

## ON THE CORROSION INHIBITION OF ALUMINIUM IN BICARBONATE BUFFER SOLUTIONS PART I: WEIGHT LOSS, POLARIZATION AND EDX STUDIES

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(Received 12<sup>th</sup> Sept. 2005; Accepted 27<sup>th</sup> Dec. 2005)

تناول الدراسة في هذا الجزء استخدام حامض الأكريليك المتبلمر (ذو وزن جزيئي ١٢٠٠٠ غرام / مول) كمثبط لتآكل الألومنيوم النقي في محاليل مائية منظمة من البيكربونات (ذات أس هيدروجيني = ٨) وذلك باستخدام طرق كيميائية (طريقة الفقد في الوزن) و طرق كهروكيميائية (الاستقطاب البوتنشيوديناميكي). و تم أيضا استخدام بعض طرق التحاليل (EDX) لمعرفة العناصر الموجودة على سطح الفلز في عدم وجود ووجود البوليمر. و قد أوضحت النتائج أن هذا المركب يعمل على تثبيط تآكل الألومنيوم عن طريق الامتزاز على سطح الفلز و أن معدل تثبيط تآكل الألومنيوم يزداد بزيادة تركيز البوليمر. و قد أوضحت النتائج أيضا أن نقطة التعادل الكهربي للألومنيوم يلعب دورا هاما في عملية امتزاز البوليمر على سطح الفلز. و قد أثبتت نتائج الاستقطاب البوتنشيوديناميكي أن هذا البوليمر له القدرة على تثبيط التفاعلين الانودي و الكاثودي. يلاحظ توافق بين نتائج طريقة الفقد في الوزن و طريقة الاستقطاب البوتنشيوديناميكي.

The main object of this part is to investigate the corrosion inhibition of Al in weakly alkaline solutions (pH 8) by polyacrylic acid (PAA ; 12000 g mol<sup>-1</sup>) at 25 °C by means of weight loss and potentiodynamic polarization measurements, complemented with ex situ energy dispersive X-ray (EDX) examinations of the electrode surface. Measurements were carried out in bicarbonate buffer solution (pH 8) containing various concentrations of PAA. The results demonstrated that the inhibition effect of this polymer is due to its adsorption on Al surface. The isoelectric point (IEP) of aluminium oxide (pH = 9) seems to be an important factor controlling corrosion inhibition and adsorption of the polymer. Polarization measurements showed that the polymer acts as a mixed-type inhibitor. The inhibition efficiency of the polymer increases with increasing its concentration. Results obtained from the chemical and electrochemical measurements are in good agreements. Studying the effect of temperature on the corrosion inhibition of Al and determination of the thermodynamic functions for both dissolution and adsorption processes will be the target of the second part of this work.

key words: Aluminium; weakly alkaline solutions; Corrosion inhibition; Adsorption; Polyacrylic acid

### INTRODUCTION

The many applications of aluminium and its alloys have resulted in research into their electrochemical behaviour and corrosion inhibition in a wide variety of media [1-10]. One of these applications is found in aluminium-air technology, firstly developed by Zaromb [11], which was of particular interest for its application to electric vehicle propulsion [4,12]. Amongst various types of anode materials, aluminium exhibits a high theoretical energy density (8.10 W.h/g) combined with a high

negative standard potential (-1.676V vs SHE) [13]. Further arguments for its consideration are its low production cost and the existence of a large base for manufacture and distribution.

Several attempts were made to develop a generator functioning in saline or acidic media [14-16], but in such conditions, the kinetics of aluminium dissolution are reduced by the presence of quite a thick oxide-hydroxide film at the anode surface [17]. This protective film can only be broken by the presence of chloride ions in the solution [18,19], or by the action of strong alkaline solutions. Apart from the recent work of

Rota [20] who does not exclude the use of an acidic electrolyte, most of the workers have directed their research towards alkaline media, which permit optimal performances of the air cathode [4] as well as a low level of aluminium polarization during normal operation. However, aluminium suffers substantial corrosion in alkaline solutions, which induce coulombic loss on discharge and fuel loss during standby. Therefore, for commercial applications of the aluminium-air battery, it is necessary to add corrosion inhibitors, either to the metal or to the electrolyte, which are able to increase the overpotential of parasitic hydrogen evolution without decreasing the oxidation rate of aluminium.

