

## Synergistic effect of I<sup>-</sup> ions on the corrosion inhibition of Al in 1.0 M phosphoric acid solutions by purine

Mohammed A. Amin<sup>a,b,\*</sup>, Q. Mohsen<sup>b</sup>, Omar A. Hazzazi<sup>c</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt

<sup>b</sup> Materials and Corrosion Lab (MCL), Faculty of Science, Department of Chemistry, Taif University, 888 Hawayia, Taif, Saudi Arabia

<sup>c</sup> Faculty of Applied Science, Department of Chemistry, Umm Al-Qura University, P.O. Box 2897, Makkah, Saudi Arabia

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### ABSTRACT

The effect of purine, as a safe inhibitor, was investigated by measuring the corrosion of Al in 1.0 M deaerated stirred H<sub>3</sub>PO<sub>4</sub> solution at 25 °C. Measurements were conducted under various experimental conditions using polarization and impedance measurements, complemented with EDX examinations of the electrode surface. According to these results, purine alone showed a poor inhibition effect. Addition of I<sup>-</sup> ions enhanced the inhibition efficiency of purine. The synergistic effect is attributed to enhanced adsorption of purine by the adsorbed I<sup>-</sup> ions. Potentiodynamic polarization studies showed that purine alone and the mixture of purine and I<sup>-</sup> ions act as mixed-type inhibitors for the corrosion of Al in 1.0 M H<sub>3</sub>PO<sub>4</sub> solution. The impedance diagram exhibited three time constants or semi-circles of which the sizes are dependent on inhibitor concentration and immersion time. The capacitive time constant at high frequencies may be related to the oxide film itself. The second capacitive time constant at low frequencies can be attributed to oxide film dissolution. The inductive loop at medium frequencies may be attributed to the relaxation of adsorbed charged intermediates. Inhibition via hydrogen bond formation is also discussed here.

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### 1. Introduction

The most important feature of aluminium is its corrosion resistance due to the presence of a thin, adherent and protective surface oxide film. Because of this advantage, aluminium and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries. Solutions of phosphoric acid are frequently employed for cleaning of Al [1,2] and in commercial pre-plating anodic oxidation and electro-polishing of Al [3]. Under these circumstances, corrosion inhibitors should be used because the solubility of the oxide film increases above and below pH 4–9 [4] range and aluminium exhibits uniform attack. Inhibitors are used to prevent metal dissolution and minimise acid consumption. Most of the efficient acid inhibitors are organic compounds that contain mainly nitrogen, sulphur or oxygen atoms in their structure.

Generally, it has been assumed that the first stage in the mechanism of the inhibitors action in aggressive acid media is the adsorption of the inhibitors onto the metal surface. The processes of adsorption of inhibitors are influenced by the nature and surface charge of the metal, the chemical structure of organic inhibitors,

the distribution of charge in the molecule and the type of aggressive electrolyte. The chemisorptions are the principle types of interaction between organic inhibitors and the metal surface [5,6].

Synergistic inhibition is an effective means to improve the inhibitive force of inhibitor, to decrease the amount of usage and to diversify the application of inhibitor in acidic media. It is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. Actually, many investigations concerning synergistic inhibition have been carried out and are being carried out [7–9].

The objective of the present work is to study the inhibitive action of purine, as a safe-inhibitor, toward the corrosion of Al in 1.0 M deaerated stirred H<sub>3</sub>PO<sub>4</sub> solution using polarization and impedance studies, complemented with EDX examinations of the electrode surface. It was also the purpose of the present work to investigate the synergistic inhibition between purine and I<sup>-</sup> ions on the corrosion inhibition of Al in phosphoric acid solutions. Adsorption via hydrogen bond formation is also discussed here.

### 2. Experimental

The working electrode employed here was made from high-purity Al sheets (for EDX examinations of the electrode surface) and cylindrical rods (for electrochemical measurements). For electrochemical measurements, the cylindrical rods were welded with Cu-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface of

\* Corresponding author. Tel.: +20 22509331; fax: +20 24836831.  
E-mail address: [maaismail@yahoo.com](mailto:maaismail@yahoo.com) (M.A. Amin).

about 0.20 cm<sup>2</sup> geometric area, to contact the test solution. These rods were first briefly ground with no. 600 emery paper, subsequently polished with no. 2000 emery paper, washed with deionized water, degreased with absolute ethanol, dried, and then rinsed with deionized water rapidly, followed by immediate rinsing with absolute ethanol.

A conventional electrochemical cell of capacity 100 ml was used containing three compartments for working, platinum spiral counter and reference electrodes. The reference electrode was a saturated calomel one used directly in contact with the working solution. The measurements were carried out in deaerated stirred 1.0 M H<sub>3</sub>PO<sub>4</sub> solutions without and with various concentrations (10<sup>-5</sup> to 5 × 10<sup>-2</sup> M) of purine, as a safe corrosion inhibitor, at 25 °C.

KI (10<sup>-4</sup> M) was also added to purine-H<sub>3</sub>PO<sub>4</sub> containing solutions to study the synergistic inhibition between KI and purine. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification.

