

Influence of N-Heterocyclic Compounds on the Corrosion of Al-Si Alloy in Hydrochloric Acid—Effect of pH and Temperature

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ABSTRACT

Two N-heterocyclic compounds were tested as inhibitors for the corrosion of an Al-11% Si alloy in hydrochloric acid (HCl) solutions by polarization and chemical measurements. Results indicated that Compound (B), containing a quinolinium moiety, was more effective than Compound (A), which contained a pyridinium moiety. Acceleration of corrosion by Compound (B) was observed to occur at low concentrations of the compound and also in alkaline media. An increase in HCl concentration caused a decrease in the inhibition efficiency. The abrupt decrease in inhibition by Compound (B) at temperatures exceeding 50°C was attributed to reorientation of the molecules at higher temperatures. Values of the apparent activation energies of adsorption support the conclusion that Compound (B) was more efficient than Compound (A) in inhibiting the corrosion of the alloy.

KEY WORDS: acceleration, Al-Si alloy, hydrochloric acid, inhibition, N-heterocyclic compounds, polarization

INTRODUCTION

Al owes its high resistance to corrosion to the naturally formed oxide film, which protects it in air or neutral solutions. Even upon immersion in acidic and alkaline media, this film is preserved for long periods to time.¹ Al is often alloyed with different elements to

improve its mechanical properties, but thus may lead to degradation of its resistance to corrosion. Al-Si alloys are of particular interest in automotive industries, where light weight and pressure tightness are decisive in the choice of the proper alloy. In recent years, several investigators have explored the electrochemical behavior of Al in aqueous media, in particular the role played by the aggressive chloride ion in the pitting corrosion of the metal.²

Since the potential of zero charge (pzc) for aluminum oxide (Al₂O₃) occurs from pH 9.0 to 9.1,³ chloride or any aggressive anion is likely to be adsorbed at pH values <9.0. This leads to localization of the corrosion attack by preferential adsorption at weak spots in the passive film. Studies on the adsorption of organic compounds at electrodes are important to the understanding not only of corrosion process inhibition but also the structure of the electrical double layer, the kinetics of electron transfer, and the role of intermediates in the mechanism of electrode processes.⁴ Inhibitors for localized corrosion of Al and its alloys at pH <9 are generally the anion type. Above the isoelectric point, the Al surface is negatively charged, and physical adsorption of the anions is impossible; if adsorption occurs, it must be involved chemically.⁵ In addition to the electrostatic forces between the hydrated oxide film and the inhibitor, short-range forces operate by forming chemical bonds between Al cations of the surface film and nucleophilic functional groups or π electrons of the molecule of the inhibitor.⁶

Hydrochloric acid (HCl) solutions are often used for pickling aluminum or in the process of chemical

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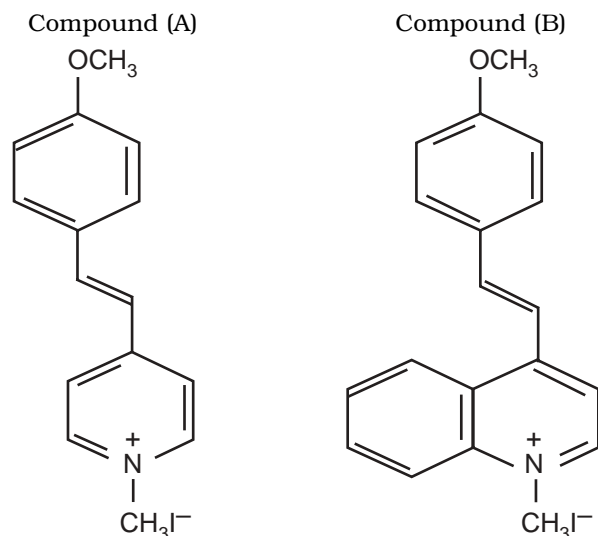
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or electrochemical etching. The inhibition of corrosion of Al or its alloys by N-heterocyclic compounds has been reported.⁷ Recently, in a study on the electrochemical behavior of some Al-Si alloys with Si content between 7% and 22.2%, the alloy containing 11.0% Si, which was almost completely eutectic, was found to have the highest corrosion rate.⁸ In the present investigation, two N-heterocyclic compounds were tested as potential inhibitors for corrosion of an Al-11.0% Si alloy in HCl. Factors that may effect this role were also studied, such as chloride ion concentration, pH, and temperature.

EXPERIMENTAL PROCEDURES

The compounds used in this study were prepared according to the literature⁹ and checked after preparation by chemical analysis, melting point measurements, and nuclear magnetic resonance (NMR). The two compounds were 1-methyl-4-[4'-(methoxy)styryl] – pyridinium iodide (denoted as “A”) and 1-methyl-4-[4'-(methoxy)styryl] – quinolinium iodide (denoted as “B”):



The Al-Si alloy used in the present investigation had the same composition as previously reported⁸ and contained, beside Al (the major component), the following: 11% Si, 0.123% Cu, 0.113% Fe, 0.073% Ni, 0.025% Cr, 0.014% Zn, 0.05% Co, and 0.002% Pb. Samples used in both the hydrogen evolution measurements (HEM) and mass loss measurements (MLM) were in the form of rods 1 cm in diameter and 5 cm in length. For polarization measurements, the Al-Si rod was inserted into a glass tube just larger than the sample and was fixed with an adhesive. The cross-sectional area exposed to the solution was 0.785 cm². Before each experiment, the sample was mechanically polished using finer grades of emery

[†] Trade name.

paper up to 4/0 and washed with deionized water. Samples used for chemical analysis were further degreased with acetone (CH₃COCH₃) and dried in a stream of hot air. Electrodes used in polarization measurements were washed after polishing with deionized water and a small portion of the test solution; then, they were inserted immediately into the test solution. All chemicals were analytical grade.

The pH was adjusted by addition of carbonate-free sodium hydroxide (NaOH), and measured by a pH meter (Jenway model 3015[†]). This was adjusted before and after each measurement with National Institute of Standards and Technology (NIST) solutions (pH 4.01 and 6.865). The test temperature was maintained at 30 ± 0.2°C with the aid of a thermostat (Julabo[†] U3 no. 8311), unless otherwise stated.

