Technical Paper

Effect of Steric Hindrances on Corrosion Inhibition Effectiveness of Piperidine Derivatives*

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Effect of steric hindrances of alkyl substituents on inhibition effectiveness of organic inhibitor for acid corrosion of iron was studied. Piperidine derivatives with methyl or ethyl substituents were used as inhibitors. Corrosion rates of 99.89% iron in 6.1 M HCl solution with and without the inhibitor at 30°C were determined by polarization measurements. Inhibition efficiencies calculated from the corrosion rates were discussed by using polarization data, base strengths, molecular coverage areas, and some substituent constants of the inhibitors. Inhibition effect of the inhibitor at a constant free amine concentration on cathodic partial reaction is linearly related to the reciprocal of dissociation constant of piperidinium cation. The molecular coverage area and steric interaction of the substituent are hardly related to the cathodic inhibition efficiency of the inhibitor. The relationship of the molecular coverage area and the polar and steric substituent constants in the Ingold-Taft equation to the anodic inhibition efficiency was established. Steric effect of substituents at 2 and 6-position on the chemisorption of inhibitor results in marked decrease of the anodic inhibition effectiveness. Steric influence of substituents at 3 and 5-position on close packing of the adsorbed inhibitor on metal may be of some importance to the decreasing anodic efficiency.

1 Introduction

Steric influences of branch groups in hydrocarbon ring of organic corrosion inhibitors on their inhibition effectiveness were studied. Two kinds of the steric effects of alkyl branches on the inhibition can be considered: one is the steric hindrance of the branches to adsorption of the inhibitor on metal surface and the other the hindrance to close packing of adsorbed inhibitor molecules¹⁾. In the previous paper²⁾, effect of the steric requirements of alkyl substituents on inhibition efficiencies of *N*-alkylpiperidines and pyrrolidines for iron corrosion in hydrochloric acid solution has been studied.

The steric interaction of alkyl branch attached to nitrogen atom in cyclic imines is responsible for difficulty in the adsorption of these imines on anodic parts, resulting in the decrease of anodic inhibition efficiency.

This study was undertaken to investigate the effect of steric hindrances of alkyl substituents attached to ring carbon on inhibition efficiencies of substituted piperidines for corrosion of iron in HCl solution. Since the steric influence is dependent on number, structure, and position of branches³⁾, piperidines with

methyl or ethyl substituents were used as inhibitors. Rigid conformation of piperidine ring may help this study.

Corrosion rates of iron in 6.1 M HCl solution inhibited with the piperidine derivatives were measured by polarization technique. Inhibition effects of these piperidines on cathodic and anodic partial reactions,

were obtained from the polarization data, assuming constant Tafel slopes as have been reported by Kaesche and Hackerman⁴⁾.

The data were discussed on the basis of the concept of general adsorption⁵⁾ and by using base strengths, molecular coverage areas, and some substituent parameters of the inhibitors. An equation derived from the Ingold-Taft equation⁶⁾ was adopted in order to explain the steric effect of substituents on the efficiency of piperidines.

2 Experimental

2.1 Inhibitors

Piperidine, 2-methylpiperidine, 3-methylpiperidine, 4-methylpiperidine, and 2,2,6,6-tetramethylpiperidine were obtained as high grade commercial reagents, and 2,6-dimethylpiperidine, 3,5-dimethylpiperidine, 2,4,6-trimethylpiperidine, 2-ethylpiperidine, 3-ethylpiperidine, and 4-ethylpiperidine were synthesized by cataly-

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tic hydrogenation of the corresponding alkylpyridines. No separation of conformational isomers was tried for di- or tri-methylated compounds. These were carefully purified by fractional distillation before use.

These piperidine derivatives were dissolved in 6.1 M HCl solution prepared by diluting reagent grade concentrated HCl solution with redistilled water.

2.2 Polarization measurement

Corrosion rates of pure iron wire (99.89%*, Mallinckrodt analytical reagent grade, 0.36 mm diameter) were determined in 6.1 M HCl solution with and without the inhibitor at 30°C by polarization measurement. Polarization was carried out galvanostatically by supplying current with a coiled Pt wire, a 90 V battery, and high resistors. Potential of the iron electrode was followed with a saturated calomel electrode and a Kiethley electrometer.

2.3 Other measurements

In order to estimate approximate area of metal surface which an inhibitor molecule would effectively cover, molecular coverage area was determined by using Stuart molecular models. Chair conformation of piperidine ring and equatorial conformation of unshared electrons were employed. Details of the measurement were given in the previous paper¹⁾.

