Polarization Study on the Inhibition of Iron Corrosion by means of Phenylalkyl Amines in Acid Solution

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The inhibition effect of ω -phenylalkyl amines and ω -cyclohexylalkyl amines on the corrosion of pure iron was studied in a 6.1M HCl solution by polarization measurement. The inhibition efficiency of these amines was determined on the basis of general adsorption behavior, using molecular coverage areas, the pK_a values, and the polar and steric substituent constants. Most of the amines inhibited the cathodic and anodic processes of the corrosion reaction. The efficiency of ω -phenylalkyl amines was lower than that of the corresponding ω -cyclohexylalkyl amines; the cations of the former are adsorbed on the cathodic surface in parallel orientation mode by electrostatic attraction and by interaction between the metal and the phenyl group. The interaction between the metal and molecules of phenylalkyl amine in its resonance structure plays an important role in its adsorption on the anodic surface. The anodic inhibition efficiency of the phenylalkyl amines can be expressed in terms of polar and steric substituent constants and in terms of a factor related to the effect of their resonance structures on adsorption.

1 Introduction

A number of investigations have been reported on the inhibition of iron corrosion by means of aniline derivatives in acid solutions. According to the concept of general adsorption, amine inhibitors are adsorbed on the metal surface by the formation of a coordination bond between the metal and the nitrogen atom and by electrostatic attraction between the cathodic surface and ammonium cations which form in the acid solutions^{1,2}. Furthermore, flat adsorption of anilines on the surface can occur by π -electron bonding between the metal and the phenyl group³. Therefore, the inhibition efficiency of aniline derivatives for iron corrosion in acid solutions is related not only to the electron density of the nitrogen atoms but also to the π -electron density of the phenyl group⁴. The present work was undertaken to elucidate the effect of the phenyl group on the corrosion inhibition efficiency of phenylalkyl amines. The efficiency of ω -phenylalkyl amines for iron corrosion in 6.1 M HCl was obtained by polarization measurements and discussed with respect to the pK_a value, the polar and steric substituent constants, and the molecular size of these amines.

2 Experimental

2.1 Inhibitors

The inhibitors used were ω -phenylalkyl amines ($C_6H_5(CH_2)_nNH_2$, where $n=0-3$), and ω -cyclohexylalkyl amines ($C_6H_{11}(CH_2)_nNH_2$, where $n=0-3$). The former were obtained as high-grade commercial reagents and purified by recrystallization of their salts with hydrochloric acid. The latter series, with the exception of cyclohexylamine, were synthesized by the catalytic hydrogenation of the corresponding ω -phenylalkyl amine and all were purified by fractional distillation before use.

2.2 Polarization measurements

Corrosion rates of a 99.89% iron electrode*¹ (Mallinckrodt analytical reagent grade) were determined at $30 \pm 0.1^\circ C$ in inhibited and uninhibited 6.1 M HCl solutions by galvanostatic polarization. The details of these measurements have previously been given⁵.

2.3 Determinations of molecular coverage area and basicity

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*¹ C, 0.03%; Mn, 0.04%; P, 0.002%; Si, 0.001%; S, 0.02%

The coverage area of each inhibitor molecule 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 metal surface. Two kinds of adsorption were assumed in determining area—coulombic adsorption of the ammonium cation, and coordination adsorption of the unprotonated amine. For both the adsorbed cation and amine, two orientation modes were assumed—in the first, the molecules are adsorbed on the surface without any interaction between the metal and the phenyl group; in the second, the phenylalkyl amine inhibitor is adsorbed by the formation of a metal-nitrogen bond under the influence of π -electron interaction between the metal and the phenyl group. In the second orientation mode, the inhibitor molecules are adsorbed in parallel with the surface. Determination of the molecular coverage area has been described in greater detail elsewhere⁹⁾.

The pK_a values for some of the inhibitors were determined by titration with $HClO_4$ in water at 25°C.

3 Results

The corrosion current i_{corr} and the corrosion

potential E_{corr} were obtained by intersection of well-defined cathodic and anodic Tafel lines. The polarization curves showed that most of the amines inhibited both the cathodic and the anodic processes of the corrosion reactions. E_{corr} and the cathodic and anodic Tafel slopes b_c and b_a at an inhibitor concentration of 0.01 M are tabulated in Table 1. The E_{corr} values for the inhibited electrodes shifted toward the less noble potential by no more than 30 mV from those for the uninhibited electrode E_{corr}^0 . There was no significant spread of values for each of the Tafel slopes.

