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Temperature Coefficient of Corrosion Inhibition of Steel by Adenine

Gamal K. GOMMA* and Mostafa H. WAHDAN†
Chemistry Department, Faculty of Education, Tanta University, Kafr El-Sheikh, Egypt
† Chemistry Department, Faculty of Science, Assuit University, Assuit, Egypt

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The inhibition of steel corrosion in 0.5 M sulfuric acid by adenine at different temperatures was shown to follow the Langmuir adsorption isotherm over a wide concentration range (10^{-5} to 10^{-3} M). The corrosion potential, corrosion current, corrosion rate, polarization resistance, as well as activation energy and thermodynamic parameters were calculated at different temperatures. From a comparison of the activation energies of uninhibited and inhibited corrosion reactions, the heat of adsorption of adenine may be obtained. The temperature coefficient for corrosion inhibition has a negative value, which may be explained by assuming that the corrosion reaction is no longer the simple metal/acid reaction, but involves the adsorbed species directly.

The rate of corrosion of steel in acidic solutions increases with increasing temperature. The inhibition characteristics of some inhibitors during acid corrosion have been reported earlier.[1—10] The protection efficiency is attributed mainly to the presence in molecule of a polar atom or several as N, S, or O atoms as active centers for adsorption of the organic molecule onto the metallic surfaces. As an extension of this work a study on potentiokinetic polarization and the temperature kinetic effect of acid dissolution of steel in the presence of adenine was investigated. Adenine is one of the bases found in DNA and it is known to function as a chelating agent with transition metal ions, because it contains more than one atom with unshared pairs of electrons, which can give the unshared pairs of electrons to the metal atoms to form a stable member ring resembling a 'claw'. The results are that the metal atom is held in a stable configuration and the chelate that is produced usually does not exhibit either the properties of the metal atom or the chelating agent.

The theory of cathodic inhibition requires that the temperature coefficient for inhibition be negative, whereas experimentally both positive and negative temperature coefficients are reported.[11]

The aim of the present work is to test some of hypotheses concerning adsorption and inhibition, and to determine the heat of adsorption from the temperature dependence of inhibition.

Experimental

The steel samples containing 0.05% C, 0.6% Mn, 0.36% P, and 0.03% S was supplied by Boehler (V. E. W. Austria). The specimens were machined into cylindrical form, 2 cm in length and 0.2 cm in diameter. They were inserted in Teflon® in such a way that only the flat surface was in contact with the solution. The surface preparation procedure was shown to give reproducible polarization curves, with an error in corrosion current density of less than 0.1%.

Reagent grade chemicals were used and solutions were made up with double distilled water. A stock solution from adenine was prepared and diluted to the appropriate concentration (10^{-5} to 10^{-3} M, 1 M=1 mol dm^{-3}) as required with 0.5 M sulfuric acid solution. Before each measurement, the solution was purged with nitrogen gas for 6 h. Measurements were carried out under the presence of N_2 gas in order to avoid oxygen entrance into the electrolyte. The sample was allowed to reach a stable open circuit potential, which was attained in about 30 min. Afterwards, cathodic and anodic polarization curves were measured at a scan rate 1 mV s^{-1}.

The cell used for polarization measurements was composed of two compartments separated by a fritted glass disc to prevent mixing of anolyte and catholyte. The cell with a double walled jacket is provided with two openings in the outer wall for inlet and outlet and can be connected to the external closed-loop water circulating system (Haakn, West Germany) for the accurate temperature control. A conventional three electrodes system was used. Platinum sheet was used for the auxiliary electrode, the working electrode was a steel bar, the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary.

Potentiokinetic studies were performed using a corrosion measurements system, a model (273 soft corr) corrosion software potentiostat/galvanostat. The cathodic polarization curves were obtained at a scan rate of 1 mV s^{-1} and the potential ranging from −500 to +100 mV.

The electrochemical parameters of this inhibitor were obtained from the potentiokinetic polarization curves at different temperatures ranging from 30 to 45 °C. These include; the corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (B_{c} and B_{a} respectively), corrosion rate and polarization resistance (R_{p}). An average of the data for five independent runs was collected for adenine. Runs in which three or more of the electrochemical parameters were out of one standard deviation from their sample average were discarded.

