

# Electrochemical Studies for Aluminium Electrolytic Capacitor Applications: Corrosion Analysis of Aluminium in Ethylene Glycol-Based Electrolytes

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## Abstract

The use of the Tafel plot electrochemical technique has been presented as a corrosion test method for aluminium electrolytic capacitor applications. This technique has been used to study the electrochemical corrosion of aluminium in ethylene glycol solvent-based electrolytes. These electrolytes consist of organic and inorganic acids, bases and conductive salts dissolved in ethylene glycol, and some of them also contain corrosion inhibitors and other additives. The Tafel plot corrosion current,  $i_{corr}$ , was measured and used to characterise all these electrolytes, showing significant differences between electrolytes (different  $i_{corr}$  values), due to their different chemical compositions. In addition, the Tafel plot technique was also used to study different corrosion inhibitors in one of the test electrolytes. From the Tafel plot results, it was found that the optimum concentrations of these inhibitors in the electrolyte were ca. 0.15–0.25 % ammonium hypophosphite; 0.75–1 % phosphoric acid; 0.1–0.2 % ammonium dihydrogen phosphate; and 0.4–0.6 % dibutyl phosphate. Therefore, this corrosion technique can be employed to investigate the aluminium corrosion caused by different electrolytes and to determine the optimum corrosion inhibitor and its concentration for each particular electrolyte.

## 1. Introduction

There is an increasing demand of aluminium electrolytic capacitors, due to their high capacitance, wide working potential range and excellent price to performance ratio.<sup>1</sup> Modern electrolytes used in aluminium electrolytic capacitors are based on organic solvents such as ethylene glycol (EG) or  $\gamma$ -butyrolactone (BLO or GBL); organic and inorganic acids and bases; conductive salts; and other additives such as corrosion inhibitors and hydrogen adsorbers.<sup>2-6</sup>

For high-performance electrolytic capacitors, these electrolytes must have the following physicochemical properties: (i) high ionic conductivity; (ii) wide operation temperature range; (iii) thermal stability and good compatibility with the capacitor parts; (iv) anodizing ability to form the edges of the anode and tab foils and allow self-healing of the aluminium oxide layer; (v) excellent wettability and swellability to the paper-separator in the capacitor; (vi) reduced vapour pressure to minimise the capacitor internal pressure at the working temperature; and (vii) specific breakdown voltage, water content and pH, depending on the capacitor applications.<sup>6-8</sup>

Aluminium electrolytic capacitors can fail due to catastrophic failure or to parametric failure. Catastrophic failures includes short circuit, open circuit or safety vent operation, whereas parametric failures are caused by severe changes in capacitance, leakage current and/or equivalent series resistance (ESR).<sup>7</sup> Capacitor short circuit, venting and parametric failure may be caused by corrosion of the aluminium foils, tabs and/or inserts, which is caused by certain ingredient/s in the electrolytes.<sup>9</sup> Therefore, a key aspect in an aluminium electrolytic capacitor is the chemical compatibility between the capacitor parts and the ingredients used in the electrolyte. Additionally, the use of corrosion inhibitors becomes critical in the electrolytes. Corrosion results in deterioration of a metal's properties such as its appearance, its surface aspect or its mechanical and electrical properties.<sup>10</sup> In an aluminium electrolytic capacitor, corrosion damages the dielectric layer and generates gas during capacitor operation (specially at high temperature, high voltage and high ripple

current).<sup>5</sup> Consequently, the development of simple and reliable corrosion test methods is extremely valuable in order to investigate the aluminium corrosion that may be caused by a given electrolyte.

Traditional corrosion test methods include weight loss measurements; electrochemical test methods including potentiodynamic and impedance measurements<sup>11</sup>; etc. Electrochemical test methods are popular because they can be carried out in a short period of time.<sup>10</sup> A very useful electrochemical technique used for corrosion studies is the so-called *Tafel plot*, where the corrosion current can be easily determined. In previous works,<sup>12</sup> the corrosion behaviour of aluminium in water-organic solvent mixtures containing hydrochloric acid was studied using the Tafel plot method. The composition of the mixtures varied from 0 to 60 % (v/v) of each of methanol, ethanol, isopropanol and ethylene glycol. In these studies, it was found that increasing concentrations of alcohol resulted in lower corrosion currents. Zhang and coworkers,<sup>1</sup> investigated the corrosion of aluminium tabs (99.85 and 99.99 % of purity) in an ethylene glycol–borate electrolyte system, showing that the corrosion current increases with the concentration of chloride ions. Other works based on Tafel plot analysis, showed the protection of aluminium (in aqueous solutions) by polypyrrole films.<sup>13</sup>