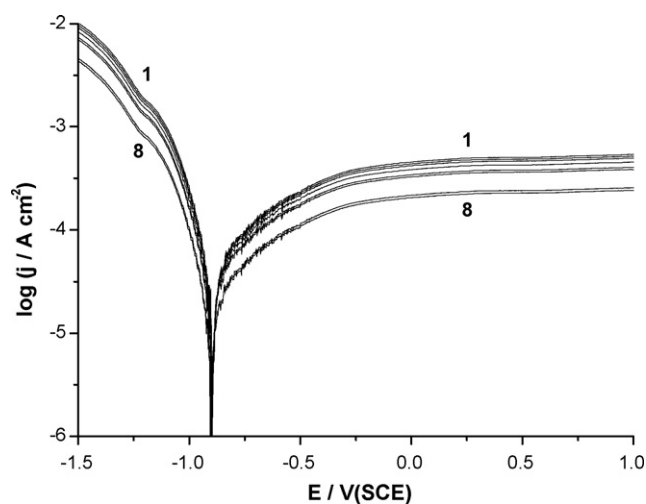
For each run, a freshly prepared solution as well as a cleaned set of electrodes was used. Each run was carried out in deaerated stirred solutions at the required temperature (±1 °C), using a water thermostat. Electrochemical measurements were performed using an Autolab Potentiostat/Galvanostat (PGSTAT30) with FRA2 module for impedance measurements and a personal computer were used with GPES and FRA (ver. 4.9) software provided by Autolab. The potentiodynamic current–potential curves were carried out at a scan rate of 0.10 mV s<sup>-1</sup> starting from –1.50 up to 1.0 V (SCE). Impedance measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open circuit potential in the frequency range 100 kHz to 1.0 mHz. All impedance data were fitted to appropriate equivalent circuits using the computer program EQUIVCRT [10]. Before each polarization and impedance experiment, the open circuit potential of the working electrode was measured as a function of time during 24 h, the time quite necessary to reach a quasi-stationary value for the open circuit potential.

### 3. Results and discussion

#### 3.1. Polarization measurements

##### 3.1.1. Effect of inhibitor concentration

The effect of purine concentration (10<sup>-5</sup> to 5 × 10<sup>-2</sup> M) on the potentiodynamic anodic and cathodic polarization curves of Al has been studied in 1.0 M deaerated stirred H<sub>3</sub>PO<sub>4</sub> solution at a scan rate of 0.10 mV s<sup>-1</sup> at 25 °C. Some of the obtained results are depicted in Fig. 1. No active passive transition was observed and the current seems to be constant at high anodic potentials, irrespective of the absence or presence of the inhibitor. In addition, it is observed that the hydrogen evolution reaction is activation controlled since the cathodic portions rise to Tafel lines. By comparing polarization curves in the absence (curve 1) and presence of various concentrations of purine (curves 2–8) it is observed that increase in purine



**Fig. 1.** Polarization curves recorded for Al in 1.0 M deaerated stirred H<sub>3</sub>PO<sub>4</sub> solution without and with various concentrations of purine at a scan rate of 0.10 mV s<sup>-1</sup> at 25 °C. (1) Blank; (2) 10<sup>-4</sup> M; (3) 2.5 × 10<sup>-4</sup> M; (4) 5 × 10<sup>-4</sup> M; (5) 10<sup>-3</sup> M; (6) 2.5 × 10<sup>-3</sup> M; (7) 5.0 × 10<sup>-3</sup> M; (8) 10<sup>-2</sup> M.

**Table 1**

Electrochemical parameters ( $j_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_c$  and  $R_p$ ) associated with polarization measurements of Al in 1.0 M H<sub>3</sub>PO<sub>4</sub> solution without and with different concentrations of purine at 25 °C.

$C_{\text{purine}} \times 10^2$ (M)	$j_{\text{corr}} \times 10^2$ (mA cm <sup>-2</sup> )	$E_{\text{corr}}$ (V) (SCE)	$-b_c$ (V dec. <sup>-1</sup> )	$R_p$ ((cm <sup>2</sup> ))	%IE
Blank	5.00	-0.897	-0.154	495	-
0.01	4.80	-0.899	-0.155	516	4.04
0.025	4.60	-0.902	-0.153	538	8.07
0.05	4.22	-0.904	-0.154	586	15.60
0.10	3.76	-0.905	-0.156	659	24.88
0.25	3.59	-0.907	-0.155	690	28.25
0.50	2.38	0.908	-0.153	1038	52.32
1.00	2.25	-0.910	-0.155	1100	55.01

concentration shifts slightly the corrosion potential ( $E_{\text{corr}}$ ) in the positive direction and reduces both the anodic and cathodic current densities. These results reveal that the presence of purine in H<sub>3</sub>PO<sub>4</sub> solution inhibits both the anodic and cathodic processes (mixed inhibitor).

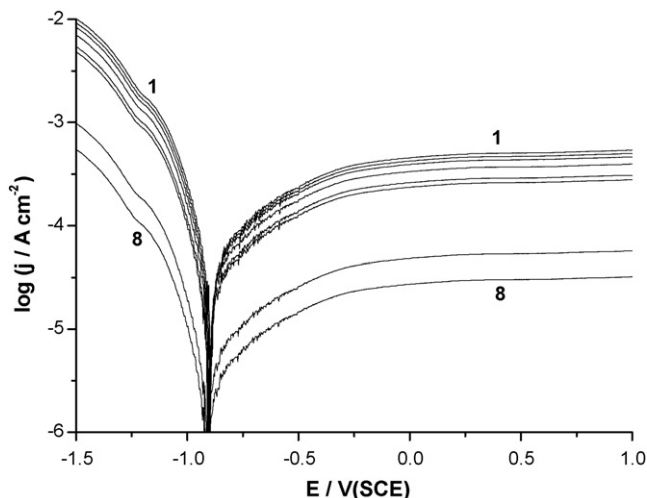
Table 1 presents the electrochemical parameters ( $E_{\text{corr}}$ ,  $j_{\text{corr}}$ ,  $b_c$ , and  $R_p$ ) associated with polarization measurements recorded for Al in 1.0 M H<sub>3</sub>PO<sub>4</sub> solutions without and with various concentrations of purine. Inhibition efficiency (%IE) values, calculated using Eq. (1), were also included in Table 1:

