Benzaldehyde, 2-Hydroxybenzoyl Hydrazone Derivatives as Inhibitors of the Corrosion of Aluminium in Hydrochloric Acid

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Received November 1, 1999; accepted January 17, 2000

The effect of benzaldehyde, 2-hydroxybenzoyl hydrazone derivatives on the corrosion of aluminium in hydrochloric acid has been investigated using thermometric and polarization techniques. The inhibitive efficiency ranking of these compounds from both techniques was found to be: 2>3>1>4. The inhibitors acted as mixed-type inhibitors but the cathode is more polarized. The relative inhibitive efficiency of these compounds has been explained on the basis of structure of the inhibitors and their mode of interaction at the surface. Results show that these additives are adsorbed on an aluminium surface according to the Langmuir isotherm. Polarization measurements indicated that the rate of corrosion of aluminium rapidly increases with temperature over the range 30–55 °C both in the absence and in the presence of inhibitors. Some thermodynamic data of the adsorption process are calculated and discussed.

Key words benzaldehyde; 2-hydroxybenzoyl hydrazone derivative; corrosion; inhibitor; aluminium; hydrochloric acid

Research on the many important applications of aluminium and its alloys has narrowed down to its electrochemical behaviour and corrosion resistance in a wide variety of media, including investigation of the properties of the surface oxide film, formed naturally or by anodization.¹⁾ Generally, this consists of a thin barrier film adjacent to the metal (*ca.* 25 nm thick) covered by a thicker porous oxide layer. In aggressive media, such as chloride solution, localized corrosion can occur leading to the breakdown of the passive layer and pit formation.

The electrochemistry of aluminium in chloride solutions has been widely investigated.^{2–10)} The effect of the presence of different ions in solutions on the electrochemical behaviour, inhibiting or enhancing corrosion, has also been studied.^{11–16)}

The aim of the present work was to examine the inhibitive action of the above mentioned inhibitors towards the corrosion of aluminium in acidic solutions. The choice of the inhibitors was based on two factors. First, it can be conveniently synthesized from relatively cheap raw materials. Secondly, the presence of an electron cloud on the aromatic ring and the high solubility of these compounds in acid medium induce greater adsorption of the compounds on the surface of aluminium which can lead to effective inhibition.

Experimental

Materials and Test Solutions Aluminium strips 100×10×0.5 mm in size (composition in Table 1) were used for thermometric measurements. For galvanostatic polarization studies, a wire 1 cm in length and ϕ 0.5 mm of the composition shown in Table 1 and embedded in araldite was used. The aluminium electrodes were mechanically polished with emery papers of 1/0, 2/0, 3/0 and 4/0 grade and degreased with alkaline solution (15 g Na₂CO₃ + 15 g Na₃PO₄ per litre). AR grade HCl (BDH) was used for preparing solutions. Double distilled water was used to prepare solutions of 2 N HCl for all experiments.

The inhibitors benzaldehyde, 2-hydroxybenzoyl hydrazone derivatives

were synthesized in the laboratory following the known procedures; their structures were characterized by NMR, IR, mp and elementary analysis and are shown in Chart 1.

Apparatus and Working Procedures The reaction vessel used was basically the same as that described by Mylius.¹⁷⁾ The reaction number (RN) is:

$$RN = (T_m - T_i)/t, \text{ } ^\circ\text{C min}^{-1} \quad (1)$$

where T_m and T_i are the maximum and initial temperatures, and t is the time in minutes taken to reach T_m . All experiments were started at $30 \pm 0.1^\circ\text{C}$ (T_i). The extent of corrosion inhibition by a certain concentration of a particular additive is evaluated from the percentage decrease in RN, *viz.*

$$\frac{(RN)_{\text{free}} - (RN)_{\text{add}}}{(RN)_{\text{free}}} \times 100 \quad (2)$$

The galvanostatic method used for steady state polarization studies consisted of a constant current device and digital ionalyzer model 701 A for measuring corrosion potentials. All experiments were carried out at $30 \pm 0.1^\circ\text{C}$. The inhibitive efficiency was calculated employing the formula:

$$\% \text{Inhibition efficiency} = \frac{I - I'}{I} \times 100 \quad (3)$$

where I and I' are the corrosion currents without and with inhibitor, respectively.

3-methyl benzaldehyde, 2-hydroxy benzoyl-hydrazone (1)

3-hydroxybenzaldehyde, 2-hydroxy benzoyl-hydrazone (2)

4-bromo benzaldehyde, 2-hydroxy benzoyl-hydrazone (3)

benzaldehyde, 2-hydroxy benzoyl-hydrazone (4)

Chart 1

Table 1. Aluminium Composition (wt%)

Si	Fe	Mn	Mg	Cu	Al
0.15	0.19	0.005	0.1	0.02	Rest

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Results and Discussion

Thermometric Measurements In this method the temperature change was followed in the absence and in the presence of different concentrations of the benzaldehyde, 2-hydroxybenzoyl hydrazone derivatives as inhibitors.

