Technical Paper

Inhibition Effect of *N*-Substituted Cyclic Imines on Iron Corrosion*

Kunitsugu ARAMAKI*

Effect of molecular structure on inhibition effectiveness of normal sized polymethyleneimines and their *N*-substituted derivatives was studied. Piperidine, pyrrolidine, quinuclidine, and their *N*-alkyl derivatives were used as inhibitors for iron corrosion in HCl solution. Corrosion rates were determined by galvanostatic polarization measurement. Results were discussed on the basis of the general adsorption behavior and by using the polarization data, base strength, molecular coverage measured with molecular models, and conformation of the inhibitor. For most of cyclic imines investigated the inhibition effect on cathodic partial reaction is greater than on anodic partial reaction. Cathodic inhibition effect is dependent on the base strength, but independent of the molecular coverage. Anodic inhibition effect depends on the base strength, the molecular coverage, and the conformation of cyclic imine. The conformation study of the inhibitor molecule adsorbed on metal surface indicates that adsorption difficulty due to steric hindrance of alkyl branch is of importance to the anode inhibition. Quinuclidine is effective in inhibiting both cathodic and anodic partial reaction without the influence of steric hindrance on the adsorption.

1 Introduction

Structure effect of cyclic polymethyleneimines, $(\text{CH}_2)_n\text{NH}$ containing 2 to 14 methylene groups on their inhibition efficiencies for iron corrosion in HCl solution has been studied¹⁻⁴. The high efficiency of small ($n=2-3$) and medium ($n=8-11$) sized imines has been concluded to be closely related to strain in imine ring.

In this study, structure effect of normal sized polymethyleneimines and their *N*-substituted derivatives on corrosion inhibition was studied. Piperidine ($n=5$), *N*-alkylpiperidines, pyrrolidine ($n=4$), *N*-alkylpyrrolidines, and ring-bridged quinuclidine, $\begin{array}{c} \text{CH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CHCH}_2\text{CH}_2\text{N} \\ \diagdown \quad \diagup \\ \text{CH}_2\text{CH}_2 \end{array}$ were used as inhibitors. Since there is little or no strain in their rings⁵, effect of the ring strain on their efficiencies seems to be of no importance. However, the presence of alkyl group attached to nitrogen atom of *N*-substituted cyclic imine may provide a possibility of strain caused by repulsion of hydrogen atoms in the imine molecule. Because of steric hindrance to adsorption of inhibitors on metal surface⁶, crowded conformation of some *N*-alkyl im-

ines with hydrogen atoms around nitrogen is presumed to play an important role in the corrosion inhibition effectiveness. Rigid conformations of piperidine and quinuclidine ring can help the study of these structural effects.

Corrosion rate of pure iron was determined in 6.1 M HCl solution at 30°C by galvanostatic polarization measurement. Inhibition effects of these imines on cathodic and anodic partial reactions,

were obtained from cathodic and anodic polarization curves. These data were discussed on the basis of concept of the general adsorption⁷. The imine inhibitor is, according to the concept, adsorbed on metal not only by means of electrostatic attraction between metal and ammonium cation but also by the formation of metal-nitrogen coordinated bond. The strong cationic adsorption should favor the inhibition effect on cathodic reaction. Establishment of the coordinated bond between metal and deionized imine should be advantageous for the inhibition of anodic reaction. These results were interpreted by using data of base strength, area of metal surface effectively covered with an inhibitor molecule, and molecular conformation of the inhibitor.

2 Experimental

2.1 Inhibitors

N-methylpiperidine, *N*-ethylpiperidine, *N*-*n*-propyl-

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** Department of Engineering, Keio University at Hiyoshi (Hiyoshi, Yokohama)

piperidine, *N*-isopropylpiperidine, *N*-*t*-butylpiperidine, *N*-methylpyrrolidine, and *N*-ethylpyrrolidine were synthesized by the reaction of piperidine or pyrrolidine with the corresponding alkyl halide. Because of being unstable, *N*-*t*-butylpiperidine was prepared as hydrochloride. Piperidine, pyrrolidine, and quinuclidine hydrochloride were obtained as high grade commercial reagents. These were carefully purified by distillation or by recrystallization.