Base strengths of the inhibitors were determined by titration with HClO_4 in water at 30°C. Densities of some inhibitors were also measured with a small pycnometer at 24°C.

3 Results

Corrosion current i_{corr} and corrosion potential E_{corr} were obtained by the intersection of extrapolated anodic and cathodic Tafel lines. The results of i_{corr} were reproducible within the error less than $\pm 4\%$. Total inhibition efficiency I_t is defined as

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

where i_{corr} and i_{corr}^0 are the corrosion current for inhibited and uninhibited electrode. Figs. 1 and 2 are the plots of I_t against the inhibitor concentration.

Substituted piperidines at 4-position of the ring are better inhibitors than unsubstituted piperidine. However, all other substituted piperidines at 2,3,5, or 6-position are less effective than the unsubstituted.

The E_{corr} values for the inhibited electrode shifts toward less noble potential within 40 mV than the corrosion potential for the uninhibited electrode E_{corr}^0 . The cathodic and anodic Tafel slopes b_c and b_a are slightly larger in many cases than those of the uninhibited electrode. However, no significant relation of the b_c and b_a values to the inhibition efficiencies of the inhibitors was found. In order to

Fig. 1 Total inhibition efficiency I_t of piperidine inhibitors (1)

- 1: Piperidine, 2: 2-methylpiperidine
3: 3-methylpiperidine, 4: 4-methylpiperidine
9: 2-ethylpiperidine, 10: 3-ethylpiperidine
11: 4-ethylpiperidine

Fig. 2 Total inhibition efficiency I_t of piperidine inhibitors (2)

- 5: 2,6-dimethylpiperidine, 6: 3,5-dimethylpiperidine, 7: 2,4,6-trimethylpiperidine
8: 2,2,6,6-tetramethylpiperidine

estimate the inhibition effect on the cathodic and anodic partial reactions, cathodic and anodic partial current of the inhibited electrode i_c and i_a were graphically obtained from current values of extrapolated Tafel lines at E_{corr} . Polarization curves indicate that these piperidine derivatives are rather cathodic inhibitors than anodic. This agrees with the polarization data for other normalized cyclic amines^{2,3)}.

Molecular coverage areas of protonated piperidinium

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

cation and of unprotonated piperidine molecule, and pK_a values are listed in Table I. Because of free orientation of the cation adsorbed on metal surface, the maximum and minimum areas are shown in the table.

Table 1 Base strength, maximum and minimum molecular coverage area of piperidinium cation $A^+_{\max}$ and $A^+_{\min}$, and molecular coverage area of piperidine A

No.	Piperidine	pK_a	$A^+_{\max}$ ($\text{\AA}^2$)	$A^+_{\min}$ ($\text{\AA}^2$)	A ($\text{\AA}^2$)
1	Piperidine	11.21	75	34	42
2	2-methyl	11.12	75	62	67
3	3-methyl	11.19	108	47	73
4	4-methyl	11.11	117	34	53
5	2,6-dimethyl	11.02	75	62	67
6	3,5-dimethyl	11.07	108	62	73
7	2,4,6-trimethyl	10.98	117	62	67
8	2,2,6,6-tetramethyl	10.85	75	62	62
9	2-ethyl	10.93	122	88	95
10	3-ethyl	11.03	155	49	88
11	4-ethyl	11.09	189	34	69

Because of the steric hindrance of the branches to the adsorption, in some cases, there is difficulty in formation of the coordination bond between nitrogen atom of unprotonated inhibitor molecule and metal. Extent of this difficulty can be estimated by means of observation in the model arranging experiment. No steric influence of the substituents at 3, 4, or 5 position of piperidine ring on the adsorption was observed. The results suggested steric effect of alkyl substituents at 2 and 6-position on the chemisorption of piperidine derivatives on iron surface.

4 Discussion

In order to discuss the effect of steric requirements on the inhibitor action of piperidines, the efficiencies at 0.01 and 0.1 M of the concentration were employed. Because of no significant difference in the Tafel slopes, no discussion on the inhibition behavior was tried with these values. As have previously been given^{2),4)}, on the assumption of constant b_c and b_a for the inhibited and uninhibited electrode (e.g., $b_c = 150 \pm 7 \text{ mV/log } i$ and $b_a = 110 \pm 3 \text{ mV/log } i$), cathodic and anodic inhibition efficiencies I_c and I_a were obtained by

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

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

Since i_c/i_{corr}^0 and i_a/i_{corr}^0 should be in agreement approximately with the ratios of cathodic and anodic exchange currents for the inhibited electrode to those for the uninhibited electrode, I_c and I_a indicate the

inhibition efficiencies for cathodic and anodic partial reaction⁴⁾.