Curves of Fig. 1 represent the behaviour observed in the presence of different concentrations of inhibitor **2**. All curves of the tested materials are characterized by an initial slow rise (due to the oxide film originally present on the metal surface¹⁸) followed by a sharp rise and finally by a decrease in temperature after attaining a maximum value. The curves for additive containing systems fall below that of the free acid. This indicates that the additives behave as inhibitors over the concentration range studied. The percentage reduction in RN

Fig. 1. Temperature-Time Curves Obtained in Absence and Presence of Different Concentrations of Compound **2**

of the studied compounds is presented in Table 2.

The results compiled in Table 2 revealed that the efficiency of corrosion inhibition as determined from the percentage reduction in RN varies with both the concentration and the type of the inhibitor. The inhibitive efficiency of additives is in the order: **2** > **3** > **1** > **4**.

Polarization Measurements The polarization curves for the system involving inhibitor **2** are shown in Fig. 2 and the electrochemical parameters in these media are given in Table 3. The corrosion current density for aluminium in 2 N HCl is: $i_{\text{corr.}}$ 19 mA cm⁻². Addition of inhibitor molecules causes a decrease in $i_{\text{corr.}}$. The decrease in $i_{\text{corr.}}$ and the increase in θ with increasing concentration in the range 1×10^{-5} — 1×10^{-3} M demonstrate the efficiency of the additive compounds as corrosion inhibitors of aluminium. Also, the slopes of anodic and cathodic Tafel slopes are approximately constant, independent of the concentration of inhibitor. This indicates that the inhibition of the dissolution of aluminium takes place without affecting the mechanism.

A correlation between θ and $\log C$ of adsorbate is given by Frumkin adsorption isotherm. The experimental results (Fig. 3) are in good agreement with the following equation:

$$KC = \left[\frac{\theta}{1-\theta} \right] \exp(-f\theta) \quad (4)$$

Table 2. The Inhibitor Efficiencies of Hydrazone Derivatives at 30 °C

Substance	% Reduction in RN			
	1	2	3	4
1×10^{-5}	32.1	37.5	32.5	31.5
5×10^{-5}	68.0	73.4	72.6	66.7
1×10^{-4}	79.5	77.6	84.8	78.2
5×10^{-4}	92.3	92.8	92.5	91.7
1×10^{-3}	93.4	96.2	94.6	92.7

Fig. 2. Effect of Concentration of Compound **2** on the Current Potential Relations of Aluminium Dissolution in 2 N HCl

The inhibition efficiency of additives decreases in the order: **2** > **3** > **1** > **4**.

Table 3. The Effect of Compound 2 Concentrations on the Free Corrosion Potential (E_{corr}), Corrosion Current Density (i_{corr}), Tafel Slopes (β_a , β_c) Inhibition Efficiency (P_i) and Degree of Surface Coverage (θ) of Aluminium in 2 N HCl at 30 °C

Conc. (M)	$-E_{\text{corr}}$ (mV)	i_{corr} (mA cm) ⁻²	β_a (mV/dec.)	β_c (mV/dec.)	% P_i	θ
0.0	848	19.0	38	164	—	—
1×10^{-6}	850	4.5	35	168	75.3	0.75
5×10^{-6}	855	3.3	36	165	83.0	0.83
1×10^{-5}	856	2.9	39	150	85.0	0.85
5×10^{-5}	835	2.2	40	136	88.0	0.88
1×10^{-4}	857	1.7	50	130	91.0	0.91
5×10^{-4}	856	1.5	52	134	92.0	0.92

Fig. 3. Effect of Compound 3 concentration on the Degree of Surface Coverage for Al in 2 N HCl

where C is the concentration of adsorbed substance in the bulk of the solution and f is a constant depending on intermolecular interaction in the adsorbed layer and on the heterogeneity of the surface. K is the modified equilibrium constant of the adsorption process, which is related to the standard free energy of adsorption according to the following equation:

$$K = \exp(\Delta G_{\text{ads}}^0 / RT) \cdot \frac{1}{55.5} \quad (5)$$

The effect of temperature on the rate of dissolution of aluminium in 2 N HCl was studied by galvanostatic polarization in the temperature range 30–60°C. For all the additives tested, the logarithm of i_{corr} is a linear function of $1/T$ (Figs. 4, 5). The activation energy values E_a^* (Table 4) increase with increasing inhibition efficiency of the compounds. Compound 2 which gives maximum inhibition efficiency yields the highest activation energy and the opposite is true for compound 4. The similar values of E_a^* suggest that the inhibitors are similar in their mechanism of action and that the order of efficiency may be related to the pre-exponential factor A by the equation:

$$\log R = \log A - \frac{E}{RT} \quad (6)$$

Fig. 4. Log K - $1/T$ Plots for Aluminium Dissolution in Presence and Absence of Compounds 1, 2 and 3

