

Research Article

Thermodynamic Properties and Inhibitor Adsorption Behaviour of *Musa acuminata* Flower Extract on Mild Steel in Phosphate Environment

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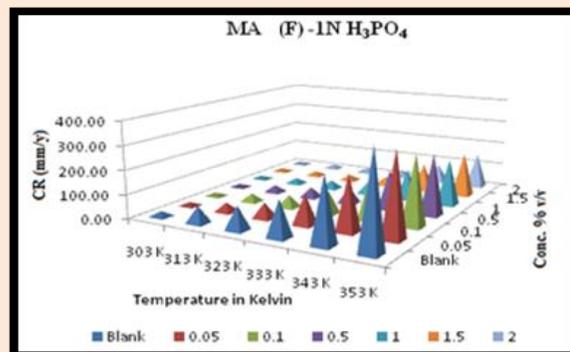
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Abstract

Corrosion inhibition and adsorption behaviour of *Musa acuminata* flower MA (F) extract on mild steel in phosphate environment was investigated at different temperature (303-353 K) by weight loss techniques. Results show that inhibition efficiency of the extract decreased as temperature increased but increased with increase in concentration of extract. Inhibition occurs through adsorption of phytonutrients on the metal surface. Adsorption data fitted well to Langmuir and Temkin adsorption isotherm. Fundamental thermodynamics functions were determined and discussed to evaluate inhibitive properties of MA (F) in phosphate environment.

Keywords: *Musa acuminata*, flower extract, mild steel, Langmuir adsorption, Thermodynamic parameters.



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Introduction

The metal gets corroded by exposure to corrosive atmosphere like moist air, salty water, refinery oil, various acids etc [1, 2]. Acids are widely used in industry for derusting and pickling, cleaning of refinery equipment, removal of calcareous deposits from boilers, radiators of vehicles, pipelines carrying water or petroleum products, heat exchangers and so on. Due to its prominent properties, hydrochloric acid, sulphuric acid and phosphoric acid are widely used in industry for acid pickling process [3]. These acids have their own advantages and disadvantages. Hydrochloric acid is cheaper and can be used for pickling at low temperature, but require a large volume for pickling due to its low activity. Sulphuric acid is costly and produces fewer fumes and involves less volume for pickling. Phosphoric acid is non toxic and used in production of fertilizers. It is a medium strong acid and shows strong corrosiveness on ferrous and ferrous alloys. Little work has been done on the inhibition of steel in phosphoric acid solutions.

The effect of temperature on inhibition reaction of inhibited acid-metal surface is highly complex, because many changes may occur on the metal surface, such as rapid etching, rupture, desorption of the inhibitor and the decomposition and/or rearrangement of the inhibitor [4]. Temperature has a great effect on the rate of metal electrochemical corrosion. In case of corrosion in an acid medium, the corrosion rate increases with temperature increase because the hydrogen evolution over potential decreases. It is generally assumed that in the acid corrosion the inhibitors adsorb on the metal surface, resulting in a structural change of the double layer and reduced rate of the electrochemical partial reaction [5]. In industrial processes like pickling and acid cleaning, the choice of optimum temperature is of particular importance as temperature modifies the interaction between the mild steel surface and the acid medium in the absence and presence of inhibitor. In the presence of inhibitor which is of adsorptive type the temperature variation affects the metal dissolution as well as the degree of metal surface coverage by inhibitor at a constant value of its bulk concentration [6]. To test the stability of the inhibitor at higher temperature, experiments were performed at different temperature in the range of 303 K – 353 K in the phosphoric acid medium.

Experimental

Materials

Preliminary treatment of mild steel: Rectangular mild steel coupons of size 5 x 1 x 0.2 cm (**Figure 1**) were polished in sequence using silicon carbide emery papers of grade, 200, 400, 600, and then washed with distilled water, degreased with acetone and dried using hot air drier.



Figure 1 Photograph of mild steel coupons

Preparation of inhibitor

Musa acuminata inflorescence was collected from the cultivated farm in Thirumalayampalayam, Coimbatore, Tamilnadu, India. The inflorescence was separated into florets and bracts (**Figure 2**). The florets were air dried under shade, ground into powder using an electronic blender, sieved and stored in air tight container. Present study has been carried out with commercial grade H_3PO_4 acid to simulate industrial conditions.