These inhibitors were dissolved in 6.1 *M* HCl solution which was prepared by diluting reagent grade concentrated HCl solution with redistilled water.

2.2 Polarization measurement

Pure iron wire (99.89%*¹ Mallinckrodt analytical reagent grade, 0.36 mm diameter) was fixed at an end of glass tubing with a Teflon joint and cut to a given length. This electrode assembly was washed with *n*-hexane, immersed in phosphoric acid solution for 1 min, carefully rinsed with water, washed with pure acetone, and dried in a vacuum desiccator. The assembly was then set in a small glass cell containing 6.1 *M* HCl solution deaerated with nitrogen gas.

Polarization was carried out galvanostatically by using a 90 V battery, high variable resistors, and a platinum counter electrode. Potential was measured with a saturated calomel electrode and an electrometer.

2.3 Molecular coverage determination

For estimating the approximate area of metal surface which the inhibitor molecule would effectively cover in adsorbed position, the area was measured with Stuart molecular models, as in the previous paper². Two kinds of the molecular structures of the inhibitor were applied; one is of ammonium cation and the other of free imine. The former is adsorbed on metal by means of the electrostatic attraction and the latter by the formation of coordinated bond between metal and nitrogen atom. Molecular models of the inhibitor corresponding to each of these structures were arranged on a plane in the adsorbed position. The metal-nitrogen bond was assumed to be perpendicular to metal surface. Chair conformation for piperidine ring, boat conformation for quinuclidine ring, and planar conformation for pyrrolidine ring were used. The models were projected on the plane and the distance from the metal-nitrogen bond to the most extreme portion of molecule was measured. The adsorbed molecule was assumed to be free to rotate on the metal-nitrogen bond as an axis, and area of circle was calculated with this distance as a radius. The molecular coverage was given by calculation of the area into square angstrom unit.

Since there are many possible shapes of ammonium

cation adsorbed on metal surface, the maximum and minimum values for each of the inhibitors were determined.

2.4 Basicity measurement

The approximate pK_a values for some inhibitors were determined by titration with HClO_4 in water at 25°C. The pH value was followed with a glass electrode and a pH meter.

3 Results

Anodic and cathodic polarization curves showed well-defined Tafel regions as in Fig. 1. The corrosion current, i_{corr} and the corrosion potential, E_{corr} were given by the intersection of extrapolated anodic and cathodic Tafel lines. The i_{corr} values for the several runs at a given inhibitor concentration were reproducible with a maximum deviation of $\pm 4\%$. Fig. 2 shows the total inhibition efficiency, I_t which is defined as

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

where i_{corr} and i_{corr}^0 are the corrosion currents for inhibited and uninhibited electrode.

Pyrrolidine and its *N*-substituted derivatives are better inhibitors than piperidine and the corresponding *N*-substituted piperidines. Orders of I_t in the homologous series of cyclic imines used are

piperidine > *N*-methylpiperidine < *N*-ethylpiperidine < *N*-*n*-propylpiperidine,
N-ethylpiperidine > *N*-isopropylpiperidine
 > *N*-*t*-butylpiperidine,

and

Uninhibited (A) and inhibited with piperidine (B), *N*-*t*-butylpiperidine (C) and quinuclidine (D) at 0.01 *M*

Fig. 1 Polarization curves of iron electrode in 6.1 *M* HCl solution at 30°C

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

1. piperidine; 2. *N*-methylpiperidine
3. *N*-ethylpiperidine; 4. *N*-*n*-propylpiperidine; 5. *N*-isopropylpiperidine
6. *N*-*t*-butylpiperidine; 7. quinuclidine
8. pyrrolidine; 9. *N*-methylpyrrolidine
10. *N*-ethylpyrrolidine

Fig. 2 Total inhibition efficiency I_t of the cyclic imine inhibitors

pyrrolidine > *N*-methylpyrrolidine < *N*-ethylpyrrolidine.