Results and Discussion

Sulfuric acid (0.5 M) containing various concentrations of adenine was used for potentiodynamic measurements. The polarization curves for these solutions are shown in Fig. 1 at 30 °C. Anodic and cathodic Tafel slopes are required for calculating the corrosion rate using the linear polarization method. Polarization data for inhibited as well as uninhibited solutions are given in Table 1.

Anodic and cathodic Tafel slopes are usually reported

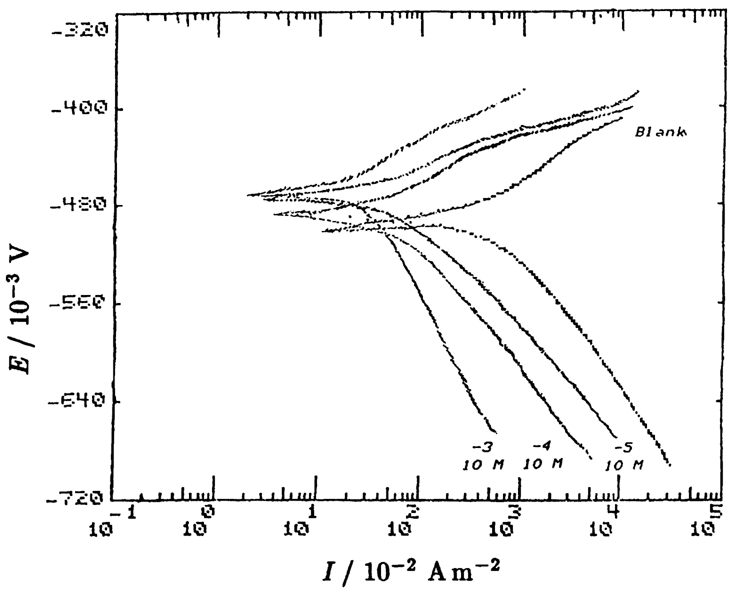

Fig. 1. Polaization curves of steel in sulfuric acid with different concentration of adenine at 30 °C.

Table 1. Electrochemical Parameters For Steel in 0.5 M Sulfuric Acid Solutions in The Presence of Adenine

[Adenine]	Corrosion potential	B_c	B_a	Polarization resistance	B
M	$-E$/mV (SCE)	mV	mV	$R_p/\Omega\,cm^2$	mV
Temperature 30 °C					
0	480	120	62	0.0175	17.77
1×10^{-5}	468	108	54	0.0774	15.65
1×10^{-4}	465	113	66	0.0968	18.11
1×10^{-3}	464	118	74	0.1251	19.77
Temperature 35 °C					
0	485	106	48	0.0141	14.55
1×10^{-5}	476	106	60	0.0510	16.65
1×10^{-4}	470	116	72	0.0742	19.31
1×10^{-3}	468	123	88	0.0978	21.30
Temperature 40 °C					
0	490	87	49	0.0131	13.62
1×10^{-5}	483	80	54	0.0232	14.01
1×10^{-4}	476	99	54	0.0350	15.19
1×10^{-3}	473	130	56	0.0452	17.01
Temperature 45 °C					
0	495	68	36	0.0054	10.23
1×10^{-5}	491	75	40	0.0080	11.34
1×10^{-4}	489	89	33	0.0132	10.46
1×10^{-3}	478	135	55	0.0242	16.98

to be in the range B_a/B_c=70/120 to 110/190.[12—15] The difference in the Tafel slopes suggests that the primary mechanisms in these studies differ.

By using the Stern–Geary[16] equation, the corrosion rate can be calculated from the linear polarization method.

$$I(\mathrm{mA}) = \left[\frac{B_a - B_c}{2.3(B_a + B_c)}\right] / R_p. \qquad (1)$$

The value in the bracket is the "B" constant and R_p is the polarization resistance generated by the linear polarization scan. The unit of R_p is in $\Omega\,cm^2$ and "B" is expressed in mV. The corrosion rate can also be calculated by extrapolating the Tafel lines of the potentiodynamic scans to the rest potential. Table 2 shows that the inhibited and uninhibited corrosion rates calculated using linear polarization and potentiodynamic methods

Table 2. Values of Corrosion Rates and Corrosion Current Densities Calculated by the Linear Polarization and Potentiodynamic Tests