Piperidine is protonated in acid solution,

and then adsorbed on the cathodic electrode through electrostatic attraction,

Equilibrium constant for the adsorption of piperidinium cation, K_{ads} is expressed by

$$K_{\text{ads}} = \frac{[\text{C}_5\text{H}_{10}\text{NH}_2^+_{\text{ads}}]}{[\text{C}_5\text{H}_{10}\text{NH}_2^+][\text{M}^-]} \quad (4)$$

The concentration of adsorbed cation on the metal surface $[\text{C}_5\text{H}_{10}\text{NH}_2^+_{\text{ads}}]$ can be written by using the dissociation constant of $\text{C}_5\text{H}_{10}\text{NH}_2^+$, K_a as

$$[\text{C}_5\text{H}_{10}\text{NH}_2^+_{\text{ads}}] = \frac{K_{\text{ads}}}{K_a} \cdot [\text{M}^-][\text{C}_5\text{H}_{10}\text{NH}][\text{H}^+] \quad (5)$$

Since the surface concentration corresponds to the inhibition efficiency, a linear relationship between I_c and $1/K_a$ is expected at a constant free amine concentration, where the I_c values obtained by interpolation from I_c vs. inhibitor concentration curve. As references, 0.01 and 0.1 M of piperidine were adopted for determining the constant free amine concentration which can be calculated from the K_a value. The value $[\text{M}^-]$ is presumed to be constant because the I_c value was determined with the current at E_{corr}^0 which is constant in the φ scale potential⁹⁾. Fig. 3 shows the linear correlation between I_c and $1/K_a$.

Fig. 3 Relationship of cathodic inhibition efficiency I_c at constant free amine concentration to $1/K_a$

Number indicates the inhibitor number shown in Table 1.

A: at 0.01 M, B: at 0.1 M of piperidine concentration as the reference

This correlation indicates that the molecular coverage areas of inhibitors are of no importance to the cathodic inhibition efficiency. However, points for 4-methyl- and 4-ethylpiperidine (No. 4 and 11) deviate from the straight lines. No reasonable explanation of these deviations is successful from the consideration of the maximum and minimum molecular coverage area of protonated piperidine. Little influence of the area on I_c is in marked contrast to enhanced effect of the area on I_a shown later. As piperidinium cation is highly hydrated, the inhibition may be independent of size and configuration of the inhibitor molecule. No influence of the steric interaction on the inhibition effect of piperidines on the cathodic partial reaction is thus concluded.

Hall¹⁰⁾ has reported that steric hindrances of methyl substituents at 2 and 6-position in piperidine ring to reaction of piperidine with proton can be neglected. Base strengths of 2,6-substituted pyridines decrease with increase in steric requirements of the reference acid in the order, $H^+ > BH_3 > BF_3 > B(CH_3)_3$ ¹¹⁾.

These indicate that the steric interactions between bulky acids and 2,6-alkyl-substituted cyclic bases are important to the formation of coordinate bond. Iron surface acts as a bulky acid in the donor-acceptor reaction during the chemisorption process of inhibitor. Therefore, the steric hindrances of alkyl substituents to the adsorption of the inhibitor by coordination may occur while the steric effect is not important of the cationic adsorption.

The I_a values for piperidines in question would be related to the basicities, the molecular coverage areas, and the steric requirements of substituents. According to linear free energy relationships, rate constant or equilibrium constant of organic reaction process for unsubstituted and meta or para-substituted benzenoid compounds is given as the Hammett equation¹²⁾ by

$$\log k/k_0 \text{ or } \log K/K_0 = \rho\sigma \quad (6)$$

where k'_s are rate constants, K'_s are equilibrium constants, the zero subscripts refer to the unsubstituted compound, and ρ and σ are the reaction and substituent (Hammett) constants. In corrosion inhibition process, equation (7) is derived on the assumption that the activation energy of corrosion reaction does not change by the adsorbed inhibitor^{13), 14)}.

$$\log \frac{I(1-I_0)}{I_0(1-I)} = \rho\sigma \quad (7)$$

where I and I_0 are inhibition efficiencies of the substituted and unsubstituted inhibitor.