Table 1 indicates E_{corr} and absolute values of cathodic and anodic Tafel slopes, b_c and b_a at 0.01 *M* of the inhibitor concentration. The E_{corr} values for inhibited electrode shifted toward less noble potential within 40 mV than the corrosion potential for uninhibited electrode, E_{corr}^0 . The b_c and b_a values of inhibited electrode are a little larger in many cases than those of uninhibited electrode, b_c^0 and b_a^0 .

In order to estimate the inhibition effect on the cathodic and anodic partial reactions, as have been shown by Kaesche and Hackerman⁹⁾, cathodic and anodic partial currents of the inhibited electrode, i_c and i_a were graphically obtained from the current values of the extrapolated Tafel lines at E_{corr}^0 . These values at 0.01 *M* of the concentration were also tabulated in Table 1. In most cases i_c of each inhibitor corresponds well to i_{corr} while i_a does not.

Table 2 shows the maximum and minimum molecular coverage of ammonium cation, A^+_{max} and A^+_{min} , the molecular coverage of free imine, *A*, and the pK_a value.

The actual shape of pyrrolidine ring is not planar but puckered because of bond opposition strain of hydrogen atoms. Since the ring members of pyrroli-

Table 1 Corrosion potential E_{corr} , cathodic and anodic Tafel slope b_c and b_a , and cathodic and anodic partial current i_c and i_a at 0.01 *M* of the inhibitor concentration

No.	Inhibitor	E_{corr} (mV)	b_c (mV/ log <i>i</i>)	b_a (mV/ log <i>i</i>)	i_c (mA/ cm ²)	i_a (mA/ cm ²)
	None	-467	153	110	—	—
1	Piperidine	-488	155	112	0.308	0.700
2	<i>N</i> -methylpiperidine	-478	155	115	0.500	0.832
3	<i>N</i> -ethylpiperidine	-500	155	112	0.356	0.836
4	<i>N</i> - <i>n</i> -propylpiperidine	-488	162	109	0.332	0.652
5	<i>N</i> -isopropylpiperidine	-496	153	114	0.399	0.992
6	<i>N</i> - <i>t</i> -butylpiperidine	-479	154	110	0.668	1.048
7	Quinuclidine	-478	153	112	0.368	0.560
8	Pyrrolidine	-493	154	109	0.300	0.704
9	<i>N</i> -methylpyrrolidine	-476	162	113	0.380	0.736
10	<i>N</i> -ethylpyrrolidine	-484	153	112	0.340	0.612

Table 2 Maximum and minimum molecular coverage of ammonium cation A^+_{max} and A^+_{min} , molecular coverage of imine *A*, and pK_a

No.	Inhibitor	A^+_{max} (Å ²)	A^+_{min} (Å ²)	<i>A</i> (Å ²)	pK_a
1	Piperidine	74.8	34.2	42.1	11.22 ^a
2	<i>N</i> -methylpiperidine	74.8	34.2	42.1	10.08 ^a
3	<i>N</i> -ethylpiperidine	74.8	34.2	60.6	10.41 ^b
4	<i>N</i> - <i>n</i> -propylpiperidine	114.4	34.2	102.4	10.47
5	<i>N</i> -isopropylpiperidine	74.8	34.2	60.4	10.34
6	<i>N</i> - <i>t</i> -butylpiperidine	74.8	34.2	—	—
7	Quinuclidine	74.8	34.0	34.0	10.58 ^c
8	Pyrrolidine	53.8	29.0	53.8	11.29 ^a
9	<i>N</i> -methylpyrrolidine	53.8	29.0	53.8	10.46 ^a
10	<i>N</i> -ethylpyrrolidine	74.7	29.0	68.8	10.74

a) S. Searles, M. Tamres, F. Block, L.A. Quarterman, *J. Amer. Chem. Soc.* **78**, 4917 (1956).

b) N.F. Hall, M.R. Sprinkle, *ibid.* **54**, 3469 (1932).

c) B.M. Wepster, *Rec. trav. chim.* **71**, 1159 (1952).

dine move up and down to the average plane of the ring⁹⁾, however, the planar conformation was applied to this study. The molecular models of *N*-*t*-butylpiperidine cannot be arranged on the metal plane in the configuration corresponding to the form of molecule adsorbed on metal by coordination because of the steric hindrance of *t*-butyl radical. Therefore, no *A* value of *N*-*t*-butylpiperidine is shown in the table. There is little difference in A^+_{min} for all the inhibitors investigated.