It is known that polymers are adsorbed stronger than their monomer analogs [21], hence it is expected that polymers will be better corrosion inhibitors than the corresponding monomers. The improved performances of the polymeric materials are ascribed to their multiple adsorption sites for bonding with the metal surface. The polymer provides two advantages: a single polymeric chain displaces many water molecules from the metal surface, thus making the process entropically favorable and the presence of multiple bonding sites make the desorption of the polymers a slower process.

The present work reports the results of weight loss and potentiodynamic polarization measurements to study the ability of polyacrylic acid (supposed to be non-toxic) to inhibit the corrosion of aluminium in bicarbonate buffer solutions (pH 8) in the absence and presence of various concentrations of PAA. Some EDX examinations of the electrode surface have been carried out.

### EXPERIMENTAL

The working electrode employed in this work were made of very pure aluminium (99.999%). Bicarbonate buffer (pH 8.0) was prepared using 0.022 M sodium carbonate + 0.821 M sodium hydrogen carbonate [22]. For weight loss measurements, corrosion inhibition tests were performed using coupons measuring  $1 \times 2 \times 0.1 \text{ cm}^3$  prepared from pure aluminium. The aluminium coupons were polished with emery papers, then degreased with acetone and washed with distilled

water. The coupons were dried and kept in a desiccator. The weight loss ( $\text{g cm}^{-2}$ ) was determined at different immersion times at  $25 \text{ }^\circ\text{C}$  by weighing the cleaned samples before and after hanging the coupon into  $50 \text{ cm}^3$  of the corrosive solution, namely the weakly alkaline solutions (pH 8), (open air) in the absence and presence of various concentrations of PAA ( $12000 \text{ g mol}^{-1}$ ). After the time elapsed the cleaning procedure consisted of wiping the coupons with a paper tissue, polishing lightly with emery paper to remove the corrosion products from the surface, washing with distilled water and acetone, followed by oven drying at  $110 \text{ }^\circ\text{C}$ .

For electrochemical measurements, the investigated materials were cut as cylindrical rods, 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 ( $0.25 \text{ cm}^2$ ) geometric area, to contact the test solution. Prior to each experiment, the surface pretreatment of the working electrode was performed by mechanical polishing (using a polishing machine model POLIMENT I, BUEHLER POLISHER) of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The electrode was then, rinsed with acetone, distilled water, and finally dipped in the electrochemical cell.

The cell used is a conventional three electrodes Pyrex glass cell with a platinum wire counter-electrode and a saturated calomel electrode (SCE) as reference to which all potentials are referred. The SCE was connected via a Luggin capillary, the tip of which was very close to the surface of the working electrode to minimize the IR drop. The experiments were carried out in aerated stagnant buffer solutions (pH 8) devoid of and containing various concentrations of high purity (99.95 %) polyacrylic acid (PAA;  $12000 \text{ g mol}^{-1}$ ) as an inhibitor.

All buffer solutions and PAA were 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. The working electrode was stabilized in the test solution for 2 h prior to each

polarization scan or impedance run. The pre-treatment served to put the electrode surface in a reproducible initial state and obtain a stable corrosion potential. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -2.0 to 2.0 V at a scan rate of 5 mV s<sup>-1</sup>. M352 corrosion software from EG&G Princeton Applied Research was used for the potentiodynamic polarization measurements.

EDX examinations of the electrode surface were performed with Traktor TN-2000 energy dispersive spectrometer. Prior to analysis, the Al specimens were kept immersed in bicarbonate buffer solution (pH 8) for 12 hours in the absence and presence of 10<sup>-7</sup> M PAA. Finally, the specimens were washed thoroughly and submitted to 5 min of ultrasonic cleaning in order to remove loosely adsorbed ions.

## RESULTS AND DISCUSSION

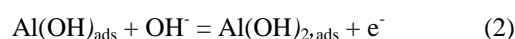
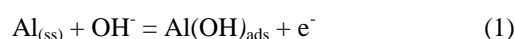
### Weight loss measurements:

#### Effect of inhibitor concentration

The variation of the weight loss (g cm<sup>-2</sup>) of Al in bicarbonate buffer solution (pH 8) with and without the addition of different concentrations (2.0×10<sup>-8</sup>-20×10<sup>-8</sup> M) of PAA with the immersion time has been studied at 25 °C; a part of the results is shown in Fig. 1. In aqueous alkaline media, Al reacts by the evolution of hydrogen. The evolution of hydrogen during this corrosion reaction may lead to serious pressure problems in industry. Detailed studies about these problems have been presented elsewhere [23,24]. Visual observations showed that the hydrogen evolution decreases (i.e., the corrosion-inhibiting effect increases) upon the addition of PAA. This could be seen from the weight loss decrease with increasing the concentration of PAA (see Fig. 1). Thus, the corrosion rate of Al decreased with the increase of the polymer concentration. This trend may result from the fact that adsorption amount and the coverage of the polymer on the electrode surface increases with increasing concentration. In other words, the inhibitive action of PAA may be related to adsorption and formation of a barrier film on the electrode surface. The formation of such a barrier film is confirmed by EDX examinations of the electrode surface (more details are shown in

EDX examinations of the electrode surface section). This surface film separates the electrode from the corrosive medium, namely the bicarbonate buffer solution, resulting in a decrease in the corrosion rate.

The corrosion process of Al in alkaline solution could be explained on the basis that the surface of Al is covered by passive film. When immersed in alkaline solutions, the outer surface of the film will dissolve, on the other hand, Al atoms in substrate will diffuse toward surface, or oxygen toward substrate, and combine to form passive film [25]. In some areas, the passive film is not very dense due to structural defects (active sites or flawed regions of the oxide film) and is relatively more soluble, where its dissolution is faster than its formation. In these areas, dissolution of Al atoms and gradual removal of these atoms through the formation of hydroxide with increased coordination number from 1 to 3 to form independent molecular species of Al(OH)<sub>3</sub> (equations 1-3) takes place. Al(OH)<sub>3</sub> species react in a pure chemical manner to form a soluble aluminate ion, AlO<sub>2</sub><sup>-</sup> that goes in solution leaving a bare surface site (ss) ready for another dissolution process (equation 4) [26,27]. Compared with the reduction of water, the reduction of oxygen can be neglected [27]. The corrosion process of Al in alkaline solution is usually considered as [6,27-29]:



As H<sub>2</sub> evolves (equation 6), the local pH on bare surface site increases. This accelerates the corrosion reaction on them, and makes it easier for the passive film to be damaged.

The inhibition efficiency (IE%) of the polymer (Table 1) is calculated from the total weight loss by the following equation [6,7]:

$$\text{IE}\% = [1 - (\text{WL} / \text{WL}^0)] \times 100 \quad (7)$$

where  $WL^{\circ}$  and  $WL$  are the weight losses of specimens without and with the inhibitor. It follows from the data of Table 1 that the polymer inhibits the alkaline corrosion of Al to an extent

depending on its concentration. Increasing the concentration of the polymer is accompanied by an increase in the inhibition efficiency.

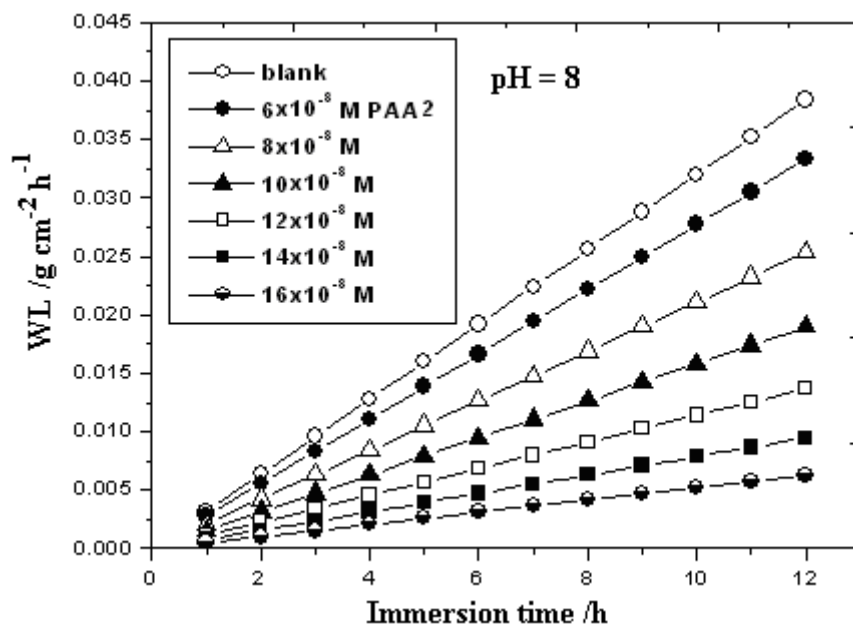


Fig. 1: Variation of the weight loss ( $g\ cm^{-2}$ ) of Al in bicarbonate buffer solution (pH 8) with and without the addition of different concentrations ( $2.0 \times 10^{-8} - 20 \times 10^{-8}\ M$ ) of PAA with the immersion time at  $25\ ^{\circ}C$ .