However, the Tafel plot technique has not been applied yet to the characterisation of different organic solvent-based electrolytes used in aluminium electrolytic capacitors or to the characterisation of different corrosion inhibitors. This technique can be a very useful approach to investigate aluminium corrosion caused by different electrolytes, and it may become crucial in the development of electrolytes. The target of this work was to use the Tafel plot as a means to characterise a series of electrolytes used in electrolytic capacitors. In addition, the Tafel plot was used to study different corrosion inhibitors in order to identify the corrosion inhibitor and the concentration providing the best protecting performance against aluminium corrosion.

## 2. Experimental

### 2.1. Instrumentation.

An Electrochemical Analyzer from CH Instruments (Model 1100A) was used for these investigations. A Ag|AgCl electrode (CHI111, also from CH Instruments) was used as pseudo-reference electrode; a stainless steel electrode was used as counter electrode; and the working electrode was an aluminium electrode of 6 mm in diameter (99.99 % purity rod from Puratronic-Alfa Aesar, embedded in Araldite adhesive to expose an aluminium surface area of 0.28 cm<sup>2</sup>).

### 2.2. Electrolyte solutions.

#### 2.2.1. Electrolyte studies.

In these investigations, a series of ethylene glycol-based electrolytes were studied. These electrolytes, namely WEY-450-1, WEY-450-2, WEY-450-3 and WEY-450-4, contained a series of acids, bases and conductive salts, as well as corrosion inhibitors (with the exception of WEY-450-3 electrolyte, which does not contain corrosion inhibitors). All these electrolytes were designed for 450 volt capacitor applications and were prepared and tested as described in a previous publication.<sup>7</sup> Table 1 summarises the electrolyte parameters.

**Table 1.** Electrolyte parameters: water content (H<sub>2</sub>O); pH; conductivity ( $\kappa$ ), and breakdown voltage (Vs).

Parameters	WEY-450-1	WEY-450-2	WEY-450-3	WEY-450-4
H <sub>2</sub> O (%)	16.0	14.5	14.3	3.3
pH (25 °C)	4.97	5.55	5.47	6.00
$\kappa$ (mS/cm, 25 °C)	0.800	0.935	0.827	1.257
Vs (V, average, 90 °C)	475	475	475	475

Before any Tafel experiment, cyclic voltammetry (CV) was carried out (60 CV cycles, from  $-0.5$  V to  $+10$  V) in the electrolyte solution in order to obtain a more stable aluminium surface (to obtain more stable and repeatable Tafel plots).

### 2.2.2. Characterisation of corrosion inhibitors.

The electrolyte WEY-450-5, containing no corrosion inhibitors, was used as reference electrolyte to investigate different inhibitors. In ethylene glycol systems, classical inhibitors include phosphoric acid, phosphates, phosphonates and hypophosphites.<sup>5,10</sup> In these works, ammonium hypophosphite (AH); phosphoric acid (PA); ammonium dihydrogen phosphate (ADHP); and dibutyl phosphate (DBP) were used as inhibitors, and in different concentrations: 0, 0.05, 0.1, 0.2, 0.5, 0.8, 1 and 1.5 %.

As mentioned above, 60 CV cycles were carried out before Tafel plot analysis. After finishing the 8 Tafel plots of WEY-450-5 (0 % inhibitor), the aluminium electrode was polished and the whole procedure (60 CV cycles and 8 Tafel plot measurements) was repeated for WEY-450-5 + 0.05 % of one of the chosen inhibitors. This process (polishing followed by CV and Tafel) was repeated for each concentration of the different inhibitors employed. These experiments were carried out at ca. 20 °C.