$$\%IE = 100 \times \left[ \frac{(j_{\text{corr}})_o - (j_{\text{corr}})_i}{(j_{\text{corr}})_o} \right] \quad (1)$$

where  $(j_{\text{corr}})_o$  and  $(j_{\text{corr}})_i$  are the corrosion current densities in the absence and presence of the inhibitor, respectively. It is obvious from this figure that accurate evaluation of corrosion rate (i.e., corrosion current density,  $j_{\text{corr}}$ ) from anodic branches, and therefore the anodic Tafel slope ( $b_a$ ), is impossible, simply because the recorded experimental anodic polarization curves do not exhibit linear Tafel regions. This is because the absence of linearity in anodic branches prevents linear extrapolation to the corrosion potential,  $E_{\text{corr}}$ . This was the reason why values of  $b_a$ , calculated from the software, were not included in Table 1. However, the cathodic branch, as will be discussed later, is under activation control and exhibit linearity in accord with Tafel relationship. The corrosion rate, and therefore the cathodic Tafel slope ( $b_c$ ) may now be estimated accurately by extrapolating the cathodic linear region back to  $E_{\text{corr}}$ .

The shapes of the polarization plots for inhibited electrodes are not substantially different from those of uninhibited electrodes. The presence of purine decreases the corrosion rate but does not change other aspects of the behaviour. This means that the inhibitor does not alter the electrochemical reactions responsible for corrosion. In addition, the absence of significant changes in the cathodic Tafel slope in the presence of inhibitor indicates that the hydrogen evolution is slowed down by the surface blocking effect of the inhibitor. This indicates that the inhibitive action of purine, may be related to its adsorption and formation of a barrier film on the electrode surface. EDX examinations of the electrode surface carried out for Al under various experimental conditions confirmed the existence of an adsorbed film of the inhibitor, see Section 3.4.

It is well-known that purine is an organic base which protonize in an acid medium, thus the inhibitor molecule becomes a cation, existing in equilibrium with the corresponding molecular form. Hence poor adsorption is expected to occur between protonated purine molecules and the positively charged electrode surface (see latter). This may explain why purine, under these conditions, provides a little inhibition efficiency (~55%).



**Fig. 2.** Polarization curves recorded for Al in 1.0 M deaerated stirred  $\text{H}_3\text{PO}_4$  solution without and with various concentrations of purine in presence of  $10^{-4}$  M KI at a scan rate of  $0.10 \text{ mV s}^{-1}$  at  $25^\circ\text{C}$ . (1) Blank; (2)  $10^{-4}$  M; (3)  $2.5 \times 10^{-4}$  M; (4)  $5 \times 10^{-4}$  M; (5)  $10^{-3}$  M; (6)  $2.5 \times 10^{-3}$  M; (7)  $5.0 \times 10^{-3}$  M; (8)  $10^{-2}$  M.

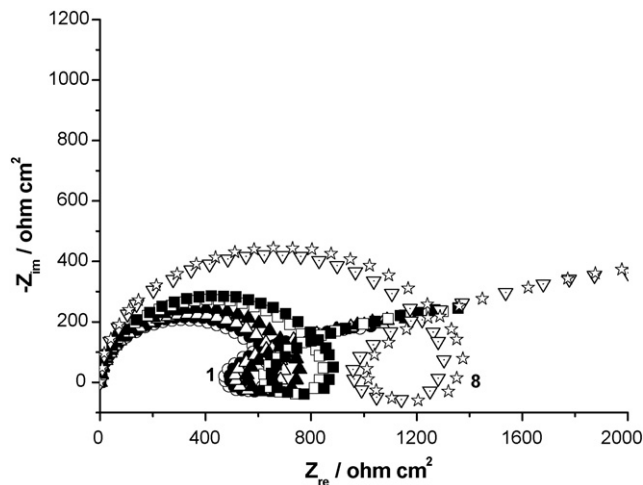
### 3.1.2. Synergistic inhibition between $\text{I}^-$ ions and protonated purine molecules

The little inhibition efficiency recorded for purine alone encouraged us to study the synergistic inhibition between  $\text{I}^-$  ions and protonated purine molecules in order to retard effectively Al corrosion under these conditions. For this purpose,  $10^{-4}$  M  $\text{I}^-$  ions has been added to purine- $\text{H}_3\text{PO}_4$  containing solutions to study the polarization response of Al, Fig. 2. Data of Fig. 2 clearly demonstrate that addition of  $\text{I}^-$  ions to purine- $\text{H}_3\text{PO}_4$  containing solutions results in a marked decrease in both anodic and cathodic current densities. A very slight shift in  $E_{\text{corr}}$  towards more negative potentials is also observed here. This indicates that purine, in presence of  $\text{I}^-$  ions, is an effective mixed-type inhibitor for Al corrosion in phosphoric acid solution. Synergism between  $\text{I}^-$  ions and purine was therefore proposed. Table 2 lists the electrochemical parameters associated with polarization measurements recorded for Al in 1.0 M  $\text{H}_3\text{PO}_4$  solution without and with various concentrations of purine in presence of  $10^{-4}$  M KI. It is obvious that the corrosion current densities, and hence the rate of corrosion, of purine alone (Table 1) are significantly decreased upon introducing KI to purine- $\text{H}_3\text{PO}_4$  containing solutions (Table 2). This decrease in the corrosion current densities enhances with an increase in the concentration of purine. Moreover, the inhibition efficiency of purine alone is increased in presence of KI. These results also confirm the existence of a strong synergism between purine and KI in the corrosion inhibition of steel in these solutions.