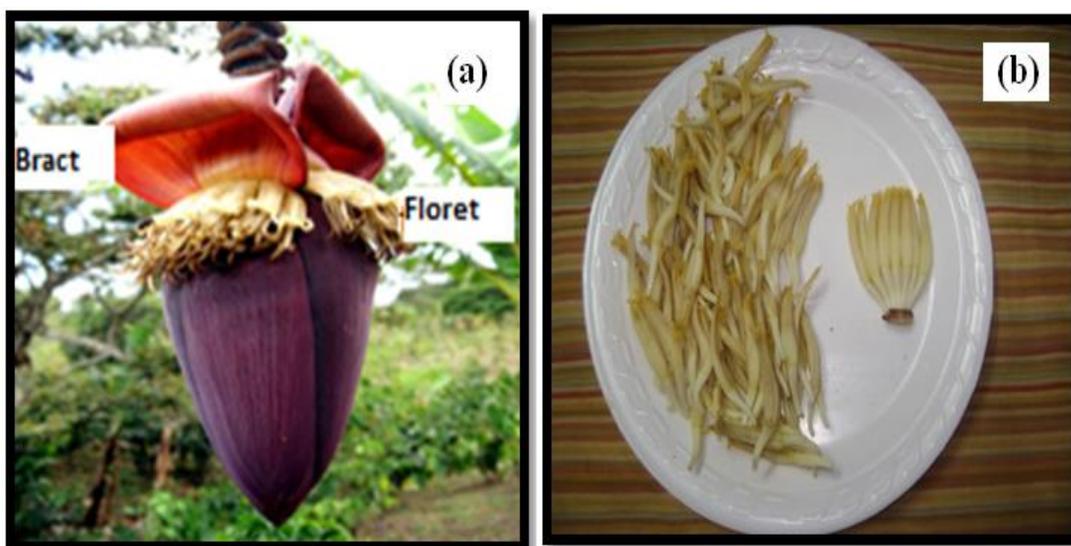


Figure 2 (a) *Musa acuminata* inflorescence (b) florets

25 gm of dried powder of floret was boiled in 500 ml of 1N H_3PO_4 acid with reflux condenser for three hours and was kept overnight to extract its phytonutrients. The extract was filtered and the filtrate volume was made up to 500 ml using H_3PO_4 acid. From this 5 % stock solution, test concentrations of 0.05, 0.10, 0.50, 1.00, 1.50 and 2.0 % v/v were prepared by diluting with 1N H_3PO_4 .

Methods

Gravimetric Experiment

Weight loss determinations were carried out at the temperature range of 303 K – 353 K. After initial weighing, the specimens were immersed in 100 ml of 1N H_3PO_4 acid without and with various concentrations of the plant extracts and kept in the thermostat (Raaga Lit pump type digital) for 1h duration (**Figure 3**). After the appropriate immersion time, the specimens were removed, washed, dried and reweighed. The loss in weight was determined. A triplicate was

run to ensure the weight loss and the results were averaged. From the weight loss, corrosion rate (CR), inhibition efficiency (IE) and surface coverage (θ) was calculated.



Figure 3 Photograph of thermostat (Raaga Lit pump type digital)

Thermodynamic parameters

Various thermodynamic parameters such as activation energy (E_a), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were calculated as described below,

Determination of activation energy

The apparent activation energies E_a for the corrosion in presence and absence of inhibitor were evaluated from Arrhenius equation,

$$CR = Ae^{\frac{-E_a}{RT}} \quad (1)$$

Where, CR is the corrosion rate, E_a is the apparent activation energy of the corrosion reaction, R is the gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential factor [7].

Determination of free energy of adsorption

The free energy of adsorption (ΔG_{ads}) at different temperature was calculated from the equilibrium constant of adsorption using the expression,

$$k = \frac{1}{55.5} \exp \left[\frac{\Delta G_{ads}}{RT} \right] \quad (2)$$

where, $k = \frac{\theta}{C(1-\theta)}$ (from Langmuir equation), θ = degree of coverage on the metal surface, C = concentration of inhibitor in mM, $\Delta G_{ads} = -RT \ln(55.5k)$.

