Technical Paper

Inhibition Effect of Chloroalkyl Amines on Acid Corrosion of Iron*

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Inhibition effect of chloroalkyl amines on corrosion of iron in HCl solution was studied. Corrosion rates were determined on 99.89% iron in 6.1M HCl solution at 30°C by polarization measurement. Inhibition efficiencies of chloroalkyl amines do not seem higher than those of the corresponding alkyl amines. These values were discussed on the basis of general adsorption concept by using polarization data, base strengths, molecular coverage areas, and polar substituent constants. The inhibition efficiency of chloroalkyl amine for cathodic partial reaction is lower than that of alkyl amine. The efficiency of alkyl amine for anodic partial reaction is also decreased by introduction of chlorine atom into alkyl group. These are caused by depression of basicity or electron density at nitrogen atom due to the inductive effect of chlorine atom. No formation of polymer molecules by the reaction of chloroalkyl amine was observed in the corrosive solution at 30°C, while chlorinated amine polymerizes in the solution at the boiling temperature, resulting in high inhibition efficiency.

1 Introduction

Structure effects of polymethyleneimines on inhibition of iron corrosion in hydrochloric acid have been studied. The inhibition efficiency of small-sized trimethyleneimine is higher than that of normal-sized imine because the former imine polymerizes in acid solution through ring-opening reaction due to marked strain in ring and the polymer molecules act as good inhibitors. In HCl solution 3-chloropropylamine also forms by the reaction of this imine with hydrochloric acid. Formation of chlorinated amine does not seem to enhance the inhibition efficiency of this imine. Polychlorinated hexadecylamines have, however, reported to be good inhibitors for steel corrosion in hydrochloric acid solution. Formation of chlorinated amine does not seem to enhance the inhibition efficiency of this imine. Polychlorinated hexadecylamines have, however, reported to be good inhibitors for steel corrosion in hydrochloric acid solution. This study was undertaken to investigate effect of chlorine atom introduced to hydrocarbon group of alkyl amine on its inhibition effectiveness.

Many kinds of this effect can be presumed. Because chlorine atom is electron-attractive, electron density at nitrogen atom is decreased by the introduction of chlorine atom into alkyl group at near position to nitrogen atom. Decrease of the electron density at nitrogen causes base strength to lower, resulting in decreasing possibility of cationic adsorption. Further, adsorption through formation of coordinate bond between metal and nitrogen atom is weaken by the depression of electron density. Matsuda et al. have presumed the adsorption possibility of chlorine atom in chlorinated hexadecylamine by discussion of cathodic Tafel slope.

Higher inhibition efficiencies of chlorinated anilines and pyridines than those of unchlorinated ones have been presented by many investigators. Grigoriev et al. have explained this result by the enhanced physical adsorption of protonated nitrogen atom. Molecular orbital calculation study by Altsybeeva et al. have suggested possibility of bifunctional adsorption with nitrogen and chlorine atom on metal. Great effect of chlorine substituent on the inhibitor adsorption is expected for aniline and pyridine molecule in which unshared electron pair on nitrogen atom is in part delocalized. Because of localized electron pair on nitrogen of alkyl amine, however, the adsorption possibility with chlorine atom of chloroalkyl amine on metal seems questionable.

Chloroalkyl amine can form polymer by the reaction of amino group with chlorine atom. If the polymerization reaction occurs in the corrosive solution, the inhibition effectiveness of chlorinated alkyl amine on the iron corrosion may increase since polymer amines are, in general, far better inhibitors than monomer amine.

In this work the inhibition efficiency of chlorinated alkyl amine was compared with that of unchlorinated amine. Corrosion rate of pure iron was determined in 6.1M HCl solution by polarization measurement. Inhibition effects of these amines on cathodic and anodic partial reactions, $2H^+ + 2e^- \rightarrow H_2$ and $Fe \rightarrow Fe^{2+} + 2e^-$ were obtained. The results were discussed

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on the basis of the general adsorption behavior\textsuperscript{14} and by using base strength, molecular coverage area, and some substituent parameters.

