



Research Article

ADSORPTION AND THERMODYNAMIC STUDIES OF N-(6-AMINO BENZO[d]THIAZOL-2-YL)BENZAMIDE ON MILD STEEL IN ACID MEDIUM

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Article Received on: 21/10/16 Revised on: 21/11/16 Approved for publication: 03/12/16

DOI: 10.7897/2230-8407.0712143

ABSTRACT

Adsorption of N-(6-aminobenzo[d]thiazol-2-yl)benzamide on mild steel in acid medium was studied at different temperature (303K-333K) by physicochemical method. Thermodynamic parameters were obtained by using Gibbs Helmholtz, Van't Hoff and basic Thermodynamic equations. Activation parameters were determined using Arrhenius and transition state equations. The surface morphology of adsorption of the inhibitor molecule on the mild steel surface was studied and confirmed by SEM and FT-IR in the presence and absence of the compound.

Keywords: Adsorption, Thermodynamic parameters, Activation parameters, SEM, FT-IR

INTRODUCTION

The containers made up of mild steel are most commonly used for storing and handling alkali, acids and salt solution. But the corrosion of mild steel is the major problem in industries. So, there is a need for introducing a new compound which inhibits this process^{1,2}. For the past decades many researchers introduced the most of the available and synthesized organic compounds used as corrosion inhibitors for mild steel corrosion³. However, heterocyclics compounds containing both sulphur and nitrogen in the same ring have received minor attention. Some authors have studied the effect of benzothiazole derivatives as corrosion inhibitor for mild steel, copper and its alloy⁴. But, 2-amino-6-nitrobenzothiazole and its derivatives have not yet been investigated as inhibitors for the corrosion of mild steel in acidic solutions⁵. In the present investigation one of the benzothiazole derivative N-(6-aminobenzo[d]thiazol-2-yl)benzamide is synthesized by using 2-amino-6-nitrobenzothiazole as parent moiety and the adsorption, thermodynamic and surface morphology was studied by using Thermodynamic calculations, SEM and FT-IR.

MATERIALS AND METHODS

Preparation of Specimens

Material: Weight loss experiments were performed with a cold rolled mild steel specimen of size 5cm x 2 cm x 0.05 cm with the composition (Wt %) C-0.07%, S-Nil, P-0.008%, Si-Nil, Mn-0.34% and the balance iron. The mild steel specimens were polished using a series of emery papers. Finally, the metal was degreased with trichloroethylene and used for the experiments immediately.

Preparation of Corrosive Solutions

1N HCl was prepared by dilution of analytical grade HCl with distilled water and standardized with a standard base. The

concentration range of inhibitors used was 100-800ppm in the acid.

Inhibitor solutions

Inhibitor was synthesized and characterized as said in references 5. 2000 ppm N-(6-aminobenzo[d]thiazol-2-yl)benzamide (ABTB) solutions were prepared by dissolving 2 gm of ABTB respectively in one litre of 1N HCl. This stock solution was diluted to different concentration using 1N HCl solutions.

Experimental procedure

Weight loss experiments were carried out by weighing the cleaned specimens before and after immersion for about 1 hour in the absence and presence of inhibitors for various concentrations in 100ml acid solution. Duplicate experiments were also carried out in each case. From the change in weight of the metal specimen before and after immersion in acid medium, the weight loss was calculated. From this weight loss value, inhibition efficiency and corrosion rate were determined. Inhibition efficiency has been determined by using the following relationship⁵.

$$\text{Inhibition efficiency (\%)} = \frac{W_b - W_i}{W_b} \times 100$$

Where, W_b is the weight loss without inhibitor, W_i is the weight loss with inhibitor.

Corrosion rate has been determined by using the following relationship.

$$\text{Corrosion rate (mpy)} = \frac{534 \times W}{A \times T \times D}$$

Where W =Weight loss in mg; A =Area in inch^2 ; T =Time of immersion in sec; D =Density in gm/cc

Surface coverage (θ) has been determined using the following relationship.

$$\text{Surface coverage } (\theta) = \frac{W_b - W_i}{W_b}$$

The procedure was repeated at various temperatures in the range 303K – 333K.