Determination of enthalpy and entropy of adsorption

Enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) was calculated from the values of free energy of adsorption (ΔG_{ads}) using Gibbs- Helmholtz relationship,

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad (3)$$

The slope and intercept of the line obtained by plotting ΔG_{ads} against T furnished ΔS_{ads} and ΔH_{ads} respectively.

Determination of adsorption isotherms

Since corrosion inhibition is a surface phenomena involving adsorption of the inhibitor on the surface of the metal, the phenomenon of interaction between the metal surface and inhibitor can be understood with adsorption isotherms [8]. Different adsorption isotherms namely Langmuir and Temkin were tested for their fit into the experimental data.

Results and Discussion

Effect of temperature on CR and IE of mild steel in 1N H₃PO₄

The temperature effect on the inhibition efficiency of mild steel in 1N H₃PO₄ containing different concentrations of inhibitors at a temperature range from 303 K to 353 K was studied. **Table 1** and **Figure 4** represent the influence of temperature on inhibition efficiency for corrosion of mild steel in 1N H₃PO₄ in absence and presence of different concentration of inhibitor. Data revealed that the inhibition efficiency increased with increasing temperature up to 323 K at 2 % v/v and decreased thereafter, indicating that the inhibitor was more effective at higher temperature up to 323 K at 2 % v/v. Popova et al (2004) has interpreted the decrease of IE value with temperature increase as an indication for a physical or columbic type of adsorption [9]. The maximum inhibition efficiency was found to be 79.93 % for 2 % v/v concentration of MA (F) extract in 1N H₃PO₄.

Table 1 Effect of temperature on mild steel corrosion in 1N H₃PO₄ in absence and presence of MA (F) extract

Conc. % v/v	303 K		313 K		323 K		333 K		343 K		353 K	
	CR mm/y	IE %										
Blank	22.51	–	70.66	–	99.41	–	151.91	–	270.27	–	394.64	–
0.05	14.93	33.66	39.68	43.85	65.09	34.53	128.28	15.55	233.49	13.61	347.39	11.97
0.10	12.59	44.06	35.22	50.16	53.05	46.64	95.96	36.83	190.80	29.40	293.89	25.53
0.50	10.92	51.49	30.98	56.15	44.47	55.27	70.21	53.78	169.07	37.44	255.00	35.39
1.00	9.70	56.93	25.30	64.20	36.11	63.68	53.05	65.08	130.40	51.75	196.93	50.10
1.50	9.03	59.90	18.72	73.50	22.96	76.91	36.11	76.23	117.47	56.54	188.35	52.27
2.00	7.24	67.82	17.83	74.76	19.95	79.93	31.43	79.31	79.02	70.76	149.68	62.07

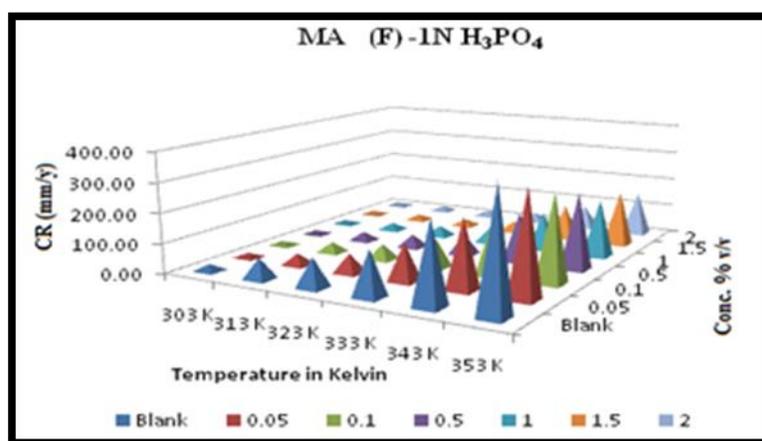


Figure 4 Effect of temperature on CR of MA (F) in 1N H₃PO₄

Energy of activation for metal dissolution in 1N H₃PO₄ medium

The values of energy of activation E_a for mild steel dissolution in 1N H₃PO₄ medium are tabulated in the **Table 2**. Comparing the E_a values of uninhibited and inhibited solutions, it was found that E_a values are higher in the inhibited solutions than that of the blank acid solution. The higher values of E_a indicate that the addition of plant extract hinders

metal dissolution and also indicate the decrease in the adsorption of inhibitor on mild steel surface with increase in temperature.

