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Corrosion Inhibition of Zn-Al-Cu Alloy by 2-Aminothiazole

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The inhibitive effect of 2-aminothiazole on corrosion of Zn-Al-Cu alloy was investigated in acid, neutral and alkaline media by impedance and polarization techniques. The impedance data were fitted to a simple equivalent circuit model and indicated control by a diffusion process. Satisfactory inhibition was obtained in alkaline and neutral media. On the other hand, quite low inhibition efficiency was observed in acid medium. Increase in concentration of the inhibitor increased the inhibitive effect, whereas the reverse was observed when the temperature was increased. Different adsorption isotherms were tested in neutral and alkaline media, the best fit was obtained for the Freundlich isotherm. The highest value for the free energy change was recorded in alkaline medium in accordance with the high inhibition efficiency observed in this medium.

Keywords Zn alloy, inhibition, concentration, adsorption isotherms-temperature

1. Introduction

Zinc-aluminum alloys can be used for manufacturing fitting exposed to steam or seawater, gears, bushings, and other components subject to friction.

Also, Al-Zn and Zn are used as coatings for the protection of steel. Zinc-aluminum alloys comprise a new family of zinc castings alloys that have proven themselves in a wide variety of demanding applications. They are engineering materials well suited to applications requiring high as-cast strength, hardness and wear resistance.

The Zn-4Al-3Cu alloy is a widely used commercial material for fabricating various construction parts through die-casting. It is also a useful mold material in the trial mold applications for stamping and injection molding. The addition of copper results in an increase in strength of the alloy; however, the material will suffer dimensional instability over a period of time at ambient temperature. Most investigations were carried out in the high aluminum-zinc alloys. However, little work has been done on Zn-Al-Cu alloy with lower aluminum content. So the effect adding Al and Cu to Zn metal was studied in this work, which was expected to alter its electrochemical behavior compared to pure Zn metal. Inhibition is one of the most important applications in corrosion protection. Inhibitors protect the metal by adsorbing onto the surface. According to Hoar and others, inhibitor molecules adsorb to a different extent at different types of surface sites and influence the anodic and the cathodic reactions unequally (Ref 1). They also concluded that the adsorption of inhibitor molecules reduces the number of electrode reaction sites, and thus, inhibition becomes more predominant when the surface is covered with a monolayer of the inhibitor. However, the degree of coverage of the metal surface by adsorbed inhibitor is often less than a monolayer, with the rate of the process reduced by several orders of magnitude. It has been proposed that organic inhibitors adsorbed on the metal surface would change the double layer structure and affect kinetics of the electrochemical reactions, thereby partly insulating the metal from attack of the corrosive medium and making it more difficult for metal ion atoms to pass from the lattice to the solution (Ref 2).

Most of the studies conducted on the electrochemical behavior of Cu-Zn alloys have centered on stress corrosion cracking and dezincification (Ref 3).

Organic materials generally are recognized as effective inhibitors for corrosion of many metals and alloys. The efficiency of organic compounds as corrosion inhibitors is associated with their chemical adsorption, which includes a variation in the charge of the adsorbed substance and a charge transfer from one phase to the other. The reaction mechanism includes the transfer of one pair of electrons from organic compounds and the formation of coordinate bonds with the metal or alloy.

The aim of the present study is to test the influence of 2-aminothiazole on the corrosion of Zn-Al-Cu alloy in acidic, neutral, and alkaline media by means of electrochemical impedance spectroscopy (EIS) and potentiodynamic measurements. The former technique is a powerful technique for the study of electrochemical systems, including corrosion (Ref 4, 5) and has found wide application in the study of corrosion phenomena on zinc and its alloys in aggressive solutions.

2. Experimental Details

The working electrode was made from Zn-Al-Cu rod jammed in a small copper mold with about 30 cm wire tail which was fixed in a glass tube with Araldite (Ciba production-Switzerland) epoxy adhesive resin. The cross-sectional area of 0.8 cm^2 was only left to contact the test solution for both electrodes. The Zn alloy was composed of 96.34%Zn-2.8%Al-0.86%Cu. A preliminary investigation with various concentrations

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of the inhibitor showed that a 0.01 M concentration was optimal, and all further investigations were carried out with this concentration. DMF was added by 0.8% for complete solubility for the inhibitor in the test solutions. These solutions are 0.01 M HCl, Na_2SO_4 and NaOH. The inhibitor, used which was 2-aminothiazole, was of Merck production. The conventional three-necked cell was used. All chemicals used were chemically pure reagents of Merck production.

Double distilled water was used for the preparation and dilution of all the solutions. The volume of the solution in the electrochemical cell was 50 ml. Measurements were conducted in unstirred solutions and at constant temperature (25 ± 1 °C) except otherwise stated.

To achieve high reproducibility, the electrodes were pre-treated always using the same procedure. Before each experiment, the electrode surface was mechanically polished with successive grades of emery papers up to 1200 grit, then washed with acetone, double distilled water and finally with fine tissue paper so that the surface appeared mirror bright. The electrode was then immersed quickly in the test electrolyte. Measurements were performed at least twice in fresh solutions and in each run the electrode pre-treatment was carried out using the same procedure. The electrochemical measurements were all carried out using an IM6 Zahner electric potentiostat, Meβtechink, Germany. Impedance measurements were conducted with excitation amplitude of 10 mV peak to peak. The working frequency range was 0.1–100 kHz. The measurements were repeated from twice to three times in order to test their reproducibility. The data is fitted to suggest equivalent circuit models and appropriate plot formats can be obtained.

Tafel experiments were carried out after steady state conditions. The potential of the electrode was then changed at a sweep rate of 1 mV s^{-1} from −250 mV to +250 mV with reference to the open-circuit potential in a single sweep. From the slope of the linear region of the E versus log i curve within 100 mV on either side from the corrosion potential (E_{corr}) value, it was possible to determine cathodic and anodic Tafel constants. The corrosion current density (i_{corr}) was determined by extrapolating the Tafel lines. The cathodic and anodic Tafel slopes were obtained by using IM6 fitting software. Each test was carried out three times with good reproducibility of results.

3. Results and Discussion

2-aminothiazole is a heterocyclic organic compound with three carbon, two nitrogen atoms (one fused in the heterocyclic ring and the other is the amino group) and one sulfur atom in the ring (Fig. 1). This compound shows different anchoring sites suitable for surface bonding: nitrogen atom (1, Fig. 1) with its lone SP^2 electron pair, the sulfur atom (3, Fig. 1), the amino group with its lone pair of electron, the C(4)H-C(5)H-"edge" and the aromatic ring (Ref 6). So 2-aminothiazole is therefore a potentially effective inhibitor. Investigations of aliphatic and cyclic amines have shown that cyclic amines are better inhibitors than aliphatic ones (Ref 2).

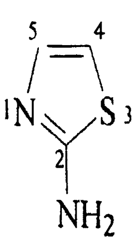

Fig. 1 Chemical structure of 2-aminothiazole

In the vicinity of the corrosion potential (E_{corr}), the polarization resistance (R_p), according to the procedure described by Mansfeld (Ref 7) can be obtained. However, in corrosion systems with discontinuous polarization curves in the vicinity of E_{corr} under steady state conditions, the determination of polarization resistance from electrochemical d.c. measurements:

$$R_p = (dE/di)_{E=E_{corr}} \quad \text{(Eq 1)}$$

and from measurements by a.c. impedance techniques according to:

$$R_p = \lim_{\omega\to 0} \mathrm{Re}\{Z_f\}_{E=E_{corr}} \quad \text{(Eq 2)}$$

was found to be problematic. In those systems the corrosion currents cannot be determined according to:

$$i_{corr} = \beta_a \beta_c / 2.303(\beta_a + \beta_c) R_p = B/R_p \quad \text{(Eq 3)}$$

where β_a and β_c are the anodic and cathodic Tafel slopes and B is a constant.