Corrosion Studies

Experiment was carried out in 1N HCl solution at different concentration of the inhibitor temperature (303, 313, 323, 333 K) using a thermostat to study the inhibition efficiency of the inhibitors. Weight loss experiment at different temperature gives detail about the nature of adsorption and activation energy.

Surface morphology

The surface morphology of the corroded and inhibited mild steel specimen was studied by SEM. The SEM photographs were recorded using a JEOL scanning electron microscope. The mild steel specimen was suspended for 5hrs in blank 1N HCl with and without the inhibitor. The plates were washed with running water, and dried. The dried plate was used for SEM studies and then the surface film formed on the mild steel surface was rubbed and mixed with KBr powder and used for recording the FT-IR spectrum.

Evaluation of thermodynamic parameters

Adsorption parameters

Arrhenius activation energy E_a was calculated from the Arrhenius plots of the log corrosion rate vs $1000/T$ for 1N HCl in the presence and absence of the inhibitors. The slopes of the straight lines permit the calculation of Arrhenius activation energy E_a . The free energy of adsorption (ΔG°_{ads}) values are calculated using the equation³

$$\Delta G^{\circ}_{ads} = -2.303 RT \log(55.5K)$$

where $K = \log(\theta/C(1 - \theta))$, θ = surface coverage from weight loss method, 55.5 is the concentration of water in solution in moles / lit.

Kinetic parameters

Transition state equation

Kinetic parameters such as the enthalpy and entropy can be calculated using the transition state equation⁷.

$$CR = \frac{RT}{Nh} \exp\left[\frac{\Delta S}{R}\right] \exp\left[-\frac{\Delta H}{RT}\right]$$

Where h is a plank constant and n is the Avogadro number respectively.

A plot of $\log(CR/T)$ versus $1000/T$ will give a straight line with a slope of $-\Delta H/2.303R$ and an intercept of $[\log(R/Nh) + (\Delta S/2.303R)]$, from which the activation thermodynamic parameters (ΔH and ΔS) were obtained.

Gibbs Helmholtz equation

Gibbs Helmholtz equation is given as follows

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} + T \left[\frac{\partial \Delta H^{\circ}_{ads}}{\partial T} \right]_p$$

which can be rearranged to give the equation

$$(\Delta G^{\circ}_{ads}/T) = (\Delta H^{\circ}_{ads}/T) + A$$

The graph plotted between $\Delta G^{\circ}_{ads}/T$ with $1/T$ gives a straight line with slope equals to ΔH°_{ads} . The standard adsorption entropy ΔS°_{ads} can be deduced using the thermodynamic equation

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} + T \Delta S^{\circ}_{ads}$$

From the values of the ΔH°_{ads} and ΔS°_{ads} we can find the nature of the corrosion process.

Adsorption isotherm

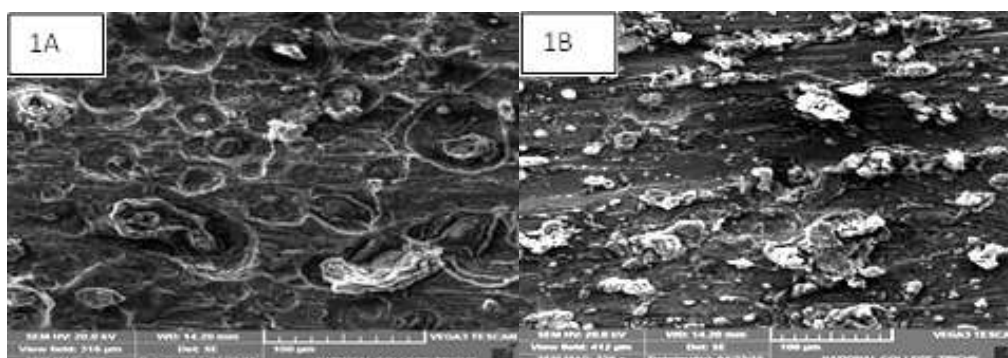
The compound follows Langmuir and Tempkin adsorption isotherm. This is given as

$$\theta/1 - \theta = KC.$$

Rearranging this equation

$$C/\theta = 1/K + C$$

Where θ is the surface coverage degree, K is the equilibrium constant of the adsorption process and C is the inhibitor concentration. It was found that a plot of C/θ vs C gives the graph of the Langmuir adsorption isotherm for the compounds⁵. Plots of θ Vs $\log C$ gives the graph of the Tempkin adsorption isotherm for the compound.