2 Experimental

2.1 Inhibitors

Primary alkyl amines containing 2 to 5 carbon atoms, 2-chloroethylamine, 2-chloropropylamine, 3-chloropropylamine, and n-butyl chloride were tested as inhibitors. Hydrochlorides of these chlorinated amines were synthesized by the reaction of the corresponding aminooalcohols with thionyl chloride in carbon tetrachloride. These hydrochlorides obtained were carefully purified by recrystallization and used as inhibitors without isolation of hydrochloric acid because free chlorinated amine can be easy to polymerize. Alkyl amines were obtained as high grade commercial reagents and distilled before use.

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

2.2 Polarization measurement

Corrosion rates of 99.89\% iron wire (Mallinkrodt analytical reagent grade) were determined in 6.1 M HCl solution at 30\(^{\circ}\)C by the polarization measurement as previously given\textsuperscript{12}. Galvanostatic polarization was carried out by supplying current with a coated platinum electrode, a 90 V battery, and variable resistors. Potential of iron electrode was followed with a saturated calomel electrode and an electrometer.

2.3 Determination of molecular coverage area

Effectively covered area per an inhibitor molecule adsorbed on metal surface was measured by using Stuart molecular models in the similar manner as has been mentioned\textsuperscript{13}. Two kinds of adsorption behavior were adopted for the area determination: one is the electrostatic adsorption of ammonium cation and the other the coordination adsorption of unprotonated amine. Staggered conformation of alkyl hydrogen was employed in this determination. Because of free orientation of the cation adsorbed on the metal plane, the maximum and minimum area \(A_{\text{max}}^+\) and \(A_{\text{min}}^+\), and the area of adsorbed molecule, which is tilted to make an angle of 60\(^{\circ}\) with the metal surface, \(A^+\) were evaluated. The coordinate bond between metal and nitrogen atom of the chemisorbed inhibitor was assumed to be perpendicular to the metal plane and to take anti-conformation to alkyl group.

2.4 Other measurements

Approximate basicity values of chlorinated alkyl amines were determined by titration of their hydrochloride with NaOH solution in water at 25\(^{\circ}\)C. For confirming the presence of polymer molecule derived from chloroalkyl amine in 6.1 M HCl solution, the solution of chlorinated amine was dried up in a vacuum desiccator at lower than 30\(^{\circ}\)C. Residual white powder was analyzed by IR spectrometry with a KBr disk.

3 Results

Corrosion current \(i_{\text{corr}}\) and corrosion potential \(E_{\text{corr}}\) were determined by intersection of extrapolated anodic and cathodic Tafel lines. The \(E_{\text{corr}}\) values were obtained in the several runs at each of inhibitor concentration. They were reproducible with the deviation within 4\%. Fig. 1 indicates total inhibition efficiency \(I_1\) which is given by

\[
I_1 = 1 - \frac{i_{\text{corr}}}{i^0_{\text{corr}}}
\]

where \(i^0_{\text{corr}}\) means the corrosion current for uninhibited electrode. The efficiency of chlorinated amine is not markedly high as compared with the value of corresponding alkyl amine. n-butyl chloride is a poor inhibitor for the iron corrosion in HCl solution within the range of concentration studied.

The \(E_{\text{corr}}\) value for inhibited electrode was less noble within 30 mV than the value for uninhibited electrode \(E^0_{\text{corr}}\,\, -467\text{mV vs. S. C. E.}\). Since the cathodic and anodic Tafel slopes for the both inhibited and uninhibited electrodes are assumed to be constant, cathodic and anodic partial current of the inhibited electrode \(i_e\) and \(i_a\) were graphically obtained from the current values of the extrapolated cathodic and anodic
Table 1  Physical parameters of the inhibitors