In the HEM, the polished specimen, in the form of a rod, was inserted into the test solution, which was aerated and unstirred. The immersion time was recorded, and hydrogen gas was collected in a graduated cylinder through a quick fit system. The volume of evolved gas was recorded as a function of time. A plot of the results produced a straight line. The slope of this line gave the rate of hydrogen evolution (R) in mL/cm²-min.

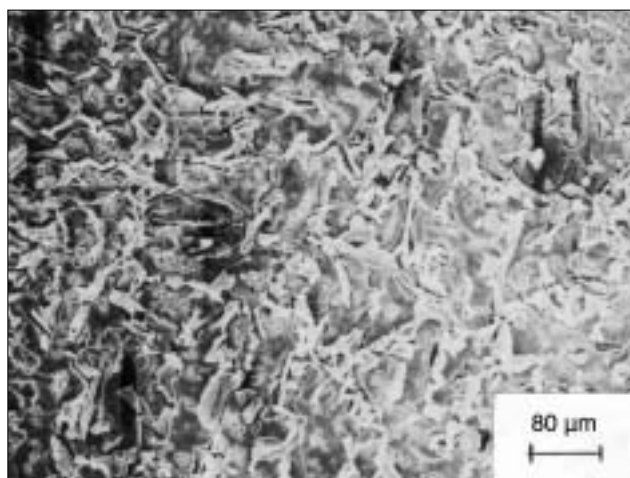
In the MLM, the polished sample was weighed before and after immersion in the test solution (90 min). The mass loss was calculated as the difference in weight before and after immersion. The rate of mass loss was obtained (g/cm²-min).

Potentiostatic polarization measurements were conducted using a potentiostat with positive feedback for IR compensation. The reference electrode was silver/silver chloride (Ag/AgCl) and the auxiliary electrode was a Pt wire. Solutions were unstirred and deaerated with 99.999% purity nitrogen gas. Upon inserting the working electrode into the test solution, the open-circuit potential between the working electrode and the reference electrode was measured. This attained a steady state within 15 min. At this point, polarization scanning started toward the noble direction.

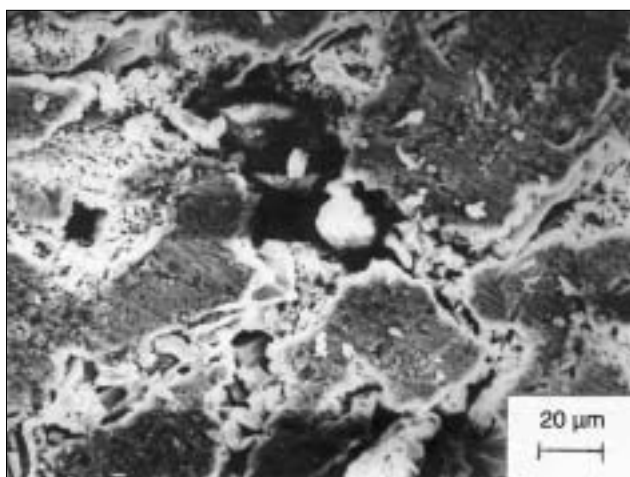
The electrode surface was examined by making photomicrographs of the surface. A scanning electron microscope (SEM) was used for this purpose.

RESULTS AND DISCUSSION

Figure 1(a) shows a SEM photomicrograph of the “as-polished” surface, while Figure 1(b) shows the same surface after immersion in 0.25 N HCl for 90 min. While Figure 1(a) shows that the alloy is uniformly composed of the eutectic dendrites, Figure 1(b) shows that general and pitting corrosion are dominant. The pits are deep and irregular; small, distinct and spherical pits would indicate improved film quality.¹⁰ Figure 1(b) shows that the alloy was severely attacked by 0.25 N HCl.



(a)



(b)

FIGURE 1. SEM for alloy surface: (a) as polished and (b) after 90 min immersion in 0.25 N HCl showing general corrosion and pitting.

The potentiodynamic polarization curves for the alloy in blank 0.25-N HCl and in the presence of the inhibitors are shown in Figures 2(a) and (b). The decrease in cathodic currents with an increase in concentration of either Compound (A) or (B) indicate that both are cathodic inhibitors.

The corrosion potential (E_{corr}) shifted to more negative values with an increase in concentration of Compound (A) or (B). These two compounds can be classified as 1:1 electrolytes, the cation being the organic part and the anion the iodide ion. The two compounds have the same adsorption centers but differ in the pyridinium group in Compound (A) and the quinolinium group in Compound (B).

Halide ions play an essential role in inhibiting the acid corrosion of positively charged metal surfaces by quaternary ammonium halides.¹¹ It has been explained that mutual stimulation or adsorption between the cations and halide ions occurs as the concentration increases, probably through physical

adsorption. The existence of halide ions (Cl^- and I^- ions in the present case) would reduce the repulsion between the positive charge of the head groups, thus facilitating formation of a closely packed layer¹² at the alloy surface. Therefore, the effectiveness of organic substances containing N-functional atoms was explained by the existence of a synergistic effect in acid media.¹³⁻¹⁴ In the present study, it was expected that the low pH of the solution would produce a positive charge on the alloy surface.

The shift of E_{corr} to more negative values,¹⁵⁻¹⁶ with an increase in the concentration of Compound (A) or (B), was caused by the potential barrier of the adsorbed species. This inhibited mainly the cathodic reaction on the electrode, while the anodic reaction was hindered only at larger concentrations,¹⁷ as shown in Figure 2.

The anodic current at the lowest concentration of Compound (B) was higher than that recorded in the absence of the compound, while higher concentrations caused a decrease in the anodic current. The value of the anodic Tafel slope (β_a) was constant and equal for Compounds (A) and (B) (60 mV/decade). The value of the cathodic Tafel slope (β_c) was also found to be equal and constant for Compounds (A) and (B). The value of β_c (110 mV/decade) was close to $2.3 (2RT/F)$,¹⁸ so the only cathodic process occurring at the electrode/solution interface was the hydrogen evolution reaction (HER). The constant values of β_a and β_c suggested that the inhibiting action of the compounds was similar and occurred by simple blocking of the available surface area.¹⁹ The constant β_c values indicated that inhibition of the corrosion of the alloy in acid media occurred predominately as a result of specific adsorption of the molecular species via interaction of the π -electrons of the conjugated bonds of the aromatic nuclei with the electrode surface. The adsorption of the cation under these conditions was probably weak since the electrode surface would have been positively charged.²⁰ The constant β_a value of 60 mV/decade is higher than the expected 40 mV/decade, corresponding to the uniform anodic dissolution of Al via hydrated Al^{3+} ions.²¹ This higher value was attributed to the participation of side reactions in film growth and to the penetration of chloride ions into the film.²²

