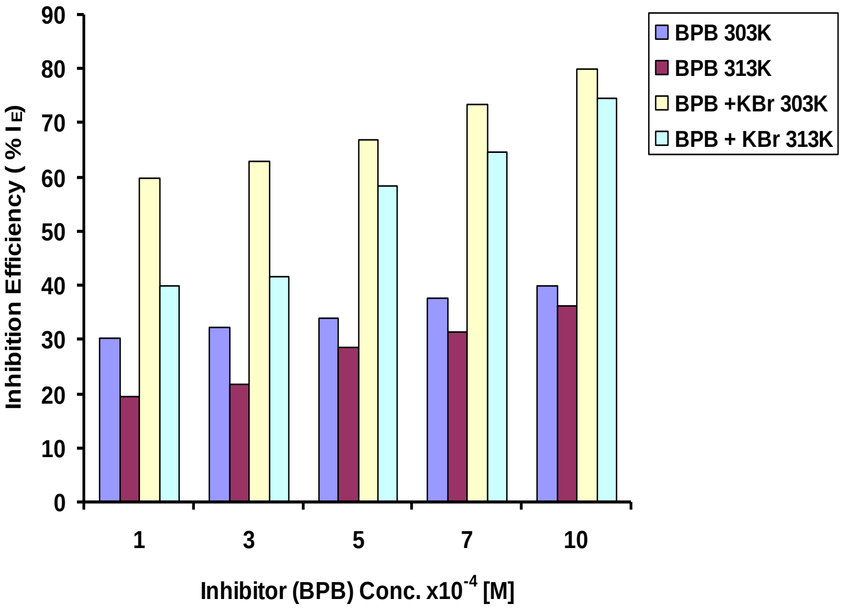

Figure 3a. Plot of Inhibition efficiency (% I_E) versus Inhibitor (BPB and BPB + KBr) Conc. at 303K and 313K.

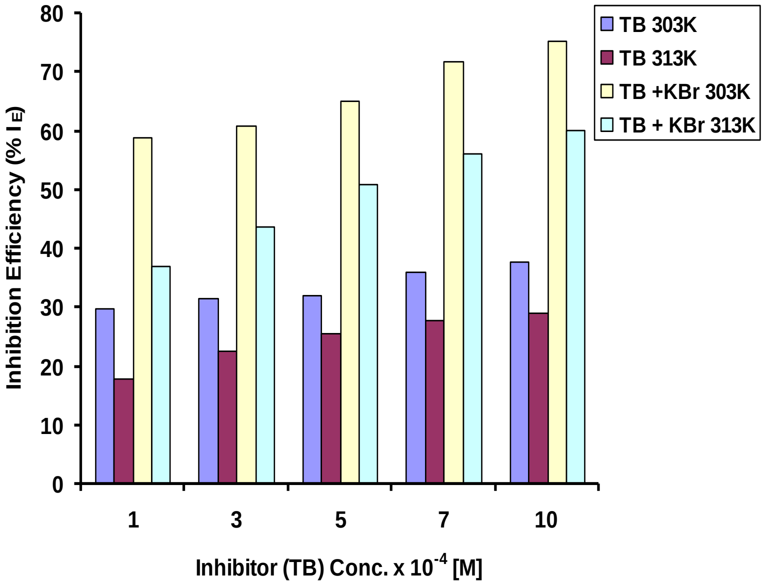

Figure 3b. Plot of Inhibition efficiency (% I_E) versus Inhibitor (BPB and BPB + KBr) Conc. at 303K and 313K.

To establish the extent of adsorption of inhibitor molecules on the steel surface, some adsorption isotherm plots were made. The linear plots obtained from the graphs of "C_{eq}"/θ against 'C' at 303 and 313K (Figs. 4a-4b) shows that the experimental data obtained within the temperature range fits Langmuir adsorption isotherm given by equation (4) below

$$`C_{eq}'/\theta = \alpha``C" + \beta \qquad (4)$$

where C_{eq} is the equilibrium concentration (concentration at which no more absorbance was observed); C is the inhibitor concentration; θ is the surface coverage calculated from equation (2); α is the slope called the binding force and β is the Langmuir constant which is the adsorptive capacity.

