

Corrosion Inhibitors Effects and adsorption properties of Theobromine for the Corrosion of Iron in Hydrochloric Acid Medium

تأثيرات مثبطات التآكل وخواص الامتزاز للثيوبرومين لتآكل الحديد في وسط حامض الهيدروكلوريك

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الخلاصة

لقد تم دراسة تأثيرات مادة الثيوبرومين كمثبطات تآكل الحديد في الوسط الحامضي بواسطة القياسات الحرارية والوزنية ، معدل كفاءة المثبط عند 303°م تتراوح من 62.9% الى 83.8% و 84.1% الى 93.4% على التوالي . وجد إن الثيوبرومين يعمل كمثبط جيد لتآكل الحديد في كل تراكيز حامض الهيدروكلوريك المستخدمة . لوحظ إن كفاءة المثبط تزداد بزيادة تركيزه . كذلك درست تأثيرات كل من درجة الحرارة، زمن الانغماس وتركيز الحامض على سلوك تآكل الحديد . وجد إن امتزاز الثيوبرومين على سطح الحديد يخضع لامتناز لانكماير . عينت طاقات التنشيط وبعض الدوال الثرموديناميكية لعملية تثبيط التآكل.

ABSTRACT

Inhibition of corrosion of iron in hydrochloric acid solutions by theobromine as natural product has been studied using thermometric and galvanometric measurements indicate that the average inhibition efficiency of theobromine at 303°C ranged from 62.9% to 83.8% and 84.1% to 93.4% respectively. It has been found that theobromine acts as a good corrosion inhibitor for iron in all concentrations of HCl solution. Inhibition was found to increase with increasing concentration of inhibitor. The effects of temperature, immersion time and acid concentration on the corrosion behavior of iron were also studied. The adsorption of theobromine on iron surface obeyed the Langmuir adsorption isotherm. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated.

Key word : Adsorption , Anticorrosion , Theobromine .

INTRODUCTION

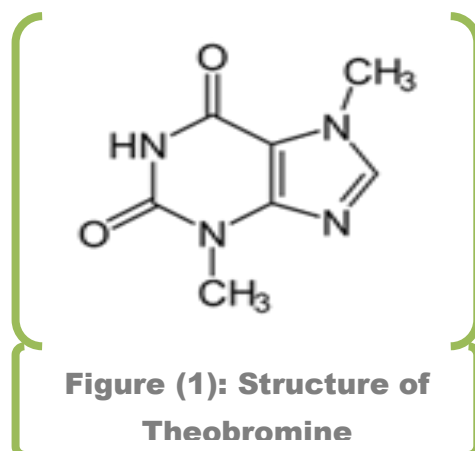
The study of corrosion of iron is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest ^[1-3].

Acid solutions are widely used in industrial acid pickling. Industrial acid cleaning and oil –well acidizing. It's requiring the use of corrosion inhibitors in order to restrain the corrosion attack on iron has been studied in some detail ^[4-7] . Corrosion is natural phenomena which can be considered either chemical or electrochemical in nature, degrades the metallic properties of metal and alloys make them until for specific role.

A corrosion inhibitor, when added in minute quantity slows down the rate of corrosion of a metal or a metal alloy. Due to their industrial importance , most corrosion inhibitors have been synthesized from cheap raw materials or chosen from organic compounds containing hetero atoms such as (O , N , S), as well as aromatic rings in their structure facilitate the adsorption of the inhibitor on the metal surface. The successful uses of naturally occurring substances to inhibit the corrosion of metals in acidic media have been reported by some research group ^[8,9] .

Theobromine is a better alkaloid that a white crystalline solid that occurs naturally in cocoa beans, from which chocolate is obtained, and in smaller amount in tea cola nuts. Theobromine belongs to a family of organic compounds known as the methylxanthines. Caffeine and Theobromine are related and have similar structures, but are very different chemicals with different

properties, effects and origins. Theobromine is extracted from cocoa beans by water or liquid carbon dioxide, which dissolves theobromine. The water or carbon dioxide is then allowed to evaporated, permitting the crystallization of the pure compound ^[10-12].



EXPERIMENTAL

Material preparation

Material used for the study was iron that composition 0.508%C, 0.309%Si, 0.6804%Mn, 0.019% P, 0.00945%S, 0.0307% Cr, 0.0036V, and the rest is Fe. The iron were mechanically pressed and cut to form rectangular specimens of dimensions (2.8, 0.9, 0.8 cm) containing a small hole of about 2mm diameter near the upper edge. Each coupon polish by Emery paper and then washing in water and in distilled water and finally with ethanol, dipped in acetone and allowed to dry in air before they were preserved in a desiccator ^[13,14].

Each coupon weight by electro balance in ± 0.0001 accuracy and the dimensions were measured in vernier, and for accuracy in all experiments the weight and dimension were fourth decimal.

All reagents used for the study were analar grade and double distilled water was used for their preparation. The inhibitor theobromine was supplied by Sigma company. The concentrations of inhibitor used for the study were (0.5 – 4) ppm.