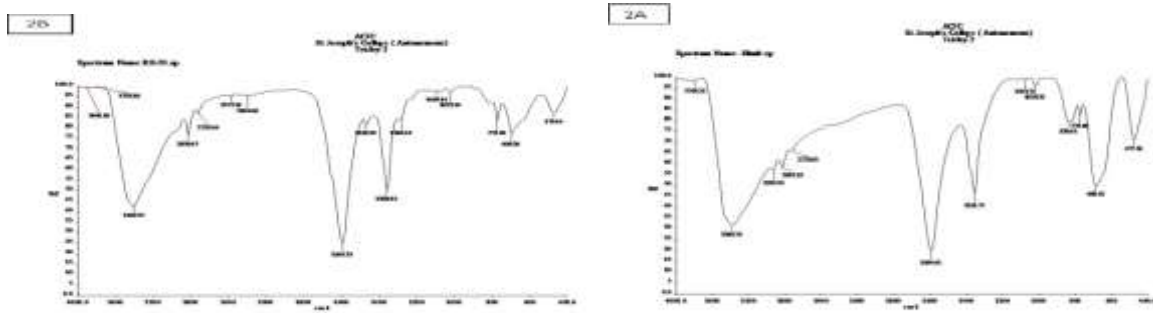


Figure 1A & 1B: SEM of mild steel in 1N HCl without and with ABTB

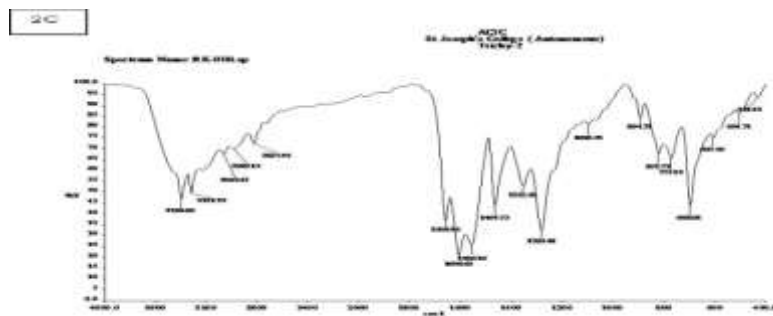


Figure 2A: FT-IR spectrum of Mild steel in 1N HCl, 2B: IR spectrum of ABTB, 2C: IR spectrum of Mild steel in 1N HCl with ABTB