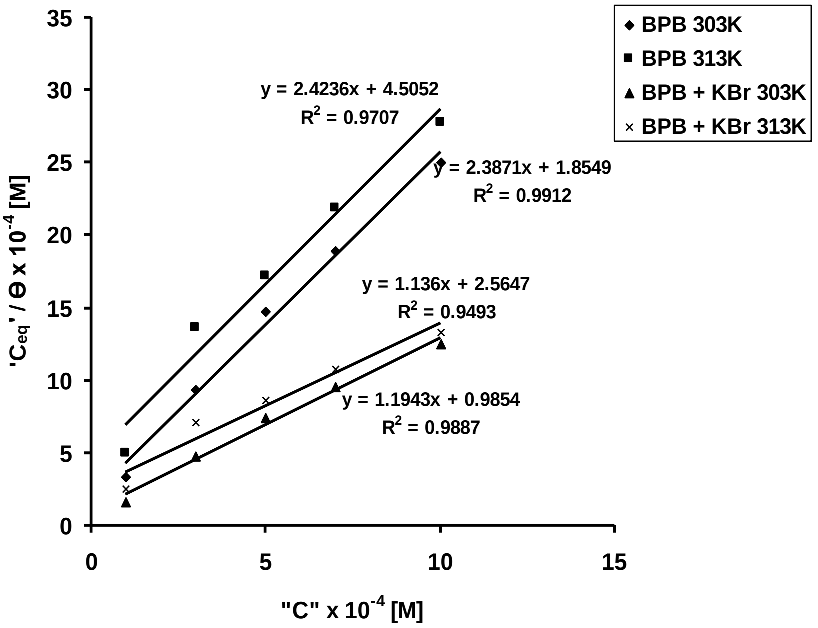

Figure 4a. Langmuir adsorption isotherm plotted as 'C_{eq}'/Θ versus "C" for Steel Corrosion in 0.5M HCl containing BPB and addition of KBr at 303K and 313K.

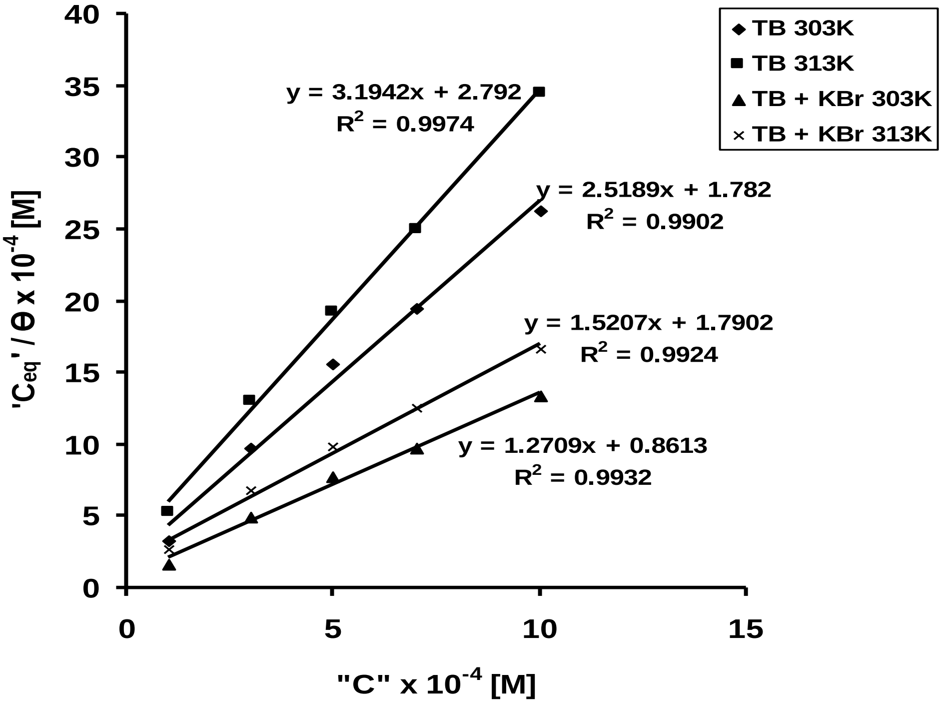

Figure 4b. Langmuir adsorption isotherm plotted as 'C_{eq}'/Θ versus "C" for Steel Corrosion in 0.5M HCl containing TB and addition of KBr at 303K and 313K.