In such cases, where the usual polarization techniques fail, the corrosion current has been determined from the charge transfer resistance, R_{ct}, according to Epelboin and coauthors (Ref 8):

$$i_{corr} = B/R_{ct} \quad \text{(Eq 4)}$$

$$R_{ct} = \lim_{\omega\to\alpha} \mathrm{Re}\{Z_f\}_{E=E_{corr}} \quad \text{(Eq 5)}$$

where R_{ct} was determined at the intercept of the capacitance loop of the a.c. impedance diagram with the real axis at medium frequencies. The results obtained by this method have shown excellent agreement with the results obtained by the Tafel extrapolation method.

The inhibition efficiency of inhibition can be calculated by:

$$\mathrm{IE\%} = \left[(i_{corr})_o - (i_{corr})i/(i_{corr})_o\right] \times 100 \quad \text{(Eq 6)}$$

or

$$\mathrm{IE\%} = \left[(R_p)_i - (R_p)_o \Big/ (R_p)_i\right] \times 100 \quad \text{(Eq 7)}$$

where $(i_{corr})_i$ and $(i_{corr})_o$ denote the corrosion current densities in solutions with or without the inhibitor, respectively. $(R_p)_i$ and $(R_p)_o$ are the polarization resistance in solutions with and without the inhibitor, respectively. The inhibition efficiency (IE%) strongly depends on the structure and chemical properties of the layers that are formed under the particular experimental conditions. The extent of adsorption is dependent on the electronic structure of the metal and the inhibitor, since chemisorption requires a chemical bond between the inhibitor and the metal.

In this work, an investigation of the inhibition of Zn-Al-Cu alloy corrosion by 2-aminothiazole compound (Fig. 1) is discussed with respect to some variables such as: effect of pH value, effect of inhibitor concentration, and effect of temperature.

3.1 Inhibition in 0.01 M HCl

The behavior of Zn-Al-Cu alloy in 0.01 M HCl containing 0.01 M 2-aminothiazole was investigated using electrochemical methods at 25 °C. Figure 2 shows the Bode plots for the alloy immersed in 0.01 M HCl with and without 0.01 M 2-aminothiazole, after 1-h immersion time. The maximum concentration used in the present study of 2-aminothiazole (0.01 M) was the highest possible concentration, as limited by the solubility of the inhibitor in aqueous media. The spectra recorded in acidic solution in absence and presences of the inhibitor used are characteristic of a diffusion process that dominates even into the medium frequency region, with the phase angle not exceeding 45°. The presence of 2-aminothiazole increases the recorded R_p value of the alloy.

Tafel plots for Zn-Al-Cu alloy in 0.01 M HCl with the addition of 0.01 M 2-aminothiazole were recorded. In each case, the polarization measurement was carried out after the corrosion potential reached an approximately stable value to ensure that the reaction system was in the steady state.

Table 1(a) shows the kinetic parameters for the alloy in the above-studied solutions obtained by using Tafel extrapolation method, while Table 1(b), shows the values calculated on the basis of determination of R_p from impedance measurements according to Epelboin et al. (Ref 8).

The results in Table 1(a) and (b) show that, in the present case, all experimental methods used are appropriate for the investigation of the efficiency of the organic compound as corrosion inhibitor. A good agreement between the electrochemical methods was observed.

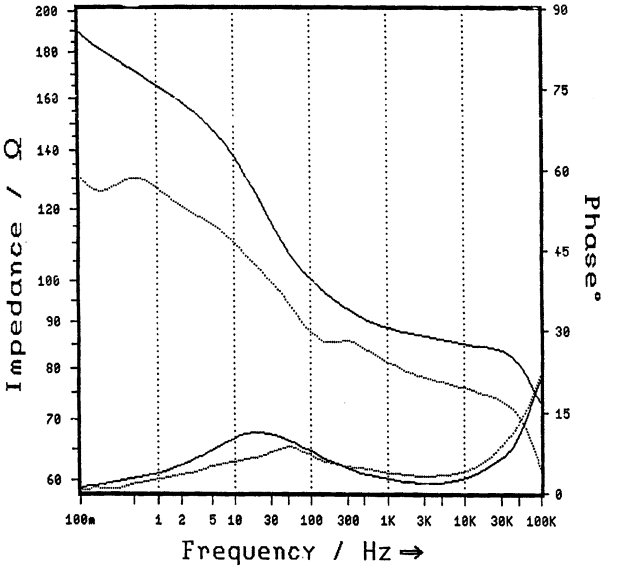

Fig. 2 Impedance plots for Zn-Al-Cu alloy in 0.01M HCl with (—) and without (….) 0.01 M 2-aminothiazole

It is evident from Table 1 that the open circuit potential of the solution was affected by the presence of inhibitor. The E_{corr} value for the inhibitor containing solution is shifted to a more negative value compared to the blank solution. Also, a slight lowering of both the anodic and cathodic current densities for the inhibitor containing solution was observed.

Also, the presence of 2-aminothiazole interferes with the cathodic reaction during the corrosion of the alloy, since only the cathodic Tafel slope is affected by the concentration of this inhibitor. This is probable, in accordance with the fact that the protonated nitrogen-containing organic compounds decrease the corrosion rate by increasing the hydrogen overvoltage on the corroding metal (Ref 9).

The decrease in the corrosion current density (i_{corr}) was associated with an appreciable shift of corrosion potential (E_{corr}) to a more negative value. This suggests that although inhibition is of a mixed type, it is predominantly under cathodic control.

The overall reaction during the corrosion of zinc in acidic solution is as follows:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \qquad \text{(Eq 8)}$$

which is the sum of the galvanic reactions (Ref 10): anodic (Ref 11):

$$Zn \rightarrow Zn^+ + e \qquad \text{(Eq 9)}$$

$$Zn^+ \rightarrow Zn^{2+} + e \qquad \text{(Eq 10)}$$

rds = rate determining step
cathodic (Ref 12):

$$H^+ + e \rightarrow H_{ads} \qquad \text{(Eq 11)}$$

$$H_{ads} + H_{ads} \rightarrow H_2 \qquad \text{(Eq 12)}$$

The 2-aminothiazole inhibitor under investigation has moderate inhibition efficiency in hydrochloric acid (IE %~27.6%), since the molecule is protonated in acidic medium, thus it becomes cation existing in equilibrium with the corresponding molecular form like:

(Eq 13)

So the protonated thiazole, becomes weakly adsorbed on the alloy surface, which is positively charged in acidic medium (Ref 2). Protonation decreases the number of lone pairs

Table 1 Kinetic parameters of Zn-Al-Cu alloy in 0.01 M HCl with and without the addition of 0.01 M 2-aminothiazole, at 25 °C after 1 h immersion time

(a) obtained using Tafel extrapolation method:

Solutions	β_a/mVdec^{-1}	β_c/mVdec^{-1}	i_{corr} /μA	E_{corr}/V	IE%
0.01 M HCl	80.5	86.7	75.6	–0.758	···
0.01 M HCl + 0.01 M inhibitor	68.9	120	54.7	–0.967	27.6

(b) As (a) but calculated on the basis of determination of R_p from impedance spectroscopy according to Epelboin et al. (Ref 8):

Solutions	B/mV	R_p/Ω	i_{corr}/μA	IE%
0.01 M HCl	18.1	239.7	75.5	···
0.01 M HCl + 0.01 M inhibitor	19	340	55.8	26.1

available for adsorption from three to two, and clearly would lower the basicity of the remaining lone pair.

The 2-aminotiazole molecule has three atoms available for coordination which are: N, S atoms in the heterocyclic ring and the N atom of amino group. The S atom of the thiazole ring is expected to have weak coordination ability (Ref 2), since the lone pair on this atom participates in the resonating structure of the molecule, resulting in a reduction of electron density on the S atom and a decrease in the electron donating power. So it is expected that 2-aminothiazole adsorbs physically on the alloy surface in acidic medium. All these factors cause the cathodic shift of E_{corr} for the alloy when immersed in acidic medium containing 2-aminothiazole.