The pK_a value of *N*-*t*-butylpiperidine is not given

here, but seems near 10 from the consideration of basicity data of *t*-butylamine derivatives.

4 Discussion

In order to elucidate the inhibition mechanism of these cyclic imines, the inhibition efficiencies were compared. As a typical inhibitor effectiveness, I_t at 0.01 *M* of the concentration was employed. The I_t values at this concentration would be interpreted through rather simple consideration with the polarization data, the base strength, the molecular coverage, and the molecular conformation, because the values are not maximum but medium for each of the inhibitors studied. More complicated discussion including lateral interaction between adsorbed molecules¹⁰ and multiple-layer adsorption would be necessary for explanation of the maximum I_t values.

Normally the I_t value increases with increase in the pK_a value. No simple correlation of I_t to any of the molecular coverages is indicated however. The result suggests an importance of the base strength to the effectiveness of these inhibitors. Discussion of polarization data should be needed for more detailed interpretation of I_t values.

Greater inhibition effect of piperidine and pyrrolidine on the cathodic polarization curve than the effect on the anodic curve has been observed in the previous study¹. Most of the cyclic imines investigated are rather cathodic inhibitors except quinuclidine as some typical curves shown in Fig. 1. The effect of quinuclidine on the anodic polarization curve is comparable to the effect on the cathodic curve, as Laengle and Hackerman have reported¹¹.

The anodic polarization curves of iron electrode inhibited with *N*-*t*-butylpiperidine in 12 runs carried out at less than 0.03 *M* of the concentration are consistent with those of uninhibited electrode with potential deviation within 5 mV. This result means no inhibition effect of *N*-*t*-butylpiperidine on anodic partial reaction. The fact agrees with the result that the impossibility of adsorption for *N*-*t*-butylpiperidine on anode by the formation of coordinated bond was confirmed in the model arranging experiment.

As b_c and b_a are larger than b_c° and b_a° , most of the inhibitors investigated exhibit both cathodic and anodic inhibitor action. Because of small values of $\Delta b_c (=b_c - b_c^\circ)$ and $\Delta b_a (=b_a - b_a^\circ)$, no further amplification of the values was tried. Instead, with the assumption of constant b_c and b_a for the inhibited and uninhibited electrode, the inhibition efficiencies for cathodic and anodic partial reaction, I_c and I_a which are given as

$$I_c = 1 - i_c/i_{c,corr}$$

$$I_a = 1 - i^\circ_{corr}$$

were calculated.

Fig. 3 shows a relationship of I_c or I_a to the pK_a value. A simple correlation between I_c and pK_a indicates an increase of I_c with increasing pK_a . Ammonium cation which is derived from cyclic imine in acid solution is adsorbed on cathode metal and forms a barrier to control the cathodic partial reaction. Therefore, the inhibitor effect of cyclic imine on the cathodic partial reaction may be attributed to stability of ammonium cation. The I_c value depends thus on the base strength.

Number indicates the inhibitor number shown in Table 1 and in Fig. 1

Fig. 3 Relationship of cathodic or anodic inhibition efficiency, I_c (○) or I_a (Δ) to pK_a value

Because of no simple relation of I_c to A^+_{max} or A^+_{min} , the molecular coverage seems to be of no importance to the inhibition effect of these imines on the cathodic reaction. A similar result has been observed in the maximum inhibition effectiveness of aniline derivatives on cathodic reaction⁹. Because of being highly hydrated in bulk solution, adsorbed ammonium cation is supposed to be kept apart from the metal surface. Therefore, the effect of molecular coverage on I_c of cation may be neglected.