<table>
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<tr>
<th>No.</th>
<th>Inhibitor</th>
<th>$pK_a$</th>
<th>$\Sigma^*$</th>
<th>$A$ (A$^2$)</th>
<th>$A_{\text{max}}^+$ (A$^2$)</th>
<th>$A_{\text{min}}^+$ (A$^2$)</th>
<th>$A^+$ (A$^2$)</th>
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<tr>
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<tr>
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<td>0.865</td>
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<td>253</td>
<td>26.9</td>
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<tr>
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<td>0.840</td>
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<td>—</td>
<td>141</td>
<td>254</td>
<td>24.6</td>
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</table>


Tafel lines at $E^0_{\text{corr}}$. Cathodic and anodic inhibition efficiency $I_c$ and $I_a$ which are defined as

$$I_c = 1 - i_c/i_{c0}$$  \hspace{1cm} (2)
$$I_a = 1 - i_a/i_{a0}$$  \hspace{1cm} (3)

should be measures of the inhibition efficiencies for the cathodic and anodic exchange currents$^{(5)}$. The $I_c$ and $I_a$ values of these inhibitors indicate that the $I_e$ values of all amines studied depend rather on $I_c$ than on $I_a$.

Table 1 shows the $pK_a$ value, the polar substituent constant $\Sigma^*$, the molecular coverage area of amine $A$, and three kinds of the area of ammonium cation $A_{\text{max}}^+$, $A_{\text{min}}^+$, and $A^+$.

4 Discussion

The cathodic inhibition efficiency of amine inhibitor is expressed by

$$I_c/A^+ = \text{const.} \frac{K_{\text{ads}}[\text{RNH}_2][\text{H}^+][\text{M}]}{K_a}$$  \hspace{1cm} (4)

where $K_{\text{ads}}$ and $K_a$ are equilibrium constants for the adsorption and dissociation of ammonium cation and $A^+$ the molecular coverage area of the cation$^{(5), (19)}$. The cathodic efficiency at a constant free amine concentration $I_c'$ can be graphically determined by interpolation of the $I_c$-inhibitor concentration curve. On the assumption of a constant $K_{\text{ads}}$ value, $I_c'/A^+$ is proportional to the reciprocal of $K_a$. Fig. 2 shows a linear correlation of $I_c'/A^+$ to $1/K_a$ at a constant free amine concentration calculated from 0.01M of ethylamine as a reference. From this result, the inhibition of cathodic partial reaction is increased with the basic strength and the molecular coverage area of the inhibitor. Since the result suggests the constant $K_{\text{ads}}$ value for each amine, there seems little effect of enhanced positive charge at ammonium nitrogen due to the presence of electron-attractive chlorine atom on the cathodic inhibition.

The anodic inhibition efficiency of free amine is dependent on the electron density at the functional atom, the molecular coverage area, and the steric requirement for the adsorption process$^{(5)}$. According

Fig. 2 Relationship between $I_c'/A^+$ and $1/K_a$
Number indicates the inhibitor number shown in Table 1

Fig. 3 Relationship between $\log I_a/(1-I_a)$ and $A$ (A$^2$)
Number indicates the inhibitor number shown in Table 1
to the linear free energy relationship, $I_n$ can be expressed without the consideration of the molecular coverage area and the steric hindrance by

$$\log I_n(1-I_n) = \rho^* \Sigma \sigma^*$$

where the zero subscripts refer to a reference compound, and $\rho^*$ and $\Sigma \sigma^*$ are the reaction and polar substituent constant, respectively. The polar substituent constant represents a measure of the electron density at nitrogen atom. The log $I_n(1-I_n)$ value for each amine at 0.01 M concentration was plotted against the molecular coverage area $A$ in Fig. 3. Alkyl amines were employed as reference compounds here. Difference of the log $I_n(1-I_n)$ value for chlorinated amine from a curve through the points for unchlorinated amines in Fig. 3, $\Delta \log I_n(1-I_n)$ was graphically obtained. This value, corresponding to the left members of equation (5), should indicate the effect of chlorine substitution on the $I_n$ value. All the values of chlorinated amines are negative, meaning unfavorable effect of chlorine substituent on the inhibition efficiency of alkyl amine. Fig. 4 shows a linear relationship between $\Delta \log I_n(1-I_n)$ and $\Sigma \sigma^*$. A minus slope of this line is reasonable because of increasing $I_n$ with increase in the electron density at nitrogen atom. Therefore, the decrease in $I_n$ of chlorinated alkyl amines is concluded to arise from the depression of electron density due to the inductive effect of chlorine substituent. The steric influence of methyl or ethyl substituent on the amine inhibition is of little importance at $\beta$-position and negligible at $\gamma$-position of hydrocarbon group. Hence, the steric effect of chlorine atom on the inhibition effectiveness of chlorinated amine was not taken in this argument into account.