Figure 1 shows the total inhibition efficiency

Table 1 Polarization data at an inhibitor concentration of 0.01 M

No.	Inhibitor	E_{corr} (mV vs. SCE)	b_c (mV/ log i)	b_a (mV/ log i)
0	none	-467	154	110
1	aniline	-474	155	112
2	benzylamine	-478	153	110
3	2-phenylethylamine	-480	155	110
4	3-phenylpropylamine	-484	153	112
5	cyclohexylamine	-479	156	111
6	cyclohexylmethylamine	-488	154	111
7	2-cyclohexylethylamine	-484	153	112
8	3-cyclohexylpropylamine	-472	158	116

Fig. 1 Total inhibition efficiency I_t

- a) for ω -phenylalkyl amines: 1, aniline; 2, benzylamine; 3, 2-phenylethylamine; 4, 3-phenylpropylamine
 b) for ω -cyclohexylalkyl amines: 5, cyclohexylamine (●: purified by recrystallization of its chloride); 6, cyclohexylmethylamine; 7, 2-cyclohexylethylamine; 8, 3-cyclohexylpropylamine

I_t given by

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

where i_{corr} and i_{corr}^0 are the corrosion currents for the inhibited and uninhibited electrodes, respectively. For both series of amines, I_t increased with an increase in the carbon number of the alkyl group. The phenylalkyl amines were found to be less effective inhibitors than the corresponding cyclohexyl compounds.

It has been reported that aromatic compounds purified only by distillation are better inhibitors than the corresponding compounds subjected to extensive purification⁷. For this reason, recrystallized ω -phenylalkyl ammonium chlorides were used in this experiment. No recrystallization of the chlorides was employed in the purification of the ω -cyclohexylalkyl amines since, as shown in Fig. 1 b, the I_t values of samples of cyclohexylamine purified by distillation were in good agreement with those purified by chloride recrystallization.

4 Discussion

If the values of b_c and b_a are constant, the inhibition effect can be given in terms of cathodic and anodic inhibition efficiencies I_c and I_a as:

$$I_c = 1 - i_c/i_{\text{corr}}^0 \quad (2)$$

$$I_a = 1 - i_a/i_{\text{corr}}^0 \quad (3)$$

where i_c and i_a are the current densities obtained by extrapolating the cathodic and anodic Tafel lines, respectively, at E_{corr}^0 .

The inhibition of the cathodic process by amine inhibitors was assumed to depend on the coulombic adsorption of ammonium cations on the cathode, as has been shown in previous papers^{8,9}. The cathodic inhibition efficiency can then be expressed by

$$I_c/A^+ = \text{const.} \cdot \frac{K_{\text{ads}}}{K_a} [\text{RNH}_3][\text{H}^+][\text{M}] \quad (4)$$

where K_{ads} and K_a are equilibrium constants for the adsorption and dissociation of the ammonium cation, respectively, and A^+ is the molecular coverage area of the cation. A 0.01M cyclohexylamine solution was adopted as the referent for determining the values of I_c at a constant concentration of free amines. The concentration of the other amines (C') at which free amine concentration equals that of

the referent was calculated by

$$C' = 0.01 K_a/K'_a \quad (5)$$

where K_a and K'_a are the dissociation constant for the ammonium cations of cyclohexylamine and of any other amine, respectively. The cathodic inhibition efficiency at C' (I'_c) was obtained by interpolation of the curve of I versus inhibitor concentration (C), but I'_c for aniline was not obtainable because K'_a is extremely large.

Since $[M]$ and $[H^+]$ in eq. (4) are constant I'_c/A^+ should be proportional to $1/K_a$ if K_{ads} is unchanged.

Fig. 2 Relationship between I'_c/A^+ and $1/K_a$

O : $A^+ = A_1^+$, Δ : $A^+ = A_2^+$

A plot of the circles in Fig. 2 indicates this correlation based on the molecular coverage area of the cation in the first orientation mode (A_1^+) (numbers refer to the inhibitors in Table 1). The diagonal line in Fig. 2 shows this correlation, which has been reported for a series of alkyl amines in the previous paper⁹. The plots for ω -cyclohexylalkyl amines were located near the line. On the other hand, the values of I'_c/A_1^+ for ω -phenylalkyl amines were higher than those for the alkyl amines. This indicates that the phenyl group causes the I'_c of aliphatic or alicyclic amines to increase.

Phenylalkyl ammonium ions may be adsorbed on the cathodic surface by means of ionic attraction and by interaction between the metal and the phenyl group.