**Table 2**

Electrochemical parameters ( $j_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_c$  and  $R_p$ ) associated with polarization measurements of Al in 1.0 M  $\text{H}_3\text{PO}_4$  solution without and with different concentrations of purine in presence of  $10^{-4}$  M KI at  $25^\circ\text{C}$ .

$C_{\text{purine}} \times 10^2$ (M)	$j_{\text{corr}} \times 10^2$ ( $\text{mA cm}^{-2}$ )	$E_{\text{corr}}$ (V) (SCE)	$-b_c$ (V dec. $^{-1}$ )	$R_p$ ( $\Omega \text{ cm}^2$ )	%IE
Blank	5.00	-0.897	-0.154	495	-
0.01	4.65	-0.900	-0.153	532	7.00
0.025	4.31	-0.902	-0.155	574	13.80
0.05	3.67	-0.903	-0.155	675	26.68
0.10	2.87	-0.906	-0.155	862	42.55
0.25	2.59	-0.907	-0.153	957	48.30
0.50	0.53	-0.909	-0.156	4701	89.47
1.00	0.30	0.912	-0.154	8347	94.07



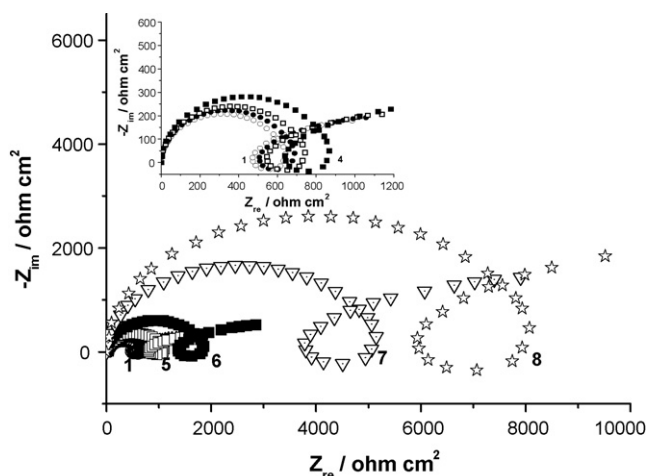
**Fig. 3.** Complex plane impedance plots recorded for Al in 1.0 M deaerated stirred  $\text{H}_3\text{PO}_4$  solution without and with various concentrations of purine at the respective corrosion potentials at  $25^\circ\text{C}$ . (1) Blank; (2)  $10^{-4}$  M; (3)  $2.5 \times 10^{-4}$  M; (4)  $5 \times 10^{-4}$  M; (5)  $10^{-3}$  M; (6)  $2.5 \times 10^{-3}$  M; (7)  $5.0 \times 10^{-3}$  M; (8)  $10^{-2}$  M.

## 3.2. Electrochemical impedance measurements

### 3.2.1. Effect of purine concentration

Fig. 3 represents Nyquist plots recorded for Al in 1.0 M deaerated stirred  $\text{H}_3\text{PO}_4$  solutions without and with various concentrations of purine at the respective corrosion potentials at  $25^\circ\text{C}$ . The synergistic inhibition of  $\text{I}^-$  ions has been also studied, Fig. 4. The shape of the impedance diagrams of Al in acidic solution is similar to those found in literature [11–13]. Here again, the presence of purine increases the impedance but does not change other aspects of the behaviour. These results indicate that almost no change in the corrosion mechanism occurred due to the inhibitor addition. The Nyquist plots presented in Fig. 3 are characterized by three time constants or semi-circles, namely: (i) a capacitive time constant at high frequencies, (ii) an inductive time constant at medium frequencies and (iii) a second capacitive time constant at low frequencies.

Before the interpretation of the impedance diagrams, it is important to make sure whether there was an oxide layer on the electrode surface. If an oxide layer is present, the measured impedance is



**Fig. 4.** Complex plane impedance plots recorded for Al in 1.0 M deaerated stirred  $\text{H}_3\text{PO}_4$  solution without and with various concentrations of purine in presence of  $10^{-4}$  M K at the respective corrosion potentials at  $25^\circ\text{C}$ . (1) Blank; (2)  $10^{-4}$  M; (3)  $2.5 \times 10^{-4}$  M; (4)  $5 \times 10^{-4}$  M; (5)  $10^{-3}$  M; (6)  $2.5 \times 10^{-3}$  M; (7)  $5.0 \times 10^{-3}$  M; (8)  $10^{-2}$  M.

determined by the metal/oxide interface, the oxide layer itself and the oxide/electrolyte interface. In our experiments, it is reasonable to assume that the electrode surface has been covered with an oxide layer because of the ex situ pretreatment of the electrode. This is also assumed in the literature. An oxide free Al surface is very difficult to produce. Even after producing such a surface, it repassivates very fast [14,15].

The time constant at high frequencies is attributed to the oxide layer formation or the oxide layer itself. Brett [11,12,16] assigned the high frequency time constant to the reactions involved at the oxide layer formation. He suggested that at metal/oxide interface, Al is oxidized to  $Al^+$  intermediates. The  $Al^+$  intermediates will subsequently be oxidized to  $Al^{3+}$  at the oxide/solution interface where also  $O^{2-}$  or  $OH^-$  is formed. Simultaneously with the formation of  $O^{2-}$ , ions hydrogen ions are formed. This results in a local acidification at the oxide/electrolyte interface, resulting in film dissolution.  $Al^+$  and  $O^{2-}$  ions must be transported through the oxide layer. This transport is due to a high electric field strength [17]. Although all these processes are present, just one semi-circle (i.e., time constant) in the Nyquist diagrams is observed. This could either mean that the time constants of the individual processes strongly overlap, or that one process dominates and, therefore, excludes the other processes in this frequency range.