Thermometric method

The inhibition efficiencies were determined using thermometric technique. This involve the immersion of single specimen measuring (2.8, 0.9, 0.8 cm) in a reaction chamber containing 50ml of test solution. Temperature changes were measured at interval of one minute using a thermometer with a precision of 0.01°K, the temperature first increased slowly then rapidly and attained a maximum value and then start decreasing. The highest temperature was recorded, the percentage inhibition efficiency was calculated according to the following equation:

$$I\% = \frac{RN_{free} - RN_{inh}}{RN_{free}} \times 100 \quad \dots \dots \dots (1)$$

Where (RN_{free}) and (RN_{inh}) are the reaction number in absence and presence of inhibitors respectively, reaction number (RN) in (°K/min) is defined as :

$$RN = \frac{(T_m - T_o)}{t} \quad \dots \dots \dots (2)$$

Where (T_m) and (T_o) are the maximum and initial temperatures respectively, and the (t) is the time required to reach the maximum temperature ^[9, 15].

Gravimetric method

In gravimetric experiment, a previously weighted metal coupon was completely immersed in 250 ml of the test solution in an open beaker; the beaker was interest into a water bath maintained at 303°K. After every 4 hours each coupon withdrawn from the test solution, by emery paper and

washing in a water and distilled water and immersed in acetone and then dried before re-weighting, the difference in weight is measured , the experiment is repeated at (308 , 313, 318 and 323°K)

From the weight loss results , the inhibition efficiency of the inhibitor (I%) , degree of surface coverage (θ) and the corrosion rate(C_R) were calculated using equations 3 , 4 and 5 respectively:-

$$I\% = \left(1 - \frac{W_1}{W_2}\right) \times 100 \quad \dots\dots\dots (3)$$

$$\theta = 1 - \frac{W_1}{W_2} \quad \dots\dots\dots (4)$$

$$C_R = \frac{\Delta W}{At} \quad \dots\dots\dots (5)$$

Where (W_1) and (W_2) are the weight losses (in gm) in presence and absence of the inhibitor in HCl solution respectively , (A) is the area of the coupon (in cm^2), (t) is the period of immersed (in hours) and W is the weight loss of iron coupon after time t ^[9,13-16].

RESULTS AND DISCUSSION

Thermometric measurement

The inhibition efficiency values were also determined by using thermometric techniques. Temperature change for iron in 1N HCl was recorded at various inhibitor concentrations . No significant temperature changes were recorded at an acid concentration 0.05, 0.1, 0.5N HCl solutions. Therefore, use of the thermometric method was restricted to 1N HCl solution. The results are listed in table (1) and plotted (2a)and(2b) broad agreement with those obtained from mass loss measurement. The variation of the reaction number (RN) with inhibitor concentrations presented graphically shows essentially linear behavior with the negative slope indicating that the reaction number decrease with increasing inhibitor concentration .

Weight loss measurement

1. Effect of inhibitor concentration

Table (2) illustrates the relationship between the concentration of inhibitor in different concentrations of HCl solution with inhibition coefficient (I%) , the corrosion rate (C_R) and the degree of the surface coverage (θ).When the concentration of the inhibitor is increased the weight loss is decreased and then the inhibition coefficient (I%) and the degree of the surface coverage (θ) are increased and on the other hand , the corrosion rate (C_R) is decreased up to their optimum level after which a further increase in inhibitor concentration did not cause any significant change in the inhibition coefficient (I%) and the corrosion rate (C_R) (figure 3) . The optimum concentration (4ppm) of inhibitor showed maximum inhibitor efficiency of 93.4% in HCl solution . Further increase in the inhibitor concentration did not cause any significant change in the performance of the inhibitor (the results were closely around the maximum inhibition coefficient (I%) for the concentrations up 4ppm) .

2. Effect of immersion time

Weight loss measurements were performed in 1N HCl in absence and presence of inhibitor for (2 to 10) days immersion time at 303°K .This illustrate in figure (4) that represents the inhibition coefficient (I%) is decreased with increasing immersion time for the inhibitor.

3. Effect of acid concentration

Figure(5) represents the effect of acid concentration on the inhibitor efficiency(I%) for theobromine that concentration 4ppm at different temperatures , the results indicate that inhibitor efficiency(I%) of theobromine increases with increasing acid concentrations .these can be attributed to increased aggressiveness of solution with increasing in acid concentration.

4. Effect of temperature and adsorption consideration

The inhibitor efficiency(I%) was found to decrease with increasing temperature [table (2) and figure(6)] . This relation portrays the mechanism of physical adsorption.