Chemisorption of this inhibitor is not expected to occur, because at this very low pH value, the molecule will be protonated. Thus, chemisorption via the lone pair electrons should be excluded as a possible mechanism for corrosion inhibition by 2-aminothiazole in hydrochloric acid. In highly acidic solution, the high dissolution rate of zinc hinders the formation of a protective layer on the alloy surface which causes a lower percentage of inhibition compared to other pH values.

3.2 Inhibition in 0.01 M Na_2SO_4

3.2.1 Effect of Inhibitor Concentration. The effect of 2-aminothiazole concentration on the corrosion of Zn-Al-Cu alloy in 0.01 M Na_2SO_4 solution was investigated. Impedance spectra are shown in Fig. 3a. In all cases the high frequency parts of the impedance and phase angle describe the behavior of an inhomogeneous surface layer (Ref 13). The low frequency contribution shows the kinetic response for the charge transfer reaction (Ref 13). Generally, the presence of increasing thiazole concentrations cause an increase in the value of R_p compared to the blank sulfate solution, which indicates more inhibition action for the used inhibitor.

The impedance data were analyzed using the equivalent circuit model shown in Fig. 3b. The fitting results of the equivalent circuit parameters for the alloy in 0.01 M Na_2SO_4 in presence of different concentration of 2-aminothiazole are listed in Table 2.

The R_p of the formed film on the alloy surface (35.8 kΩ) was much higher than that of the blank solution (8.77 kΩ) (cf. Table 2). This change is due to the effective film formed on the alloy surface.

It can be observed that the R_p increases and the double layer capacitance (C_{dl}) decreases in the presence of inhibitor. The decrease in C_{dl} values in presence of inhibitor suggests that the coverage of the metal surface with reaction product increases the double layer thickness.

At higher inhibitor concentration, R_p increases and C_{dl} decreases. The latter may result from a reduction in the local dielectric constant and/or from increased electrical double layer thickness. Either of these can be related to adsorption at the metal/solution interface (Ref 14). The fractional coverage value θ can be obtained from the corrosion current via (Ref 15):

$$\theta = 1 - \left[(i_{corr})_i / (i_{corr})_o\right] = \left[(i_{corr})_o - (i_{corr})_i\right] / (i_{corr})_o \qquad \text{(Eq 14)}$$

Or

$$\theta = 1 - \left[(R_p)_o \Big/ (R_p)_i\right] = \left[(R_p)_i - (R_p)_o\right] \Big/ (R_p)_i \qquad \text{(Eq 15)}$$

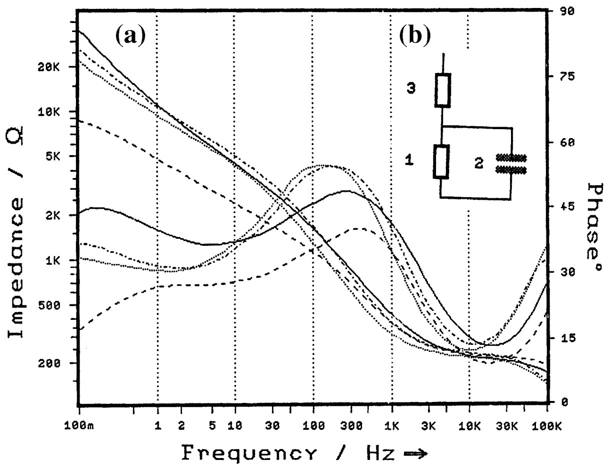

Fig. 3 (a) Effect of concentration in neutral environment (0.01 M Na_2SO_4) containing different concentration of 2-aminothiazole(M): (- - -) nil; (…) 10^{-3}; (-·-·) 5×10^{-3} and (—) 10^{-2} (b) Fitted equivalent circuit model: (1) R_p(polarization resistance; (2) CPE (constant phase element) and (3) R_s (solution resistance)

Table 2 Effect of inhibitor concentration on the electrochemical parameters of the alloy in 0.01 M Na_2SO_4

C, M	R_p/kΩ	CPE/nF	n	R_s/Ω	θ	IE%
0	8.77	415.5	0.524	100	···	···
10^{-3}	22.16	513.1	0.553	117.6	0.60	60.4
5×10^{-3}	26.6	404	0.539	121.3	0.67	67
10^{-2}	35.8	372.8	0.485	136.9	0.75	75.5

The values of θ are calculated using Eq 15 where the R_p values are obtained from impedance measurements. The values obtained in this way are also shown in Table 2.

It seems that complex formation occurs between 2-aminothiazole compound and the metal cations in the Zn-Al-Cu alloy. These complexes can form an adsorbed stable layer on the alloy surface which causes a decrease in the rate of corrosion when the 2-aminothiazole is added.

Figure 4 shows the typical Nyquist plot with and without the inhibitor, where two time constants can be clearly observed by two slightly distorted capacitive loops. The capacitive loop with inhibitor appearing at low frequency presents a phase angle close to 45°, typical of Warburg type behavior. The presence of two capacitive loops (two time constants) in the Nyquist plot is associated with the presence of two processes, in this case corresponding to oxidation and reduction reactions.

Table 3 represents the results obtained by a.c. impedance measurements for the results after fitting the data by the equivalent circuit shown in Fig. 3b. This equivalent circuit represents the Zn alloy/Na_2SO_4 interface. This model is similar to that usually proposed for the simple metal/electrolyte interface, but with a constant phase element (CPE) which substitutes the capacity of the double layer (C_{dl}) and which takes into account phenomena related to the heterogeneous surface and the diffusion processes.

As can be seen from the Bode plot (Fig. 3a), the impedance of the solution containing inhibitor has a high value compared to the blank free solution. Also the capacitance value is lower for the solution containing the inhibitor (C_{dl} = 372.8 nF) compared to the uninhibited one (C_{dl} = 415.5 nF). The values of the exponent (*n*) are close to 0.5, which indicates a diffusion control process and consequently the CPE represents a Warburg diffusion component.

The phase angle maximum in the inhibited solution is larger than that in the uninhibited one. All these observations confirm the inhibiting character of the 2-aminothiazole in the neutral sulfate medium. Hence, these two different methods (a.c. impedance and Tafel plots) told a consistent story about the efficiency of this molecule for inhibition of Zn-Al-Cu alloy corrosion. Furthermore, the agreement between the inhibition efficiency (IE%) values obtained from the a.c. impedance method (Table 3a) agreed well with the corresponding value obtained from the linear polarization method (Table 3b).

3.2.2 Effect of Temperature. The effect of temperature on the corrosion rate of Zn-Al-Cu alloy was investigated in 0.01 M Na_2SO_4 solution with addition of 0.01 M 2-aminothiazole. Bode plots for the alloy immersed in 0.01 M Na_2SO_4 containing 0.01 M 2-aminothiazole at different temperature values showed a decrease in the R_p and in the phase angle maximum as the temperature increased.

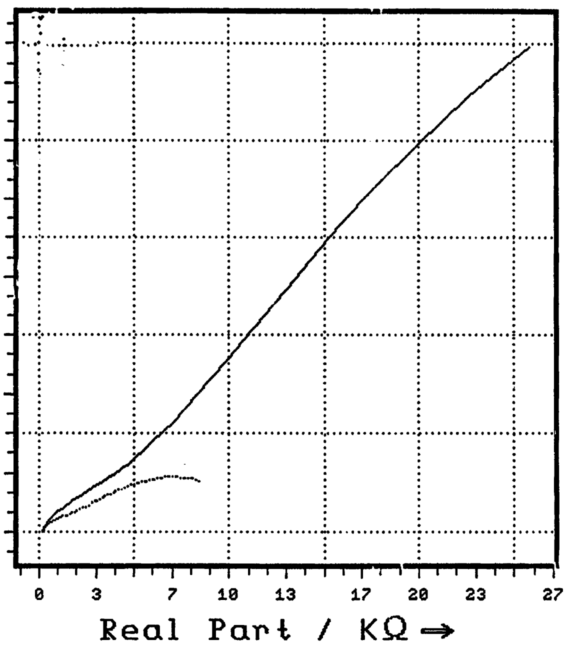

Fig. 4 Nyquist plots in neutral environment (0.01 M Na_2SO_4) containing 0.01 M 2-aminothiazole: (….) blank solution and (—) 0.01 M 2-aminothiazole + 0.01 M Na_2SO_4

The impedance data were analyzed using the equivalent circuit model in Fig. 3b. The electrochemical parameters are listed in Table 4. As would be expected, the i_{corr} values, obtained from Tafel plots, increase considerably as the temperature increase, indicating that the inhibitor efficiency decreases at higher temperatures. Temperature-dependent data were also obtained for the inhibitor at the optimal concentration of the inhibitor.