This confirms that corrosion inhibition is often due to the formation and maintenance of a thin protective layer on the metal surface. This is in agreement with the findings of Ebenso *et al*, [21] and Onen and Shinggu [42].

3.4. Inhibition Mechanism

Table 2 shows calculated values of activation energy , $E_{a.}$ The average values of the activation energy, E_a for the inhibitors studied, (6.85 and 6.32kJmol^{-1}) are lower than 40.0kJmol^{-1} indicating that the compounds are physically adsorbed on the steel surface.

Table 2. Some thermodynamic data for Mild Steel corrosion in 0.50M HCl containing BPB and TB from Absorbance difference measurements

Inhibitor Conc. (M)	Activation energy, Ea (kJmol^{-1}) 303K - 313K	Heat of adsorption, Q_{ads} (kJmol^{-1}) 303K - 313K
Blank	5.88	-
BPB		
0.0001	6.10	-4.24 (--63.95)
0.0003	6.41	-4.05 (-67.43)
0.0005	7.31	-1.84 (--30.39)
0.0007	8.89	-1.74 (-29.62)
0.001	5.55	-6.03 (-22.69)
Average	6.85	-3.58 (-42.82)
TB		
0.0001	7.38	-9.50 (-70.68)
0.0003	5.96	-19.33 (-54.29)
0.0005	8.89	-5.82 (-45.66)
0.0007	5.23	-16.38 (-55.46)
0.001	4.14	-9.87 (-54.66)
Average	6.32	-12.18 (-56.15)

( ) = Values obtained on addition of 0.06M KBr (halide)

Physical adsorption requires that the average E_a be $\leq$ 40.0kJmol^{-1} and the percent inhibition efficiency increases at lower temperatures. This agrees with an earlier report by Onen [37].

3.5. Thermodynamic Considerations

The activation energy values presented in Table 2 were computed from the modified Arrhenius equation (5)

$$E_a = 2.303R\frac{T_1T_2}{T_2 - T_1}\log\frac{\rho_2}{\rho_1} \qquad (5)$$

Where ρ_1 and ρ_2 are corrosion rates at 303 and 313K respectively [43]. The values of rate constants, k were obtained from plots of log Ad versus time (days) as shown in Figs. 5 and 6.

The values of heat of adsorption, Q_{ads} (in Table 2) were computed from the relation:

$$Q_{ads} = 19.147\left(\log\frac{\Theta_2}{1-\Theta_2} - \log\frac{\Theta_1}{1-\Theta_1}\right)\left(\frac{T_1T_2}{T_2-T_1}\right) \qquad (6)$$

where Θ_1 and Θ_2 are degree of surface coverage at 303K and 313K respectively.

Table 3. Adsorption parameters derived from Langmuir adsorption isotherm plot for PBP and TB at different temperatures.

Inhibitor	Temperature (K)	ΔG (kJ mol^{-1})	K (M^{-1})	Slope	R^2
BPB	303	–8.56	0.54	2.39	0.991
	313	–6.53	0.22	2.42	0.971
TB	303	–8.85	0.61	2.53	0.990
	313	–7.78	0.36	3.19	0.997

