

ACID CORROSION INHIBITION OF STEEL BY ORGANIC NITROGEN CONTAINING COMPOUNDS.

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المخلص

تم دراسة الخواص التثبيطية لحمض الارثوأمينوبنزويك و 8-هيدروكسيدي أكوينولين والكولونولين على تأكل الحديد الصلب في وسط 0.5 مولاري حمض الهيدروكلوريك / 10% إيثانول عند درجة حرارة 30 درجة مئوية وذلك باستخدام طريقة فقدان الوزن. تم تطبيق نموذج الحركية - الديناميكي الحراري الحديث على البيانات المتحصل عليها وذلك لغرض دراسة آلية التثبيط، كما تمت دراسة وتوضيح الارتباط بين التغيرات في التركيب الجزيئي وكفاءة التثبيط لهذه المركبات. أظهرت النتائج كفاءة تثبيط عالية (أكبر من 80%) للتآكل الحمضي لحديد الصلب بمركب الكولونولين بتركيز منخفض قدره 7.5×10^{-3} M. ولقد وجد أن تثبيط التآكل الحمضي لهذه المركبات يزداد حسب الترتيب: حمض الامينوبنزويك > 8-هيدروكسي موانولين > كوانولين.

ABSTRACT

The corrosion characteristics of ortoaminobenzoic acid, 8-hydroxy quinoline and quinoline on steel in 0.5 M, HCl / 10% Ethanol medium are investigated at 30°C using weight loss method. Recent Kinetic-Thermodynamic model was applied on the data obtained in order to study the inhibition mechanism.

Correlation of the structural changes with the protection efficiency of these compounds was reported. The results showed a high protection efficiency (greater than 80%) of quinoline for acidic corrosion of steel at its low concentration (7.5×10^{-3} M). The inhibition of acid corrosion by these compounds was found to increase in the order: quinoline > 8-hydroxy quinoline > ortoaminobenzoic acid.

KEYWORDS: Acid corrosion inhibition; Protection efficiency; Kinetic thermodynamic model; Inhibition mechanism.

INTRODUCTION

The electrochemical corrosion proceeds as a heterogeneous reaction of the electrified interface metal / environment. Consequently adsorption processes are domination the electrode kinetics [1].

Acid inhibitors are usually used in several industrial processes to control the corrosion of metals. They find wide applications as components in pretreatment composition, in cleaning solutions for industrial equipments, and in acidification of oil

wells. Most of the well-known are organic compounds containing Nitrogen, Sulphate and Oxygen. The influence of organic compounds containing Nitrogen, Such as amines and heterocyclic compounds, on the corrosion of steel in acidic solutions has been investigated by several works [2-6].

The primary step of the action of corrosion inhibitors in acid solutions is usually adsorption of the inhibitor on the metal surface. This phenomenon could take place via (i) electrostatic between the charged metal and the charged inhibitor molecules, (ii) dipole type interaction between uncharged pairs in the inhibition with the metal (iii) π – interaction with the metal and (iv) a combination of all the above [7].

The adsorption of an organic adsorbate on the surface of a metal is regarded as a substitutional adsorption process between the inhibitor molecule in aqueous phase $I_{(aq)}$ and the water molecules adsorbed on the electrode surface $H_2O_{(s)}$ [8].



where x is the size ratio which is the number of water molecules replaced by one inhibitor molecule.

Basically all available isotherms are of the form: $f(\theta, x) \exp(-a\theta) = kc$

where a is a molecular interaction parameter depending on the molecular interactions in the adsorption layer and on the degree of heterogeneity of the surface, $f(\theta, x)$ is the configurational factor which depends essentially on the physical model and assumptions underlying derivation of the isotherm [9]. In the limit when $x = 1$ and $a = 0$ all isotherms reduce to Langmuir isotherm and is given by the equation:

$$\frac{\theta}{(1-\theta)} = k [I] \quad (2)$$

in which K is the equilibrium constant of the adsorption reaction and I is the inhibitor concentration in the bulk of the solution [10].

This work deals with the study of corrosion inhibition properties of nitrogen containing compounds namely O-aminobenzoic acid (O.A.B.A), Quinoline (Q) and 8-hydroxyquinoline (8-H.Q). The corrosion inhibition efficiency of these compounds will be correlated to their structure in 0.5 M HCl / 10% Ethanol at 30 °C.

EXPERIMENTAL

The rate of dissolution of steel samples in 0.5 M HCl was determined by weight loss Method. The specimens used were cut in the form of rods of dimensions 30mm length and 10mm diameter.

The commercial steel rods that collected from Musrata steel factory were of composition given as: C = 0.37, Si = 0.27, Mn = 0.16, P = 0.13, S = 0.06, Cr = 0.13, Ni = 0.11, Cu = 0.1, Fe to 100 (by weight percent). Before the measurements, the samples were mechanically polished with a series of emery papers starting with a coarse one and proceeding in steps to the finer grades. They were washed thoroughly with distilled water and dried with acetone, the steel specimens were placed vertically in a beaker containing 100 ml solution. Both sample and solution were allowed to attain temperature equilibrium for a minimum of 20 min. prior to starting the corrosion

experiments. The reactions were under stagnant conditions at 30 °C and rates followed for a maximum of 1hr to avoid drastic changes in surface characteristics.