As the temperature increases the corrosion rate also increases, probably as a result of desorption of the inhibitor molecules from the metal surface.

Desorption of inhibitor molecules with increase in temperature is usually observed in cases of physisorption; chemisorption is often increased with increase in temperature. Also as the temperature increases the value of E_{corr} was shifted to more negative values. This corresponds to a more active state of the alloy surface.

The following activation parameters: E_a (activation energy), ΔH (the enthalpy change of activation) and ΔS (the entropy change of activation) are obtained from Arrhenius-type plot (Eq 16) and Eyring transition-state graph (Eq 17).

$$\ln \psi = \ln A + (-E_a/RT) \qquad \text{(Eq 16)}$$

$$\ln \psi/T = -\Delta H/RT + \ln R/Nh + \Delta S/R \qquad \text{(Eq 17)}$$

where ψ is the corrosion rate of Zn-Al-Cu alloy in presence of inhibitor, *A* is the Arrhenius pre-exponential constant, *R* is the universal gas constant (8.314 J mol^{-1} K^{-1}), *N* is Avogadro's number, and h is Plank's constant. A plot of ln ψ versus $1/T$ and ln (ψ/T) versus $1/T$ produced straight lines with slopes of ($-E_a/R$) and ($-\Delta H/R$), respectively. The intercepts are ln *A* and [ln ($R/N\,h$) + $\Delta S/R$] for the Arrhenius and Eyring transition-state equation, respectively.

Figure 5a represents the least—square plot for ln ψ vs. $1/T$ for the alloy in 0.01 M Na_2SO_4 in presence of 2-aminothiazole, where $\psi = 1/R_p$ which is the corrosion rate of the alloy. The E_a was determined from the slope of this plot and it was found to be 32 kJ mol^{-1}. Figure 5b illustrates the relation between ln (ψ/T) vs. ($1/T$) at different concentrations of 2-aminothiazole. The plot also produced a straight line, the calculated value of ΔH was +31.2 kJ mol^{-1} and ΔS was −230.7 J mol^{-1} K^{-1}.

Table 4 Electrochemical parameters for Zn-Al-Cu alloy in 0.01 M 2-aminothiazole + 0.01 M Na_2SO_4, at different temperature values

Temp/°C	R_p/kΩ	CPE/nF	*n*	R_s/Ω	i_{corr}/nA	E_{corr}/V
25	35.8	372.8	0.485	136.9	10.9	−0.950
30	22.96	383.7	0.448	143	71.9	−1.065
40	13.33	695.2	0.506	60.4	263	−1.075

Table 3 Kinetic parameters of Zn-Al-Cu alloy in 0.01 M Na_2SO_4 with and without the addition of 0.01 M 2-aminothiazole, at 25 °C after 1 h immersion time

(a) obtained by fitting					
Solutions	R_p/kΩ	CPE, nF	*n*	IE%	
0.01 M Na_2SO_4	8.77	415.5	0.524	–	
0.01 M Na_2SO_4 + 0.01 M inhibitor	35.8	372.8	0.485	75.5	
(b) obtained using Tafel extrapolation method:					
Solutions	β_a/mVdec^{-1}	β_c/mVdec^{-1}	i_{corr} /nA	E_{corr}/V	IE%
0.01 M Na_2SO_4	46.2	124	40	−1.016	···
0.01 M Na_2SO_4 + 0.01 M inhibitor	139	124	10.9	−0.950	72.7

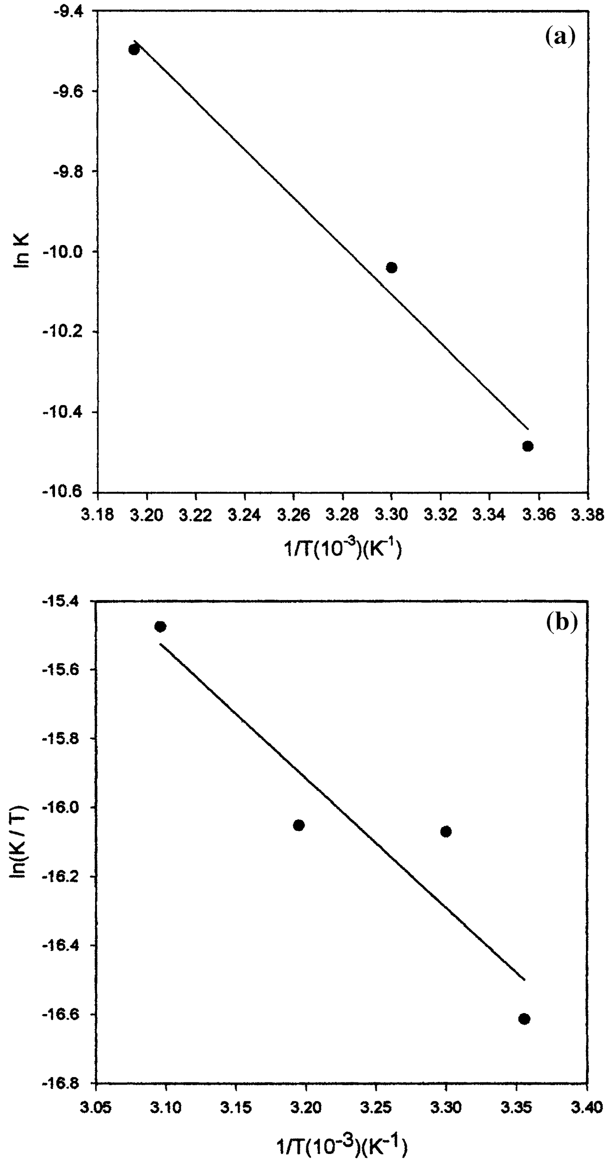

Fig. 5 (a) Arrhenius plot for Zn-Al-Cu alloy in 0.01 M Na_2SO_4 containing 0.01 M 2-aminothiazole. (b) Eyring plot of corrosion rate of Zn-Al-Cu alloy in presence of 0.01 M 2-aminothiazole at different temperatures in neutral medium

3.2.3 Choice of Adsorption Isotherm. The adsorption of an organic adsorbate on the surface of a metal is regarded as a substitution adsorption process between the organic compound in the aqueous phase (org(aq)) and the water molecules adsorbed on the electrode surface (H_2O(s)) (Ref 16).

$$\mathrm{Org(aq)} + x\mathrm{H_2O(s)} \rightarrow \mathrm{Org(s)} + x\mathrm{H_2O(aq)} \qquad \text{(Eq 18)}$$

where x is the size ratio, and is simply the number of water molecules replaced by one molecule of organic adsorbate. It must be emphasized that in addition to the electronic characteristics of the inhibitor, the adsorption process depends on the nature of the surface, temperature, and pressure.

A number of mathematical relationships representing adsorption isotherms that characterize the dependence of the surface coverage function, θ, on the inhibitor concentration have been suggested to fit the various experimental data. Some of these isotherms are empirical and others are theoretical. An adsorbed molecule may make adsorption more difficult or less difficult if it is attached to another neighboring molecule. Thus, multilayer adsorption may take place through occupation of more than one surface site by an inhibitor molecule or the adsorption of more than one inhibitor molecule per surface site. A number of mathematical expressions have thus been developed to take into consideration some of the non-ideal effects. The most used expressions are Freundlich, Frumkin, Hill de Boer, Parsons, Temkin, Flory-Huggins, Bockris-Swinkels adsorption isotherms and kinetic-thermodynamic model (Ref 17). Some of the corresponding mathematical expressions are listed below.