The corrosion currents, i_{corr} , were obtained by Tafel interpolation and are plotted as a function of concentration in Figure 3. The figure shows that Compound (B) is a more effective inhibitor than Compound (A) at higher concentrations. Previous studies have shown that inhibition of related compounds increases with an increase in electron density in the functional group (i.e., by substitution of electron-releasing groups elsewhere in the molecule). Increase in the electron density leads to easier electron transfer from the functional group of the inhibitor to the metal, thus producing stronger coordinate bonding

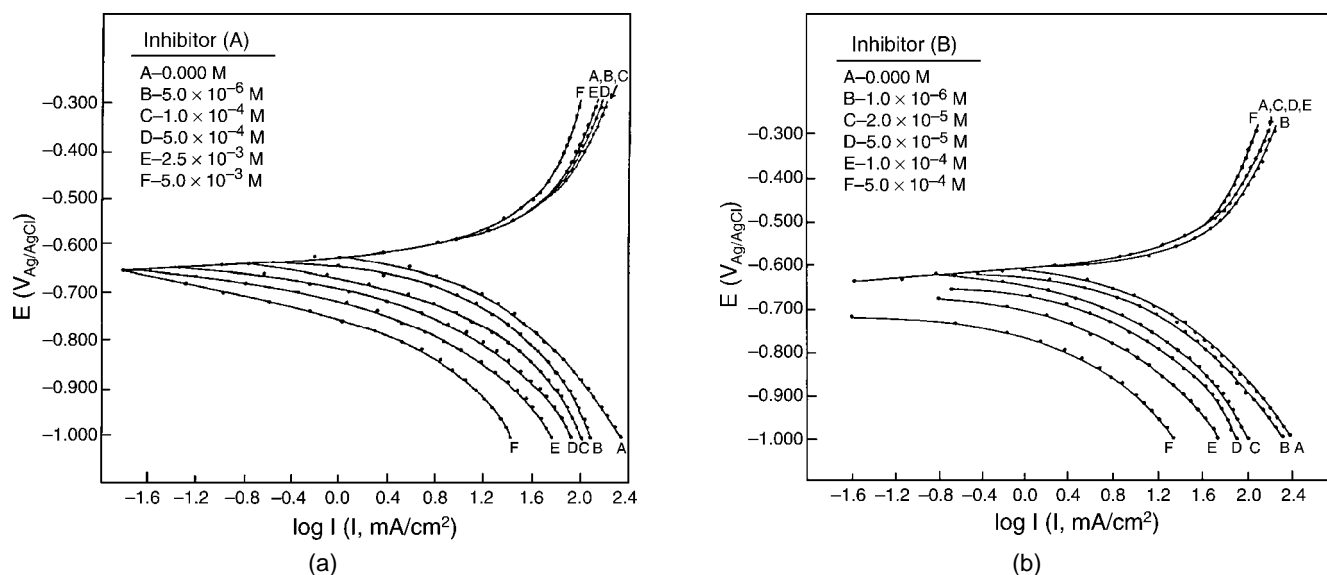


FIGURE 2. Effect of concentration on the polarization curves in 0.25 N HCl at 30°C: (a) Compound (A) and (b) Compound (B).

and, hence, greater adsorption.²³ Substitution of the phenyl group in the pyridinium moiety evidently increased the electron density in the quinolinium moiety in the molecule of Compound (B). The observed lower inhibition efficiency of Compound (A) compared to (B) was caused by the lower electron density of the pyridinium group that resulted from a lacking phenyl group. The larger molecule size of Compound (B) as compared to (A) was another factor determining the efficiency of the inhibitor. The present results agree with recent reports that the inhibition efficiency of N-heterocyclic organic compounds increases with the number of aromatic systems and the availability of electronegative atoms in the molecule.²⁴

The action of Compounds (A) and (B) was also studied by the HEM in 0.25 N HCl and over a wide range of concentrations starting from 10^{-7} M to concentrations determined by the solubility of each compound. The percentage of inhibition ($\text{Inh}_H\%$) was calculated from the following relation:

$$\text{Inh}_H\% = \left(1 - \frac{R}{R^0}\right) \times 100 \quad (1)$$

where R and R^0 are the rates of hydrogen evolution ($\text{mL}/\text{cm}^2\text{-min}$) in the presence and absence of the compound. The relation between $\text{Inh}_H\%$ and concentration of the compound is given in Figure 4. The characteristic S-shaped adsorption isotherm indicated a one-step adsorption process²⁵ and that, at concentrations $>1.5 \times 10^{-5}$ M, Compound (B) was more effective than (A) in inhibiting the corrosion of the alloy, as substantiated from polarization curves.

It is interesting to note that Compound (B) had a dual action—it stimulated corrosion at low concentrations and inhibited it at higher concentrations.

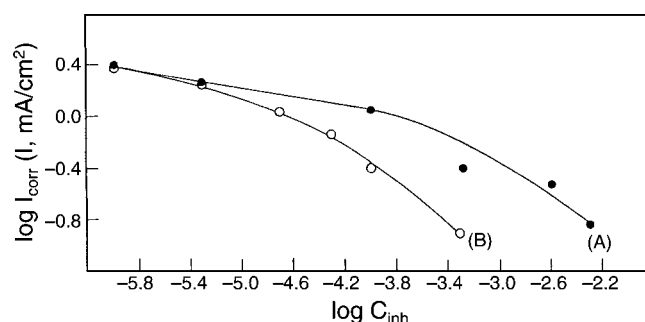


FIGURE 3. Dependence of i_{corr} on concentration of (A) and (B).