In the case of aliphatic or alicyclic compounds, equation (6) is given as the Ingold-Taft equation¹⁵⁾ by

$$\log k/k_0 \text{ or } \log K/K_0 = \rho^*\sigma^* + E_s \quad (3)$$

where ρ^* and σ^* mean the reaction and polar substituent (Taft) constants, and E_s is the steric substituent constant. Hence, equations (6), (7), and (8) lead to

$$\log \frac{I(1-I_0)}{I_0(1-I)} = \rho^*\sigma^* + E_s \quad (9)$$

Linear correlations of $\log I/(1-I)$ to the Hammett constant have been reported in many papers¹³⁾⁻²¹⁾. However, no complete relationship on equation (9) seems to be established. Donahue and Nobe¹³⁾ have shown linear relations of $\log(1-I)$ to σ^* for *N*-alkyl anilines and aliphatic primary amines. No linear relation between $\log I/(1-I)$ and σ^* for aliphatic amines and *N*-alkyl anilines has, however, been reported by Altsybueva, Dorokhov, and Levin^{21), 22)}. A linear relationship of $\log(1-I)$ at maximum inhibition to the E_s value for alkyl mercaptans and sulfides has been established by Brandt, Fischer, and Schwabe²³⁾. Some correlations of the Taft constant to values related to corrosion inhibition processes have further be confirmed^{24), 25)}.

Assuming that the I value increases linearly with the molecular coverage area $A^{26)}$, I and I_0 are re-

Table 2 Polar and steric substituent constant $\Sigma\sigma^*$ and ΣE_s , steric substituent constant calculated with equation (11) $\Sigma E'_s$, and density of piperidine derivatives

No.	Piperidine	$-\Sigma\sigma^*$	ΣE_s	$\Sigma E'_s$ (0.01 M)	$\Sigma E'_s$ (0.1 M)	Density at $t^\circ\text{C}$
1	Piperidine	-0.35	0	0	0	0.8606 ^{20a}
2	2-methyl	-0.25	-0.40	-0.86	-0.85	0.8436 ^{24a}
3	3-methyl	-0.33	-0.57	-0.39	-0.28	0.8446 ^{24a}
4	4-methyl	-0.34	0.04	-0.12	-0.01	0.8583 ^{24b}
5	2,6-dimethyl	-0.15	-0.80	-1.50	-1.44	0.8158 ^{25a}
6	3,5-dimethyl	-0.31	-1.14	-0.47	-0.32	0.8203 ^{24b}
7	2,4,6-trimethyl	-0.14	-0.76	-1.47	-1.36	0.8315 ^{19a}
8	2,2,6,6-tetramethyl	0.05	-2.94	-2.83	-2.77	0.8367 ^{16a}
9	2-ethyl	-0.235	-1.06	-1.10	-1.04	0.8557 ^{24b}
10	3-ethyl	-0.315	-1.23	-0.58	-0.48	0.8563 ^{23a}
11	4-ethyl	-0.33	-0.62	-0.21	-0.10	0.8652 ^{24b}

a: I. Heilbron et al. ed., "Dictionary of Organic Compounds", (1965), Maruzen Co. Tokyo.

b: Present investigation.

placed with I/A and I_0/A_0 as

$$\log \frac{I(A_0 - I_0)}{I_0(A - I)} = \rho^* \sigma^* + E_s \quad (10)$$

If A and $A_0 \gg I$ and I_0 ,

$$\log \frac{A_0 I}{A I_0} \approx \rho^* \sigma^* + E_s \quad (11)$$

Exact values of the Taft and steric substituent constants for the piperidine derivatives except piperidine²⁷⁾ are not available but the approximate values of substituents can be calculated from the constants of analogous alkyl groups²⁾. These constants of substituents are summed as $\Sigma\sigma^*$ and ΣE_s for each inhibitor. They are shown in Table 2. The ΣE_s values for substituted piperidines at 3, 4, or 5-position seem erroneous because the values are obtained from those of alkyl groups which are more flexible than piperidine ring.

Substituting I_a and I_{a0} for I and I_0 in equation (11), Fig. 4 shows the correlation of $\log A_0 I_a / A I_{a0} - \Sigma E_s$ to $\Sigma\sigma^*$ at 0.01 M of the inhibitor concentration. Points for 2,6-substituted piperidines are arranged on a straight line with a slope $\rho^* = -5.9$. The similar result was obtained from the I_a data at 0.1 M with $\rho^* = -5.8$. The $-\Sigma\sigma^*$ value, which corresponds to the electron density at nitrogen atom of the inhibitor, is responsible for ability of chemical adsorption on metal. Therefore, these minus values of ρ^* 's are quite reasonable because I_a increases with decreasing $\Sigma\sigma^*$.