INHIBITORS

All compounds were obtained from Alderich chemical company and were used without further purification.

RESULTS AND DISCUSSION

Rates of dissolution were determined chemically by weight loss at 30°C. Table (1) gives the corrosion rate and inhibitor efficiency for mild steel in 0.5 M HCl %

Table 1: Corrosion parameters obtained from weight loss data for mild steel in 0.5 M HCl /10% Ethanol in absence and presence of different concentrations of studied inhibitors at 30°C.

Concent. (M)	Log C	O-aminobenzoic acid		Quinoline		8-hydroxy quinoline	
		CR (gm min ⁻¹ Cm ⁻² ×10 ⁵)	%Inh.	CR (gm min ⁻¹ Cm ⁻² ×10 ⁵)	%Inh.	CR (gm min ⁻¹ Cm ⁻² ×10 ⁵)	%Inh.
0		6.526	0	6.526	0	6.526	0
0.0001	-4			5.752	11.68	6.365	2.49
0.0005	-3.30103	6.335	2.96	4.568	30.02	5.564	14.77
0.0008	-3.09691	6.127	6.14				
0.001	-3	5.813	10.96	3.444	47.23	5.413	17.06
0.002	-2.69897					4.012	38.54
0.0025	-2.60206			2.172	66.73		
0.004	-2.39794	4.806	26.37				
0.005	-2.30103			1.495	77.08	1.653	74.67
0.0075	-2.12494			1.233	81.1	1.434	78.02
0.008	-2.09691	3.375	48.29				
0.01	-2	3.195	48.95	1.127	82.71	1.369	79.02
0.0125	-1.90309			1.037	84.08	1.267	80.58
0.015	-1.82391	2.733	58.12	0.979	84.99	1.123	82.79
0.0175	-1.75696			0.939	85.06		
0.02	-1.69897	2.104	67.76	0.927	85.79	1.049	83.92
0.035	-1.45593	1.224	82.78				

10% Ethanol in absence and presence of different concentration of (O.A.B.A), (Q) and (8-H.Q) at 30 °C. This shows that the corrosion rate decreases and inhibitor efficiencies increase with increasing concentration of each inhibitor at a given temperature.

Figure (1) shows the variation of the corrosion rate as a function of the concentration of O-aminobenzoic acid, quinoline and 8-hydroxyquinoline at 30 °C. As shown in this figure at a gain temperature on increasing the concentration of inhibitors the corrosion rate of steel decreases.

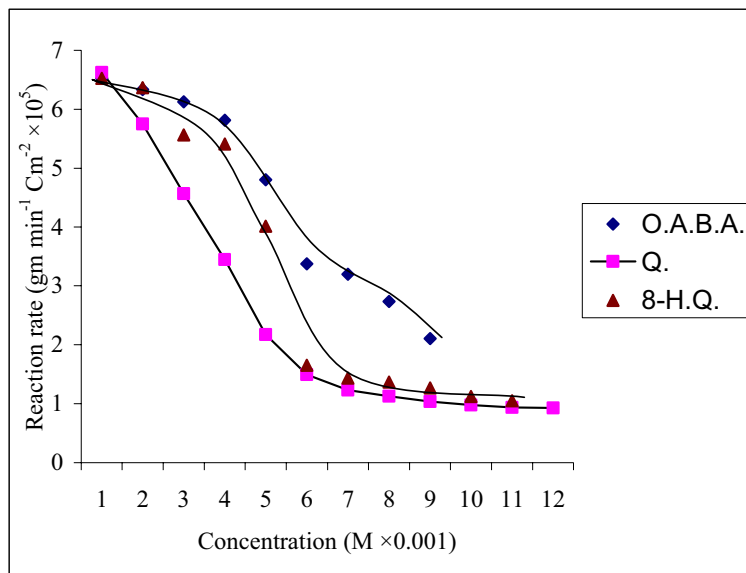


Figure 1: Variation of corrosion rate with the concentration of O.A.B.A, Q. and 8-H.Q. at 30°C.

Figure (2) represents the variation of percentage inhibition as a function of the logarithm of the concentration of O-aminobenzoic acid, quinoline and 8- hydroxyquinoline at 30 °C. As shown in this figure, the results have characteristics of S-shaped adsorption isotherms indicate of adsorption mechanism for the inhibition processes. This inhibition behavior could be attributed to the presence of electron donation groups of these compounds on clean positionally changed steel surface. The curves in Figure (2) also show that the efficiency of inhibition of acid corrosion of steel by the above mentioned compounds increases in order:

Quinoline > 8-hydroxyquinoline > O-aminobenzoic acid.

It is evident that the presence of different withdrawing groups has clear influence on inhibition efficiency created by adsorption centers - N, -NH₂ and - OH.