[Adenine]	Linear Polarization		Potentiodynamic Tests	
	Corrosion current	Corrosion rate	Corrosion current	Corrosion rate
M	μA cm^{-2}	MPY	μA cm^{-2}	MPY
Temperature 30 °C				
0	1001	1041	1010	1050
1×10^{-5}	192	200	202	210
1×10^{-4}	183	190	187	195
1×10^{-3}	154	160	158	165
Temperature 35 °C				
0	1017	1057	1025	1066
1×10^{-5}	312	325	326	339
1×10^{-4}	250	260	260	270
1×10^{-3}	227	236	228	273
Temperature 40 °C				
0	1036	1077	1038	1079
1×10^{-5}	578	601	604	628
1×10^{-4}	416	432	434	451
1×10^{-3}	370	385	376	391
Temperature 45 °C				
0	1742	1811	1863	1937
1×10^{-5}	1316	1368	1416	1472
1×10^{-4}	970	1009	1030	1071
1×10^{-3}	673	700	690	718

are in good agreement. All the values reported were obtained from triplicate experiments.

Since corrosion rate is directly related to corrosion current, the inhibition efficiency ($P\%$) at different concentrations and temperatures for adenine can be calculated from the equation.

$$P\% = \frac{i_\mathrm{a} - i_\mathrm{c}}{i_\mathrm{a}} \times 100, \tag{2}$$

where i_a and i_c are the corrosion rates in uninhibited and inhibited solutions respectively. Also the degree of coverage θ at constant potential is given by[17,18)]

$$\theta = 1 - i_\mathrm{c}/i_\mathrm{a}. \tag{3}$$

The inhibition efficiencies calculated from linear polarization are equal to the values obtained by potentiodynamic method. These types of comparison between the inhibitor efficiencies evaluated by the two methods have also been reported and explained by several other workers too in the literature.[19—21)] At lower inhibitor concentration, the protection is generally less than that at a higher concentration. This is in good agreement with lower values of cathodic Tafel slopes at lower inhibitor concentration. Since the efficiency decreases with the increase in temperature, it is effective at lower temperature. The protection efficiencies were found to have 83, 77, 64, and 61% for 10^{-3} M adenine in 0.5 M sulfuric acid solution at 30, 35, 40, and 45 °C, respectively.

If it is assumed that adenine forms a monolayer adsorption over steel surface, then at any instance the fraction of the surface covered and not exposed to corrosion media is equal to $(i_\mathrm{a}-i_\mathrm{c})/i_\mathrm{a}$, within a certain range of inhibitor and temperature where monolayer adsorption is readily maintained over the steel surface.

Figure 2 represents the Langmuir adsorption isotherm which may be expressed from the equation.

$$[\theta/(1-\theta)] = A{\cdot}C{\cdot}\exp{(Q/RT)}, \tag{4}$$

where A is a constant, C is inhibitor concentration, Q is the heat of adsorption, θ is the occupied and $(1-\theta)$ is the vacant sites not occupied by inhibitor. The equation can be represented in the form

$$\log{[\theta/(1-\theta)]} = \log A + \log C + Q/2.3\ RT. \tag{5}$$

Thus, a plot of $\log{[\theta/(1-\theta)]}$ against $\log C$ should be linear. This expectation is realized from the plots in Fig. 2. It can be seen however, that at a particular concentration the change in relative surface coverage with the change in temperature is not so prominent as was found in the case of dicyandiamide.[22)] A plot of $\theta/(1-\theta)$ against $1/T$ at constant concentration of adenine is shown in Fig. 3. Although Langmuir's general adsorption theory is inadequate to explain the above re-