The inhibition effectiveness of the imine inhibitors on the anodic partial reaction should be related to the basicity, the molecular coverage, and the conformation of adsorbed molecule. The basicity is considered to be a measure of electron-donating ability for deionized cyclic imines, but the result in Fig. 3 indicates no simple relationship between I_a and pK_a . In order to see the correlation of the I_a value with both pK_a and A , the anodic inhibition per a unit molecular coverage, I_a/A was calculated and plotted against pK_a in Fig. 4. With an assumption of linear relationship of I_a to A , the I_a/A value should be related to the

Number indicates the inhibitor number

Fig. 4 Relationship between I_a/A and pK_a

adsorption ability of the inhibitor on anode metal.

From the observation of molecular conformation for these inhibitors adsorbed on metal by formation of coordinated bond, adsorption of piperidine, *N*-methylpiperidine, pyrrolidine, *N*-methylpyrrolidine, and *N*-ethylpyrrolidine was confirmed to occur readily. Quinuclidine is very easily adsorbed without the influence of steric hindrance. There is some difficulty of the adsorption for *N*-ethylpiperidine and *N*-*n*-propylpiperidine. *N*-isopropylpiperidine and *N*-*t*-butylpiperidine are more difficult and even impossible to be adsorbed on the metal surface.

Fig. 4 indicates a linear relation of I_a/A to pK_a for piperidine, *N*-methylpiperidine, pyrrolidine, *N*-methylpyrrolidine, and *N*-ethylpyrrolidine, increasing I_a/A with increase in pK_a . Since there is no difficulty in the adsorption, this correlation is reasonable. Higher value of I_a/A for quinuclidine placed upper than the straight line exhibits easier adsorption, while lower values for the other imines imply the influence of steric hindrance on the adsorption.

Difference in I_a/A from this line, $\Delta I_a/A$ obtained graphically may be taken to be a measure of the adsorbability under the influence of steric interaction. As shown in Table 3, the values of piperidine derivatives correspond roughly to the steric substituent constant, E_s of the Ingold-Taft equation¹²⁾,

$$\log(k/k_0) = E_s + \rho^* \sigma^*$$

where k and k_0 are the rate constants of alkaline hydrolysis for carboxylic ester, RCOOR' and for standard ester, $\text{CH}_3\text{COOR}'$, σ^* is the polar substituent constant, and ρ^* is a constant 2.48. Since the steric hindrance of radical R to the reaction is related to the E_s value, $\Delta I_a/A$ can be used as the measure of the effect of steric hindrance with alkyl branch of the inhibitor on the anodic adsorption.

Table 3 Effect of steric hindrance $\Delta I_a/A$ and steric substituent constant E_s

Alkyl branch	$\Delta I_a/A \times 10^3$	E_s^*
Piperidine derivatives		
H	+0.9	+1.24
Methyl	-0.1	0
Ethyl	-1.9	-0.07
<i>n</i> -propyl	-1.9	-0.36
Isopropyl	-4.4	-0.47
<i>t</i> -butyl	-4.8**	-1.54
Quinuclidine	+7.9	
Pyrrolidine derivatives		
H	-0.5	
Methyl	+0.1	
Ethyl	0	

* Reference 12

** The pK_a value of *N*-*t*-butylpiperidine was assumed to be 10.

The $\Delta I_a/A$ value of piperidine is higher than that of *N*-alkylpiperidine because of the steric interaction of alkyl branch to the adsorption. Aroney and Le Fèvre¹³⁾ suggested that in the conformation of piperidine hydrogen atom attached to nitrogen atom is axial to the ring and, therefore, unshared electron pair is equatorial. If this implication is correct, piperidine may easily be adsorbed on the anode surface by the formation of metal-nitrogen coordinated bond without the influence of steric hindrance with hydrogen atoms.