The observations reported by Chauhan (2007) and Bentiss et al (2001), explained that the increase of E_a value in the presence of plant extract may be interpreted as physical adsorption that occurs in the first stage, that is important because it is the preceding stage of chemisorption of plant extract on mild steel [10, 11]. The increase in E_a can be attributed to an appreciable decrease in the adsorption of the inhibitor on mild steel surface with increase in temperature. A corresponding increase in the corrosion rate occurs because of the greater area of the metal that is frequently exposed to acid environment. The Arrhenius plots for the extract in 1N H_3PO_4 medium is shown in **Figure 5**.

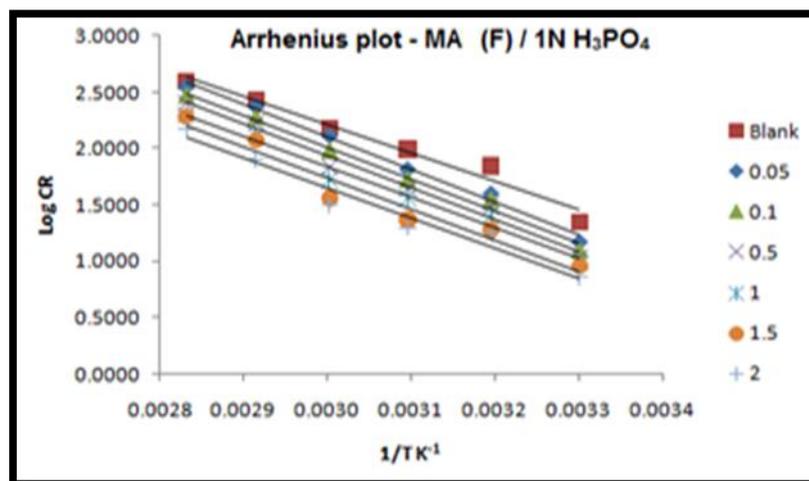


Figure 5 Arrhenius plots of Log CR vs. $1/T$ for mild steel in 1N H_3PO_4

Table 2 Activation energy (E_a) for mild steel in absence and presence of various concentration of MA (F) extract in 1N H_3PO_4

Extract Conc. (% v/v)	E_a (kJ/mol)
Blank	47.96
0.05	55.43
0.10	54.57
0.50	54.20
1.00	51.75
1.50	53.43
2.00	50.76

Adsorption Isotherms

Corrosion inhibition is a surface phenomenon. The interaction of surface-inhibitor can be estimated from the experimental data. The inhibition efficiency depends on the type, number of active sites at the metal surface, charge density, molecular size of inhibitor, metal-inhibitor interactions and the metallic complex formation. Adsorption isotherms give information on the metal-inhibitor interaction [12].

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface [13]. The performance of the studied inhibitor as a corrosion inhibitor may be attributed to the presence of electron donor groups (N, O and aromatic rings) in the molecular structure of inhibitor which favours the greater adsorption of it on the metal surface. The unshared and pi electrons interact with d-orbital of mild steel to provide a protective film. To quantify the effect of inhibitor concentration on the corrosion rate, it is a common practice to fit the corrosion rate data to equilibrium adsorptions such as Langmuir, Temkin equation [14]. The experimental data obtained with the various inhibitor concentrations of the plant extract in 1N H_3PO_4 medium at different temperatures from 303 K to 353 K were applied to Langmuir and Temkin adsorption isotherm equations.

The plots of C/θ against C yield a straight line providing that the adsorption of *Musa acuminata* from the acid media on the mild steel surface obeys the Langmuir adsorption isotherm. The linear regression parameters are listed in **Table 3**. Straight lines of C/θ vs. C at different temperature are shown in **Figure 6**. The strong correlation (> 0.95)

for the Langmuir adsorption isotherm plot confirmed the validity of the approach. It is observed that all linear correlation coefficients (r) are almost equal to 1 and all slopes are close to 1 which indicates the adsorption of *Musa acuminata* plant extracts on mild steel surface obeys Langmuir adsorption isotherm.

