Inhibition Effect of Organic Electron-Accepting Compounds on Corrosion of Iron in Acid Solution

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In order to confirm the adsorption of organic corrosion inhibitors on metals by means of back-donation of the metal electrons to an vacant orbital of the inhibitor, the inhibition efficiency of electron-accepting inhibitors was determined for pure iron in a 6.1 M HCl solution by polarization measurements. Nitrobenzene derivatives were used as the electron-accepting inhibitors. They accelerated the cathodic reaction because of their reduction, whereas they inhibited the anodic reaction. The inhibition efficiency of these inhibitors for the anodic reaction was expressed by the Hammett-like equation associated with the Hammett constant, σ . The efficiency of the compounds with an electron-attracting substituent ($\sigma > 0$) increased with a decrease in the electron density of the nitro group. Since the efficiency of these compounds was closely related to the half-wave potential of reduction, the back-donation of metal electrons to the antibonding π -orbitals was concluded to play an important role in the adsorption of the nitrobenzene derivatives on the iron surface.

1. Introduction

It is generally accepted that organic corrosion inhibitors adsorb on metallic surface by means of three principal types of interaction between the inhibitor molecule and the metal¹⁾. They are an electrostatic, a covalent, and a π -bonding interactions. An ionic inhibitor like a quaternary ammonium cation adsorbs on the negatively charged surface by the electrostatic force. Most of polar organics chemisorb on the metal by the formation of covalent bond between the polar atom and metal. In general, a pair of unshared electrons in the polar atom is donated to a vacant d-orbital of the metal. A flat adsorption of aniline and allyl amine, oriented in parallel to the surface, occurs by π -electron bonding between the metal and the phenyl and the allyl groups^{2), 3)}. Therefore, the inhibition efficiency of aniline derivatives and olefinic amines is related not only to the electron density of nitrogen atom but also to the π -electron density of the phenyl group and the double bond. The π -bonding interaction also relates to back-coordination of metal electrons to a vacant orbital of polar atom. For example, tetra-n-propylsilane (C_3H_7)₄Si, which

holds no pair of unshared electrons, inhibited the cathodic reaction of various transition and non-transition metals in an acid solution^{4), 5)}. This result has been explained by occurrence of the back-donation of metal electrons to the vacant d-orbital of Si atom. The back-donation of metal electrons to an antibonding π -orbital of the olefinic compounds has also been suggested, since a decrease in the density of π -electron enhanced the π -electron adsorption of double bond on the cathode^{6), 7)}.

The present work was undertaken to elucidate a possibility of the adsorption by the formation of back-donation linkage between the metal and electron-accepting inhibitor. The inhibitors used were nitrobenzene derivatives which are the electron acceptors for charge transfer complexes. Inhibition efficiency of the inhibitors was determined on pure iron in a 6.1 M HCl solution by polarization measurements, and discussed with respect to the substituent constant, the electron affinity, and the molecular size of these compounds.

2. Experimental

2.1 Inhibitors

Eleven ring-substituted nitrobenzene derivatives, listed in Table 1, were used as the inhibitors. They were obtained as high-grade commercial

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Table 1 Effectively covered area, S and polarization data at the inhibitor concentration of 1×10^{-3} M.

No.	Inhibitor	S (A ²)	E_{corr} (mV)	b_a (mV/log i)
0	none	—	-467	109
1	nitrobenzene	51.6	-461	112
2	o-dinitrobenzene	61.3	-455	110
3	m-dinitrobenzene	64.3	-433	113
4	p-dinitrobenzene	64.2	-440	112
5	1,3,5-trinitrobenzene	77.7	-422	110
6	p-chloronitrobenzene	59.4	-448	111
7	2,4-dinitrofluorobenzene	66.4	-437	112
8	p-nitrotoluene	58.3	-450	112
9	p-nitroanisole	61.6	-449	112
10	p-nitrophenol	55.2	-449	110
11	p-nitroaniline	60.0	-446	110

reagents and purified by distillation or recrystallization before use. The inhibitors were dissolved in the 6.1 M HCl solution prepared by diluting reagent-grade concentrated HCl with re-distilled water.

2.2 Polarization measurements

Corrosion rates of a 99.89% iron electrode* (Mallinckrodt analytical reagent grade) were determined in the inhibited and uninhibited HCl solutions by galvanostatic polarization measurements. The inhibitor solution was deaerated by passing nitrogen gas and kept at $30 \pm 0.1^\circ\text{C}$. The cathodic and anodic polarization runs were carried out independently. The details of the measurements have been given elsewhere⁸.

2.3 Determination of effectively covered area

The area of metal surface effectively covered by an inhibitor molecule, S was determined by arranging the Stuart-Briegleb molecular models on a plane in the position corresponding to the appropriate conformation and orientation mode of the molecule adsorbed on the surface. The nitrobenzene derivatives were assumed to adsorb in parallel with the surface and not to rotate on the surface. The determination of the area has been described in more detail elsewhere⁹.