The Arrhenius equation was used to calculate the activation energy E_a for corrosion of iron in presence of inhibitor^[9,17]:-

$$\log C_R = \log A - \frac{E_a}{2.303RT} \dots \dots \dots (6)$$

Figure (7) shows the Arrhenius plots for the corrosion of iron in 0.1N and 1N HCl solutions. Values of the activation energy E_a calculated from slope of straight line are recorded in table (3). These values indicated that the activation energy E_a increases with increasing concentration of inhibitor which suggests that there is increasing ease of adsorption of the inhibitor with increasing concentration. The activation energies are also lower than the threshold value of 80 kJ/mol required for the mechanism of chemical adsorption, therefore, the adsorption of inhibitor on iron surface supports the mechanism of physical adsorption.

The thermodynamic parameters for the adsorption (ΔH_{ads} and ΔS_{ads}) of inhibitor on iron surface can be calculated by the alternative formulation of Arrhenius equation^[9,17]:-

$$\log \left(\frac{C_R}{T} \right) = \log \frac{R}{Nh} + \left(\frac{\Delta S_{ads}}{2.303R} \right) - \left(\frac{\Delta H_{ads}}{2.303RT} \right) \dots \dots \dots (7)$$

Where (h) is the Planck's constant, (N) is Avogadro number, (R) is the universal gas constant, (ΔH_{ads}) is the enthalpy of adsorption and (ΔS_{ads}) is the entropy of adsorption.

The slope of straight line for plot of $\log (C_R/T)$ versus $(1/T)$ is equal to $(-\Delta H_{ads}/2.303R)$ and the intercept is equal to $(R/Nh + \Delta S_{ads}/2.303R)$, (figure 8). From which the values of ΔH_{ads} and ΔS_{ads} were calculated and listed in table (3). The positive signs of enthalpies reflected the endothermic nature of dissolution process. This suggests that iron dissolution required more energy in the presence of inhibitor. The large negative values of entropies (ΔS) and positive values of enthalpy indicate that the corrosion of iron inhibited by theobromine is endothermic and that controlled by activation complex^[17].

In order to study the adsorption characteristics of inhibitor on iron surface used the Langmuir adsorption isotherm assuming that the inhibitor adsorbed on the metal surface decrease the surface area available for corrosion. Langmuir isotherm equation should give a straight line of unit gradient for the plot of the degree the surface coverage with the concentration of the inhibitor as follows^[14,16]:-

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \dots \dots \dots (8)$$

Where (K_{ads}) is the equilibrium constant of adsorption. figure (9) shows Langmuir isotherm for the adsorption of theobromine on iron surface. Values of adsorption parameters deduced from the Langmuir plots are recorded in table(4). From the results obtained, the R^2 values are very close to unity indicating a strong adherence of the adsorption data to the assumptions of Langmuir isotherm^[8].

The free energy of adsorption (ΔG_{ads}) of theobromine on iron surface was calculated using the following equation^[14,16]:-

$$\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \dots \dots \dots (9)$$

Where R is the universal gas constant, T is the absolute temperature and the value 55.5 is the concentration of water in solution in mol/L.

Calculated values of ΔG_{ads} are also presented in table (5). From the results obtained the free energies are negatively less than the threshold value (-40 kJ/mol) required for chemical adsorption indicating that the adsorption of theobromine on iron surface is spontaneous and supports the mechanism of physical adsorption^[9].

Mechanism of inhibition

The transition of metal /solution interface from a state of active dissolution to the passive state is attributed to the adsorption of the inhibitor molecules at the metal /solution interface, forming protective film. The rate of adsorption is usually rapid and hence, the reactive metal surface is shielded from the aggressive environment. In aqueous acidic solution, main constituents exist

either as neutral molecules or as protonated molecules (cations) . The inhibitors may adsorb on the metal /acid solution interface by one and / or more of the following ways :(a) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (b) donor-acceptor

interactions between the Π – electrons of aromatic ring and vacant d orbital of surface iron atoms, (c) interaction between unshared electron pairs of hetero atoms and vacant d orbital of iron surface atoms^[17].

Table (1): Variation of the inhibitor efficiency and reaction number with the concentration of the inhibitor for iron in 1N HCl solution at 303°K .

CONC.	RN	I%
B [*]	0.308	
0.5	0.114	62.987
1	0.105	65.909
1.5	0.095	69.156
2.5	0.078	74.675
3	0.074	75.974
3.5	0.058	81.117
4	0.050	83.766
* solution without inhibitor		

Table (2): Variation between the concentration of the inhibitor, concentration of acid and the temperature with the inhibitor efficiency, the corrosion rate and the surface coverage .