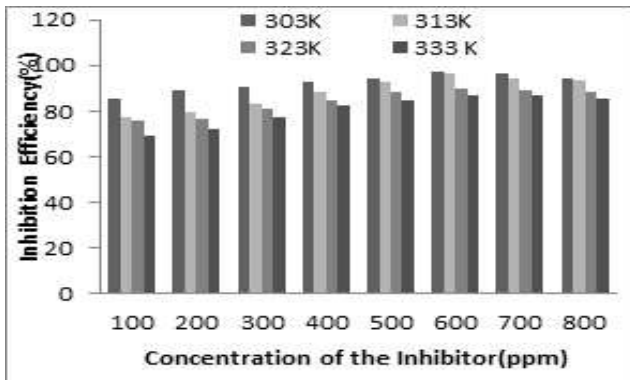


Figure 3: Effect of temperature

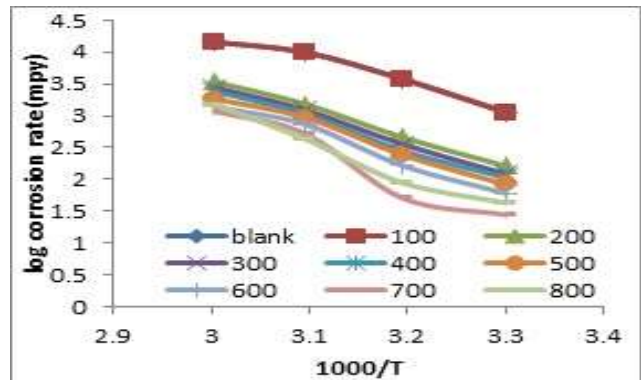


Figure 4: Arrhenius plot

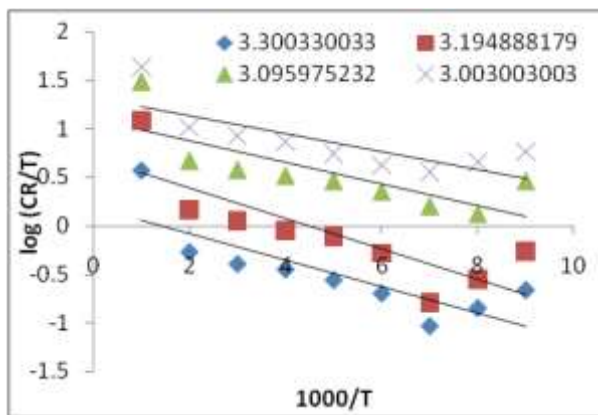


Figure 5: Transition state plots

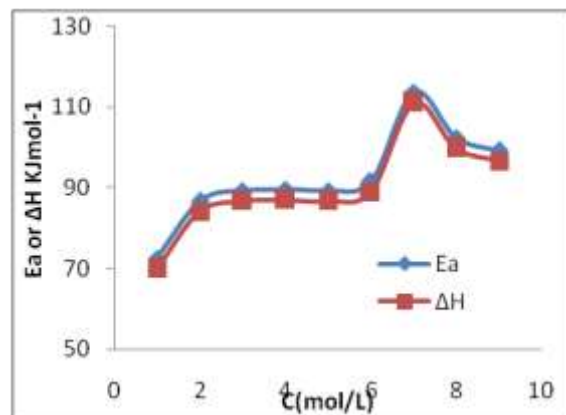


Figure 6: The relationship between Ea and ΔH

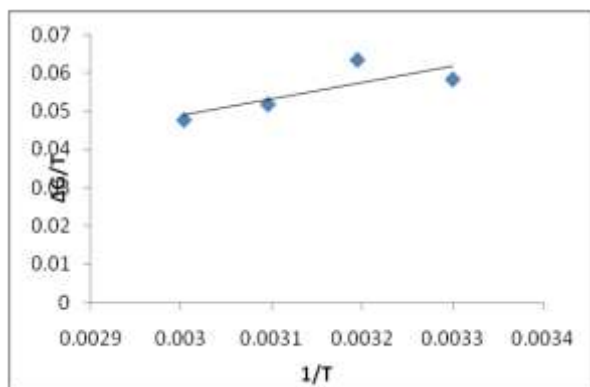


Figure 7: The relationship between $\Delta G/T$ with $1/T$ (ABTB)