3. Results

Typical polarization curves of the iron electrode in the uninhibited solution and the inhibited solution with nitrobenzene are shown in Fig. 1, indicating acceleration of the cathodic reaction in the presence of nitrobenzene. All the curves showed that the nitrobenzene derivatives stimu-

Fig. 1 Polarization curves of iron electrode in 6.1 M HCl uninhibited (A) and inhibited with nitrobenzene at 1×10^{-3} M (B) and at 3×10^{-3} M (C).

Fig. 2 Anodic inhibition efficiency, I_a , of nitrobenzene derivatives (1).

1, nitrobenzene; 2, o-dinitrobenzene; 3, m-dinitrobenzene; 4, p-dinitrobenzene; 5, 1,3,5-trinitrobenzene. s: saturated in the solution.

lated the cathodic reaction. This stimulation is attributed to the electrochemical reduction of the nitro compounds to hydroxylamines and finally to amines. Nitrobenzene is cathodically reduced to aniline in an acid medium¹⁰, as

* Impurities: C, 0.03%; Mn, 0.04%; P, 0.002%; Si, 0.001%; S, 0.02%.

Fig. 3 Anodic inhibition efficiency, I_a of nitrobenzene derivatives (2).

6, p-chloronitrobenzene; 7, 2,4-dinitrofluorobenzene; 8, p-nitrotoluene; 9, p-nitroanisole; 10, p-nitrophenol; 11, p-nitroaniline. s: saturated in the solution.

Therefore, the inhibition effect of the adsorbed molecule on the cathodic reaction could not be determined in this experiment.

The nitro compounds, however, inhibited the anodic reaction of the iron electrode in the acid solution. The well-defined anodic Tafel lines were observed in the potential region between -280 and -380 mV (vs. SCE). The corrosion potential for the inhibited electrode shifted toward the less noble potential by less than 90 mV from that for the uninhibited electrode, E_{corr}^0 . The potential, E_{corr} and the anodic Tafel slope, b_a at the inhibitor concentration of 1×10^{-3} M are listed in Table 1. There was no significant spread of anodic Tafel slopes. The effectively covered area, S of the inhibitors is also tabulated in the table.

On the assumption that the values of b_a are constant, the anodic inhibition efficiency, I_a is given by

$$I_a = 1 - i_a / i_{\text{corr}}^0 \quad (1)$$

where i_a is the current density obtained by extrapolating the anodic Tafel line at E_{corr}^0 and i_{corr}^0 is the corrosion current density obtained by intersection of the extrapolated anodic and cathodic Tafel lines for the uninhibited electrode.

Fig. 4 Relationship between I_a/S and dipole moment of inhibitors, μ . The numbers refer to the inhibitors in Table 1.

Fig. 2 and 3 show the anodic inhibition efficiency of the nitrobenzene derivatives.

4. Discussion

The nitrobenzene derivatives are effective inhibitors for the corrosion of titanium in acid media¹¹. These compounds are electrochemically reduced on the titanium surface, which leads to passivation of the metal. The corrosion potential of Ti shifts toward the noble potential by several hundreds millivolts by the addition of the effective inhibitors¹². Rosenfeld has been described that amine nitrobenzoate and 3,5-dinitrobenzoate shifted the potential beyond the passivation potential, and thus facilitated passivation of iron in neutral media¹³.

In order to confirm no reduction of the nitro compounds during the anodic polarization measurement in this experiment, UV spectra of the inhibitor solution were determined at the concentration of 1×10^{-3} M. The concentration of the nitro compound was decreased during the cathodic polarization, while no change in the concentration was observed during the anodic one. The effect of the reduction on the anodic Tafel line was estimated to be negligible. The reduction potential of the nitro compounds examined in this study was less noble than the potential range of the anodic polarization and the corrosion potential of the inhibited electrode shifted toward the more noble potential by less than 45 mV at the inhibitor concentration of 1×10^{-3} M, as shown in Table 1. Thus, it is concluded that the inhibition of the anodic reaction is not attributed to the passivation of iron surface but to the adsorption of the inhibitor.

Some adsorption modes of the nitro compounds

Fig. 5 Relationship between $\log(I_a S_0 / I_{a0} S)$ and Hammett constant, σ at the inhibitor concentrations of 1×10^{-3} M (O) and 3×10^{-3} M (Δ). The numbers refer to the inhibitors in Table 1.

on the iron surface were considered. Because the nitro group is electron-attracting, the compounds can adsorb on the surface by the electrostatic interaction between the metal and dipole. Fig. 4 shows the relationship between I_a/S and dipole moment of the nitro compounds, μ , exhibiting no evident correlation between them. From this result, it was concluded that the dipole-metal interaction is of a minor importance to the adsorption of nitro compounds.