As early emphasized, samples in this paper were polished in water and after the mechanical polishing, no chemical or electrochemical polishing was done. This means that after the polishing, protective oxide or hydroxide film should formed before the EIS experiment and this film may not change in this solution. Accordingly, the other possible explanation for the capacitive time constant at high frequencies is the oxide film itself. The oxide film is considered as a parallel circuit of a resistor due to ionic conduction in the oxide, and a capacitance due to the dielectric properties of the oxide. We believe that if oxide film formation or dissolution of metal or oxide film takes place during EIS measurement, time constant should change at each frequency. This time constant or semi-circle makes an angle approaching  $65^\circ$  with the real axis and its intersection gives a value of  $1.85 \Omega \text{ cm}^{-2}$  for the resistance of the solution ( $R_s$ ) enclosed between the working electrode and the counter electrode.

The low frequency inductive loop is often attributed to surface or bulk relaxation of species in the oxide [18]. Adsorbed charged intermediates may result in an inductive loop [19,20]. This is more pronounced when the intermediates are strongly adsorbed. Lenderink et al. [13] have attributed this loop to the relaxation of adsorbed species like  $H_{ads}^+$ . A possible candidate, suggested by Valand and Heusler [21], is an adsorbed oxygen ion. The point of intersection between the inductive loop and the real axis represents ( $R_s + R_{ct}$ ) [22]. To obtain  $C_{dl}$ , the frequency ( $f_{max}$ ) at which the imaginary component of the impedance is maximal was found and used in Eq. (2):

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \quad (2)$$

Finally, the time constant at low frequencies can be associated with the dissolution of the oxide layer.

Tables 3 and 4 collect, respectively, the impedance parameters, namely  $R_{ct}$  and  $C_{dl}$ , recorded for Al in 1.0 M  $H_3PO_4$  solution without and with various concentrations of purine in the absence and presence of  $I^-$  ions at 25 °C. As Tables 3 and 4 clearly show, the value of the charge-transfer resistance,  $R_{ct}$ , increases with the inhibitor concentration.  $R_{ct}$  values are always greater in presence of  $I^-$  ions. This result is related to the corrosion protection (inhibiting) effect of purine molecules, particularly with  $I^-$  ions. This inhibiting effect, which obviously increases in presence of  $I^-$  ions, of purine is not only due to the decrease of the surface area in contact with electrolyte, but also to the slowing down of the charge-transfer process

**Table 3**

Impedance parameters ( $R_{ct}$  and  $C_{dl}$ ) recorded for Al in 1.0 M  $H_3PO_4$  solution without and with different concentrations of purine at the respective corrosion potentials at 25 °C.

$C_{\text{purine}} \times 10^2$ (M)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	%IE
Blank	480	27.00	–
0.01	500	25.94	3.92
0.025	521	24.89	7.83
0.05	566	22.91	15.13
0.10	633	20.48	24.13
0.25	661	19.60	27.40
0.50	975	13.30	50.75
1.00	1029	12.59	53.36

at the interface. However, the existence of an inductive loop in the impedance spectra indicates that the electrode is still dissolved by the direct charge-transfer at the purine-adsorbed electrode surface.

A tendency towards a decrease in  $C_{dl}$  values is observed with increasing purine concentration, and this decrease in  $C_{dl}$  is enhanced upon addition of  $I^-$  ions to the corrosive environment (inspect data listed in Tables 3 and 4). These results suggest that the purine molecules function by adsorption at the metal/solution interface, and this adsorption is reinforced by  $I^-$  ions. Here again, in agreement with polarization studies, synergism between  $I^-$  ions and purine is confirmed. This decrease in  $C_{dl}$  may be explained on the basis that the double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of the inhibitor on the electrode surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with increase in inhibitor concentration may be attributed to the formation of a protective layer on the electrode surface. The thickness of this protective layer increases with increase in inhibitor concentration, since more inhibitor molecules adsorb on the electrode surface, resulting in a noticeable decrease in  $C_{dl}$  (inspect the  $C_{dl}$  values in Table 3). This trend is in accordance with Helmholtz model, given by Eq. (3) [23]:

$$C_{dl} = (\varepsilon \varepsilon_0 A) / d \quad (3)$$

where  $d$  is the thickness of the protective layer,  $\varepsilon$  the dielectric constant of the medium,  $\varepsilon_0$  the vacuum permittivity and  $A$  is the effective surface area of the electrode.

The inhibiting effect of purine can also be assessed, assuming that  $j_{corr}$  is reciprocally proportional to  $R_{ct}$  values. Accordingly, the %IE values were calculated from Eq. (4) under various experimental conditions and also listed in Table 3:

$$IE\% = 100 \times \frac{R_{ct} - R_{ct}^0}{R_{ct}} \quad (4)$$

where  $R_{ct}^0$  and  $R_{ct}$  are the charge-transfer resistances for uninhibited and inhibited solutions, respectively. It is apparent that the inhibition efficiency increases with increase in inhibitor concentration. It

**Table 4**

Impedance parameters ( $R_{ct}$  and  $C_{dl}$ ) recorded for Al in 1.0 M  $H_3PO_4$  solution without and with different concentrations of purine in presence of  $10^{-4}$  M KI at the respective corrosion potentials at 25 °C.

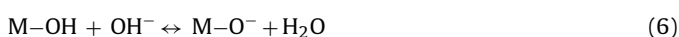
$C_{\text{purine}} \times 10^2$ (M)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	%IE
Blank	480	27.00	–
0.01	515	25.17	6.76
0.025	555	23.35	13.51
0.05	650	19.95	26.10
0.10	822	15.76	41.62
0.25	910	14.24	47.27
0.50	3852	3.36	87.54
1.00	6038	2.15	92.05

is worth noting from Tables 1–4 that the inhibition efficiency values obtained from impedance measurements are comparable and run parallel with those obtained from polarization measurements.