Some organic compounds behave as good corrosion inhibitors in certain concentration ranges while they exhibit more or less remarkable stimulation at lower concentrations.^{11,26-27} The stimulation of corrosion of the alloy by Compound (B) at low concentrations can be explained on the basis of the synergistic effect of the halide (Γ) ions present,¹³⁻¹⁴ the molecular weight of Compound (B), and the solubility of the intermediate corrosion products. It has been explained that halide ions at low concentrations may be chemisorbed and become integrated with the metal surface,²⁶⁻²⁷ giving a net negative charge that favors adsorption of cations in the solution. However, Compound (B), which had a higher electric charge density than (A), might have undergone repulsion with the net negative charge existing on the metal surface as a result of the presence of both Cl^- and Γ^- . As the concentration increased, this effect was overcome and inhibition set in. With an increase of concentration, inhibition was observed to increase. These results are supported by a previous report that Γ^- gives maximum synergistic effect at concentrations up to 10^{-4} M while a decrease in concentration reverses this ef-

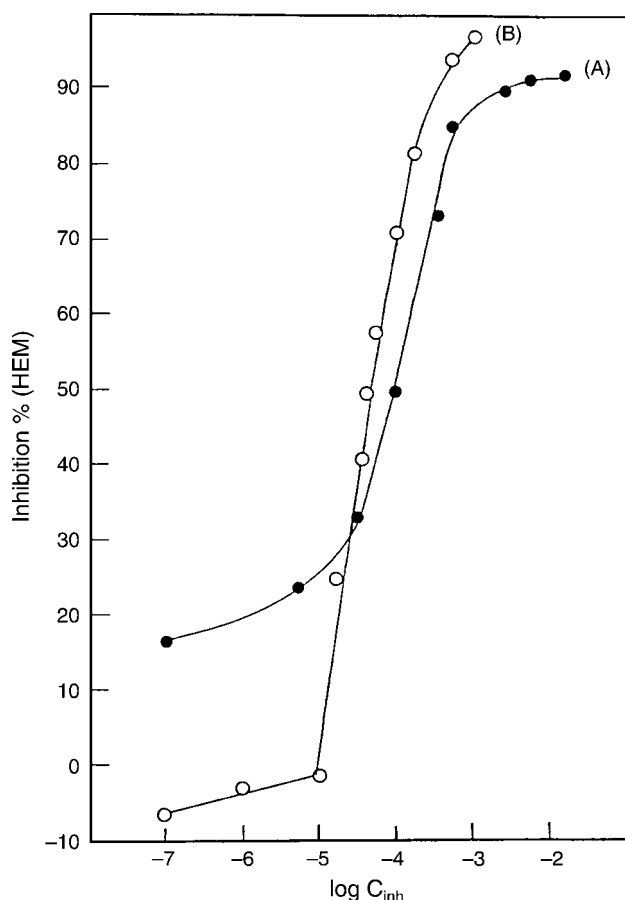


FIGURE 4. Relation between percentage of inhibition and concentration of Compounds (A) and (B).

fect.¹⁴ Inhibition of corrosion in the case of quaternary ammonium ions was attributed to the co-adsorption of Br⁻ with these ions, with the whole compound behaving as a nonionic one,²⁸ which was probably the case in this study at higher concentrations of the inhibitor. The formation of soluble intermediates as products of the corrosion process may have also facilitated the stimulation of corrosion at low concentrations.²⁹ As the concentration of Compound (B) increased, the aggressiveness of I⁻ ions decreased as a result of the decrease in ionization of the compound.²⁹ This may have been accompanied by a decrease in the solubility of the intermediate corrosion products, thus reversing stimulation of corrosion to inhibition.

Several trials were made to determine the suitable isotherm fitting the surface coverage, θ , with the inhibitor concentration from the hydrogen evolution and polarization measurements. The linear relations shown in Figure 5 indicate that both inhibitors underwent adsorption fitting the kinetic-thermodynamic model:

$$\log \frac{\theta}{1-\theta} = K' + y \log C \quad (2)$$

where K' is a constant, C is the concentration (mol/L), and y is the number of inhibitor molecules occupying one active site. $1/y$ represents the number of active sites occupied by one molecule on the surface. The constant K' is related to the binding constant K by the following relation:

$$K = K'^{(1/y)} \quad (3)$$

Values of $1/y$ greater than unity imply the formation of multilayers of the inhibitor on the surface while values less than unity indicate that the molecule will occupy more than one active site.

The slope of the lines in Figure 5 represent y for Compound (A) or (B). The value of $1/y$ for (A) was 2.00, indicating formation of multilayers on the alloy surface, whereas $1/y$ for (B) was close to unity (1.06), indicating that each molecule was attached to one active site on the surface. The adsorption took place through the same center so that the alkyl moiety was directed to the bulk of the solution.

The intercept in Figure 5 gives $\log K'$, from which K was calculated and found to increase from a value of 36,901 for Compound (A) to 56,076 for (B). Thus, the protection efficiency for Compound (B) was higher than for (A) because of stronger electrical interactions between the adsorbed molecules and the alloy surface in the case of Compound (B).

Values of the constant K' are related to the standard free energy of adsorption, ΔG_{ads}^0 , by the following equation:

$$K' = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{\text{ads}}^0}{RT}\right) \quad (4)$$

Values of ΔG_{ads}^0 for Compounds (A) and (B) were -36.6 KJ/mol and -37.7 KJ/mol, respectively. These values are within the range of -20.8 KJ/mol to -45.2 KJ/mol recorded for organic inhibitors of various types in aqueous media.^{19,30} The high negative values of ΔG_{ads}^0 are a characteristic feature of strong adsorption and indicate that the adsorption of these molecules occurs in the flat configuration.

The more negative ΔG_{ads}^0 value of Compound (B) indicates that it is adsorbed more strongly on the alloy surface than Compound (A). This energy change increases with the increase of the solvating energy of the adsorbed species, which, in turn, increases with increasing size of the organic molecule.³¹

Effect of HCl Concentration

The effect of HCl concentration on the inhibiting action of the compounds was studied by chemical methods. In both the HEM or MLM, the concentration of the inhibitor was fixed at 5×10^{-4} M, which produced high inhibition rates for either Compound (A) or (B) in 0.25 N HCl. The inhibition by HEM ($\text{inh}_H\%$) or by MLM ($\text{inh}_M\%$) was calculated by deter-

mining the corrosion rate in the presence and absence of the inhibitor at the same acid concentration. The corrosion rate was always lower in the presence of the inhibitor at this high concentration than in the absence of the inhibitor. The percentage inhibition for both compounds was found to decrease with an increase in acid concentration (Figure 6). It is clear that Compound (B) imparted better inhibition at all acid concentrations as a result of its superior properties as an inhibitor.