Formation of a surface complex has been proposed by Riggs et al. for the adsorption of nitro compound on the titanium surface¹⁴⁾. The oxygen atoms of the nitro group attracting electrons from the phenyl group form the complex linkage with the titanium. If the nitro group plays an important role in the adsorption of the inhibitor, the inhibition efficiency should relate to a substituent constant.

According to the linear free energy relationship, if the activation energy of corrosion process is not changed by the adsorption of inhibitor and I_a is low enough to be proportional to S , I_a is expressed approximately by the equation

$$\log(I_a S_0 / I_{a0} S) = \rho^* \Sigma \sigma^* + \delta E_s + \Psi_r + \alpha \quad (2)$$

where zero subscripts refer to a reference inhibitor, $\Sigma \sigma^*$ and E_s denote the polar and steric substituent constants, Ψ_r is a parameter related to the electron-delocalized structures, and ρ^* , δ , and α are constants, respectively²⁾. Since all the inhibitors used in this study are benzene derivatives, the terms $\rho^* \Sigma \sigma^*$ and Ψ_r are replaced by

Fig. 6 Relationship between $\log(I_a S_0 / I_{a0} S)$ and half-wave potential of reduction, $E_{1/2}^{\text{red}}$ at the inhibitor concentrations of 1×10^{-3} M (O) and 3×10^{-3} M (Δ). The numbers refer to the inhibitors in Table 1.

$\rho\sigma$, the product of the reaction and Hammett constants. The term δE_s which is related to the steric requirements for the adsorption of inhibitor was taken to be negligible. Therefore, Eq. (2) was written as

$$\log(I_a S_0 / I_{a0} S) = \rho\sigma + \alpha \quad (3)$$

The reference inhibitor was nitrobenzene.

The value of $\log(I_a S_0 / I_{a0} S)$ was plotted against σ in Fig. 5, which showed two straight lines intersecting at the plot of nitrobenzene. For the nitro compounds in the range of $\sigma < 0$, it is reasonable that the inhibitor chemisorbs on the metal by the electron donation of the nitro group to the metal orbital because an increase in the electron density of the nitro group enhances the inhibition efficiency. In the range of $\sigma > 0$, however, the efficiency increases with a decrease in the density. This result cannot be explained by the chemical adsorption associated with the electron donation of the nitro group to the metal.

The inhibitors in the range of $\sigma > 0$ are polynitro compounds except p-chloronitrobenzene. These inhibitor molecules can adsorb on the metal by the interaction between the plural functional groups and metal surface. The multi-functional adsorption results in the flat adsorption which is favorable for the π -electron bonding between the molecule and the metal.

The anodic inhibition efficiency of m-dinitrobenzene was lower than that of o- or p-dinitrobenzene, though the electron density in the nitro groups of the former molecule is higher by means of the resonance effects than the density in the groups of the latter two. This finding suggests

the occurrence of adsorption by the different mode from the electron donation of inhibitor.

Since the electron-accepting inhibitor like the nitro compound can adsorb on the metal by the back-donation, the inhibition efficiency was confirmed to be correlated to the polarographic half-wave potential of reduction, $E_{1/2}^{red}$ as a measure of the electron affinity. The value of $\log(I_a S_0/I_{a0} S)$ was plotted in Fig. 6 against $E_{1/2}^{red}$, which was determined in 0.1 M tetraethyl ammonium perchlorate at 25°C by Peover¹⁵⁾. The figure exhibits a straight line at each of the concentrations and the increase of I_a with the ability of electron acceptance. This result shows that the chemisorption by the back-donation is of an importance to the adsorption of such the electron-accepting inhibitors as the nitro compounds.

The polar organic inhibitors like alkyl amines chemically adsorb by the donation of electrons in the polar group to the metal orbital, in general. Because of no electron-acceptable orbital in the molecule of the amines, the adsorption by the back-donation is impossible to occur. However, the inhibitors like anilines and olefinic amines, which can accept the electrons in the antibonding π -orbital, may readily adsorb by the back-coordination on the cathode. The possibility of the back-donation has also been shown in the previous studies on the cathodic inhibition efficiency of these inhibitors^{2), 3)}. The adsorption of these inhibitors by the donation of π -electrons to the metal orbital must be reinforced by the back-donation of metal electrons to the antibonding π -orbitals of the double bonds.

5. Conclusion

The polarization study was made on the iron electrode in the HCl solution inhibited with the nitrobenzene derivatives. These compounds accelerated the cathodic reaction because of their reduction, while they inhibited the anodic reaction. The inhibition efficiency of these inhibitors for the anodic reaction was correlated to the Hammett constant, σ of substituent in the benzene ring. As for the compounds of which σ is less

than zero, the efficiency increased with the electron density of the nitro group. The efficiency of the compounds for $\sigma > 0$ was enhanced with the decrease in the electron density. Because the efficiency of the latter compounds was correlated to the half-wave potential of reduction, the formation of inhibitor-metal bond by the back-donation was concluded to be a major factor for the adsorption of the nitro benzene derivatives.

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