Table 3 Adsorption parameters for various adsorption isotherms for mild steel in 1N H₃PO₄ in the presence of the extracts

Temp. in K	MA (F) extract in 1N H ₃ PO ₄					
	Langmuir			Temkin		
	Correlation	Slope	Intercept	Correlation	Slope	Intercept
303	0.988	1.475	0.158	0.945	5.270	-3.111
313	0.991	1.297	0.129	0.923	4.963	-3.356
323	0.983	1.205	0.176	0.934	3.633	-2.521
333	0.991	1.158	0.264	0.976	2.664	-1.805
343	0.953	1.341	0.419	0.923	3.052	-1.676
353	0.973	1.513	0.424	0.952	3.442	-1.713

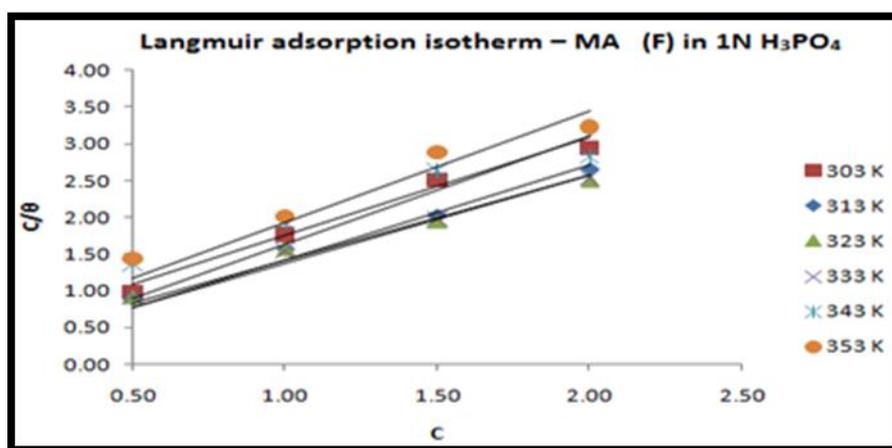


Figure 6 Langmuir isotherms for adsorption of inhibitor on mild steel surface in 1N H₃PO₄

The plot of surface coverage (θ) obtained from weight loss method versus $\log C$ at different concentrations of the inhibitors showed a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Temkin's adsorption isotherm. This also points out that the corrosion inhibition by these compounds is being a result of their adsorption on the metal surface [15]. **Figure 7** show the Temkin's adsorption isotherm plots for MA (F) 1N H₃PO₄. It was found that the data fitted the Langmuir adsorption and Temkin adsorption isotherms with correlation coefficients greater than 0.90.

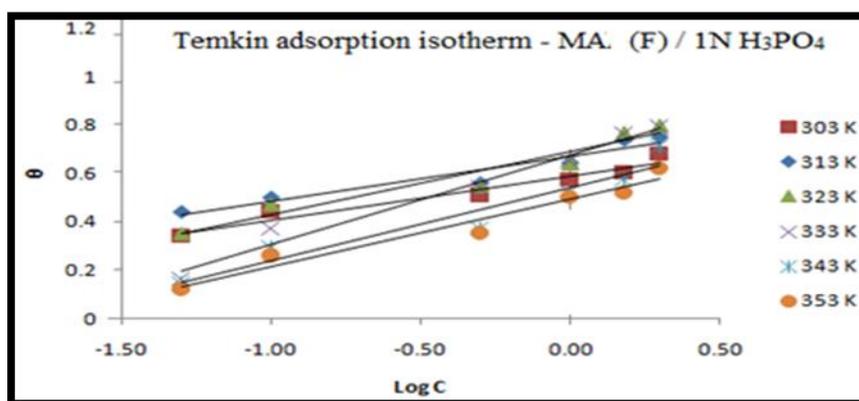


Figure 7 Temkin adsorption isotherms for mild steel in 1N H₃PO₄

Thermodynamic parameters of adsorption of the plant extracts in 1N H₃PO₄ medium

In this system, the ΔG_{ads} is in the range -10.09 kJ/mol to -17.60 kJ/mol for MA (F) extract which authenticates physical adsorption. This implies that the constituents of plant extracts adhere on the surface of the corroding system and gives a strong inhibition.