Fig. 5. Log K - $1/T$ Plots for Aluminium Dissolution in Presence and Absence of Compound 4

This is further related to concentration, steric effects, metal surface characteristics, etc. Also, the results show that compound 2 gives maximum efficiency and exhibits the highest negative ΔG_{ads}^0 , indicating that it is strongly adsorbed on the aluminium surface.

Table 5 summarizes the inhibition efficiency of the additives at various concentrations from polarization measurements.

Table 4. Energy of Activation, Free Energy of Adsorption and Modified Equilibrium Constant of Hydrazone Derivatives During Corrosion of Aluminium in 2 N HCl

Inhibitor	% Inhibition	E^* (kcal mol ⁻¹)	$-\Delta G_a^0$ (kcal mol ⁻¹)	B
1	76.0	8.0	10.1	3.2×10^5
2	85.0	10.6	10.6	7.0×10^5
3	77.0	9.1	10.2	3.4×10^5
4	73.7	5.3	10.0	2.9×10^5
Free	—	4.8	—	—

Table 5. Inhibition Efficiency of Different Inhibitors at Various Concentrations at 30 °C

Conc. (M)	% Inhibition efficiency			
	1	2	3	4
1×10^{-6}	66.3	75.3	67.4	67.0
5×10^{-6}	70.0	83.0	70.3	68.4
1×10^{-5}	76.0	85.0	77.0	73.7
5×10^{-5}	84.0	88.0	85.0	83.7
1×10^{-4}	89.0	91.0	90.0	86.0
5×10^{-4}	90.5	92.0	92.0	88.0

Chemical Structure and Corrosion Inhibition of Aluminium Inhibition efficiency was shown,¹⁹⁾ to depend on the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption and formation of metallic complexes.

Variation in structure of the inhibitor molecules (1—4) takes place through the phenyl group of benzaldehyde side chain. Thus variation in inhibition efficiency would probably originate from this part of the molecule.

Vertical adsorption of the additive molecules on the aluminium surface is suggested as evidenced by the presence of the substituent effect on inhibition action. Skeletal representation of the mode of adsorption of the inhibitor molecules is shown in Chart 2.

Adsorbed molecules on the surface of the corroding metal interfere with cathodic and/or anodic reactions.²⁰⁾ Inhibition of these reactions would obviously depend on the degree of coverage of the metal with the adsorbate. Competitive adsorption is assumed to occur on the surface of the metal between the aggressive Cl⁻ ions on one hand and the inhibitor molecules on the other. Experimental results indicated that the decrease inhibition efficiency of the additives used for aluminium dissolution in hydrochloric acid over the concentration range 1×10^{-6} — 5×10^{-4} M is in the order $2 > 3 > 1 > 4$.

In the *p*-substitutions the inductive effects are small due to the great distance that separates the substituent from the reaction center. In *m*-substitution, inductive effects are more significant than resonance effects. In *o*-substitution both a strong inductive effect and resonance are observed. Compound 2 is the most efficient inhibitor due to the presence of three active centers (one C=O and two -OH groups). Compound 3 comes after compound 2 in spite of the fact that it contains the same number of active centers (one -OH, one C=O and one Br atom). This is because the OH group in compound 2 increases the electron charge density on the molecule more than Br atom in compound 3 and hence it in-

Chart 2. Skeletal Representation of the Mode of Adsorption of the Inhibitor Molecules

creases the inhibition efficiency. Compounds 1 and 4 have the same number of active centers, but in compound 1 the *m*-substituent in the phenyl group of benzaldehyde (*m*-CH₃) has some inductive and resonance effects which increase the electron charge density on the molecule, and hence increase the inhibition efficiency. So, compound 1 is superior to compound 4 in inhibition efficiency. The higher inhibition efficiency values of the compounds used can be attributed to their large surface coverage of the aluminium surface, and to the presence of electrodonating groups in *m*- or *p*-substitution in the phenyl group of benzaldehyde.

Conclusions

The tested benzaldehyde, 2-hydroxybenzoyl hydrazone derivatives act as mixed type inhibitors but the cathode is more polarized against pure aluminium in 2 N hydrochloric acid at 30 °C. All the compounds are adsorbed on the metal surface following the Langmuir adsorption isotherm. Inhibition efficiency increases with increase in the concentration of the inhibitor as well as its electron donor character.

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