Flory-Huggins adsorption isotherm:

$$\theta/x(1-\theta)^x = \psi C \qquad \text{(Eq 19)}$$

Kinetic-thermodynamic model:

$$\log(\theta/1-\theta) = \log\psi + y\log\psi \qquad \text{(Eq 20)}$$

where Θ is a constant related to the binding constant, ψ, by the following relationship:

$$\psi = \Theta^{(1/y)} \qquad \text{(Eq 21)}$$

where y is the number of inhibitor molecules occupying one active site and $1/y$ represents the number of active sites of the surface occupied by one molecule of the inhibitor. It is of importance to realize that a value of $1/y$ greater than unity implies the formation of a multilayer of the inhibitor on the surface of the metal, while values of $1/y$ less than unity, mean that a given inhibitor molecule will occupy more than one active site. Larger values of the binding constant mean better inhibition efficiency of a given compound, i.e., stronger electrical interaction between the double layer existing at the phase boundary and the adsorbing molecules. A small value of the binding constant indicates weaker interaction by the adsorbing molecules and the metal surface which means that the molecules are easily removable by the solvent molecules from the surface.

Basically, all the above isotherms having the form (Ref 18):

$$F(\theta, x)\exp(-a\theta) = \psi C \qquad \text{(Eq 22)}$$

where $F(\theta, x)$ is the configurational factor which depends essentially on the physical model and assumptions underlying deviation of the isotherm. θ is the degree of surface coverage, (a) is the molecular interaction parameter depending on the molecular interactions in the adsorption layer and the degree of heterogeneity of the surface and C is the concentration.

Moreover, all above expressions include the equilibrium constant of the adsorption process, ψ, which is related to the standard free energy of adsorption

$\Delta G_{\mathrm{ads}}{}^{\mathrm{o}}$ by (Ref 15):

$$\psi = 1/55.5\exp\left[-\Delta G^{\mathrm{o}}_{\mathrm{ads}}/RT\right] \qquad \text{(Eq 23)}$$

The value 55.5 in the above equation is the concentration of water in the solution in mol dm^{-3}.

The different isotherms mentioned previously were tested to evaluate the most suitable isotherms, describing adsorption of the inhibitor on the Zn-Al-Cu alloy surface.

Excellent fit was obtained using Freundlich, Kinetic-thermodynamic, and Flory-Huggins models. The curve fitting of the data obtained from EIS measurement using 2-aminothiazole to Freundlich isotherm is given in Fig. 6. By far the best fit was

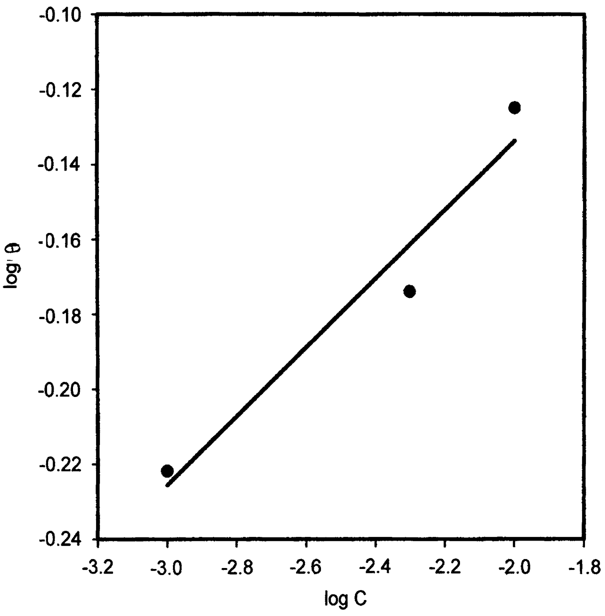

Fig. 6 Freundlich adsorption isotherm for 2-aminothiazole on Zn-Al-Cu alloy in 0.01 M Na_2SO_4

Table 5 Number of active sites ($1/y$), binding constants (Θ,ψ), number of water molecules replaced by one molecule of organic adsorbate (x) and free energy change (ΔG_{ads}^o) obtained from kinetic-thermodynamic model and Flory-Huggins isotherm for Zn-Al-Cu alloy in 0.01 M Na_2SO_4

Kinetic-Thermodynamic Model			Flory-Huggins Isotherm		
$1/y$	Θ	ΔG_{ads}^o	x	ψ	ΔG_{ads}^o
1.15	426.6	−10	1.25	430	−10

obtained with the Freundlich isotherm. The Freundlich model has been used for other inhibitor systems (Ref 19).

According to this isotherm, θ is related to the equilibrium adsorption constant ψ and concentration C via:

$$\theta = \psi C^n \qquad \text{(Eq 24)}$$

where $0 < n < 1$. In the logarithmic form the above equation becomes

$$\log\theta = \log\psi + n\log C \qquad \text{(Eq 25)}$$

which predicts that a plot of log θ vs. log C is linear (Fig. 6). The equilibrium constant of adsorption is related to the standard energy of adsorption. The standard free energy of adsorption (ΔG_{ads}^o) was calculated from equation (23) having the value of −10.6 kJ/mol.

Fitting the results by Kinetic-thermodynamic model for Zn-Al-Cu alloy in 0.01 M Na_2SO_4 containing different inhibitor concentration is given in Table 5. A good straight line fit was obtained for this isotherm. The slope of the line represents, y, the number of the inhibitor molecules occupying a single active site. The intercept is log Θ. As stated previously, $1/y$, gives the number of active sites occupied by a single-inhibitor molecule. The binding (equilibrium) constant for the adsorption process ψ is equal to $\Theta^{(1/y)}$.

The results also have been found to fit Flory-Huggins adsorption isotherm. Table 5 gives the curve fitting for the alloy in neutral sulfate medium containing different inhibitor concentrations. A very satisfactory fit was obtained for data of this inhibitor. The slope of the straight line is equal to x, and the intercept is log ψ K.

The results in Table 5 show that the numbers of active sites occupied by one molecule of inhibitor, $1/y$, is approximately equal to unity indicating that the adsorption process takes place by the occupation of one active site per single inhibitor molecule. The large negative value for the standard free energy of adsorption, ΔG_{ads}^o, indicates that the reaction proceeds spontaneously and is accompanied by an efficient adsorption.

Comparing the value of ΔG_{ads}^o obtained from Freundlich isotherm ($\Delta G_{ads}^o = -10.6$ kJ/mole), from the kinetic-thermodynamic model ($\Delta G_{ads}^o = -10$ kJ/mole) and from Flory-Huggins isotherm ($\Delta G_{ads}^o = -10$ kJ/mole) which confirms that these isotherms best fit the adsorption process occurring at the alloy surface using 2-aminothiazole as an inhibitor in neutral medium.

Molecules which adsorb by strong interaction have high values for the standard free energy of adsorption (Ref 20). This is in general agreement with Nuzzo's measurements of the bond energies for thiols chemisorbed to gold (Ref 21).

On the other hand, Metikos-Hukovic et al. describe the interaction between thiourea and iron ($\Delta G_{ads}^o = 39$ kJ/mol) as chemisorption (Ref 22). The ΔG_{ads}^o values obtained in this work show that in the presence of 0.01 M Na_2SO_4, chemisorption of this inhibitor does not occur. The low value of ΔG_{ads}^o obtained here support the physisorption-based mechanism.

3.3 Inhibition in 0.01 M NaOH

3.3.1 Effect of Inhibitor Concentration. Impedance behavior of Zn-Al-Cu alloy in 0.01 M NaOH solution containing different concentrations of 2-aminothiazole is somewhat similar to that in 0.01 M Na_2SO_4 solution containing different concentrations of this inhibitor, as shown in Fig. 7. The increase in the R_p value is observed when the inhibitor is added to the blank hydroxide solution. Splitting of the phase angle shift is observed, with an increase in the phase angle shift with the addition of 2-aminothiazole. This splitting in the phase angle shift means that the formation of inhibitor film changed the electrode interfacial structure and resulted in an extra time constant. The continuous increase in the phase angle shift obviously correlates with the inhibitor film growth.