## 3. Results and discussions

### 3.1. Electrolyte studies

The Tafel plot analysis can be used to determine the corrosion current ( $i_{corr}$ ) and the corrosion potential ( $E_{corr}$ ), using the Butler-Volmer equation:<sup>14</sup>

$$i = i_{corr} \left( \exp^{\left(\frac{2.303\eta}{b_a}\right)} + \exp^{\left(-\frac{2.303\eta}{b_c}\right)} \right) \quad (1)$$

where  $i$  is the measured current,  $\eta$  is the difference between the applied potential and the corrosion potential ( $\eta = E - E_{corr}$ );  $i$  is the measured current;  $b_a$  and  $b_c$  the anodic and cathodic constants.

For large anodic overpotentials ( $\eta/b_a \gg 1$ ), equation 1 can be simplified:

$$\eta = \log i_{corr} + b_a \log i \quad (2)$$

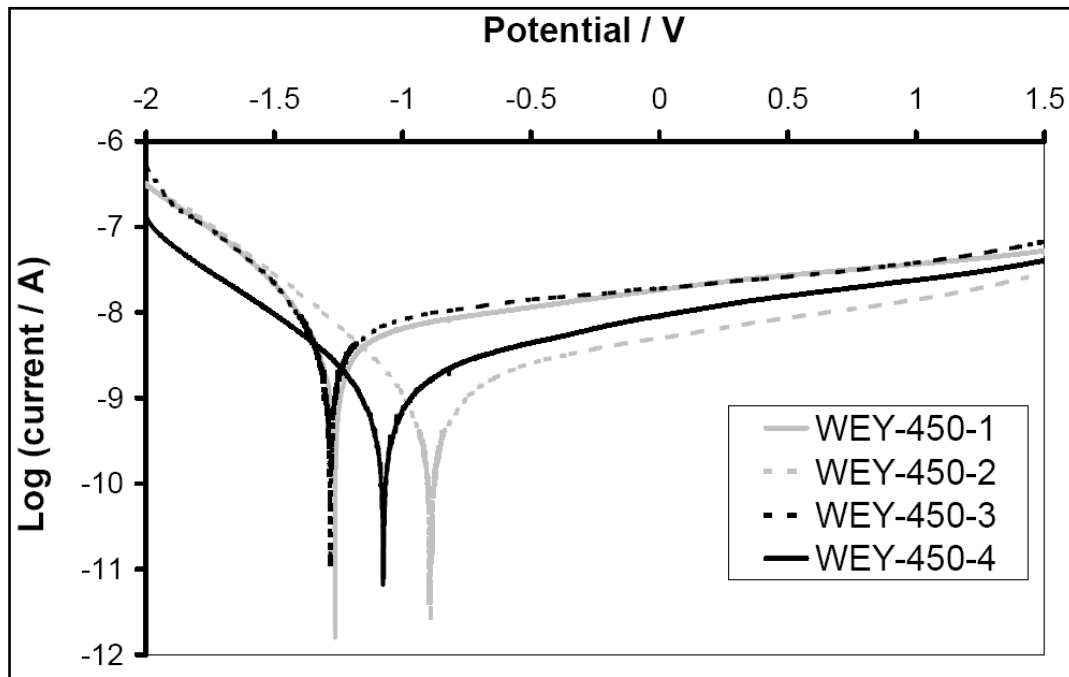
Conversely, for large cathodic overpotentials ( $\eta/b_c \ll 1$ ), equation 1 becomes:

$$\eta = \log i_{corr} - b_c \log |i| \quad (3)$$

In Tafel plot analysis, the curved line obtained is the total current (the sum of the anodic and cathodic currents). The sharp point in the curve is due to the logarithmic scale and it is the point where the current changes from cathodic to anodic or viceversa. This intersection point shows both the  $i_{corr}$  and the  $E_{corr}$ . The key parameter is the  $i_{corr}$  as it is directly proportional to the corrosion rate of the metal.

The Tafel plot analysis was used to study and compare the corrosion current (which is a measure of the corrosion rate) of the four test electrolytes used in this work, *i.e.* WEY-450-1, WEY-450-2, WEY-450-3 and WEY-450-4 electrolytes. Figure 1 shows the results and Table 2 summarises the  $i_{corr}$  values.