In the case of *N*-substituted piperidines, however, alkyl radical is probably equatorial and unshared electrons axial since an unfavorable repulsion between ring and alkyl hydrogen atoms occurs in molecule with the axial radical. When *N*-alkylpiperidine is adsorbed on metal surface, the axial conformation of unshared electrons may be changed to the equatorial, because the equatorial unshared electrons on nitrogen atom favors the formation of coordinated bond with such a bulky electron acceptor as metal surface. Therefore, the equatorial unshared electrons of piperidine may be advantageous over the axial unshared electrons of *N*-substituted piperidine for the adsorption on anode metal, resulting in the higher $\Delta I_a/A$ value of piperidine than of *N*-alkylpiperidine.

The geometry of nitrogen atom in pyrrolidine is not sp^2 hybridization but sp^3 , as has been discussed⁴⁾. As the conformation of pyrrolidine seems to be nearly eclipsed with hydrogen atoms in the planar ring, there is neither axial unshared electron pair nor equatorial to the ring, and pyrrolidine and its derivatives can rather easily be adsorbed on metal without change of the conformation. Since the effect of steric hindrance with alkyl branch on the anode adsorption is less for pyrrolidine derivatives than for piperidines, the $\Delta I_a/A$

values are higher for the former.

Unshared electrons on nitrogen atom of cage-shaped quinuclidine are located in an extreme portion apart from the ring. Because of the easy adsorption on the anode, the great $\Delta I_a/A$ value of quinuclidine is shown in Fig. 4.

The order of I_t for *N*-substituted piperidine is explained as follows. The stronger basicity and the more favorable conformation for the adsorption give rise to higher I_c and I_a for piperidine than *N*-methyl piperidine, resulting in the more enhanced I_t value. The pK_a value increasing with the carbon number of straight alkyl branch in *N*-alkylpiperidine favors the increase of I_c . Although the steric interaction of alkyl branch acts to decrease the effectiveness, a little enhancement of I_a with the increase of branch carbon number is caused by the increase in both pK_a and A . As a result, the order of I_t is *N*-methyl- $<$ *N*-ethyl- $<$ *N*-*n*-propylpiperidine. The I_t values of piperidine derivatives with α -methyl substituted branch are arranged in the order, *N*-ethyl- $>$ *N*-isopropyl- $>$ *N*-*t*-butylpiperidine, because of decreasing I_c with pK_a and of lowering I_a under the influence of steric hindrance.

The order of I_t for pyrrolidine derivatives, pyrrolidine- $>$ *N*-methyl- $<$ *N*-ethylpyrrolidine can be explained by the same order of I_c and I_a responsible for the basicity and/or the molecular coverage.

Because of the lack of adsorption difficulty on anode metal, the enhanced inhibition effect of quinuclidine on the anodic partial reaction results in a high total efficiency.

5 Conclusion

The inhibition efficiency of piperidine and pyrrolidine derivatives can be interpreted with the effect on cathodic and anodic partial reaction. The cathodic inhibition efficiency of these inhibitors is not related to the molecular coverage but closely to the base strength. The anodic inhibition efficiency depends either on the molecular coverage or on the basicity. The difficulty in the adsorption on the anode electro-

de due to the steric hindrance of alkyl branch is also responsible for decreasing the anodic efficiency.

The inhibition effect on the cathodic partial reaction is predominant over the effect on the anodic partial reaction for most of the inhibitor investigated. The high cathodic inhibition effectiveness is attributed to the high pK_a value. Therefore, a stronger base is a better inhibitor for these cyclic imines.

In this paper, the total inhibition efficiency is argued on the basis of the general adsorption concept and in terms of the inhibition effect on cathodic and anodic partial reactions. The formation of metal-nitrogen coordinated bond on cathode surface is left out of consideration. Co-adsorption of the inhibitor and halide anion¹⁴⁾ must be of some importance to the anodic efficiency. Nevertheless, the effectiveness of normal sized polymethyleneimine derivatives can be explained successfully by using the cathodic and anodic inhibitor efficiency together with the base strength, the molecular coverage, and conformation of these imines. Further detailed studies on the effectiveness of nitrogen-containing inhibitors will be needed for elucidating the inhibition mechanism.

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