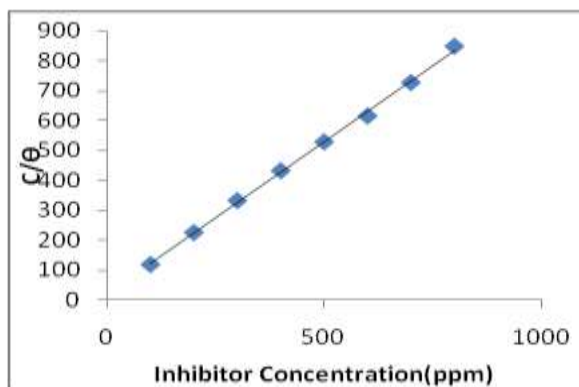


Figure 8: Langmuir adsorption isotherm

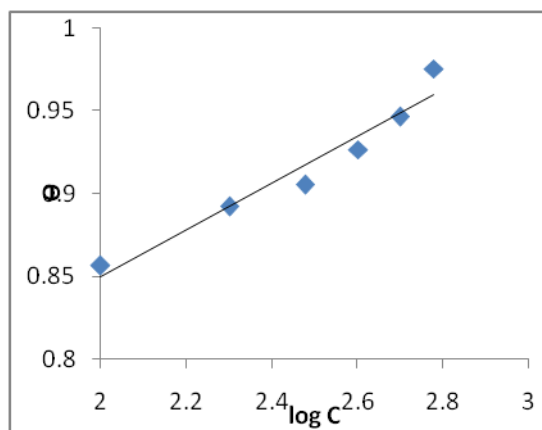


Figure 9: Temkin adsorption isotherm

Table 1: FT-IR Peak Value (cm^{-1}) of ABTB Mild steel in 1N HCl and Mild steel in 1N HCl with inhibitor (ABTB)

S.no	FT-IR Peak Value(cm^{-1})			Possible groups
	Mild steel in 1N HCl	ABTB	Mild steel in 1N HCl with ABTB	
1		3399.60	3402.37	Amine
2	3386.76	-		ν O-H
3	-	3321.33	3402.37	Amide
4		3063.47	2830.47	-C-H- group in the aromatic ring
5		1659.05	1595.31	C=O attached to amidegroup
6	1594.41	-	1595.31	δ HOH
7		1464.72	1469.94	-C=C- group in the aromatic ring
8	686.52			γ OH
9		698.03	698.36	Aromatic monosubstitution (C-H deforming)
10	477.51		475.45	γ FeO

Table 2: Inhibition efficiency of ABTB on mild steel corrosion in 1N HCl at 303K- 333K

Inhibitor concentration (ppm)	Temperature							
	303K		313K		323K		333K	
	Corrosion rate	IE (%)	Corrosion rate	IE (%)	Corrosion rate	IE (%)	Corrosion rate	IE (%)
Blank	1130.49		3768.3		9881.32		14403.28	
100	162.11	85.66	456.34	87.89	1512.83	84.69	3410.69	76.32
200	121.75	89.23	355.72	90.56	1223.30	87.62	2801.43	80.55
300	106.94	90.54	280.36	92.56	1061.25	89.26	2412.54	83.25
400	82.978	92.66	243.05	93.55	933.78	90.55	1834.97	87.26
500	60.36	94.66	164.29	95.64	727.26	92.64	1392.797	90.33
600	27.69	97.55	50.87	98.65	515.80	94.78	1183.95	91.78
700	42.61	96.23	88.17	97.66	428.84	95.66	1492.18	89.64
800	65.45	94.21	171.08	95.46	932.79	90.56	1914.196	86.71

Table 3: ΔG_{ads}° KJ mol⁻¹ and Ea (calculated using arrhenius plot) for the corrosion of mild steel in 1N HCl

Inhibitor Concentration (ppm)	$-\Delta G_{ads}^{\circ}$ KJ mol ⁻¹				Ea(KJ mol ⁻¹)
	303K	313K	323K	333K	
100	17.65	18.74	18.61	17.69	86.80
200	16.34	17.26	17.00	16.04	89.37
300	15.81	17.01	16.47	15.56	89.62
400	15.84	16.73	16.15	15.72	89.38
500	16.02	17.11	16.16	15.84	91.61
600	17.65	19.82	16.71	15.88	113.76
700	16.18	17.99	16.85	14.79	102.43
800	14.64	15.79	14.19	13.56	99.26

Table 4: Activation parameters of mild steel corrosion in 1N HCl with ABTB (using transition state plots)