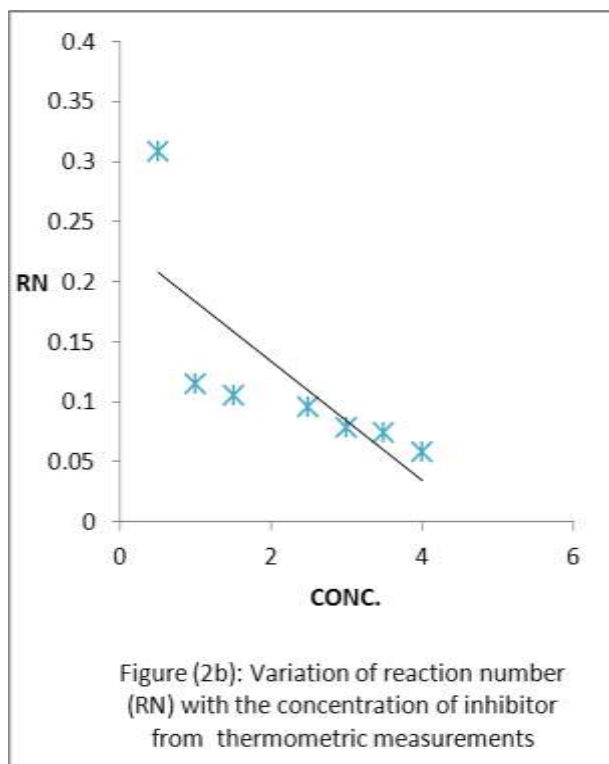
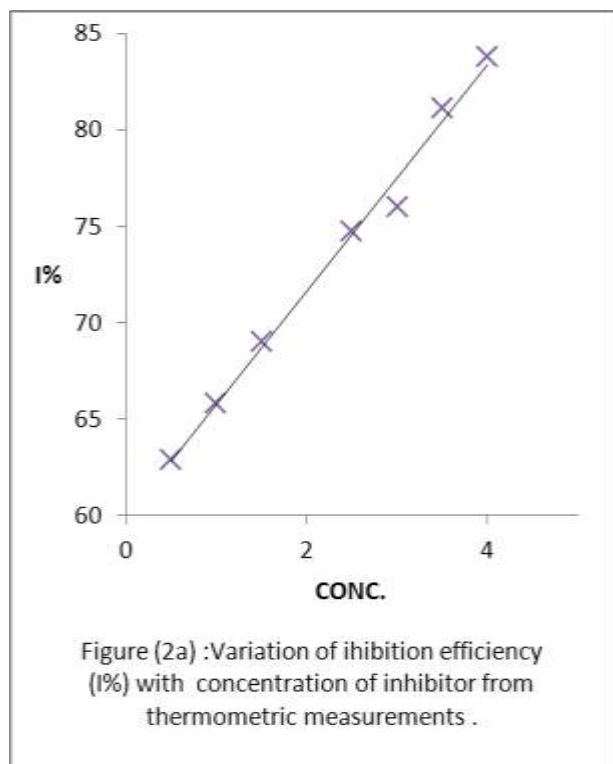
Temp.	C	0.05N HCl			0.1N HCl			0. 5N HCl			1N HCl		
		I%	θ	CR	I%	θ	CR	I%	θ	CR	I%	θ	CR
303°K	0.5	77.666	0.777	0.350	80.455	0.805	0.491	82.888	0.829	0.278	84.075	0.841	0.371
	1	77.737	0.777	0.350	81.077	0.811	0.476	83.703	0.837	0.265	84.812	0.848	0.355
	1.5	82.323	0.823	0.278	83.385	0.834	0.418	84.211	0.842	0.257	85.422	0.854	0.341
	2.5	86.933	0.869	0.206	86.323	0.863	0.345	86.465	0.865	0.219	86.531	0.865	0.315
	3	86.413	0.864	0.213	88.915	0.889	0.280	87.733	0.877	0.200	88.117	0.881	0.278
	3.5	90.855	0.908	0.144	91.239	0.912	0.222	92.037	0.920	0.130	91.300	0.913	0.203
	4	91.637	0.916	0.132	92.454	0.924	0.192	92.911	0.929	0.115	93.434	0.934	0.154
308°K	0.5	72.927	0.729	0.554	74.133	0.741	0.747	74.866	0.749	0.508	79.144	0.791	0.576
	1	73.816	0.738	0.535	75.901	0.759	0.695	76.285	0.763	0.480	82.308	0.823	0.488
	1.5	78.239	0.782	0.446	79.038	0.790	0.605	79.222	0.792	0.421	83.810	0.838	0.446
	2.5	81.731	0.817	0.374	84.206	0.842	0.456	86.115	0.861	0.282	86.323	0.863	0.378
	3	82.110	0.821	0.366	85.645	0.856	0.415	87.342	0.873	0.257	88.711	0.887	0.311
	3.5	84.021	0.840	0.327	87.226	0.872	0.369	88.937	0.889	0.225	90.248	0.902	0.270
	4	84.312	0.843	0.321	89.311	0.893	0.309	91.767	0.918	0.166	93.931	0.939	0.168
313°K	0.5	70.333	0.703	0.623	72.123	0.721	0.667	74.344	0.743	0.553	75.041	0.753	0.630
	1	71.917	0.719	0.590	73.344	0.733	0.638	75.486	0.755	0.528	76.855	0.769	0.582
	1.5	73.221	0.732	0.562	74.033	0.740	0.622	76.322	0.763	0.510	77.645	0.776	0.564
	2.5	77.538	0.775	0.472	76.411	0.764	0.564	77.745	0.777	0.482	78.806	0.788	0.534
	3	79.123	0.791	0.439	80.307	0.803	0.471	81.632	0.816	0.396	81.535	0.815	0.466
	3.5	80.834	0.808	0.403	82.222	0.822	0.426	83.249	0.832	0.362	83.936	0.839	0.405
	4	82.121	0.821	0.376	83.941	0.839	0.385	83.516	0.835	0.355	84.442	0.844	0.393
318°K	0.5	68.906	0.689	0.857	69.502	0.695	0.913	71.104	0.711	0.765	72.412	0.724	0.927
	1	70.320	0.703	0.818	71.019	0.710	0.868	72.746	0.727	0.722	74.467	0.745	0.856
	1.5	71.619	0.716	0.783	72.124	0.721	0.835	73.322	0.733	0.706	76.109	0.761	0.802
	2.5	73.333	0.733	0.736	73.901	0.739	0.781	74.856	0.748	0.667	77.319	0.773	0.762
	3	74.547	0.745	0.703	74.725	0.747	0.757	75.331	0.753	0.654	78.242	0.782	0.732
	3.5	75.107	0.751	0.686	76.129	0.761	0.715	76.544	0.765	0.622	78.200	0.782	0.732
	4	75.134	0.751	0.686	77.348	0.773	0.679	77.877	0.779	0.585	80.213	0.802	0.665
323°K	0.5	68.124	0.681	0.955	69.728	0.697	0.918	71.210	0.712	0.725	72.041	0.720	0.807
	1	69.500	0.695	0.913	70.903	0.709	0.881	72.083	0.721	0.703	73.019	0.732	0.778
	1.5	70.817	0.708	0.874	72.012	0.720	0.848	73.045	0.730	0.680	74.033	0.740	0.750
	2.5	72.323	0.723	0.829	73.803	0.738	0.794	74.428	0.744	0.645	75.420	0.754	0.709
	3	73.321	0.733	0.799	74.823	0.748	0.763	75.137	0.751	0.627	76.333	0.763	0.683
	3.5	74.733	0.747	0.757	75.534	0.755	0.742	76.444	0.764	0.594	76.510	0.765	0.678
	4	75.012	0.750	0.748	76.202	0.762	0.721	77.205	0.772	0.574	78.377	0.784	0.623