Table 1: Values of inhibition efficiency (IE%) for Al in bicarbonate buffer solution (pH 8) containing various concentrations of PAA at  $25\ ^{\circ}C$  (weight loss and polarization measurements).

$(C \times 10^8) / M$	Inhibition efficiency (IE%)	
	Weight loss	Polarization
2.0	4.95	5.00
4.0	7.00	7.13
6.0	15.25	15.35
8.0	37.33	37.88
10.0	55.22	55.75
12.0	71.05	71.12
14.0	82.04	82.31
16.0	92.55	93.00
18.0	94.57	94.92
20.0	96.00	97.00

**Mechanism of Adsorption:**

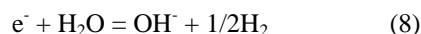
It is well known that adsorption of organic inhibitors on a corroding metal depends mainly on the charge of the metal surface, the charge or the dipole moment of the inhibitor, and the adsorption of other ionic species if it is electrostatic in nature [19]. The charge of the metal surface at the open circuit potential plays a very important role in the electrostatic adsorption process. This could be explained with the isoelectric point (IEP) of aluminium oxide. It has been pointed out that in aqueous alkaline solutions, aluminium is always covered with aluminium oxide (or hydrated oxide) [22,23,30]. Since the IEP of aluminium oxide is at about 9 [30], hence at pH 8 (below the IEP) the surface is positively charged. Aliphatic carboxylic acids (e.g. PAA) have pKa values < 5 [23] and can be considered as dissociated to anions both at pH 8. So, at pH 8 (below the IEP) there should be an electrostatic attraction between the positively charged aluminium oxide surface and the negatively charged PAA (i.e., high IE%).

**Polarization measurements:****Effect of inhibitor concentration**

Figure 2 shows the effect of PAA concentration on the potentiodynamic anodic and cathodic polarization characteristics of Al in bicarbonate buffer solution (pH 8) at a scan rate of 5 mV s<sup>-1</sup> and at 25 °C. The data clearly show that, the addition of the polymer shifts the corrosion potential ( $E_{\text{corr}}$ ) slightly in the positive direction and reduces both the anodic and cathodic current densities. The anodic current was however, reduced, more significantly than the cathodic current. These results indicate that the polymer acts as a mixed-type inhibitor. This means that the inhibitor has significant effects on retarding the cathodic hydrogen evolution reaction and inhibiting the anodic dissolution of aluminium.

The cathodic reaction which occurs when Al corrodes in weakly alkaline solutions has been investigated by Burstein and Liu [31]. Under the conditions used by Burstein and Liu, the cathodic

reaction is primary the reduction of water to hydrogen according to the following reaction:



The overall anodic reaction in the corrosion of Al in weakly alkaline solutions is :