### 3.3. Mechanism of purine adsorption and explanation for synergism

#### 3.3.1. Surface charge of the electrode surface

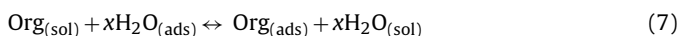
It is well-known that terminal oxygen atoms at metal oxide surfaces react with water, forming hydroxylated sites, or hydroxide layers at the surface (M–OH), that impart a pH-dependent surface charge. The polar hydroxyl ( $\text{OH}^-$ ) groups may cause the surface to attract and physically adsorb a single or several additional layers of polar water molecules. An oxide or hydroxide surface (M–OH) becomes charged by reacting with  $\text{H}^+$  or  $\text{OH}^-$  ions due to surface amphoteric reactions, Eqs. (5) and (6). At low pH, hydroxide surface adsorbs protons to produce positively charged surfaces (M– $\text{OH}_2^+$ ). At high pH they lose protons to produce negatively charged surfaces (M– $\text{O}^-$ ):



The number of these sites and the surface charge of the oxide are determined by the pH of the solution. Surface charge influences adsorption of ions from solution and other interfacial phenomena [24]. The pH of the potential of zero charge (PZC) for aluminium oxides/hydroxides is between 6 and 9, and in acidic solution, the accumulation of Al– $\text{OH}_2^+$  species accounts for the surface charge [25,26].

In acidic solution, therefore the positively charged surface sites will electrostatically attract any anions present in solution, and repel cations. Hence poor adsorption is expected to occur between protonated purine molecules and the positively charged surface oxide film. This may explain why purine, under these conditions, provides a little inhibition efficiency ( $\approx 55\%$ ).

The adsorption of an organic adsorbate on a metal surface is regarded as a substitutional adsorption process between the organic molecule in the aqueous solution ( $\text{Org}_{(\text{sol})}$ ), and water molecules adsorbed on the metallic surface ( $\text{H}_2\text{O}_{(\text{ads})}$ ) [27]:



where  $x$  is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate. The adsorption of organic compounds can be described by two main types of interaction: physical adsorption and chemisorption. In general, the proceeding of physical adsorption requires the presence of both electrically charged surface of the metal and charged species in the bulk of the solution. Chemisorption process involves charge sharing or charge-transfer from the inhibitor molecules to the metal surface to form a coordinate type of a bond. This is possible in case of a positive as well as a negative charge of the surface. The presence of a transition metal, having vacant, low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair of electrons is necessary [28,29].

However, the inhibitor under investigation, namely purine is an organic base which protonize in an acid medium. Thus the inhibitor molecule becomes a cation, existing in equilibrium with the corresponding molecular form. This is in accordance with the distribution diagram for purine species calculated using the data for acid–base equilibria ( $\text{p}K_{\text{a}1} = 4.25$ ,  $\text{p}K_{\text{a}2} = 9.83$ ) [30]. It has been shown that protonated cationic species of purine, are the dominant inhibitor in the range of pH 0–2.

Therefore, it was assumed that protonated purine molecules are adsorbed directly on the positively charged electrode surface via the delocalized  $\pi$ -electrons of the pyrimidin and imidazole rings and the partial negative charges of N-atoms. It is probable that the adsorbed N-atoms are oriented with the two ring structures parallel to the metal surface (due to aromaticity of purine molecule). The adsorption of purine on the electrode surface makes a barrier for mass and charge transfers. This situation leads to the protection of the electrode surface from the acid corrosion. However, it seems that this adsorption is not quite sufficient to make an effective corrosion inhibition, as the maximum inhibition efficiency recorded under these conditions is low (55% at the maximum concentration of purine used).

In addition to the physical (electrostatic) adsorption, there should be chemical adsorption due to the coordinate bonds that may be formed, after prolong immersion times, between the lone electron pairs of the unprotonated N-atoms and the empty p-orbital of Al atoms which enhance the attraction between the purine molecules and electrode surface.

Moreover, there is a great possibility that adsorption may also take place via hydrogen bond formation between the N–H linkage in purine molecule and the oxygen atoms of the oxidized surface species. This type of adsorption should be more prevalent for protonated N-atoms, because the positive charge on the N-atom is conducive to the formation of hydrogen bonds. Unprotonated N-atoms may adsorb by direct chemisorption, as mentioned previously, or by hydrogen bonding to a surface oxidized species. The extent of adsorption by the respective modes depends on the nature of the metal surface. Adsorption by direct chemisorption, for unprotonated N-atom, is more probable on an exposed metal atom. In addition, the unprotonated N-atom can also interact with oxidized metal by hydrogen bonding. Effective inhibition is predominantly provided by the direct coordination of unprotonated N-atom to metal atoms. As the metal surface is covered by an adherent oxide protective layer, the direct coordination of nitrogen to an exposed metal atom is a remote event. Protonated and unprotonated N-atoms are adsorbed onto the metal through hydrogen bond formation. The criteria for inhibitor selection can also be inferred from above considerations. A good inhibitor must have strong affinity for the bare metal atoms. The requirement is different in case of Al, a compact passive oxide film is always present on the electrode surface, where hydrogen bond formation accounts for most of the inhibition action. An effective inhibitor, is one that forms hydrogen bonds easily with the oxidized surface. Adenine, previously used as a corrosion-safe inhibitor for copper in chloride solutions [31] and steel in acid medium [32], was used alongside purine to verify the criteria. A comparison of the inhibition performance of adenine and purine (data not shown here) was that adenine is more effective corrosion inhibitor than purine itself; similar results were previously obtained [32].