The impedance data were analyzed using the equivalent circuit model shown in Fig. 3b. The fitting results are listed in Table 6. It is clear from Table 6, that the value of the solution resistance (R_s) obtained in the pure medium (0.01 M NaOH) was increased in the presence of inhibitor. This can be attributed to the change in the conductivity of the medium. Besides the increase in the value of R_p for the solution containing the inhibitor, the value of CPE obtained in the blank solution (CPE = 4.132 μF) is drastically decreased to half its value in the presence of the organic inhibitor (CPE = 2.08 μF). This can be correlated to the decrease in the area of Zn-Al-Cu alloy surface exposed to corrosive solution (increase in the area covered with the inhibitor) as a result of adsorption. On the other hand, the value of the exponent of CPE, n, can be used as a gauge of the heterogeneity of the surface. The data in Table 6 indicate that the value of n obtained in the blank medium

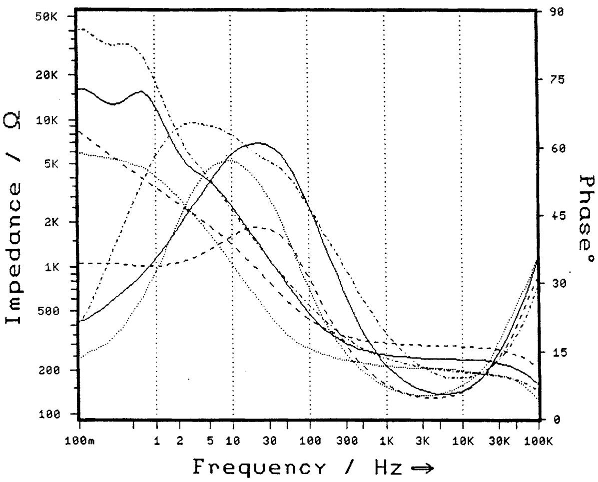

Fig. 7 Effect of concentration in alkaline environment (0.01 M NaOH) containing different concentrations of 2-aminothiazole(M): (…) nil; (. . .)10^{-4}; (- - -) 10^{-3}; (-·-·) 5×10^{-3} and (—) 10^{-2}

Table 6 Effect of inhibitor concentration on the electrochemical parameters of the alloy in 0.01 M NaOH

C, M	R_p, kΩ	CPE, μf	n	R_s, Ω	θ	IE%
0	11.19	4.132	0.776	170.7	···	···
10^{-3}	16.4	3.97	0.79	180.1	0.32	32
5×10^{-3}	32	2.65	0.75	183.6	0.65	65
10^{-2}	55.1	2.08	0.814	184.7	0.797	79.7

increases in the presence of the organic compound. This can be due to the adsorption of a uniform layer of inhibitor on the alloy surface.

The data recorded in alkaline medium are dominated also by diffusion ($n \approx 0.7$). The term, n, considers how far the interface is from an ideal capacitor. The capacitor is considered ideal when $n = 1$, and non-ideal (roughness surface) when $0.5 < n < 1$. The change in the value of the exponent was associated with the presence of a more complex surface layer.

The increase in the R_p and the decrease in C_{dl} when the organic inhibitor was added suggest that the coverage of the metal surface with reaction increases the double layer thickness.

Table 6 represents the results obtained by a.c. impedance measurements after fitting the data by the equivalent circuit shown in Fig. 3b.

Figure 8 represents the polarization curves of the Zn-Al-Cu alloy sample treated at 25 °C for 1 h in 0.01 M NaOH with and without 0.01 M 2-aminothiazole. Treatment with the organic compound resulted in a shift of the corrosion potential (E_{corr}) toward a more positive value by 328 mV in comparison to the blank solution. Both the cathodic and anodic currents decreased in presence of the inhibitor. The higher corrosion resistance was exhibited by the alloy treated with 0.01 M 2-aminothiazole solution indicating that the surface exposed to the corrosive medium is less active, due to the improvement of the surface coverage by the inhibitor solution. Thus, inhibition may be caused by active site blocking.

3.3.2 Effect of Temperature. The increase in temperature from 25 °C to 50 °C resulted in an increase in corrosion rate and a decrease in R_p value. These increases in the corrosion rate as the temperature increased is a result of desorption of inhibitor molecules from the metal surface.

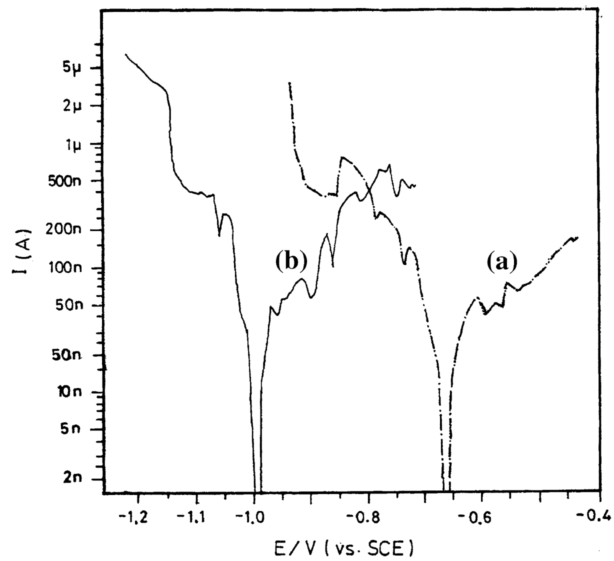

Fig. 8 Tafel plot for Zn-Al-Cu alloy with (a) and without (b) 0.01 M 2-aminothiazole in alkaline medium (0.01 M NaOH)

Table 7 Effect of temperature on the electrochemical parameters for the alloy in 0.01 M 2-aminothiazole + 0.01 M NaOH

Temp/°C	R_p/kΩ	CPE/μF	n	R_s/Ω	i_{corr}/nA	E_{corr}/V	IE%
25	55.1	2.08	0.776	184.7	10.9	−0.670	79.7
30	31.49	2.68	0.723	183.3	12.5	−0.797	64.5
40	29.92	4.82	0.684	119.2	19.1	−0.877	62.6
50	16.28	7.69	0.611	98.25	22.5	−0.901	31.26

A simple relationship was plotted for the effect of temperature on the inhibition efficiency. It was observed that, as the temperature increased the inhibition efficiency (IE%) decreased. This suggests that the inhibition of Zn-Al-Cu alloy corrosion in presence of this inhibitor occurs by adsorption at sites on the metal surface.

Table 7 shows the electrochemical parameters obtained from EIS and polarization measurements for the inhibited Zn-Al-Cu alloy in 0.01 M NaOH containing 0.01 M 2-aminothiazole at different temperatures, with the values of inhibition efficiency for each temperature. As the temperature increases, the protection of the surface by the inhibitor decreases as indicated by decrease in R_p and increase in the corrosion current, i_{corr}. This is also supported by the shift of E_{corr} to more negative values. Also, the decrease in n with increase in temperature indicates that the surface film tends toward better capacitive properties at lower temperatures.

The process of inhibition also was found to obey Arrhenius relation (cf. equation (16)). The activation energy value (E_a) was calculated from the slope of the straight line and found to be 48 kJ mol^{-1}. This is in a good agreement with the inhibition efficiency order recorded from the a.c. and d.c. measurements.

The relation between ln (ψ/T) vs. ($1/T$) at different concentrations of 2-aminothiazole in presence of 0.01 M NaOH gave a straight line, the calculated value of $\Delta H = +47.45$ kJ mol^{-1} and $\Delta S = -173.2$ J mol^{-1} K^{-1}.

Comparing the value of E_a for both solutions in neutral and alkaline medium, the large E_a value in the latter indicates the strong adsorption of the inhibitor molecules at the metal surface in alkaline medium compared to the neutral solution, where better inhibitors show the highest values of activation energy for the corrosion process. ΔH value is higher in alkaline medium rather than in neutral medium which suggests a higher protection efficiency observed in the alkaline medium. This could be attributed to the presence of an energy barrier which increases in the alkaline medium. Also, it is observed that the ΔS value has a lower value compared to the neutral solution.