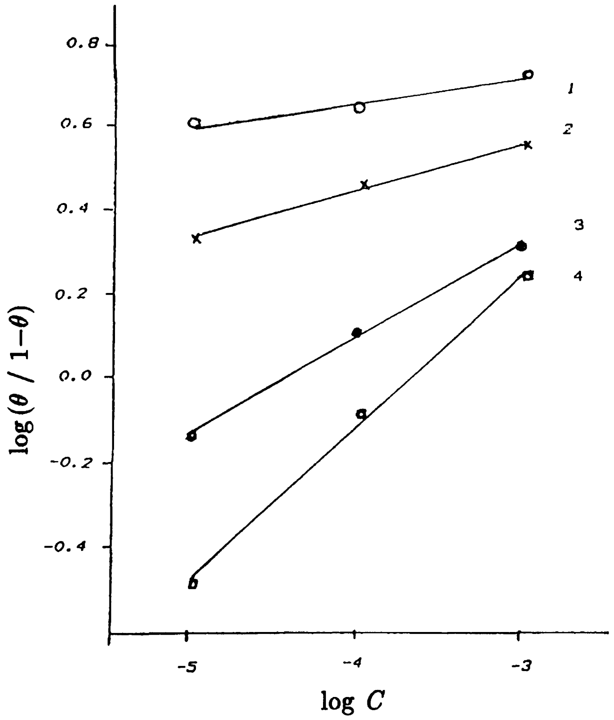

Fig. 2. Plots of log $\theta/1-\theta$ vs. log C at different temperatures (1) 30 °C, (2) 35 °C, (3) 40 °C, and (4) 45 °C.

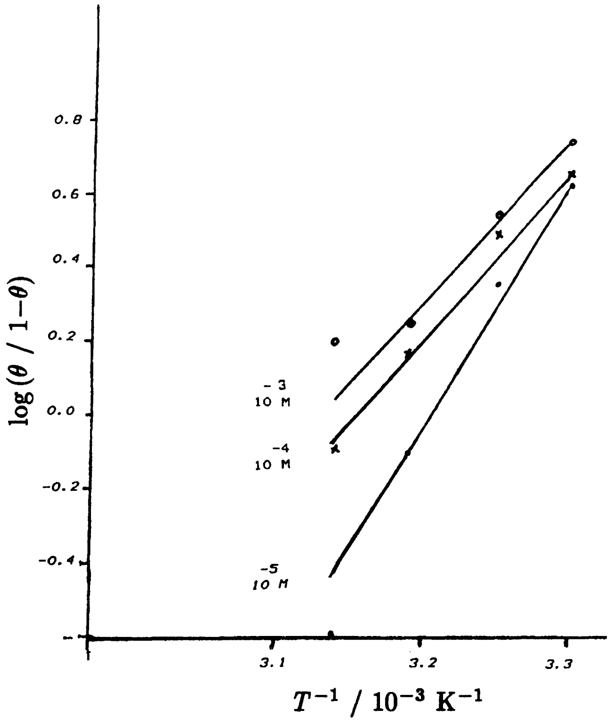

Fig. 3. Plots of $\log(\theta/1-\theta)$ vs. $1/T$ at different concentrations of adenine (1) 10^{-5} M, (2) 10^{-4} M, (3) 10^{-3} M in presence of H_2SO_4.

sults at all concentrations and at all temperatures, heat of adsorption can be estimated by two similar, but not equivalent methods. The first involves plotting values of $\log[\theta/(1-\theta)]$ taken at any single concentration of inhibitor from Fig. 2 versus the reciprocal of temperature. This is a direct application of the Langmuir equation. Heat of adsorption as estimated by this method is 81 kJ mol^{-1} for 10 M^{-4} adenine.

In the second method the total measured corrosion rate is expressed as the sum of two rates.

$$\frac{-\mathrm{d[Fe]}}{\mathrm{d}t} = K_1(1-\theta) + K_2\theta, \tag{6}$$

where θ is the fraction of the surface coverage by the adsorbed adenine, K_1 is the rate constant for the uninhibited reaction, and K_2 is the rate constant for corrosion of the completely covered surface. By combining some mathematical expression for adsorption with Eq. 6, additional insight may be gained as to the changes in activation energy with adenine concentrations.

Langmuir equation is accepted generally as the most appropriate in the system steel/inhibited acid. In one of its forms, it is expressed by Eq. 4.