These findings could be explained on the basis that the ability of an amine to provide corrosion inhibition is related to its tendency to form hydrogen bonds with the oxide or hydroxide species on the metal surface. Such capability should be proportional to the number of NH linkages in the amine molecules. Adenine has the highest number of NH bonds (due to the presence of an extra  $\text{-NH}_2$  group, which is not present in the purine structure) and therefore the most tendency to form hydrogen bonds with an oxidized surface. These results confirmed the importance of hydrogen bonding in effective corrosion inhibition. However, the extent of chemisorption as well as adsorption via hydrogen bonding needs further study. This study is presently under investigation in this laboratory.

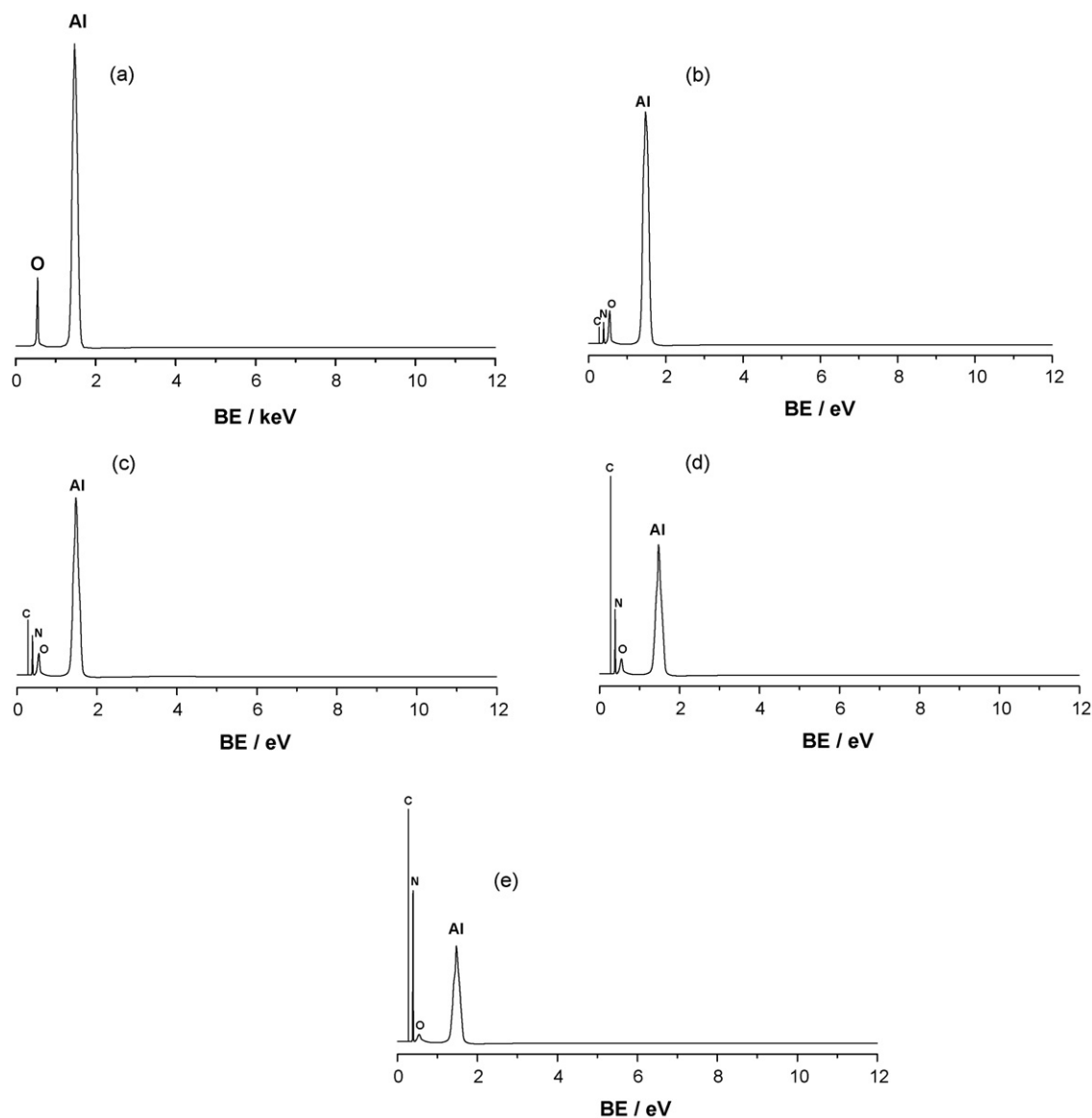
On the other hand, it is well-known that the protective properties of a cation type of an inhibitor in any aggressive environment

can be improved with the addition of halide ions to the solution. This results in the observation of a synergistic effect in the corrosion inhibition [33–36]. For this reason we have also studied the synergistic inhibition between purine and iodide ion on the corrosion inhibition of Al in phosphoric acid solutions. Iodide ions are usually characterized by strong adsorbability on the metal surface.  $I^-$  ions first adsorbed at the oxide/solution interface at the corrosion potential through electrostatic attraction force due to the excess positive charge at the oxide/solution interface. This process changes the charge of the solution side of the interface from positive to negative. This change in the charge of the solution side of the interface facilitates physical adsorption of the inhibitor's cations. Thus the protonated purine molecules are able to electrostatically adsorb on the electrode surface covered with primary adsorbed  $I^-$  ions. It is obvious that  $I^-$  ions promote the physical adsorption of purine on the Al surface. Therefore, the Al corrosion might be markedly suppressed by purine in the presence of  $I^-$  ions.