3.3.3 Choice of Adsorption Isotherm. Basic information on the interaction between the inhibitor and the electrode surface can be provided by the adsorption isotherm. In this respect, the coverage concentration data of 2-aminothiazole in 0.01 M NaOH was best fitted to Freundlich adsorption isotherm. This isotherm was found to describe the experimental results well, and the correlation coefficient of the fitted data was about 0.96. The isotherm is shown in Fig. 9. The calculated value of $\Delta G_{\mathrm{ads}}^{\circ}$ from the isotherm was found to be −14.3 kJ/mol. So it is believed for the relation between the 2-aminothiazole and the alloy surface to undergo a physisorption mechanism on the alloy surface.

Fitting the results by Kinetic-thermodynamic model for Zn-Al-Cu alloy in 0.01 M NaOH containing different inhibitor concentrations is given in Fig. 10. A good straight line fit is obtained for this inhibitor. The results also have been found to fit Flory-Huggins adsorption isotherm. Figure 11 gives the curve fitting for the alloy in alkaline medium containing different inhibitor concentrations. Very satisfactory fit is obtained for data of this inhibitor.

Table 8 gives the adsorption parameters obtained from kinetic-thermodynamic model and Flory-Huggins isotherm for Zn-Al-Cu alloy in 0.01 M NaOH using 2-aminothiazole at 25 °C. The results show that the numbers of active sites occupied by one molecule of inhibitor, $1/y$, for the inhibitor used has a value greater than unity, i.e., ($1/y = 3.5$). This suggests that the 2-aminothiazole form multilayer film. The large negative value for the standard free energy of adsorption,

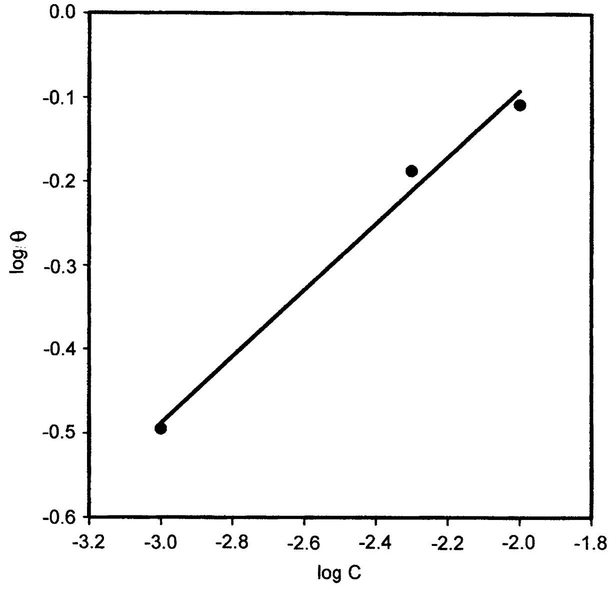

Fig. 9 Freundlich adsorption isotherm for 2-aminothiazole on Zn-Al-Cu alloy in 0.01 M NaOH

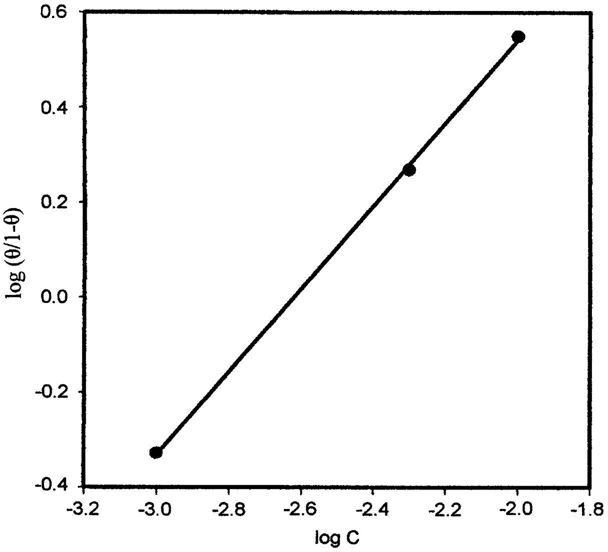

Fig. 10 Kinetic-Thermodynamic model curve fitting of the corrosion data of Zn-Al-Cu alloy in 0.01 M NaOH in presence of different concentrations of 2-aminothiazole

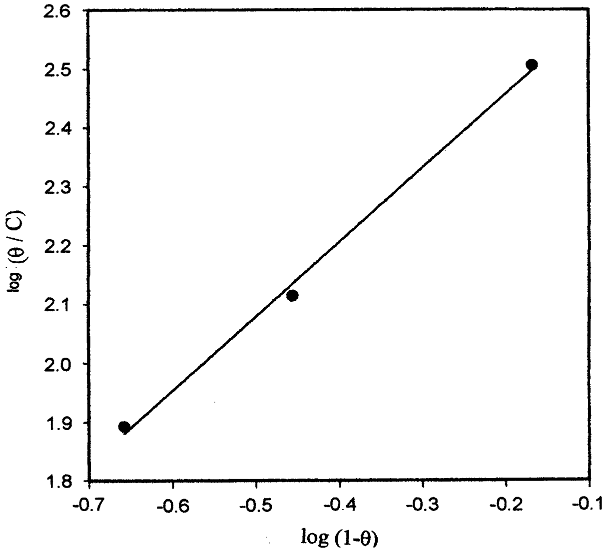

Fig. 11 Flory-Huggins isotherm curve fitting of the corrosion data of Zn-Al-Cu alloy in 0.01 M NaOH in presence of different concentrations of 2-aminothiazole

Table 8 Number of active sites ($1/y$), binding constants (Θ,ψ), number of water molecules replaced by one molecule of organic adsorbate (x) and free energy change ($\Delta G_{\mathrm{ads}}^{\circ}$) obtained from kinetic-thermodynamic model and Flory-Huggins isotherm for Zn-Al-Cu alloy in 0.01 M NaOH

Kinetic-Thermodynamic Model			Flory-Huggins Isotherm		
$1/y$	Θ	$\Delta G_{\mathrm{ads}}^{\circ}$	x	ψ	$\Delta G_{\mathrm{ads}}^{\circ}$
3.5	3548	−13.1	4.2	3000	−13.04

Table 9 Possible reactions at zinc electrodes in aqueous solutions

Reactions	Standard eq. potential E/V, SHE
(1a) $Zn \leftrightarrow Zn^{2+} + 2e$	−0.763
(1b) $Zn + OH^{-} \leftrightarrow Zn(OH)^{+} + 2e$	−0.893
(1c) $Zn + 2OH^{-} \leftrightarrow Zn(OH)_2 + 2e$	−1.244
(1d) $Zn + 2OH^{-} \leftrightarrow ZnO + H_2O + 2e$	−1.247
(1e) $Zn + 3OH^{-} \leftrightarrow HZnO_2^{-} + H_2O + 2e$	−1.188
(1f) $Zn + 4OH^{-} \leftrightarrow ZnO_2^{2-} + 2H_2O + 2e$	−1.214
(2) $2H_2O + 2e \leftrightarrow H_2 + 2OH^{-}$	−0.828
(3) $O_2 + H_2O + 4e \leftrightarrow 4OH^{-}$	+0.401
(4a) $Inh.aq + Zn \leftrightarrow (Zn\text{-}Inh)_{ad}$	...
(4b) $HInh + Zn^{2+} \leftrightarrow ZnInh^{+} + H^{+}$	...
(4c) $HInh + ZnInh^{+} \leftrightarrow Zn(Inh)_2^{+} + H^{+}$	...

ΔG_{ads}^{o}, indicates that the reaction proceeds spontaneously and is accompanied by efficient adsorption.