Inserting values for θ and $(1-\theta)$ from this equation into the rate equation (6), there results:

$$\frac{-\mathrm{d[Fe]}}{\mathrm{d}t} = \frac{K_1}{1+AC\mathrm{e}^{Q/RT}} + \frac{K_2AC\mathrm{e}^{Q/RT}}{1+AC\mathrm{e}^{Q/RT}}. \tag{7}$$

The rate constants K_1 and K_2 of Eq. 7 can be replaced by their exponential forms, using K_1' and K_2' for the pre-exponential factors, to give

$$\frac{-\mathrm{d[Fe]}}{\mathrm{d}t} = \frac{K_1'\mathrm{e}^{-E_1/RT}}{1+AC\mathrm{e}^{Q/RT}} + \frac{K_2'AC\mathrm{e}^{Q/RT\ -E_2/RT}}{1+AC\mathrm{e}^{Q/RT}}. \tag{8}$$

When the steel is uninhibited, C equals 0, and the activation energy for steel corrosion is E_1. Terms of Eq. 8 reveal that as the term $AC\mathrm{e}^{Q/RT}$ increases the activation energy should increase.

As $AC\mathrm{e}^{Q/RT}$ becomes much larger than one, which occurs at higher θ values, the activation energy approaches (E_1+Q). At even higher values of θ, the second term of Eq. 7 begins to assume some importance and because $AC\mathrm{e}^{Q/RT}$ is much larger than one, this expression cancels out of the second term and the measured activation energy will approach E_2.

From the above analysis, it may be concluded that the temperature coefficient of inhibited acid corrosion depends on the concentration of the inhibitor and that if Langmuir adsorption is followed over an intermediate range of coverage, an estimate of heat of adsorption can be obtained from the trend of activation energy with concentration. Thus, heat of adsorption is obtained by using the corrosion rate data against reciprocal of temperature (Fig. 4). Activation energy is determined from this, and then plotted against the inhibitor concentration (Fig. 5). The heat of adsorption can be estimated from the value of E_1+Q(maxima in the curve) and E_1 for uninhibited rate,[23] and is obtained to be 68 kJ mol^{-1} for 10^{-4} mol. This value is

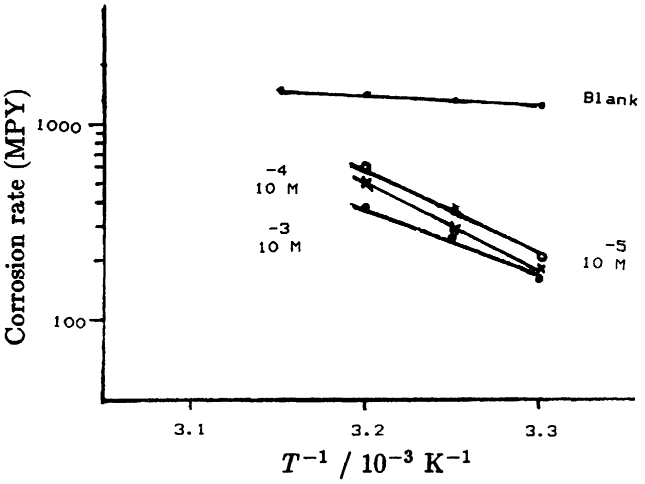

Fig. 4. Arrhenius plots of inhibited corrosion rate for adenine.

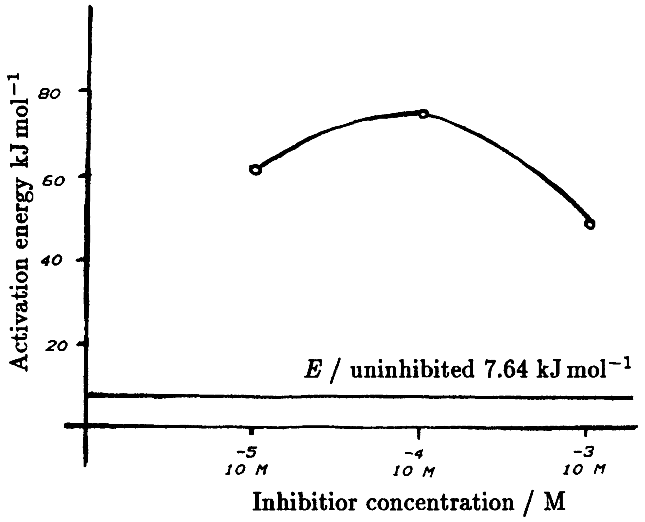

Fig. 5. Activation energies of inhibited corrosion of steel in 0.5 M H_2SO_4.

in reasonable agreement with that estimated by simple application of the Langmuir equation.