### 3.4. EDX examinations of the electrode surface

The goal of this section was to confirm the results obtained from electrochemical measurements that a protective surface film of inhibitor is formed on the electrode surface. To achieve this goal, EDX examinations of the electrode surface were performed in 1.0 M deaerated stirred  $H_3PO_4$  solution in the absence and presence of various concentrations of purine at different immersion times. Some experiments were also performed in presence of  $10^{-4}$  M KI to support the synergism between purine and KI to inhibit the acid corrosion of Al.

Fig. 5 presents a panorama of EDX survey spectra recorded for Al exposed for 2.0 and 4.0 h in 1.0 M  $H_3PO_4$  solution without and with two different concentrations, namely 0.001 and 0.005 M purine at 25 °C. Some EDX experiments were also performed in presence of  $10^{-4}$  M KI to see and confirm synergistic effect of  $I^-$  ions on the shape of the EDX spectra. For the electrode without inhibitor treatment (Fig. 5a), only aluminium and oxygen were detected, which



**Fig. 5.** EDX spectra of Al specimens: (a) after 2.0 h of immersion in 1.0 M  $H_3PO_4$  solution; (b) after 2.0 h of immersion in 1.0 M  $H_3PO_4$  solution containing 0.001 M purine; (c) after 2.0 h of immersion in 1.0 M  $H_3PO_4$  solution containing 0.005 M purine; (d) after 4.0 h of immersion in 1.0 M  $H_3PO_4$  solution containing 0.005 M purine; (e) after 4.0 h of immersion in (1.0 M  $H_3PO_4$  + 0.005 M purine) solution containing  $10^{-4}$  M KI.

indicated that the passive film contained only  $\text{Al}_2\text{O}_3$ . However, in inhibited  $\text{H}_3\text{PO}_4$  solutions (Fig. 5b–d), the EDX spectra showed an additional line characteristic for the existence of the existence of N. In addition, the intensity of C signal is enhanced. The appearance of the N signal and this enhancement in the C signal upon introducing purine to the corrosive medium is due to the N and C atoms of the adsorbed purine species. These data show that a carbonaceous material containing N atoms has covered the electrode surface. This layer is undoubtedly due to the inhibitor, because of the existence of N signal and the high contribution of the C signal observed in presence of purine. The N signal and this high contribution the C signal is not present on the electrode surface exposed to uninhibited  $\text{H}_3\text{PO}_4$  solutions (see Fig. 5a). In addition, the intensity of the N and C signals increases with increasing purine concentration and immersion time (see Fig. 5b–f), since more purine molecules adsorb on the electrode surface. The intensity of the N and C signals also increases upon introducing KI to purine- $\text{H}_3\text{PO}_4$  containing solutions (compare Fig. 5d with Fig. 5e), since more protonated purine molecules electrostatically adsorb on the electrode surface already charged with a negative layer of adsorbed  $\text{I}^-$  ions. These results confirm those obtained from electrochemical measurements that a synergism exists between purine and  $\text{I}^-$  ions.

The spectra of Fig. 5b–e show that the aluminium and oxygen signals are considerably suppressed relative to the samples prepared in 1.0 M  $\text{H}_3\text{PO}_4$  solution, and this suppression increases with increasing purine concentration and immersion time. Introduction of KI to purine- $\text{H}_3\text{PO}_4$  containing solutions enhances this suppression (see Fig. 5e). The suppression of the aluminium and oxygen signals takes place because of the overlying inhibitor film. These results confirm those from polarization measurements which suggest that a surface film inhibited the metal dissolution, and hence retarded the hydrogen evolution and metal dissolution reactions. The effect of purine (Fig. 1) alone and purine combined with KI (Fig. 2) on the cathodic branch of polarization curves may be explained on the basis that the inhibitor surface film acts as a barrier to the diffusion of  $\text{H}_3\text{O}^+$  ions from solution to electrode surface [37], which may increase the overpotential of cathodic reduction of  $\text{H}_3\text{O}^+$  ions. This surface film also increases the overpotential of the anodic dissolution of Al, slowing down the corrosion rate, see anodic branches presented in Figs. 1 and 2. Therefore, EDX examinations of the electrode surface support the results obtained from polarization and impedance methods that purine, in presence of  $\text{I}^-$  ions, is a good inhibitor for Al corrosion in  $\text{H}_3\text{PO}_4$  solutions.

#### 4. Conclusion

Polarization and impedance measurements together with surface analysis (EDX examinations of the electrode surface) were used to study the corrosion inhibition characteristics of purine, as a safe-inhibitor, for Al corrosion in 1.0 M deaerated stirred  $\text{H}_3\text{PO}_4$  solutions. The principle conclusions are

- (i) The acid corrosion of Al is moderately reduced upon the addition of purine.
- (ii) Inhibition efficiency increases with increase in purine concentration and immersion time. The inhibition efficiency of purine is markedly enhanced in presence of KI (synergism).
- (iii) A surface film of inhibitor is formed on the electrode surface via electrostatic adsorption of protonated purine molecules on

the positively charged Al surface covered with a chemisorbed layer of negatively charged  $\text{I}^-$  ions.

- (iv) EDX observations of the electrode surface showed that a surface film of inhibitor is formed on the electrode surface. This film retarded the reduction of  $\text{H}^+$  ions and inhibited metal dissolution in phosphoric acid solutions (mixed-type inhibitor).
- (v) Physisorption, followed by chemisorption, is proposed as the mechanism for corrosion inhibition.
- (vi) Using adenine, a safe-inhibitor too, alongside with purine confirmed the importance of adsorption via hydrogen bonding.
- (vii) The inhibition efficiencies obtained from polarization measurements are comparable with those obtained from impedance measurements.

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