The results in Figure 6 demonstrate the adverse effect of increasing HCl concentration on the inhibition efficiency of the compounds, especially Compound (A). A similar observation was made of N-heterocyclic compounds as corrosion inhibitors for Al-Cu alloy⁷ and for hydrazine compounds as corrosion inhibitors for Cu and Al.³² In the latter case, this behavior was attributed to the fact that the inhibitors undergo decomposition at higher acid concentrations, which was not the case for the present results. There are several reasons for this effect; for example, the desorption of the inhibitor might be aided by the heat of hydration of Cl⁻ ions, which increases with Cl⁻ ion concentration³³ and thus leads to less inhibition. Another reason is the expected increase in positive charge on the alloy surface as the pH falls, resulting from the increase in HCl concentration (pH corresponding to the pzc for Al₂O₃ = 9). This would result in an increased attraction of Cl⁻ ions at the alloy/solution interface. It was evident that the electrostatic attraction of Cl⁻ to the positively charged surface was higher than the short-range forces caused by the π -bond interaction. As Cl⁻ concentration increased, the space available for adsorption on the surface decreased, and thus inhibition by the compound decreased. The effect of acid concentration was less pronounced for Compound (B) because of its strong adsorption on the surface.

Results indicate that inhibition by HEM was always higher than that recorded by MLM. This was observed in other cases and may be attributed to permeation of some hydrogen through the alloy surface³⁴ or to the nonadherence of the adsorbed film, which is partially removed by washing and leads to higher weight loss.

Effect of pH

To study the effect of pH, the inhibitor efficiency was first tested in 0.25 M HCl, 1 M phosphoric acid (H₃PO₄), and 0.05 M NaOH by MLM on the alloy. These concentrations were chosen on the basis of comparable values of the alloy corrosion rate in these media in the absence of the inhibitor. The corrosion rates in 0.25 M HCl, 1 M H₃PO₄, and 0.05 M NaOH in the absence of the inhibitor were 2.318, 1.474, and 2.416 g/cm²-min, respectively. The concentration of Compound (A) was 3.5 × 10⁻⁴ M, while that of (B) was 1 × 10⁻⁴ M; these concentrations were found to give

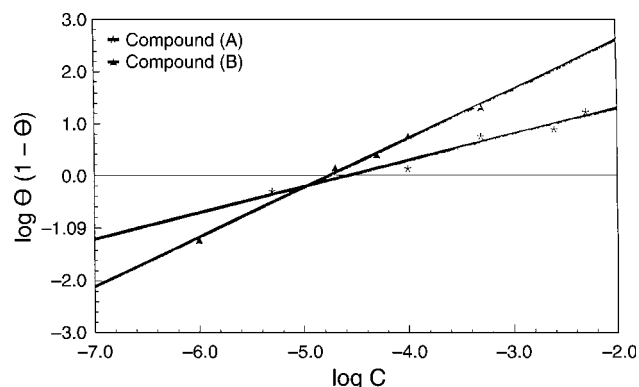


FIGURE 5. Fitting of the results obtained by polarization measurements to the kinetic thermodynamic model.

close values of inhibition in 0.25 N HCl for Compounds (A) and (B). Results are shown in Table 1.

It was clear that, in acid media, where the alloy surface was positively charged, electrostatic attraction between the alloy surface and the delocalized π -electrons on the compounds led to adsorption of the molecules in the flat configuration, and good inhibition was observed in acid media. In NaOH, the alloy surface was negatively charged and there was repulsion between the surface and the π -electrons. As Al dissolved in alkaline media as AlO₂⁻, which was attracted to the cationic part of the compound in the bulk of solution, this caused continuous removal of the AlO₂⁻ from the electrode surface and enhanced dissolution, which led to acceleration of the corrosion process in the presence of the compound, so that the corrosion rate was higher than in the absence of the compound. Thus, negative values of the inhibition process were recorded.

The inhibition by Compound (B) was essentially the same in HCl as in H₃PO₄. However, Compound (A), which adsorbed less on the alloy surface, was found to be affected by the medium. Since phosphate ions adsorb less on metal surfaces than chloride ions, more sites were available for adsorption of Compound (A) in H₃PO₄. This led to higher inhibition than in HCl, where chloride ions adsorbed strongly and left fewer sites free to adsorb the inhibitor. Similar effects were recorded in the presence of chloride and sulfate ions in inhibition studies of corrosion of mild steel.³⁵⁻³⁶ The results indicated the importance of pH in determining the action of the compounds on the corrosion process.

The effect of pH was examined through the polarization behavior of the alloy in 10⁻¹ N HCl in the presence of 5 × 10⁻⁵ M of Compound (B) at 30°C and at pH values 2, 5, 7, 10, and 12. The results are shown in Figure 7. There was a shift of E_{corr} to more negative values with an increase in pH. The value of i_{corr} was minimum at neutral pH and increased in both acidic and alkaline directions, the increase being substantially greater in alkaline media. Inhibition

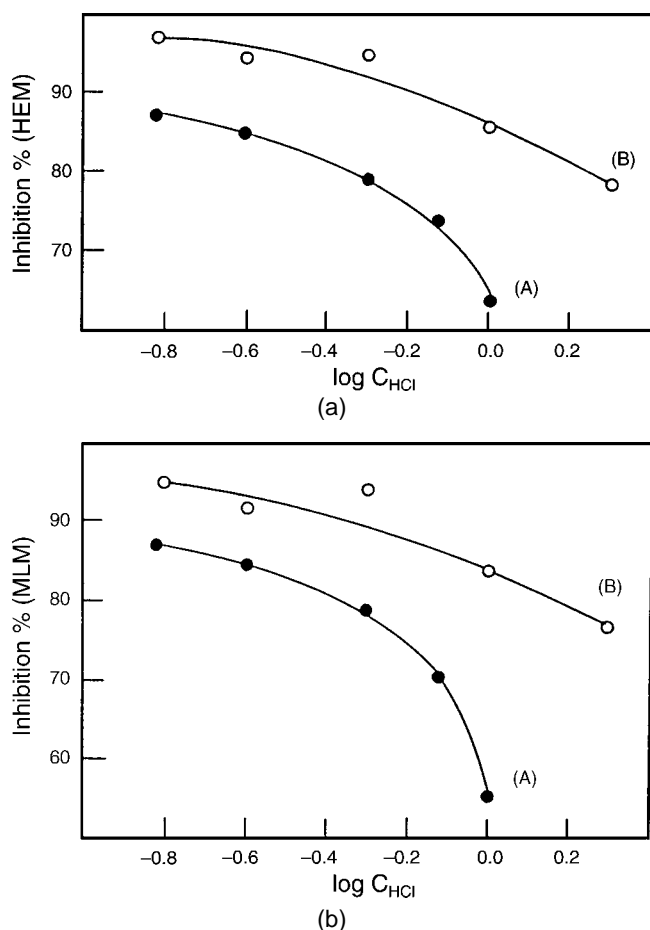


FIGURE 6. Effect of HCl concentration on the inhibition efficiency by: (a) HEM and (b) MLM.