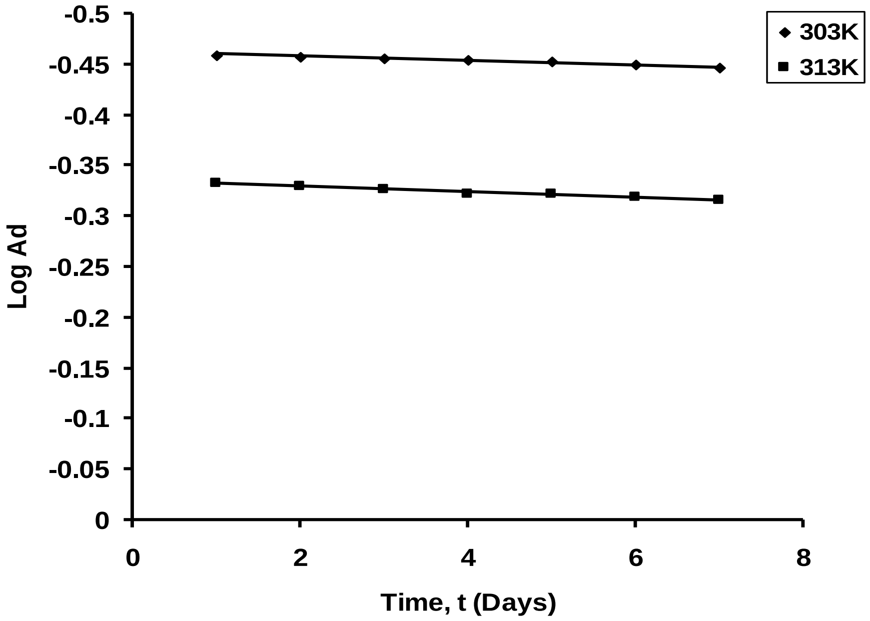

Figure 5. Plot of Log Ad versus Time, t (Days) in 0.50 M HCl at 303K and 313K

All the values of Q_{ads} are negative for steel corrosion as shown in Table 2. This implies that the inhibition process is spontaneous. It is also an indication that adsorption and inhibition efficiency decrease with increase in temperature which agrees with earlier findings by otherauthors [44]. Values of Gibbs free energy, ΔG are presented in Table 3 obtained from the Langmuir adsorption isotherm plots which still points towards physisorption.

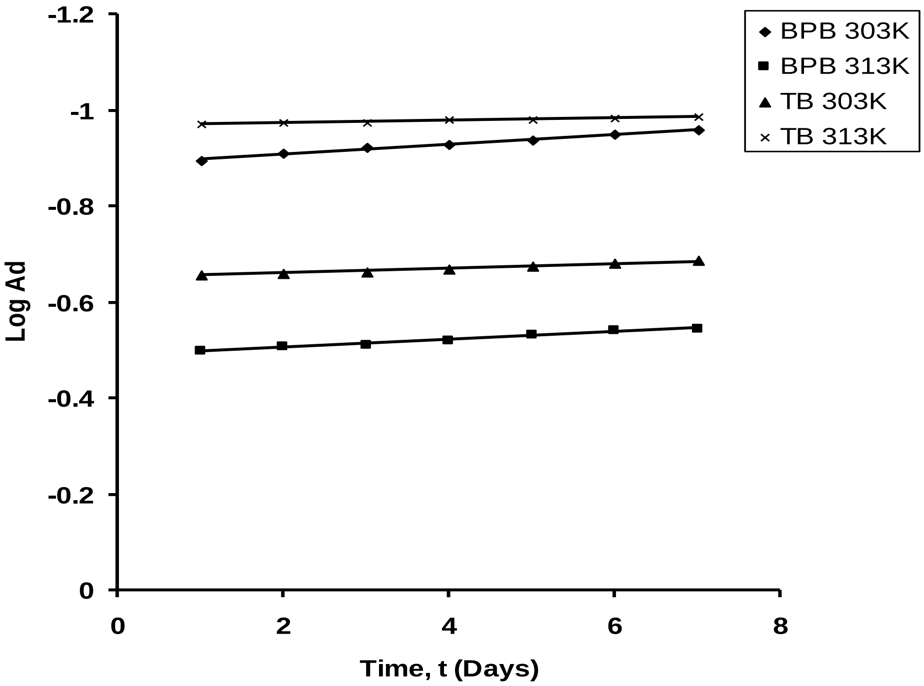

Figure 6. Plot of Log Ad versus Time, t (Days) in 0.50M HCl containing 0.001M Inhibitors (BPB and TB) at 303K and 313K