In theory, electrolytes with high water content should result in more corrosion (higher  $i_{corr}$  values), compared to electrolytes with low water content,<sup>12</sup> *i.e.* WEY-450-1, WEY-450-2 and WEY-450-3 electrolytes (with water content ca. 15 %) should show considerably higher  $i_{corr}$  values, compared to WEY-450-4 electrolyte (water content ca. 3 %). However, the  $i_{corr}$  of aluminium in WEY-450-4 is higher than the  $i_{corr}$  in WEY-450-2 electrolyte (water content ca. 15 %), which indicates that either one or some of the ingredients in WEY-450-4 electrolyte are more aggressive to the aluminium surface, or that WEY-450-2 contains more efficient corrosion inhibitors.



**Figure 1.** Tafel plot of aluminium in glycol-based electrolytes. Scan rate: 0.01 V/s.

**Table 2.** Corrosion current ( $i_{corr}$ ) measured from the Tafel plot curves in Figure 1.

Electrolyte	Corrosion inhibitor	Concentration of corrosion inhibitor	$i_{corr}$ . (nA)
WEY-450-1	ADHP	~ 0.2%	2.276
WEY-450-2	AH	0.2%	0.332
	PA	0.8%	
WEY-450-3	-	-	2.477
WEY-450-4	ADHP	~ 0.2%	0.459

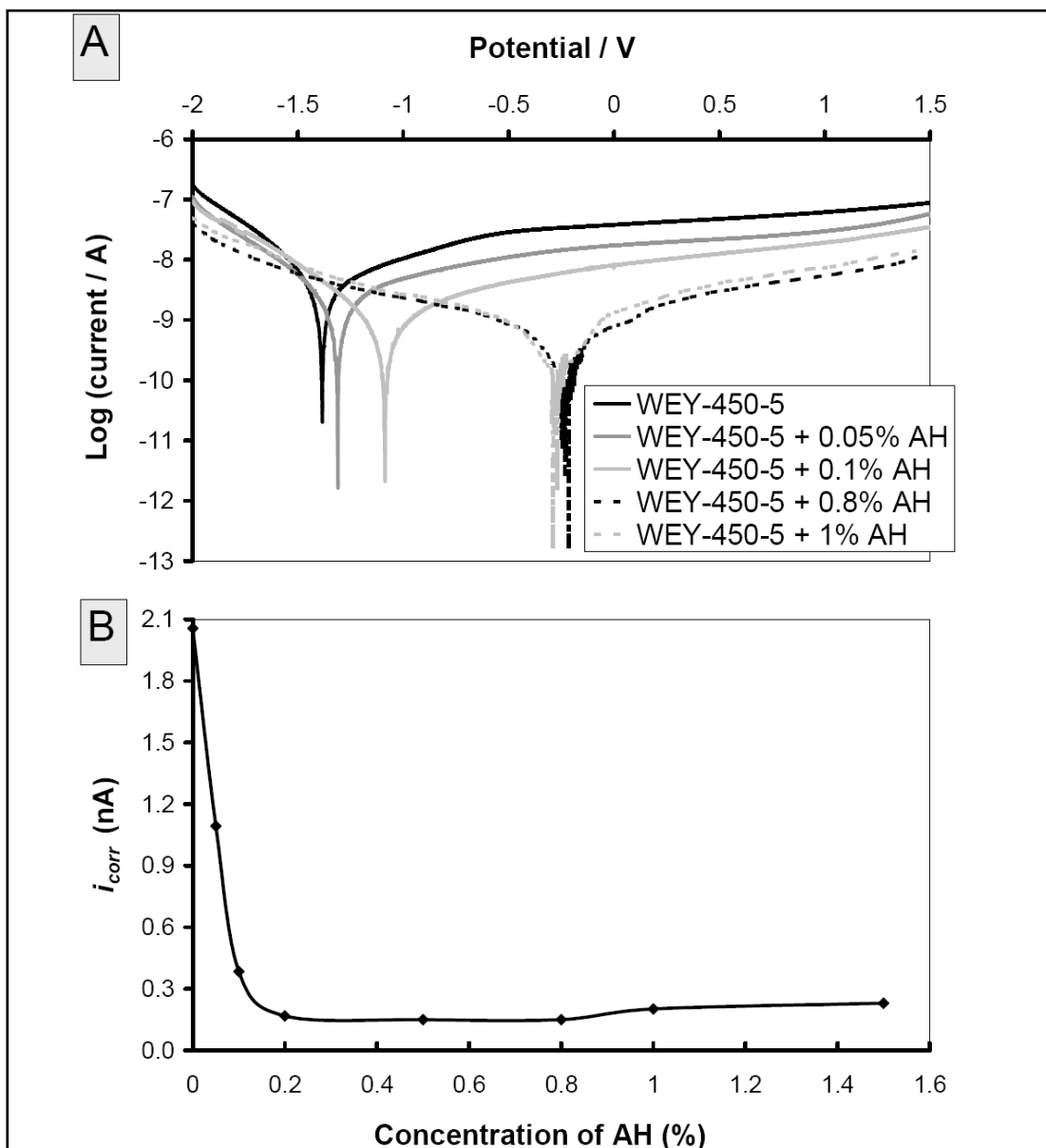
On the other hand, WEY-450-3 electrolyte is expected to be the electrolyte with higher corrosion (higher  $i_{corr}$ .) because it does not contain corrosion inhibitors. Nevertheless, its  $i_{corr}$  is only a little bit higher than the  $i_{corr}$  using WEY-450-1, which means that either the ingredients used in WEY-450-3 are excellent in terms of chemical compatibility with aluminium, or that the ingredients used in WEY-450-1 are more aggressive. In addition, WEY-450-2 electrolyte has the same chemical composition as WEY-450-3, but with the difference that WEY-450-2 contains two types of corrosion inhibitors. This explains the great differences in  $i_{corr}$  between the two electrolytes: the  $i_{corr}$  of aluminium in WEY-450-2 is approximately 7 times lower than in WEY-450-3.