TABLE 1

Effect of Medium on the Inhibition Efficiencies of Compounds (A) and (B) Taken from Mass Loss Measurements

Compound/ Medium	NaOH (0.05 M)	H ₂ PO ₄ (1.0 M)	HCl (0.25 M)
A	-33.35	83.65	69.57
B	-30.05	68.78	68.92

percentages were calculated from i_{corr} values in the absence and presence of the inhibitor, with the pH of the solutions adjusted to the same values. The results are shown in Table 2.

There was a remarkable decrease of percentage inhibition with the increase in pH. At neutral pH, no inhibition was observed, as in the case of alkyl quaternary ammonium salts in acid corrosion of steel.³⁷ At high pH values, there was an acceleration of corrosion. A similar observation was reported on inhibition and stimulation of corrosion depending on the pH of solution.³⁸ Since there was a gradual change in the charge on the alloy from positive to negative with an increase in pH, there would be a simultaneous

change from attraction to repulsion of the decolorized π -electrons with the alloy surface, which probably led to a change of orientation from the flat configuration to the vertical configuration, and thus a decrease in inhibition was observed at pH values 2 to 5. At pH values 10 and 12, inhibition was completely absent, and acceleration of corrosion occurred at a rate that increased with pH, according to the mechanism proposed in the case of NaOH.

Effect of Temperature

The effect of temperature on the inhibition efficiency of Compounds (A) and (B) in 0.25 N HCl was studied by chemical methods in the temperature range from 30°C to 70°C. Polarization measurements were not possible since the glass tube encasing the electrode cracked at higher temperatures, presumably because of differences in the coefficients of expansion of glass and the alloy. Increase in temperature increased the rate of corrosion of the alloy in the absence or presence of the inhibitor. However, calculation of the percentage of inhibition showed that, as the temperature increased, the inhibition decreased for both Compounds (A) and (B) by either HEM or MLM (Figure 8). There was a monotonic decrease in inhibition with temperature for Compound (A), whereas (B) exhibited a plateau in the temperature range of 30°C to 50°C, indicating that the rise in temperature in this range did not seriously affect the percentage of inhibition. At higher temperatures, an abrupt limited decrease was observed in the inhibition. This change in inhibition efficiency may be correlated with a reorientation process during which a change occurs from π -bonding to adsorption via the functional group.²⁰ This leads to a decrease in inhibition caused by a change from adsorption in the planar to the vertical orientation, as has been observed for many organic compounds. The reorientation process is sensitive to many factors such as concentration, pH, temperature, type of anions present, and applied potential.³⁹

Arrhenius plots are shown in Figure 9 as deduced from HEM and MLM, respectively. The apparent activation energy (ΔE_{app}) was calculated from the following relation:

$$R \text{ (or } R') = Ae^{(-\Delta E_{\text{app}}/RT)} \quad (5)$$

where R or R' is the rate of corrosion as determined from HEM or MLM, respectively. Values of ΔE_{app} were equal to 42.1 KJ/mol and 43.4 KJ/mol, from HEM and MLM, respectively, in uninhibited solutions. The respective values for Compound (A) were 63.8 KJ/mol and 66.4 KJ/mol, and for Compound (B) 71.7 KJ/mol and 81.5 KJ/mol. These values of ΔE_{app} are comparable and suggest a similar mechanism of action for both inhibitors.⁷ Moreover, these values are of the order of activation energies of diffusion processes,⁴⁰

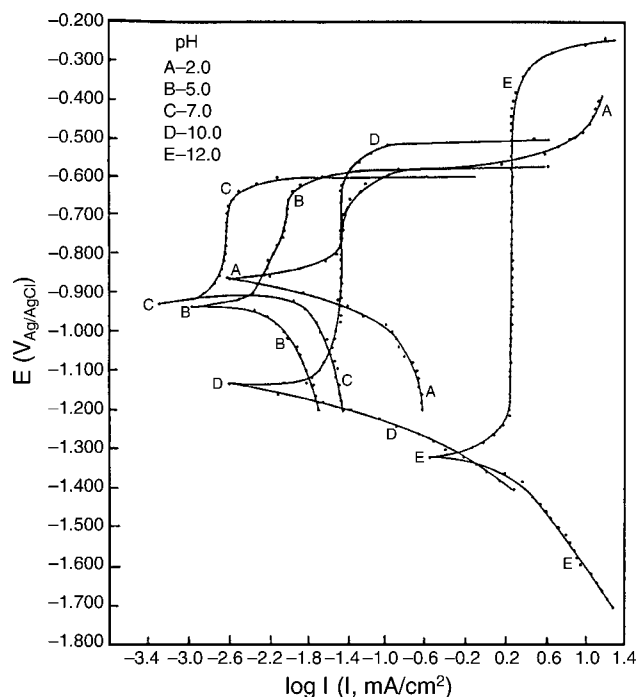


FIGURE 7. Effect of pH on the polarization curves in 0.1 N HCl at 30°C in the presence of 5×10^{-5} M (Compound B).