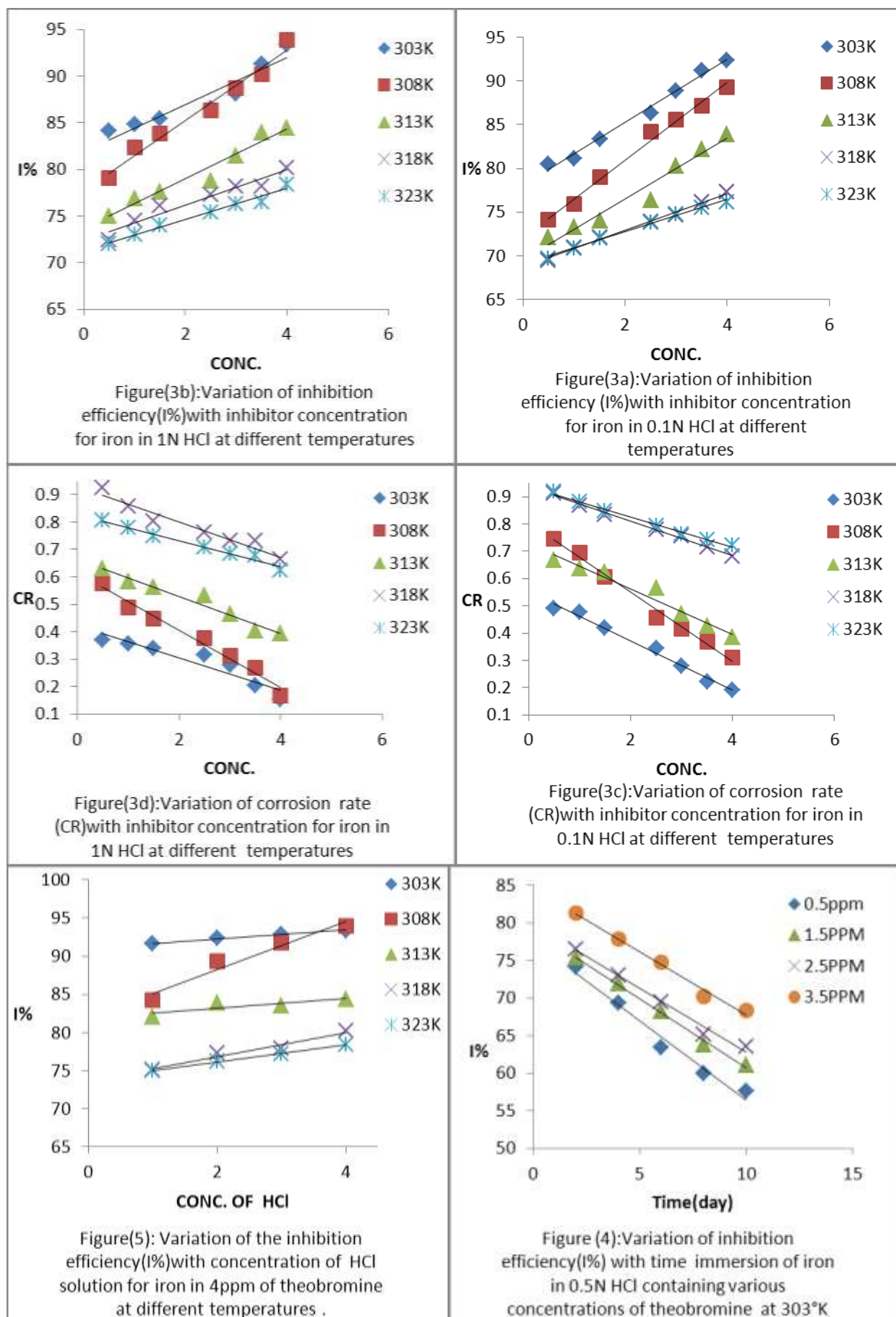
Table (3): Thermodynamic parameters for the adsorption of theobromine on iron surface.