The value of I'_c/A_2^+ (*i.e.* coverage are in the second mode) for each of the ω -phenylalkyl amines is plotted as a triangle in Fig. 2. The second mode plots for benzylamine and 2-phenylethylamine were also above the diagonal line. This result shows that the phenyl group increases K_{ads} in eq. (4). The amounts by which the values of I'_c/A_2^+ for the phenyl alkyl amines deviated from the values for the alkyl amines shown by the diagonal line in Fig. 2 ($\Delta I'_c/A_2^+$) were measured, and plotted

Fig. 3 Correlation of I'_c/A_2^+ to σ^*_1 (○) and σ^*_2 (△)

in Fig. 3 against σ^*_1 , the polar substituent constant of the ω -phenylalkyl group attached to the nitrogen atoms. The value of $\Delta I'_c/A_2^+$ increased with increases in σ^*_1 and this is similar to the result obtained for olefinic amines in the previous paper⁹). The above correlation indicates that cathodic inhibition efficiency increases with a decrease in electron density of the nitrogen atoms. The increase in the I_c of the phenylalkyl amines cannot, therefore, be attributed to coordination adsorption of the unprotonated amine, but may in part be caused by the reinforced coulombic adsorption of the phenylalkyl ammonium cation on the cathode by an enhanced positive charge due to the inductive effect of the phenyl group¹⁰).

In order to investigate the interaction between the metal and the phenyl group of the cation, $\Delta I'_c/A_2^+$ was also plotted against σ^*_2 , the polar substituent constant of substituents $(-CH_2)_nNH_3^+$ ($n=1-3$) (see Fig. 3). This correlation showed that $\Delta I'_c/A_2^+$ increased with decreasing π -electron density of the phenyl group. It can be

supposed from this correlation that the increase in I_c for the phenylalkyl amines is caused not by the coordination of π -electrons on the phenyl group to the metal orbitals, but by other interactions such as a back-donation of metal electrons to vacant orbitals in the phenyl group.

If the activation energy of the corrosion process is not changed by the adsorption of inhibitors, I_a is expressed approximately by the Hammett-like equation

$$\log (I_a A_o / I_{a0} A) = \rho^* \Sigma \sigma^* + \delta E_s + \alpha \quad (6)$$

where zero subscripts refer to a reference inhibitor, A is the molecular coverage area of free amines, $\Sigma \sigma^*$ and E_s denote the polar and steric substituent constants, respectively, and ρ^* , δ , and α are constants¹¹). The term δE_s is a measure of the steric requirements for the adsorption of inhibitors. Although the values of E_s for some of the substituents in the amines used were unknown, δE_s was neglected in this discussion because the constant δ was taken to be negligible for primary amines¹²). The reference inhibitor was cyclohexylamine.

Fig. 4 Relationship between $\log (I_a A_o / I_{a0} A)$ and $\Sigma \sigma^*$

○ : $A=A_1$, △ : $A=A_2$

The plot of circles in Fig. 4 shows the relationship given by eq. (6), based on the coverage area of the adsorbed free amine in the first orientation mode (A_1). Each circle shows the average value and the error limits of the values of $\log (I_a A_{1,0} / I_{a0} A_1)$ at the four inhibitor concentrations adopted in this experiment (num-

bers refer to the inhibitors in Table 1). A straight line having a slope $\rho^* = -0.584$ (the value obtained for alkyl amines¹³⁾) was drawn so as to intersect the circles for the cyclohexylalkyl amines. Thus, if this line shows the relationship in eq. (6) for the cyclohexylalkyl amines, the values of $\log(I_a A_{1,o}/I_{a0} A_1)$ for the phenylalkyl amines will be larger than those for the amines previously studied. On the assumption that the phenylalkyl amines are adsorbed parallel to the surface, the molecular coverage area in the second orientation mode (A_2) was substituted in eq. (6), and $\log(I_a A_{2,o}/I_{a0} A_2)$ was also plotted against $\Sigma\sigma^*$ (triangles in Fig. 4). The logarithmic values for most of the phenylalkyl amines were larger than those for the cyclohexylalkyl amines. This increment of I_a can be attributed to the increased adsorbability of ω -phenylalkyl amines due to the π -electron interaction between the metal and the phenyl group.

The difference of amount, by which the values of $\log(I_a A_{2,o}/I_{a0} A_2)$ for the phenylalkyl amines deviated from the values for the cyclohexylalkyl amines shown by the diagonal line in Fig. 4, (ϕ_r) was plotted in Fig. 5 against n , the number

Fig. 5 Correlation of ϕ_r to n

of methylene groups in the ω -phenylalkyl group ($C_6H_5(CH_2)_n$). This value decreased with an increase in n , reaching zero at $n=3$. The electron density of the nitrogen atoms in aniline is relatively low compared with those in the cyclohexylalkyl amines because of the resonance effect of the phenyl group. Therefore, the density of delocalized π -electrons in the aniline molecule should be high. The π -electron density tends to decrease with increasing values of n

since the resonance effect of the phenyl group on the electrons of the nitrogen atoms is blocked by the methylene groups. The tendency toward a decrease in the π -electron density can be presumed from the $\Sigma\sigma^*$ values or from the basicity constants of ω -phenylalkyl amines. The difference ϕ_r is thus attributed to reinforced adsorption by virtue of the interaction between the metal and inhibitor molecules using the delocalized π -electrons of the phenylalkyl amines.