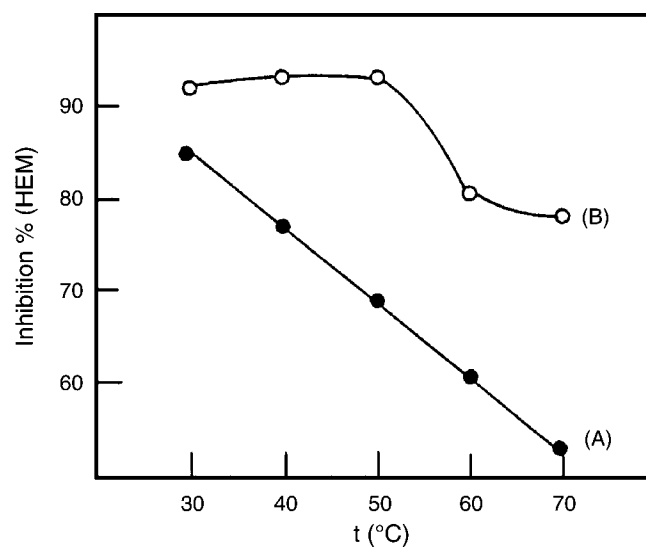
TABLE 2
Effect of pH on Inhibition
of Corrosion by Compound (B) in 0.1 N HCl

pH	2	5	7	10	12
Inh _p %	80.95	10.88	0.04	-34.90	-69.82

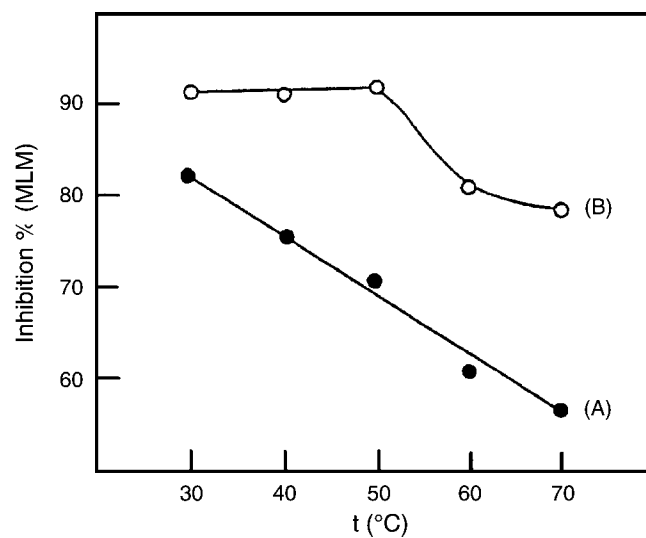
indicating that the diffusion of metal ions through the protective film on the alloy surface is rate controlling. The value of ΔE_{app} was somewhat higher for Compound (B) in accordance with its better inhibition properties. The higher values of ΔE_{app} in the presence of the inhibitors as compared to the uninhibited solutions suggest that the presence of the inhibitor at the electrode/electrolyte interface leads to an increase in the energy barrier of the alloy dissolution.

CONCLUSIONS

- ❖ Adsorption of the molecular form of the compound occurred through the delocalized π -electrons of the aromatic systems; however, the synergistic effect of the Cl^- and I^- ions was probably responsible for the initial stage of attracting the molecule to the alloy surface. This is supported by the accelerating effect observed at low concentrations of Compound (B), where the specific adsorption of Cl^- ions overcame the attraction between the surface and the short-range forces of the π -electrons.
- ❖ Compound (B) was also observed to provide inhibition at low pH values, which decreased with an in-



(a)



(b)

FIGURE 8. Relation between percentage of inhibition and temperature for Compounds (A) and (B) by: (a) HEM and (b) MLM.

crease in pH. At high pH values, acceleration of corrosion was observed.

- ❖ The remarkable decrease in adsorption as the pH of the solution was increased from 2 to 7 was explained by reorientation of the molecules from flat to vertical configuration as a result of the decrease in the positive charge on the alloy surface, as the pH of the solution approached the pzc.
- ❖ At temperatures $>50^\circ C$, it was assumed that Compound (B) underwent reorientation to the vertical configuration, which led to the abrupt decrease in surface coverage.
- ❖ Results in highly acidic media, as well as at higher temperatures, suggest that Compound (B) can be used as an inhibitor during pickling and etching of Al-Si alloys.

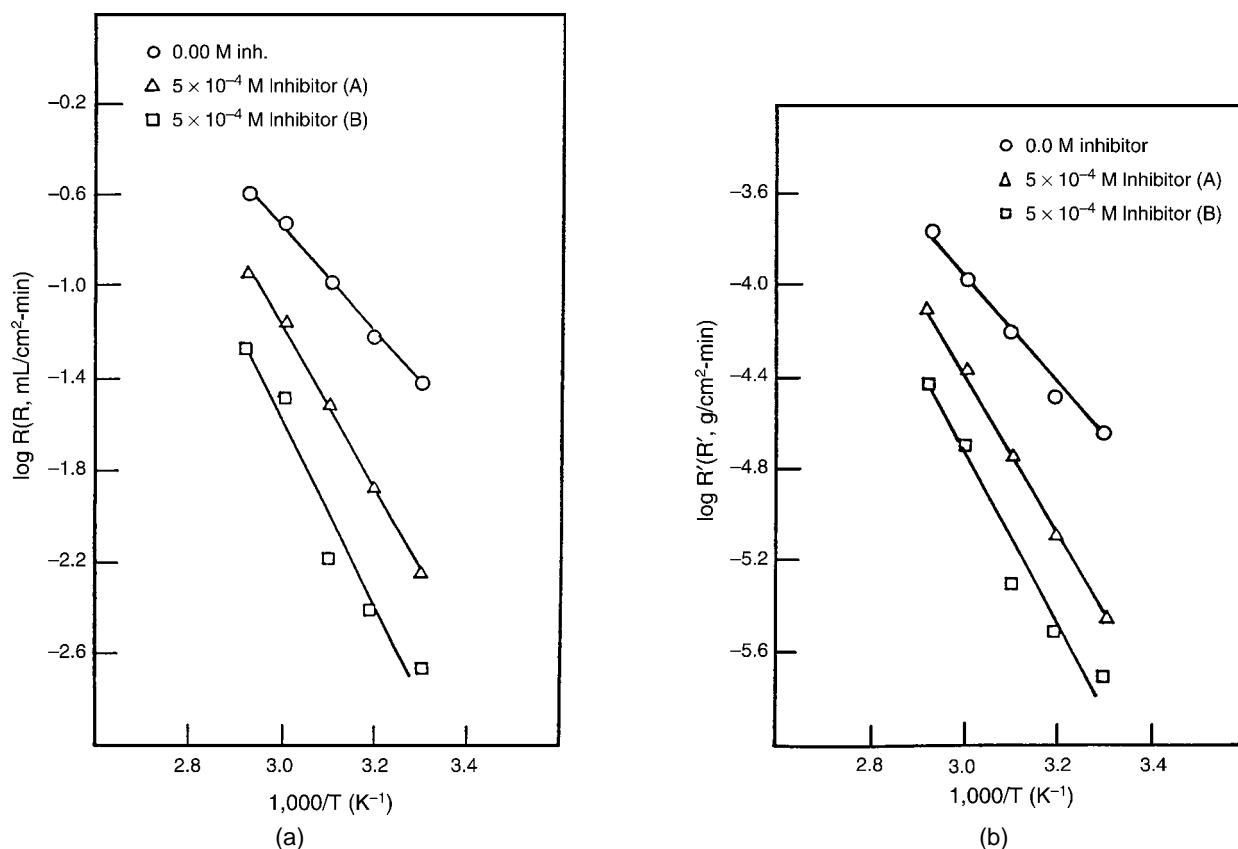


FIGURE 9. Arrhenius plots deduced from HEM for (A) and (B): (a) HEM and (b) MLM.