Fig. 4 Relationship of $\log A_0 I_a / A I_{a0} - \Sigma E_s$ to $-\Sigma\sigma^*$

Number indicates the inhibitor number shown in Table 1.

The relationship of the anodic inhibition efficiency to the polar and steric substituent constants on the basis of the Ingold-Taft equation was thus established for alkyl substituents at 2 and 6-position of piperidine ring. Because the adopted ΣE_s values of substituents at 3, 4, or 5-position are supposed to be lower than the expected values, the points of 3, 4, or 5-substituted piperidines are deviated from the line. If corrections of the E_s values are made for the effect of flexible conformation, this relationship may be established for all piperidines investigated. From this result it follows that the ΣE_s value relates to the I_a value, which implies the steric hindrance of substituents to the adsorption process of the inhibitor on anodic parts of metal. Therefore, the coordination reaction between nitrogen atom and bulky metal surface is influenced by the steric requirements of alkyl substituents located near to nitrogen atom.

In order to investigate relationship between the steric effect and the I_a values of 3, 4, or 5-substituted piperidines, the ΣE_s values of piperidine derivatives were calculated with equation (11) using $\rho^* = -5.9$ and $\Sigma E_s = 0$ for unsubstituted piperidine as a reference. These values $\Sigma E_s'$ at 0.01 and 0.1 M of the inhibitor concentration, also shown in Table 2, can be considered to be a measure of the steric influences of substituents on the adsorption of piperidines on the anodic surface. The $\Sigma E_s'$ value for 3, 4, or 5-substituted piperidine is higher than ΣE_s of each inhibitor. According to this result, with regard to the substituents at 3, 4, or 5-position of the rigid ring, the steric effect on the adsorption of piperidines on the anodic electrode is weaker than the effect presumed from the data of flexible alkyl group. There is little steric interaction of the substituent at 4-position but the some hindrance at 3 and 5-position. Recall the difficulty in the chemical adsorption of inhibitors. The adsorption difficulty for 2 and 6-substituted piperidine agrees well with the result of E_s' value. No difficulty in the adsorption of 3 and 5-substituted piperidine can be observed in the model arranging experiment, however.

The molecular coverage area of 3 and 5-substituted piperidine is larger than that of corresponding 2 and 6- or 4-substituted piperidine as shown in Table 1. This is due to possibility of far extending alkyl branch at 3 and 5-position from metal-nitrogen linkage. Therefore, packing in adsorbed layer of the 3 and 5-substituted piperidine molecule on the anode surface may be supposed to be less close as compared with that of other piperidine. This can be considered from the densities of piperidines shown in Table 2. The values of 3-methyl and 3-ethylpiperidine are smaller than those of the corresponding 4-substituted

ones. This means closer packing of 4-substituted piperidine liquid than that of 3-substituted one. Formation of the loose packing for 3-substituted piperidine molecule may be caused by disorder of molecular arrangement. From these arguments, the steric influence of substituents at 3 and 5-position on the close packing of the inhibitor adsorbed on metal may be related to the anodic inhibition efficiency.

The loose packing of adsorbed inhibitor molecules results in depression of intermolecular interaction between hydrocarbon groups of adjacent molecules²⁸⁾. To confirm the effect of the steric requirements of substituents on this interaction of liquid molecules, boiling points of these inhibitors were compared. Since the boiling point of monoalkylpiperidine changes in the order,

2-alkyl- < 3-alkyl- < 4-alkylpiperidine,

this interaction seems to be depressed with increase in the steric influence of substituent from 4 to 2-position. It may be concluded that the steric hindrances of substituents at 2 and 3-position to the close arrangement of adsorbed piperidines on metal cause the decrease of anodic inhibition efficiency.

5 Conclusion

The cathodic inhibition efficiency of substituted piperidine for iron corrosion in 6.1 M HCl solution is closely related to the dissociation constant of the piperidine. Little relationship of the molecular coverage area and the steric requirements of substituents to the cathodic inhibition efficiency was observed.

The correlation of the molecular coverage area, the polar substituent constant, and the steric substituent constant of the inhibitor to the anodic inhibition efficiency was established. The steric hindrances of substituents at 2 and 6-position to the adsorption of piperidines by formation of coordinate bond between metal and nitrogen atom give rise to the decrease of anodic inhibition efficiency, and moreover the steric influence of substituents at 3 and 5-position on the packing closeness of the adsorbed inhibitors on the anode surface may be the cause of decreasing anodic

inhibition efficiency.

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