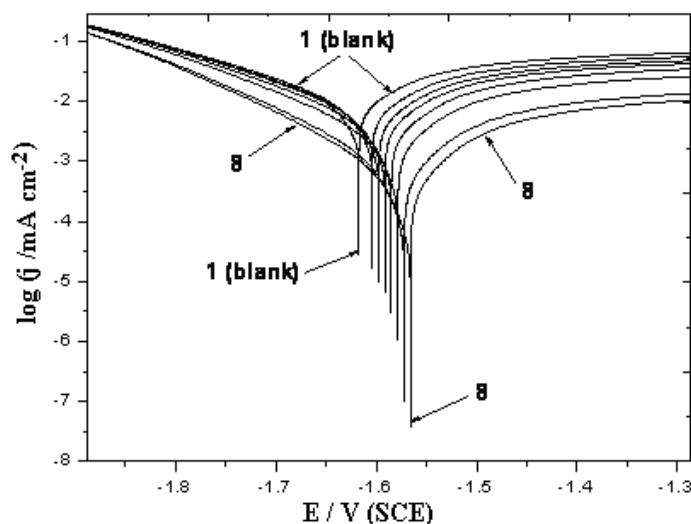


The electrochemical parameters ( $j_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_c$  and  $b_a$  and  $R_p$ ) associated with polarization measurements of the polymer at different concentrations were simultaneously determined (using M352 corrosion software from EG&G Princeton Applied Research) and are listed in Table 2. According to the data of Table 2, it is obvious that the slopes of the anodic ( $b_a$ ) and cathodic ( $b_c$ ) Tafel lines remain almost constant upon the addition of PAA. These results indicate that, the inhibitor acts by simple blocking the available surface area for both anodic and cathodic processes. In other words, the inhibitor decreases the surface area for corrosion without affecting the mechanism of corrosion and only causes inactivation of a part of the surface with respect to the corrosive medium.

Since electrochemical theory shows that, the reciprocal of the polarization resistance ( $1/R_p$ ) is a direct measure of the corrosion rate [8], the inhibition efficiencies at different concentrations of PAA are calculated at pH 8 and listed in Tables 1 and 2, respectively, using the following equation:

$$\text{IE}\% = 100 \times [1 - [(1/R_p) / (1/R_p)^0]] \quad (10)$$

where  $R_p^0$  and  $R_p$  are the electrode polarization resistances without and with inhibitor, respectively. It is worthy noting from the data of Table 1 that the inhibition efficiencies obtained from polarization measurements are comparable and run parallel with those obtained from weight loss method.



**Fig. 2:** Potentiodynamic anodic and cathodic polarization curves of Al in bicarbonate buffer solution (pH 8) in the absence and presence of various concentrations of PAA at a scan rate of  $5 \text{ mVs}^{-1}$  and at  $25^\circ\text{C}$ . (1) blank; (2)  $6.0 \times 10^{-8} \text{ M}$ ; (3)  $8.0 \times 10^{-8} \text{ M}$ ; (4)  $10 \times 10^{-8} \text{ M}$ ; (5)  $12 \times 10^{-8} \text{ M}$ ; (6)  $14 \times 10^{-8} \text{ M}$ ; (7)  $16 \times 10^{-8} \text{ M}$ ; (7)  $18 \times 10^{-8} \text{ M}$ ; (8)  $20 \times 10^{-8} \text{ M}$ .

**Table 2:** The electrochemical parameters ( $j_{\text{corr.}}$ ,  $E_{\text{corr.}}$ ,  $b_c$  and  $b_a$  and  $R_p$ ) associated with polarization measurements for Al in bicarbonate buffer solution (pH 8) in the absence and presence of different concentrations of PAA at  $25^\circ\text{C}$ .

$(C \times 10^8) / \text{M}$	$E_{\text{corr.}} / \text{V (SCE)}$	$j_{\text{corr.}} / \text{mA. cm}^{-2}$	$b_a / \text{mV dec.}^{-1}$	$-b_c / \text{mV dec.}^{-1}$	$R_p / \text{W cm}^2$
Blank	-1.615	2.00	51	26	300
2.0	-1.604	1.90	52	25	316
4.0	-1.598	1.84	49	24	325
6.0	-1.592	1.70	50	24	354
8.0	-1.585	1.23	49	23	489
10.0	-1.579	0.85	51	24	704
12.0	-1.572	0.54	49	25	1113
14.0	-1.566	0.29	48	22	2078
16.0	-1.562	0.07	49	23	10399
18.0	-1.560	0.06	49	24	10011
20.0	-1.557	0.04	52	25	14320

#### EDX examinations of the electrode surface:

EDX survey spectra were used to determine which elements were present on the Al surface before and after exposure to the inhibitor solution. After aluminium has been immersed in bicarbonate buffer solution (pH 8) in the absence and presence of  $10^{-7} \text{ M}$  PAA for 12 h, its surface film composition was determined by EDX. The results are displayed in Fig. 3. For the electrode without

inhibitor treatment (Fig. 3a), only aluminium and oxygen were detected, with a ratio of about 2:3, which indicated that the passive film contained only  $\text{Al}_2\text{O}_3$ . However, in inhibited buffer solutions (Fig. 3b), the EDX spectra showed an additional line characteristic for the existence of C (due to the carbon atoms of the PAA). In addition, the O signal is significantly enhanced (due to the oxygen atoms present in the PAA). These data show that a

carbonaceous material containing oxygen atoms has covered the electrode surface. This layer is undoubtedly due to the inhibitor, because the carbon signal and the high contribution of the oxygen signal are not present on the electrode surface exposed to uninhibited buffer solutions (Fig. 3a).