3.6. Influence of Molecular Structure of the Inhibitors

The results obtained in this study (Table 1) show the order of increase inhibition efficiency of the compounds in solution and the extent of their ability to adsorb and hence protect steel surface are as follows: TB (37.8%) < BPB (40.0%) at 303K using absorbance difference. Similar trend was observed at 313K. The sequence may be attributed to the electronic structures of these compounds. The lone pairs of electrons on the sulphur and nitrogen atoms are delocalized and hence produce resonance stabilization energy which stabilizes the compounds. The bromo-substitients of BPB contributed greatly to its inhibition effectiveness due to its high electronegativity. As a halide, Br^- substituents in solution will exhibit synergism, thus, increasing the inhibition of BPB. More so, BPB has a sulphur atom as one of its substituents. The S atom is known to be the centre of adsorption onto the metal [44]. The electron density on S atom is made available to the electron accepting bromo-atoms. This stabilizes the compound at the reaction site. Both compounds studied, inhibited the acid corrosion of steel but BPB inhibited better. This may be ascribed to the higher molecular mass of BPB ($699.99 gmol^{-1}$) compared to that of TB ($466.59 gmol^{-1}$). The assertion that inhibition increases with high molecular masses, according to which, the number of substituents on the functional groups of the inhibitor increases, the inhibitive action increases is supported by other authors [44-45]. As the substituent groups increase in size, interaction between the atoms reduces thus exposing more adsorption sites to favour attractions between the inhibitor molecules and steel surface. This in turn increases inhibition efficiency. It suffices it to mention that inhibition efficiency may decrease or increase with increase in the number of substituents on the functional groups of the inhibitor depending on whether the substituents are electron – withdrawing or electron – donating.

3.7. Synergistic effect of KBr addition

It is generally accepted that the presence of halide ions in acidic media synergistically increases the inhibition efficiency of some organic compounds.

Table 4. Synergism parameter for different concentrations of PBP and TB at 303 and 313 K.

Inhibitor concentration (M)	**Synergism parameter, S_1**		
	303 K	313 K	Average
PBP			
0.0001	1.84	1.79	1.82
0.0003	1.83	1.82	1.83
0.0005	1.81	1.69	1.75
0.0007	1.78	1.68	1.73
0.001	1.75	1.65	1.70
TB			
0.0001	1.84	1.82	1.83
0.0003	1.85	1.79	1.82
0.0005	1.79	1.74	1.77
0.0007	1.78	1.71	1.75
0.001	1.77	1.69	1.73

It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism according to Oguzie et al. [46] results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions. The synergistic ability of the halides increases in the order Cl- < Br- < I- [47,48], and is initiated by the specific adsorption of the anion onto the metal surface. The synergism parameter, S_I was evaluated using the relationship given by Aramaki and Hackerman and reported elsewhere [48, 49]. The S_I values for both methods employed as shown in Table 4 for different concentrations of BPB and TB are greater than unity. This indicates that the improved inhibition efficiency caused by the addition of bromide ions to BPB and TB is only due to synergistic effect. Similar results have been documented elsewhere [50, 51]. The synergistic effect between BPB / TB and KBr can be explained by the fact that the addition of the KBr component stabilized the adsorption of the inhibitor dyes on the steel surface. This stabilization may be caused by the interaction between the dyes and Br^- ions. Thus, the interaction enhances the inhibition efficiency to a considerable extent due to the increase of the surface coverage in the presence of bromide ions.

4. CONCLUSIONS

The compounds (BPB and TB) studied as inhibitors retarded the acid corrosion of steel to some extent being physically adsorbed on the metal surface. The inhibition efficiency (%1_E) increases with increase in inhibitor concentration and decreases with increase in temperature in the order TB < BPB. The values of Q_{ads} obtained at 303K and 313K are all negative indicating that the inhibitors are strongly adsorbed on steel surface and the adsorption process is spontaneous. Molecular structures, number of substituents and molecular masses of the compounds studied greatly influenced the inhibitory action of these compounds. Synergistic effects between the dye inhibitors and KBr have been observed. The addition of KBr enhanced the inhibition efficiency significantly.

The adsorption of BPB, TB, KBr and BPB/TB + KBr on mild steel surface in 0.5M HCl obeyed Langmuir adsorption isotherm.

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