The values of other thermodynamic parameters such as enthalpy ΔH_{ads} and entropy ΔS_{ads} provide supplementary information about the mechanism of corrosion [16]. The thermodynamic data of adsorption are depicted in **Table 4**. The values confirm the exothermic behaviour of the adsorption process of MA (F) on the mild steel surface in phosphoric acid. While endothermic adsorption process ($\Delta H > 0$) is attributed unequivocally to chemisorption, and exothermic adsorption process ($\Delta H < 0$) may involve either physisorption or chemisorption or a mixture of both process. The negative values of ΔH_{ads} show that the adsorption is exothermic with an ordered phenomenon ascribed by the negative values of ΔS_{ads} . This order may probably be explained by the possibility of formation of iron complex on the metal surface or inhibitor molecules may freely move in the bulk solution before the adsorption process. During the adsorption, the inhibitor molecules are adsorbed orderly on the metal surface which resulted in the decrease in entropy [17].

Table 4 Thermodynamic parameters of adsorption of mild steel in 1N H₃PO₄ in the presence of MA (F) extract

Conc. % v/v	ΔG_{ads} kJ/mol						ΔH_{ads} kJ/mol	ΔS_{ads} kJ/mol
	303 K	313 K	323 K	333 K	343 K	353 K		
0.05	-15.97	-17.60	-17.14	-14.80	-14.79	-14.71	-31.83	0.049
0.10	-15.29	-16.42	-16.62	-16.00	-15.44	-15.45	-18.46	0.008
0.50	-11.94	-12.86	-13.16	-13.46	-11.89	-11.98	-14.81	0.007
1.00	-10.80	-11.93	-12.31	-12.81	-11.66	-11.76	-7.67	-0.013
1.50	-10.09	-12.09	-12.92	-13.16	-11.07	-10.81	-10.96	-0.002
2.00	-10.25	-11.48	-12.62	-12.84	-12.00	-11.16	-5.79	-0.018

The results presented in Table 4 shows that the enthalpy of activation values are almost negative in the phosphoric acid medium, The negative sign of the enthalpies reflects the exothermic nature of the mild steel dissolution process. Also, the entropies of activation were positive and negative for different acid media and different inhibitor concentration indicating that the activation complex represents both association and dissociation steps. The complex chemical composition of *Musa acuminata* plant extract make it rather difficult to attribute the inhibiting action to a particular constituent or group of constituents. Alkaloid compounds have been shown to possess significant anticorrosion activity, which is principally based on their structural characteristics (nitrogen atoms and other groups in conjugation). It is very important to note that discussion of the adsorption behaviour using natural product extracts as inhibitors in terms of thermodynamics parameters (ΔG_{ads} , ΔH_{ads} and ΔS_{ads}) is not possible because the molecular mass of the extract components is not known. For example, there are several alkaloid compounds in the extracts. Authors like Abdel-Gaber (2009) in their study on acid corrosion with plant extract, noted the same limitation [18].

Conclusions

The corrosion of mild steel is significantly reduced upon addition of *Musa acuminata* flower extract in phosphate environment. Inhibition efficiency increased with increasing concentration of inhibitor. Maximum inhibitor efficiency of 79.93 was observed at an optimum concentration of 2% v/v. Corrosion rate decreased with increase in inhibitor concentration at all temperatures. Inhibition efficiency increases up to 323 K and thereafter decreases with increasing temperature indicating adsorption – desorption process. Adsorption of *Musa acuminata* plant extracts onto metal surface followed Langmuir and Temkin adsorption isotherms with a correlation coefficient greater than 0.9. Activation energy E_a was higher for inhibited acid than for uninhibited acids showing temperature dependence of inhibitor efficiency. Negative values of ΔG_{ads} with increase in temperature indicate spontaneous adsorption of inhibitor on mild steel surface. Negative value of ΔG_{ads} and ΔH_{ads} also indicate physisorption nature of adsorption by inhibitor.

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