Comparing the value of ΔG_{ads}^{o} obtained from Freundlich isotherm ($\Delta G_{ads}^{o} = -14.3$ kJ/mole), from the kinetic-thermodynamic model ($\Delta G_{ads}^{o} = -13.1$ kJ/mole) and from Flory-Huggins isotherm ($\Delta G_{ads}^{o} = -13.04$ kJ/mole) which confirms that these isotherms best fit the adsorption process occurring at the alloy surface using 2-aminothiazole as an inhibitor in alkaline medium.

It is also observed that the value of the binding constant, Θ, increases from 426.6 in 0.01 M Na_2SO_4 to 3548 in 0.01 M NaOH which supports more protection efficiency. This clearly indicates that the strength of electrical interaction by adsorbed molecule and the metal surface increases in alkaline solution compared to the neutral one.

The large negative value of ΔG_{ads}^{o} for the inhibitor in 0.01 M NaOH compared to the inhibitor in 0.01 M Na_2SO_4 indicates that the adsorption of this inhibitor is stronger on the alloy surface in alkaline medium compared to neutral medium.

3.3.4 Comparison Among the Different Studied Media. The data recorded in alkaline pH (0.01 M NaOH) were similar to those shown in neutral medium (0.01 M Na_2SO_4). In acidic medium zinc dissolution proceeds on the bare metal surface while in neutral and alkaline medium passive corrosion has to be considered. In case of pure zinc which has high hydrogen overpotential, hydrogen evolution is only important in strongly acidic solutions. At higher pH values oxygen reduction is the dominating cathodic corrosion reaction. Because of the almost equal thermodynamic stability of ZnO and $Zn(OH)_2$ with a difference of 3 mV (reactions 1c/d, Table 9) a potentiometric differentiation between the two forms is not possible. Therefore the higher inhibition efficiency (72%) observed in neutral medium is due to the formation of the above species in addition to $Zn(Inh)_2$.

In alkaline medium, the passivity due to the formation of soluble zincate ions ($HZnO_2^{-}$, ZnO_2^{2-}), has to be taken into account. These compounds are formed in addition to $Zn(Inh)_2$ which cause high inhibition efficiency (80%).

3.3.5 The Formation and Composition of Zinc Thiazole Complex. When zinc is present in a neutral solution containing the inhibitor the pH decreases. This can be explained by an overall complex formation reaction:

$$Zn^{2+} + 2\,HInh \leftrightarrow Zn(Inh)_2 + 2H^{+} \qquad \text{(Eq 26)}$$

Thus, quantitative formation of $Zn(Inh)_2$ complex occurs only if the protons emanating from this equilibrium are removed, e.g., by reaction with hydroxyl ions. Therefore, the influence of complex formation on the inhibition efficiency of the thiazole should increase with pH. This confirms the high inhibition efficiency of the studied thiazole in alkaline medium, as compared to the neutral medium, and to a higher extent, the acidic medium.

4. Conclusions

1. The inhibitor 2-aminothiazole shows good inhibition efficiency for corrosion of Zn-Al-Cu alloy in Na_2SO_4 and NaOH solutions.
2. The inhibition efficiency increases with an increase in inhibitor concentration and decreases with an increase in temperature.
3. Analysis of the impedance data indicates control by diffusion process.
4. The calculated values for the activation energy, enthalpy change, and free energy change in presence of the inhibitor are higher in NaOH solution than Na_2SO_4 solution which suggests higher protection efficiency in the former solution.

References

1. T.P. Hoar, *International Conference on Surface Reactions*. Pitts-urgh Corrosion Publishing Co, Pittsburgh, PA, 1948, p 127
2. I.L. Rozenfeld, *Corrosion Inhibition*. McGraw-Hill Inc., New York, NY, 1981, p 327
3. H.W. Pickering and C. Wagner, Electrolytic Dissolution of Binary Alloys Containing a Noble Metal, *J. Electrochem. Soc.*, 1967, **224**, p 698 (in English)
4. K. Jüttner, The Role of Chloride and Sulphate Anions in the Iron Dissolution Mechanism Studied by Impedance Measurements, *J. Electrochim. Acta*, 1990, **35**, p 1000 (in English)
5. W.J. Lorenz and F. Mansfeld, Determination of Corrosion Rates by Electrochemical DC and AC Methods, *Corros. Sci.*, 1981, **21**, p 647 (in English)
6. E.M. Kosower, *An Introduction to Physical Organic Chemistry*. John Wiley and Sons Inc, New York, NY, 1968, p 13
7. F. Mansfeld, Simultaneous Determination of Instantaneous Corrosion Rates and Tafel Slopes from Polarization Resistance Measurements, *Corrosion*, 1973, **29**, p 397 (in English)
8. I. Epelboin, M. Keddam, and H. Takenouti, Use of Impedance Measurements for the Determination of the instant Rate of Metal Corrosion, *J. Appl. Electrochem.*, 1972, **2**, p 71 (in English)
9. C.A. Mann, Brazing Assembled Metal Sheet, *Trans. Electrochem. Soc.*, 1936, **69**, p 115
10. R.J. Brodd and V.E. Leger, *Encyclopedia of Electrochemistry of the Elements*, vol. 5. A.J. Bard, Ed., (New York), Marcel Dekker Inc., 1976, p 49
11. T. Hurlen, Kinetics of the Zn/Zn++ aq. Electrode, *Acta Chem. Scand.*, 1962, **16**, 1337 and 1346
12. N. Pentland, J.O.M. Bockris, and E.Sheldon, H-Evolution Reaction on Cu,Au,Mo,Pd, Rh, and Fe-Mechanism and Measurement Technique Under High Purity Conditions, *J. Electrochem. Soc.*, 1957, **104**, p 182 (in English)
13. M.S. Abd El Aal and M.S. Morad, Inhibiting Effects of Some Quinolines and Organic Phosphonium Compounds on Corrosion of Mild Steel in 3M HCl Solution and their Adsorption Characteristics, *Brit. Corros. J.*, 2001, **36**, p 253 (in English)
14. E. McCafferty and N. Hackerman, Double Layer Capacitance of Iron and Corrosion Inhibition with Polymethyene Diamines, *J. Electrochem. Soc.*, 1972, **119**, p 146 (in English)
15. M. Kaminski and Z. Szklarska-Smialowska, Adsorption of Thiophene Derivatives on Steel in Sulfuric Acid Solutions, *Corros. Sci.*, 1973, **13**, p 557 (in English)
16. D. Schweinsberg, G. George, A. Nanyakkara, and D Steinert, The Protective Action of Epoxy Resins and Curing Agents-Inhibitive Effects on the Aqueous Acid Corrosion of Iron and Steel, *Corros. Sci.*, 1988, **28**, p 33 (in English)

17. A. El-Awady, B. Abd El-Nabey, and G. Aziz, Kinetic-Thermodynamic and Adsorption Isotherms Analyses for the Inhibition of Acid Corrosion of Steel by Cyclic and Open-Chain Amines, *J. Electrochem. Soc.*, 1992, **139**, p 2149 (in English)
18. E. Khamis, F. Bellucci, R. Latanision, and E. El-Ashry, Acid Corrosion Inhibition of Nickel by 2-(Triphenosphoranylidene) Succinic Anhydride, *Corrosion*, 1991, **47**, p 677 (in English)
19. M. Kliskic, J. Radosevic, and S. Gudic, Pyridine and its Derivatives as Inhibitors of Al Corrosion in Chloride Solution, *J. Appl. Electrochem.*, 1997, **27**, p 947 (in English)
20. J. Heyrovsky and J. Kuta, *Principles of Polarography.* Corrosion Academy of Science, Prage, 1965; Academic Press, New York, 1966
21. R.G. Nuzzo, F.A. Fusco, and D.L. Allara, Spontaneously Organized Molecular Assemblies 3. Preparation and Properties of Solution Adsorbed Monolayers of Organic Disulfides on Gold Surface, *J. Am.Chem. Soc.*, 1987, **109**, p 2358 (in English)
22. M. Metikos-Hukovic, R. Babic, Z. Grubac, and S. Brinic, Study of the Thiourea Adsorption on Iron in Acid Solution, *J. Appl. Electrochem.*, 1996, **26**, p 443 (in English)