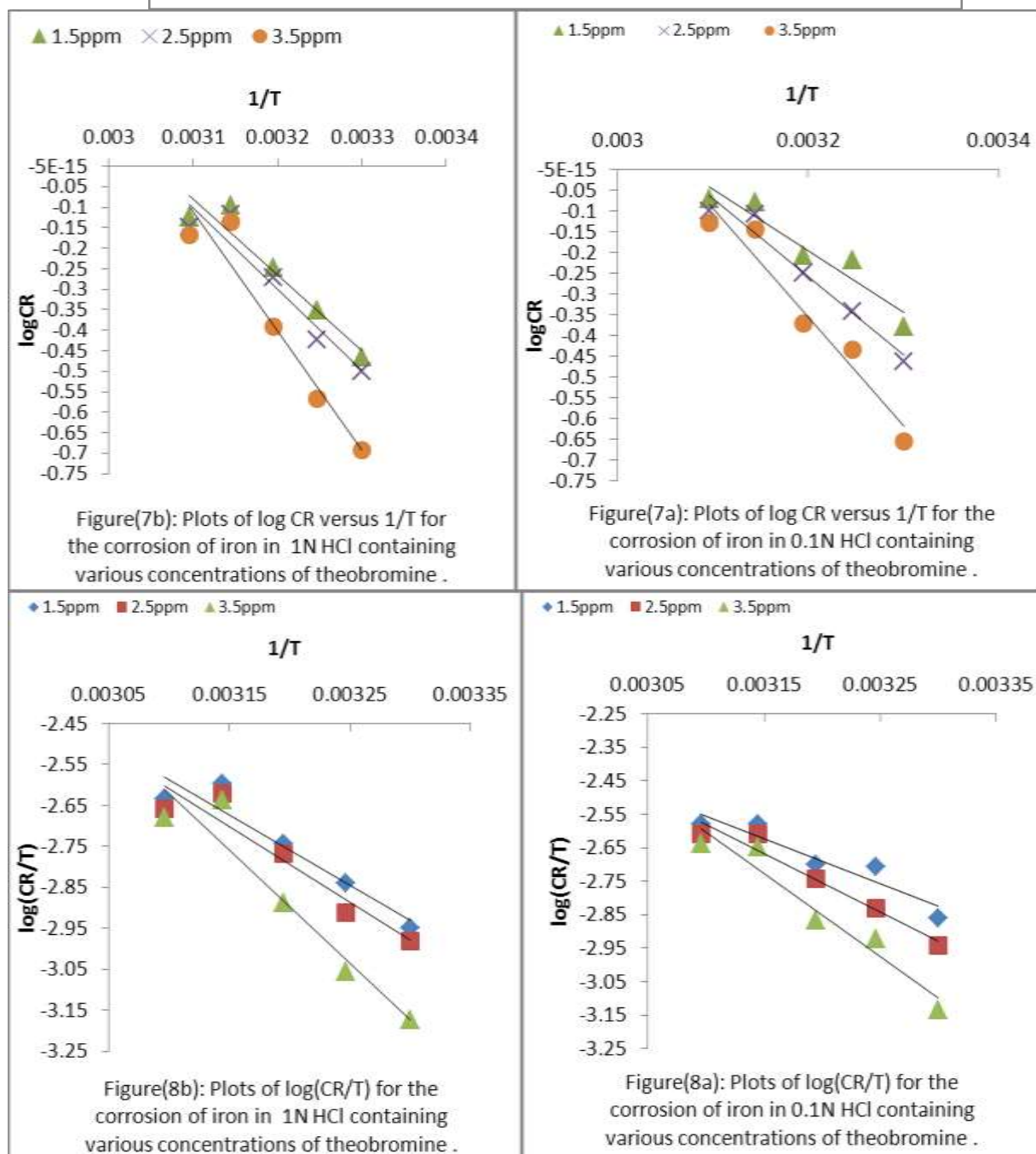
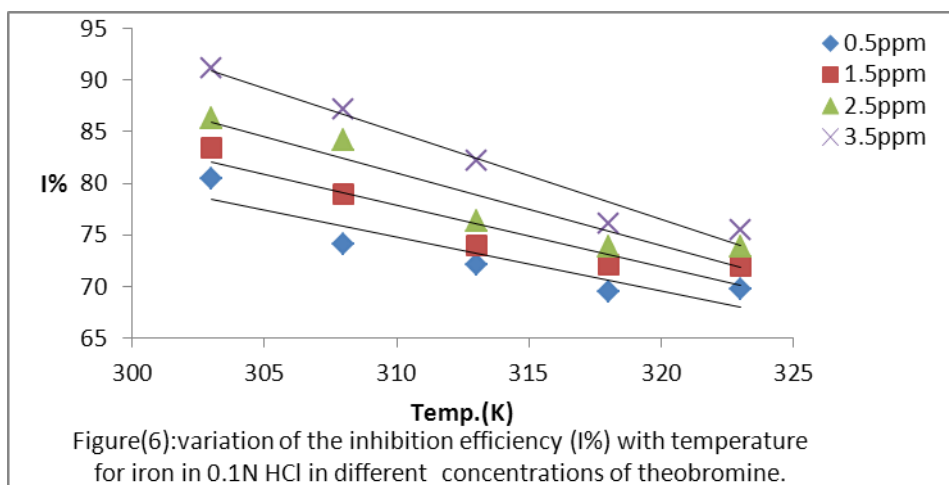
CONC. _{acid}	CONC. _{inh.}	E _a (J/mol)	R ²	ΔS(J/mol.K)	ΔH(J/mol)	R ²
0.1N HCl	1.5	28300.86703	0.959	-166.4432889	25704.47	0.889
	2.5	35910.45264	0.907	-143.2921058	33314.05	0.953
	3.5	50144.58104	0.944	-99.60281814	47548.18	0.938
1N HCl	1.5	35262.84013	0.914	-145.4664932	32666.44	0.909
	2.5	37878.61671	0.921	-137.782298	35282.22	0.903
	3.5	55463.95163	0.928	-83.45612674	52867.55	0.921