It is obvious from the spectra of Fig. 3b that the Al peaks are dramatically suppressed relative to the samples prepared in the buffer solution. The suppression of the Al lines undoubtedly occurs

because of the overlying inhibitor film. These results confirm the results obtained from polarization measurements that the inhibitor surface film retarded the cathodic hydrogen evolution reaction and inhibited the anodic dissolution of aluminium. It is possible that the inhibitor surface film acted as a barrier to the diffusion of water molecules from solution to electrode surface, which may increase the overpotential of the cathodic hydrogen evolution reaction, as shown in Fig. 2.

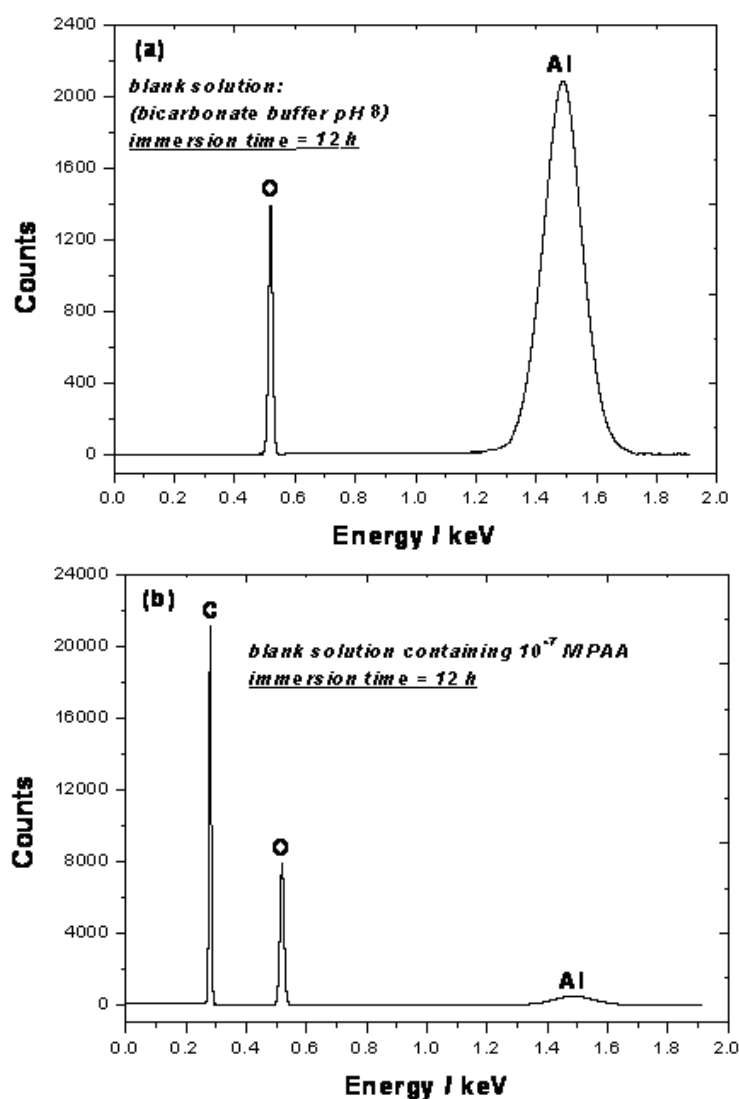


Fig. 3: EDX spectra recorded for Al specimens immersed in bicarbonate buffer solution (pH 8) for 12 h in the absence and presence of  $10^{-7}$  M PAA at 25°C.

**Conclusion:**

Weight loss and potentiodynamic polarization studies of the corrosion inhibition process of Al in bicarbonate buffer solutions (pH 8) using polyacrylic acid as a corrosion inhibitor showed that:

- i) Addition of the polymer to the weakly alkaline solution inhibits the corrosion of Al. The inhibition is due to the adsorption of the polymer on the surface of Al.
- ii) Polarization measurements showed that the polymer functions as a mixed-type inhibitor.
- iii) The inhibition efficiency of the polymer increases with increase in polymer concentration.
- iv) The inhibition efficiency of the inhibitor obtained from weight loss and potentiodynamic polarization methods are in good agreements.

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