In order to substantiate the adsorption possibility by action of chlorine atom attached to hydrocarbon group, the effectiveness of $n$-butyl chloride which is soluble in 6.1 M HCl solution within the range of concentration studied was determined and compared with that of $n$-butylamine or 3-chloropropylamine. They are alike in the molecular coverage area. Data that $I_n$ of the chloride is close to zero suggests a lack of the adsorption possibility by the formation of chlorine-metal bond.

Since no $pK_a$ value of $n$-butyl chloride in water is measurable, a relative base strength corresponding to the ability of electron--donation was determined by shift of O-H stretching frequency from dissociated phenol to hydrogen--bonded one with $n$-butyl chloride or $n$-butylamine in $n$-hexane at 30°C. The shift $\Delta \nu$ is 57 cm$^{-1}$ for $n$-butyl chloride and 547 cm$^{-1}$ for $n$-butylamine. These values mean far lower electron-
donation ability of chlorine atom than nitrogen. The $J_0$ value cannot be measured for chlorinated amines because hydrochlorides of these amines are insoluble in n-hexane. The value for chlorine atom in chloroalkyl amine studied is presumed to be as low as the value for n-butyl chloride. These results draw the conclusion that the presence of chlorine atom in alky group does not improve the inhibitor effectiveness of alky amine but rather causes the efficiency to be lowered since the electron density at nitrogen atom is decreased by the inductive effect.

In order to confirm the possibility of polymerization reaction of chlorinated alky amine, 6.1M HCl solutions of 3-chloropropylamine, $n$-butylamine, and $n$-butyl chloride at the concentration 0.003M were refluxed at 107°C and then the polarization measurements were carried out on iron electrode in these solutions at 30°C. The $I_1$ values are shown in Fig. 5 as the function of time at the boiling temperature. The $I_1$ value for 3-chloropropylamine increases with the time, while there are little changes in the values for the other two. Because polymerization product of 3-chloropropylamine is expected to be more effective on the corrosion inhibition than monomer amine, this result implies the reaction between amino group and chlorine atom at the boiling temperature.

Fig. 6 shows IR spectra of 3-chloropropylamine hydrochloride (a) and the reaction product of 3-chloropropylamine in boiling HCl solution (b). Marked difference in absorption intensity of C-Cl stretching band at about 830 cm$^{-1}$ between (a) and (b) indicates the formation of polymer molecules. It is concluded from the results that chlorinated alky amine polymerizes in the corrosive solution at 107°C and the polymer molecules formed act as good inhibitors. However, there is no improvement of the inhibition efficiency by the polymerization of chloroamine in HCl solution at 30°C, since a similar spectrum to Fig. 6 (a) was obtained for the reaction product of 3-chloropropylamine at 30°C.

5 Conclusion

The inhibition effectiveness of chloroalkyl amines on the iron corrosion in HCl solution is not higher than that of the corresponding alky amine. The inhibition efficiency of alky amine for the cathodic partial reaction is decreased by the introduction of chlorine atom to the alky group because of the basicity lowered under the influence of inductive effect. This effect also causes the depression of electron density at nitrogen atom, resulting in decrease of the efficiency for the anodic partial reaction. There seems little adsorption possibility of the chlorinated inhibitor by the formation of metal-chlorine bond. The formation of polymer by the reaction of chloroalkyl amine molecules in boiling HCl solution at 107°C improves the efficiency, but no polymerization was detected to occur in the solution at 30°C.

References:
14) N. Hackerman, *Corrosion* 18, 332t (1962).