Concentration of inhibitor (ppm)	Activation Energy (KJmol ⁻¹)	Enthalpy (KJmol ⁻¹)	Entropy (Jmol ⁻¹ K ⁻¹)	Ea- ΔH (KJmol ⁻¹)
Blank	72.53	69.90	45.35	2.64
100	86.80	84.16	74.93	2.64
200	89.37	86.73	81.06	2.64
300	89.62	86.98	80.49	2.64
400	89.38	86.74	78.07	2.64
500	91.61	88.97	82.51	2.64
600	113.76	111.12	147.15	2.64
700	102.43	99.79	113.61	2.64
800	99.26	96.62	108.04	2.64

Table 5: Activation parameters of mild steel corrosion in 1N HCl with ABTB (using Gibbs Helmholtz equation)

Temperature in Kelvin	Gibbs free energy (KJmol ⁻¹)	Enthalpy (KJmol ⁻¹)	Entropy (Jmol ⁻¹ K ⁻¹)
303	-17.65	-43.04	141.854
313	-19.82		137.31
323	-16.71		133.09
333	-15.88		129.11

RESULTS AND DISCUSSION

Surface morphology SEM

SEM figure 1A shows that the metal surface consists of many pits in the absence of the inhibitor molecule but in the Figure 1B shows no evidence of pitting but shows a protective film like surface. This protective film blocks the active sites present on the mild steel surface and inhibits the corrosion process⁵.

FT-IR Spectral Analysis

FT-IR spectrum of mild steel in 1N HCl, with ABTB and molecule ABTB are shown in figure 2A, 2B & 2C. The corresponding peak values and the corresponding possible group's values are given in Table 1. The film formation is due to the interaction of oxygen, nitrogen atoms present in ABTB with Fe in mild steel thereby Fe- ABTB complex was formed. It retards the corrosion process⁶. The peaks appeared between the ranges of 400-700 cm⁻¹ is mainly due to Fe₂O₃.

Weight loss experiment at different temperature

The experiments were carried out in 1N HCl medium at different temperature (303-333K) for the duration of 1hr. The results obtained are given in Table 2 and figure 3 which illustrates that the maximum inhibition efficiency observed was 98.65% (at 313K) whereas with increase in temperature the inhibition efficiency was found to be decreased and the corrosion rate of the metal surface was found to be increased. It is due to the fact that the protective films formed on the metal surface by the inhibitor protected the metal up to 313K after that the film formed starts to breakdown with increasing

temperature. After 313K, desorption of the inhibitor molecule from the metal surface at higher temperature⁶ which accelerate the corrosion process.

Thermodynamic parameters and adsorption isotherm

The Ea values calculated using Arrhenius plots are given in Table 3. The Arrhenius plots are shown in figure 4. The values of energy of activation Ea increases in the presence of inhibitor up to 600ppm which is shown in the Table 3 indicates that the energy barrier for corrosion reaction increased up to 600ppm in the presence of inhibitor without changing the dissolution mechanism. The increase in Ea value in the presence of ABTB indicates the strong adsorption of inhibitor on the metal surface formation up to 600ppm. The increase in Ea value in the presence of the inhibitor (ABTB) implies that the bonding between the molecules of the inhibitor and the mild steel surface is of physical or weak bonding³. This type of inhibitor will retard the corrosion at room temperature but with increase in temperature the inhibition activity gets diminished⁵.

The negative value of ΔG_{ads}° shown in Table 3 ensures the spontaneous adsorption of inhibitor on mild steel and the stability of the adsorbed layer. Generally, values of ΔG_{ads}° up to -20KJ mol⁻¹ are consistent with physical adsorption, while those around -40KJ mol⁻¹ are consistent with chemical adsorption⁷. Here, in this case the values of ΔG_{ads}° less than -20KJ mol⁻¹ which are consistent with physical adsorption i.e. electrostatic interactions between the charged molecules and the charged metal surface⁸.