REFERENCES

- M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions (Houston, TX: NACE International, 1974), p. 168.
- J.B. Bessone, D.R. Salinas, C.E. Mayer, M. Ebert, W.J. Lorenz, *Electrochim. Acta* 37 (1992): p. 2,283.
- M. Tschapek, C. Wasowski, R.M. Torres Sanchez, *J. Electroanal. Chem.* 74 (1976): p. 167.
- S. Trasatti, *Electrochim. Acta* 37 (1992): p. 2,137.
- B. Müller, M. Gampper, *Werkst. Korros.* 45 (1994): p. 272.
- C. Monticelli, G. Brunoro, A. Frignani, F. Zucchi, *Corros. Sci.* 32, 7 (1991): p. 693.
- J.D. Talati, D.K. Gandhi, *Corros. Sci.* 23, 12 (1983): p. 1,315.
- A.A. Mazhar, S.T. Arab, E.A. Noor, *J. Appl. Electrochem.* 31 (2001): p. 1,131.
- M.S.A. Abd El-Mottaleb, A.M.K. Sherief, *Z. Phys. Chem., Leipz.* 263 (1984): p. 154.
- K.S.N. Murthy, E.S. Dwarakadasa, *Br. Corros. J.* 30, 2 (1995): p. 111.
- R. Driver, R.J. Meakins, *Br. Corros. J.* 12, 1 (1977): p. 46.
- R.J. Meakins, M.G. Stevens, R.J. Hunter, *J. Phys. Chem.* 73 (1969): p. 112.
- A. Rauscher, G. Kutsan, Z. Lukacs, E. Kalman, *Proc. 7th European Symp. Corrosion Inhibitors, Ann. Univ. Ferrara, N.S., Sez V. Suppl. no. 9 (1990)*, p. 293.
- S. Syed Azim, S. Muralidharan, S. Venkatakrishna Iyer, *J. Appl. Electrochem.* 25 (1995): p. 495.
- R. Agrawal, T.K.G. Nambodhiri, *Corros. Sci.* 30, 1 (1990): p. 37.
- T.P. Hoar, R.D. Holliday, *J. Appl. Chem.* 3 (1953): p. 502.
- L. Mészáros, B. Lengyel, T. Garai, G. Trabaneli, *Acta Chim. Hung.* 127, 1 (1990): p. 113.
- M. Metikos-Hukovic, Z. Grubac, E. Stupnisek-Lisac, *Corrosion* 50, 2 (1994): p. 146.
- E. Khamis, M. Atea, *Corrosion* 50, 2 (1994): p. 106.
- M. Metekos-Hukovic, R. Babic, Z. Grubac, S. Brinic, *J. Appl. Electrochem.* 24 (1994): p. 325.
- J.W. Diggle, A.K. Vijh, *Oxides and Oxide Films*, vol. 4 (New York, NY: Marcel Dekker, 1976), p. 171.
- N. Hackerman, H. Kaesche, *J. Electrochem. Soc.* 105 (1958): p. 191.
- B.A. Abd-El-Naby, M.M. Essa, M.A.E. Shaban, *Surf. Technol.* 26 (1985): p. 165.
- S.L. Granese, B.M. Rosales, C. Oviedo, J.O. Zerbino, *Corros. Sci.* 33 (1992): p. 1,439.
- A.S. Fouda, M.M. El-Semongy, *J. Indian Chem. Soc.* 59, 89 (1982): p. 89.
- H. Yamaoka, H. Fischer, *Electrochim. Acta* 10 (1965): p. 679.
- V. Carassiti, G. Trabaneli, F. Zucchi, 2nd European Symp. Corrosion Inhibitors, *Annal. Univ. Ferrara, N.S., Suppl. n. 4 (Univ. Ferrara, 1966)*, p. 417.
- R. Driver, R.J. Meakins, *Br. Corros. J.* 9, 4 (1974): p. 227.
- L. Jha, R.R. Singh, G. Singth, *J. Electrochem. Soc.* 39, 2 (1990): p. 71.
- W.W. Damaskin, O.A. Pieterij, *Elekrodudch (Maskwa)* (1968).
- E. Blomgren, J.O.M. Bockris, C. Jesch, *J. Phys. Chem.* 65 (1961): p. 2,000.
- S. Sankarapavinasam, F. Pushpanaden, M.F. Ahmed, *J. Appl. Electrochem.* 21 (1991): p. 625.
- A.E. Fouda, H.A. El-Nadar, M.N. Moussa, *Acta Chim. Hung.* 124, 4 (1987): p. 581.
- S. Rengamani, S. Muralidharan, M. Anbu Kulandainathan, S. Venkatakrishna Iyer, *J. Appl. Electrochem.* 24 (1994): p. 355.
- S. Muralidharan, K.L.N. Phani, S. Pitchumani, S. Ravichandran, S.V.K. Iyer, *J. Electrochem. Soc.* 142, 5 (1995): p. 1,478.
- T. Vasudevan, B. Muralidharan, S. Muralidharan, S.V.K. Iyer, *Anti-Corros. Methods Mater.* 45, 2 (1998): p. 120.
- R.J. Meakins, *J. Appl. Chem.* 13 (1963): p. 339.
- B. Müller, K. Franze, D. Mebarek, *Corrosion* 51, 8 (1995): p. 625.
- H.A. Ghaly, A.A. Mazhar, *Surf. Technol.* 16 (1982): p. 323.
- J. Heyrovsky, J. Kuta, "Principles of Polarography," in *Proc. of Corrosion Academy of Science (New York, NY: Academic Press, 1966)*, p. 228.