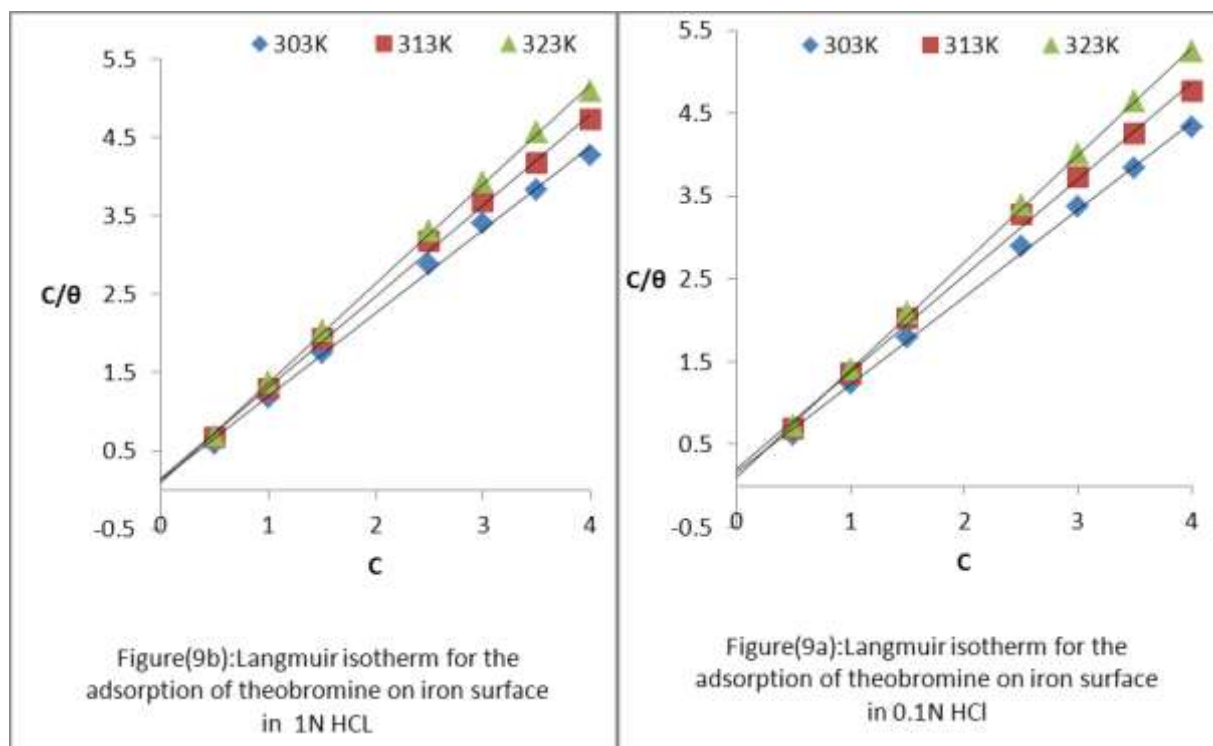
Table (4): Langmuir adsorption parameters for adsorption of theobromine on iron surface at different temperatures.