The effective activation energies may be expressed[24] as

$$E_{\text{eff}} = -2.3 \times 8.31 \times \mathrm{d}(\log i)/\mathrm{d}(1/T)\ \text{kJ mol}^{-1}. \quad (9)$$

Figure 4 shows that the activation energy is higher in the presence of inhibitor than in its absence. This type of inhibitor[25] retards corrosion at ordinary temperatures but inhibition is considerably diminished at elevated temperatures.

The cathodic Tafel lines corresponding to hydrogen evolution in the absence of inhibitor have slopes (B_c) 120, 106, 87, and 68 mV at 30, 35, 40, and 45 °C, respectively. The values obtained for B_c agree with the mechanism of hydrogen evolution suggested by Bockris et al.[26] The lower values of Tafel slopes at higher temperatures indicate higher evolution as well as hydrogen inclusion into the metal.

Table 3. Calculated Equilibrium Adsorption Parameters for Adenine Inhibition by Different Methods

Langmuir	Frumkin	
K	K	f
Temp 30 °C		
400000	515872	0.71
Temp 45 °C		
31579	33120	1.80

Table 4. Thermodynamic Data for Adenine by Different Methods

Temperature	$\Delta G°_T$	$\Delta H°_T$	$\Delta S°_T$	Temp Coeff.
	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	dE/dT
Langmuir isotherm				
30 °C	−42.42	−135.48	−307.12	−0.16×10^{-2}
45 °C	−37.79			
Frumkin isotherm				
30 °C	−43.50	−146.51	−339.98	−0.17×10^{-2}
45 °C	−37.92			

The steel dissolution reaction is characterized by anodic Tafel slopes B_a which are, in the absence of inhibitor, 62, 48, 49, and 36 mV at 30, 35, 40 and 45 °C, respectively. The magnitude of the anodic Tafel slopes indicates the mechanism of steel dissolution as given by Kelly for the sulfuric acid system.[27] The higher B_a values than those of pure iron may be due to the higher order of metal dissolution due to impurities in the steel.

The inhibitor studies have shown a little shift in the corrosion potential into the negative direction at all examined temperatures, indicating cathodic control. These results are in conformity with the fact that nitrogen containing organic compounds are mostly cathodic polarizers for the corrosion of metals in acid medium.[28]

The corrosion behavior of steel at different temperatures in the presence of an inhibitor as reported in this paper reveals that the inhibitor molecules are well adsorbed over the metal surface and that surface coverage changes with temperature together with concentration of the inhibitor.

If there is an interaction between the adsorbed molecules, thus fitted line is based on Frumkin isotherm.

$$KC = (\theta/1-\theta)\ e^{f\theta}, \quad (10)$$

where K is an average adsorption equilibrium constant and f reflects the variation of adsorption potential with coverage:

$$f = (\Delta G°_{\theta=1} - \Delta G°_{\theta=0})/RT.$$

If there is no lateral interaction, then according to Langmuir,

$$KC = [\theta/(1-\theta)]. \quad (11)$$

Equations 10 and 11 , respectively, gave the results displayed in Table 3. From the comparison of the Frumkin and the Langmuir isotherms, an interaction between the adsorped molecules increases the adsorption energy due to the increase of coverage on surface. The positive values of *f* indicates that the free energy of adsorption becomes more positive with coverage; a condition which may be attributed to lateral repulsion among adsorbate molecules.

The thermodynamic parameters for adsorption shown in Table 4 were calculated using the results in Table 3, and were obtained from

$$\Delta G^{\circ}{}_{T} = -RT\ln(K \times 55.5) \qquad (12)$$

$$\Delta H^{\circ}{}_{T} = R(T_1T_2/T_2 - T_1)\ln K(T_2)/K(T_1) \qquad (13)$$

$$\Delta S_T = \frac{\Delta H^{\circ}{}_{T} - \Delta G^{\circ}{}_{T}}{T}. \qquad (14)$$

The temperature coefficient can be calculated from the Eq. 15

$$\Delta G^{\circ} = \Delta H^{\circ} - ZFT\ (\mathrm{d}E/\mathrm{d}T). \qquad (15)$$

We see that ΔG°, ΔH°, and ΔS° are negative.

The large ΔS values suggest a liberation of particles during the adsorption process, possibly formation and release of reaction products of inhibitor.

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