To evaluate the kinetic parameters and correlate them to their corrosion inhibition mechanism, it is now of value to analyze the kinetic data obtained in the presence of the investigated inhibitors from the stand point of the generalized mechanistic scheme proposed by El-Awady et. al. [11,12]. This model has been applied on some sulphur containing compounds as acid corrosion inhibitors [13].

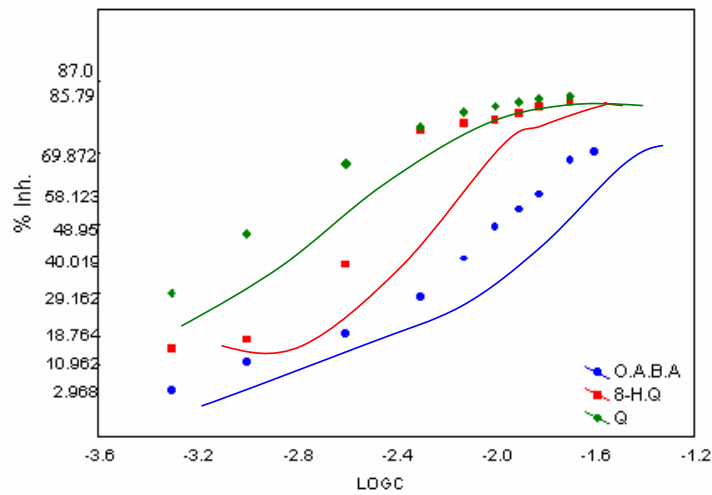


Figure 2: Variation of percentage inhibition with the logarithmic concentration of O.A.B.A, Q. and 8-H.Q. at 30°C.

The curve fitting of O.A.B.A., 8-H.Q. and Q. data to kinetic -thermodynamic model (Eq. 3) at 30°C are given in Figure (3).

$$\frac{\theta}{(1-\theta)} = K' [I]^y \quad (3)$$

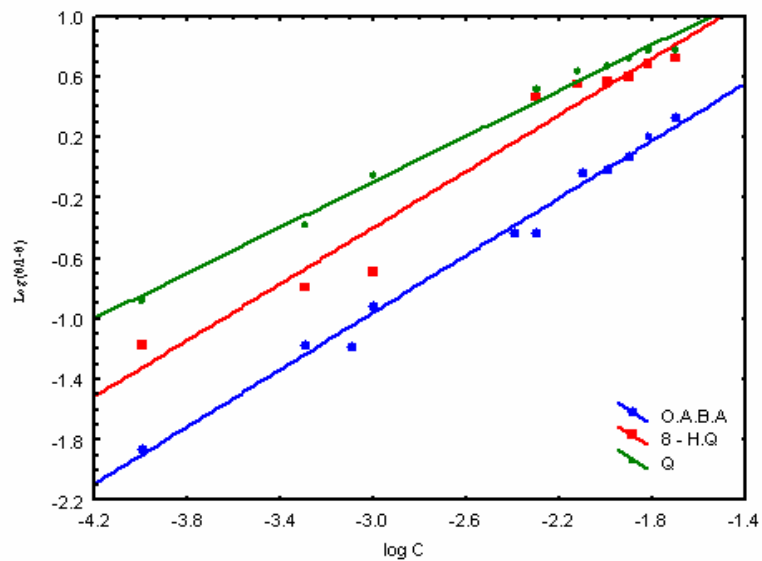


Figure 3: Corrosion data fitting curve of steel in 0.5 M HCl / 10% Ethanol in presence of tested inhibitors to the kinetic - thermodynamic model at 30°C

As seen, good straight line fits are given for the compounds used hence, the suggested model satisfactory fits the obtained experimental data. The slope of such lines is the number of inhibitor molecule occupying a single active site y and the intercept is $(\log K')$. The binding constant (K) corresponding to that obtained from the adsorption isotherms curve fitting is given by:

$$K = K' (1/y) \quad (4)$$

where $(1/y)$ represents the number of active site of the surface occupied by one molecule of the inhibitors. Table (2) gives the values of $(1/y)$ and (K) for the studied compounds. This table shows that the number of active sites occupied by one molecules increased from O.A.B.A to Q.

Quinoline > 8-hydroxyquinoline > O-aminobenzoic acid.

Table 2: Curve fittings of O.A.B.A., 8-H.Q and Q to kinetic - thermodynamic model at 30°C

compound	1/y	k~
O.A.B.A	1.0582	76.033
8- H.Q	1.074	147.9108
Q	1.326	251.1886

Inspection of these results, also show that the values of active sites occupancy and binding constants are in good agreement with the inhibition efficiency characteristics of tested compounds.

More recently M. Athar et. al. [14] investigated the inhibiting action of some organic compounds containing heteroatoms on the corrosion of steel in 1M HCl. High inhibition effect was reported at different temperatures ranging from 30 to 60°C. The inhibition effect of these compounds was discussed to be take place by adsorption process. This effect of adsorption was further supported from the fact that all the inhibitors followed Temkin adsorption isotherm.

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