Temp. (°K)	0.1N HCl			1N HCl		
	K _{ads}	ΔG(J/mol)	R ²	K _{ads}	ΔG(J/mol)	R ²
303	5.80014	-14524.3	0.998	7.556448	-15189.6	0.997
313	4.63225	-14419.5	0.996	6.526843	-15310.3	0.998
323	8.73351	-16580.5	0.999	9.685236	-16857.8	0.999









Conclusions

From the results and findings of the study, the following conclusions are made:-

- 1- The results obtained from gravimetric and thermometric methods indicate that theobromine is a good inhibitor for the corrosion of iron in HCl solution. However, the average inhibition efficiency of theobromine (obtained from gravimetric method) is better than its instantaneous inhibition efficiency (obtained from thermometric method).
- 2- The occurrence of a physical adsorption mechanism for the adsorption of theobromine on iron surface is supported by pattern of variation of inhibition efficiency of theobromine with temperature; range of values obtained for the activation and free energies. Furthermore, the adsorption of theobromine on iron surface is spontaneous and endothermic.
- 3- The inhibitor acts by being adsorbed on the surface of iron according to classical Langmuir adsorption isotherm.

References

1. V.S.Sastri, New York 1998, (Corrosion Inhibitors :Principle and Application), p 25.
2. M.Lebrini, F.Robert and C.Roos, 2010, (Corrosion inhibition of aluminium in acid media by citrullus colocynthis extract), Int.J.Electrochem. Sci. 5, 1698-1712.
3. N.Hasirci, 2000, (Adsorption of iron or ferritin by chitosan), TurkJ.Med.Sci. 30, 623-624.
4. N.O.Eddy and E.E.Ebenso, 2010, (Corrosion inhibition properties of ethanol extract), Int.J.Electrochem. sci. 5, 731-746.
5. T.X.Soror and M.A.Elzaidy, 2003, (Effect of acetyl trimethylammonium bromide on the corrosion of carbon steel in acids), Materials chemistry and physics 77(3), 697-703.
6. A.P Pakter, M.K. Shalimora and M.A. Lambin, 2002, (The effect of polar substituent in aniline and pyridine derivatives on the inhibition of steel corrosion in acids), Zashchita Metallov 38(3), 250-253.
7. M.A.Malik, M.A.Hashim, S.A.Al-thabaiti and Z.Khan, 2011, (Anti-corrosion ability of surfactants), J.Electrochem.Sci. 6, 1927-1948.

8. K.K.Al-Neami, A.K.Mohamed ,I.M.Kenawy and A.S.Fouda,1995 ,(Inhibition of the corrosion by oxygen and nitrogen containing compound),Monatshefte for chemie 126(4), 369-376 .
9. J.Nnabuk , E.E.Ebenso and Udo.J.Ibok , 2009, (Adsorption and quantum chemical studies of the inhibitive properties of tetracycline) , J.of the Argentine Chemical Society 97, 178-194 .
- 10.Theobromine,2011,<http://en.Wikipedia.org/wiki/theobromine>.
11. J.B.Thomas, J.H.Yen and M.M.Schlutz,2004,(Determination of caffeine ,theobromine and theophylline in standard reference) , J.Agric. Food chem. 52(11), 3259-3263 .
12. M.R.Brunetto and L.Gutierrez , 2007, (Determination of caffeine, theobromine and theophylline in cocoa samples by HPLC chromatography),J.Food Chem., 100(2), 459-467 .
- 13.T.Sethi , A.Chaturvedi and R.K.Upadhyay , S.P.Mathur , 2007,(Corrosion inhibitory effects of some schiff's bases) , J.Chil. Chem. Soc. 52 (3), 1206-1213 .
14. A.O.Odiongenyi ,S.A.Odoemelam and N.O.Eddy , 2009,(Corrosion and adsorption properties of ethanol extract of Vernonia amygdalina) , Portugalian Electrochemica Acta 27(1),33-45 .
- 15.R.Chauhan , U.Garg and R.K.Tak ,2011,(Corrosion inhibition of aluminium acid media by citrullus colocynthis extract) ,E-Journal of Chemistry 8(1), 85-90 .
16. E.E.Ebenso, N.O.Eddy and A.O.Odiongenyi,2008,(Corrosion and adsorption properties of ethanol extract of piper guinensis),Afr.J.Pure Appl.Chem. 2(11),107-115 .
17. A.Singh , V.K.Singh and M.A.Quraishi , 2010, (Effect of fruit extracts of some environmentally benign green corrosion inhibitors) , J.Matter. Environ. Sci. 1(3) , 162-174 .