Equation (6) can be rewritten using ϕ_r , as

$$\log(I_a A_o/I_{a0} A) = \rho^* \Sigma\sigma^* + \delta E_s + \phi_r + \alpha \quad (7)$$

The reinforced adsorption of allylamine, described in a previous paper¹⁴⁾, may also be related to this term.

5 Conclusion

Most ω -phenylalkyl and ω -cyclohexylalkyl amines inhibited both the cathodic and anodic processes of iron corrosion in a 6.1M HCl solution. It was found that the phenylalkyl ammonium ions are adsorbed on the cathodic surface in the parallel (second) orientation mode by electrostatic attraction and by the interaction between the metal and the phenyl group. The anodic inhibition efficiency showed that the phenylalkyl amine molecules are adsorbed on the anode in the parallel mode by the formation of coordination bonds between the metal and the nitrogen atoms and also between the metal and the resonating molecules. The anodic inhibition efficiency of ω -phenylalkyl amines was expressed as a Hammett-like equation in terms of the effect of the resonance structures on the anodic inhibition efficiency (ϕ_r), the value of which decreased with increases in the number of methylene groups in ω -phenylalkyl amines, becoming zero for 3-phenylpropylamine.

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References:

- 1) H. Kaesche and N. Hackerman, *J. Electrochem. Soc.* **105**, 191 (1958).
- 2) J. Vosta, J. Eliasek and P. Knizek, *Corrosion* **32**, 183 (1976).
- 3) E. Blomgren and J. O'M. Bockris, *J. Phys. Chem.* **63**, 1475 (1959).
- 4) A.I. Altsybeeva, S.Z. Levin and A.P. Dorokov, "Proceedings 3rd European Symposium on Corro-

- sion Inhibitors", p. 501 (1971). Università Degli Studi di Ferrara, Ferrara.
- 5) K. Aramaki and N. Hackerman, *J. Electrochem. Soc.* **115**, 1007 (1968).
 - 6) K. Aramaki, *This Journal* **42**, 75 (1974).
 - 7) R.C. Ayers, Jr. and N. Hackerman, *J. Electrochem. Soc.* **110**, 507 (1963).
 - 8) K. Aramaki, *This Journal* **42**, 566 (1974).
 - 9) K. Aramaki, *ibid.* **44**, 771 (1976).
 - 10) V.P. Grigoryev and O.A. Osipov, "Proceedings 3rd International Congress on Metallic Corrosion" Vol. 2, p. 48 (1966), Swets-Zeitlinger, Amsterdam.
 - 11) K. Aramaki, *This Journal* **41**, 321 (1973).
 - 12) K. Aramaki, *Boshoku Gijutsu* **26**, 297 (1977).
 - 13) K. Aramaki, *This Journal* **41**, 875 (1973).
 - 14) K. Aramaki, *ibid.* **43**, 696 (1975).

E x e r g y

近頃、エネルギーの有効利用との関連で、エクセルギーということばをよく耳にする。エクセルギーとは、熱力学の用語であって、最小作用の原理、最大仕事の原理とまったく同様の物理的意味をもっており、

$$\varepsilon = (H - H_0) - T_0 (S - S_0)$$

によって定義される状態量である。ここで、 H_0 , T_0 , S_0 はおのおのの系が与えられた環境（通常 1 気圧, 25°C）と平衡になったときのエンタルピー, 温度, エントロピーである。最大仕事の原理からわかるように、エクセルギーは系が与えられた状態より環境と平衡となるまでの間に可逆過程においてなし得る最大の仕事量をあらわしている。したがってこの過程の間に不可逆過程が含まれていればそれ以下の有効仕事しか系はなし得ない。この差はしばしばエクセルギー損失と呼ばれる。エクセルギー損失はエントロピー生成によって表わすことができる。すなわち、上式の微分をとると

$$d\varepsilon = dH - T_0 dS$$

エントロピー変化をエントロピー流とエントロピー生成に分けて、 $dS = d_e S - d_i S$ と表記すれば、

$$d\varepsilon = dH - T_0 d_e S - T_0 d_i S$$

すなわち、不可逆過程が含まれているとき、 $T_0 d_i S$ がエクセルギー損失となる。このエントロピー生成は系が環境と平衡にない任意の温度におけるものであり、そのためのエクセルギー損失は $T d_i S$ ではなく $T_0 d_i S$ と環境との関連で定義されることに注意していただきたい。

(S Y)