Kinetic Parameters

Kinetic parameters such as the enthalpy and entropy can be calculated using the transition state equation⁸ and shown in figure 5. The activation thermodynamic parameters (ΔH and ΔS) were obtained, and listed in table 4. The positive values of the enthalpy revealed that the corrosion inhibition process is endothermic and positive value of ΔS proved that increase in disordering takes place during the conversion of reactant to activating complex⁹. Both the E_a and ΔH values increases in the presence of the inhibitor proved that there is a increase in energy barrier for the corrosion process and it further support the physical adsorption mechanism. E_a values are higher than the calculated ΔH values shown in the Figure6 indicates that the gas is evolved during the corrosion process, that is the evolution of hydrogen takes place during the reaction in addition to the decrease in total reaction volume¹⁰. The difference between E_a and ΔH permits us to verify the known thermodynamic relations.

$$E_a - \Delta H = RT$$

The calculated values shown in the table are too close to RT (i.e) 2.64 KJ/mol., where T is the experimental temperature, indicating that the corrosion process follows the unimolecular reaction and it is characterized from the above equation¹⁰. The results confirmed that the corrosion inhibition process of the inhibitor acted equally on the E_a and ΔH ⁹. The mechanism was again confirmed by using the Gibbs Helmholtz equation

$$\Delta G = \Delta H - T(\partial \Delta G / \partial T)$$

The plot of $\Delta G/T$ versus $1/T$ shown in figure7 gives a straight line with the slope represents the value of ΔH for a concentration of 600ppm. By using the ΔG value obtained from the Arrhenius plot and ΔH from the slope, we have calculated the ΔS using the equation

$$\Delta G = \Delta H - T\Delta S$$

The negative value of ΔH value indicates that the reaction undergo endothermic adsorption process. The positive value of ΔS proved that there is an increase in the disorderness taking place during the formation of reactant into activated complex¹². On considering both the enthalpy and entropy value obtained from the transition state equation and GibbsHelmholtz equation it is concluded that the inhibitor behaves both endothermic ($\Delta H=111.12 \text{ KJmol}^{-1}$) and exothermic ($\Delta H= -43.04 \text{ KJmol}^{-1}$) adsorption on the exact range of given temperature. The average $\Delta H=34.04 \text{ KJmol}^{-1}$ obtained for this inhibitor molecule indicate that the inhibitor follow both the physisorption and chemisorptions mechanisms.(i.e. comprehensive adsorption). Since the absorption heat approaches the general chemical reaction heat, the chemical adsorption takes place in combination with the physical adsorption.

Adsorption isotherm

In order to determine the mechanism of organic electrochemical reactions adsorption isotherms are very important. The most frequently used isotherms are Langmuir, Tempkin and Frumkin. This compound obeys Langmuir and Tempkin adsorption isotherms which are shown in figure 8 and 9. As the adsorption process of the inhibitor molecule on the mild steel in the acid medium obeys Langmuir and Tempkin isotherm, the organic inhibitor molecule is attached as a monolayer on the metal surface through physical mechanism¹³.

CONCLUSION

SEM and FT-IR studies confirm the formation of the film of the inhibitor on the steel surface due to adsorption. Adsorption of the inhibitor molecule takes up to 313K after that with increase in temperature desorption takes place in acid medium. The negative value of ΔG_{ads}^0 and increase in E_a value ensures the spontaneous absorption of inhibitor on mild steel and the stability of the adsorbed layer. The positive value of ΔS proved that there is an increase in disordering takes place during the conversion of reactant to activating complex. The average $\Delta H=34.04 \text{ KJmol}^{-1}$ obtained for this inhibitor molecule indicate that the inhibitor follow both the physisorption and chemisorptions mechanisms.(i.e. comprehensive adsorption). E_a values are higher than the calculated ΔH values proved that the evolution of hydrogen takes place during the adsorption process. This adsorption process follows unimolecular reaction. Adsorption process obey Langmuir and Tempkin adsorption isotherm

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Cite this article as:

S. Rekha, K. Kannan. Adsorption and thermodynamic studies of N-(6-aminobenzo[d]thiazol-2-yl)benzamide on mild steel in acid medium. *Int. Res. J. Pharm.* 2016;7(12):35-41 <http://dx.doi.org/10.7897/2230-8407.0712143>

Source of support: Nil, Conflict of interest: None Declared

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