### 3.2. Corrosion inhibitor studies

WEY-450-5 electrolyte was used in these corrosion studies (WEY-450-5 electrolyte is more stable than WEY-450-3). This electrolyte does not contain corrosion inhibitors, and it has the following parameters: (i) water content: 15.2 %; (ii) pH = 5.06 (at 25 °C); (iii) conductivity  $\kappa = 0.840$  mS/cm (at 25 °C); and (iv) breakdown voltage  $V_s = 475$  V.

#### 3.2.1. Ammonium hypophosphite (AH).

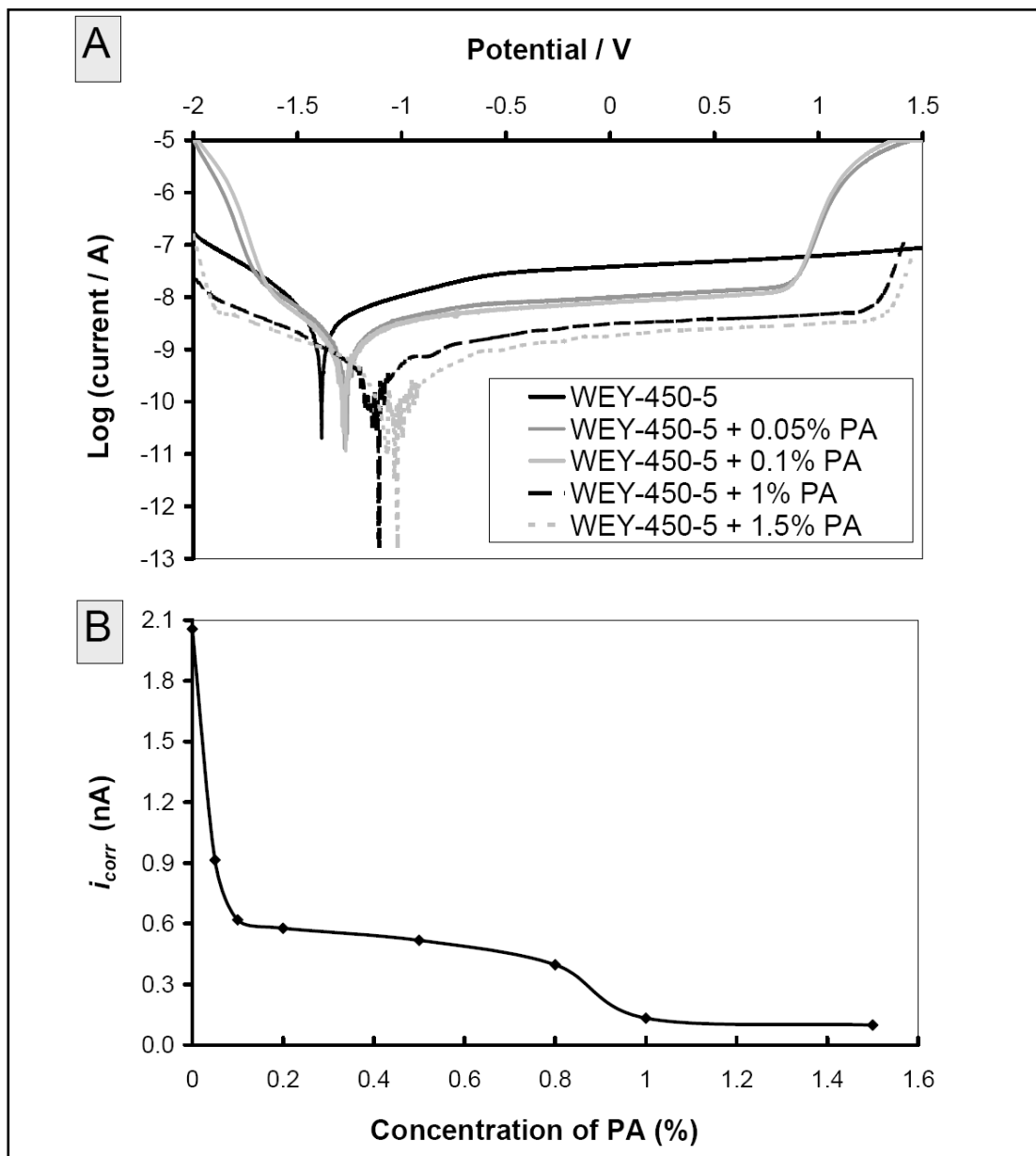
Figure 2 shows the Tafel plot of aluminium in WEY-450-5 and the effect of increasing concentrations of AH in the  $i_{corr}$ . The Tafel plot of aluminium in WEY-450-5 results in a  $i_{corr} \approx 2$  nA and  $E_{corr} \approx -1.4$  V (black curve in Figure 2(A)). The addition of increasing concentrations of AH corrosion inhibitor leads to a shift of  $E_{corr}$  to less negative voltages (which means that more energy or voltage is required to induce corrosion). The most important parameter in these studies is the  $i_{corr}$ . In this case, the addition of increasing concentrations of AH inhibitor causes a dramatic  $i_{corr}$  reduction. However, the  $i_{corr}$  does not decrease any more when the concentration of AH is above 0.2 %. There is some  $E_{corr}$  shift to less negative voltages when the concentrations are greater than 0.2 %, but  $i_{corr}$  does not change from 0.2 % to 1.5 % (as shown in Figure 2(B)), which may be due to saturation of the aluminium surface. This means that ca. 0.2 % of AH is the optimum concentration in this system.



**Figure 2.** (A) Tafel plot of aluminium in WEY-450-5. Effect of increasing concentrations of ammonium hypophosphite (AH) in the  $i_{corr}$ . Scan rate: 0.01 V/s. (B)  $i_{corr}$  as a function of the concentration of AH.

### 3.2.2. Phosphoric acid (PA).

The effect of increasing concentrations of PA in the Tafel plot of aluminium in WEY-450-5 is shown in Figure 3(A). As in the case of AH inhibitor, additions of increasing concentrations of PA results in  $i_{corr}$  reduction and  $E_{corr}$  shift to less negative voltages. However, the optimum PA concentration is 0.9 to 1.1 % (see Figure 3(B)). Effectively, the actual optimum concentration of PA should be ca. 0.75 to 1 % because the PA used is 85 % in purity.



**Figure 3.** (A) Tafel plot of aluminium in WEY-450-5. Effect of increasing concentrations of phosphoric acid (PA) in the  $i_{corr}$ . Scan rate: 0.01 V/s. (B)  $i_{corr}$  as a function of the concentration of PA.

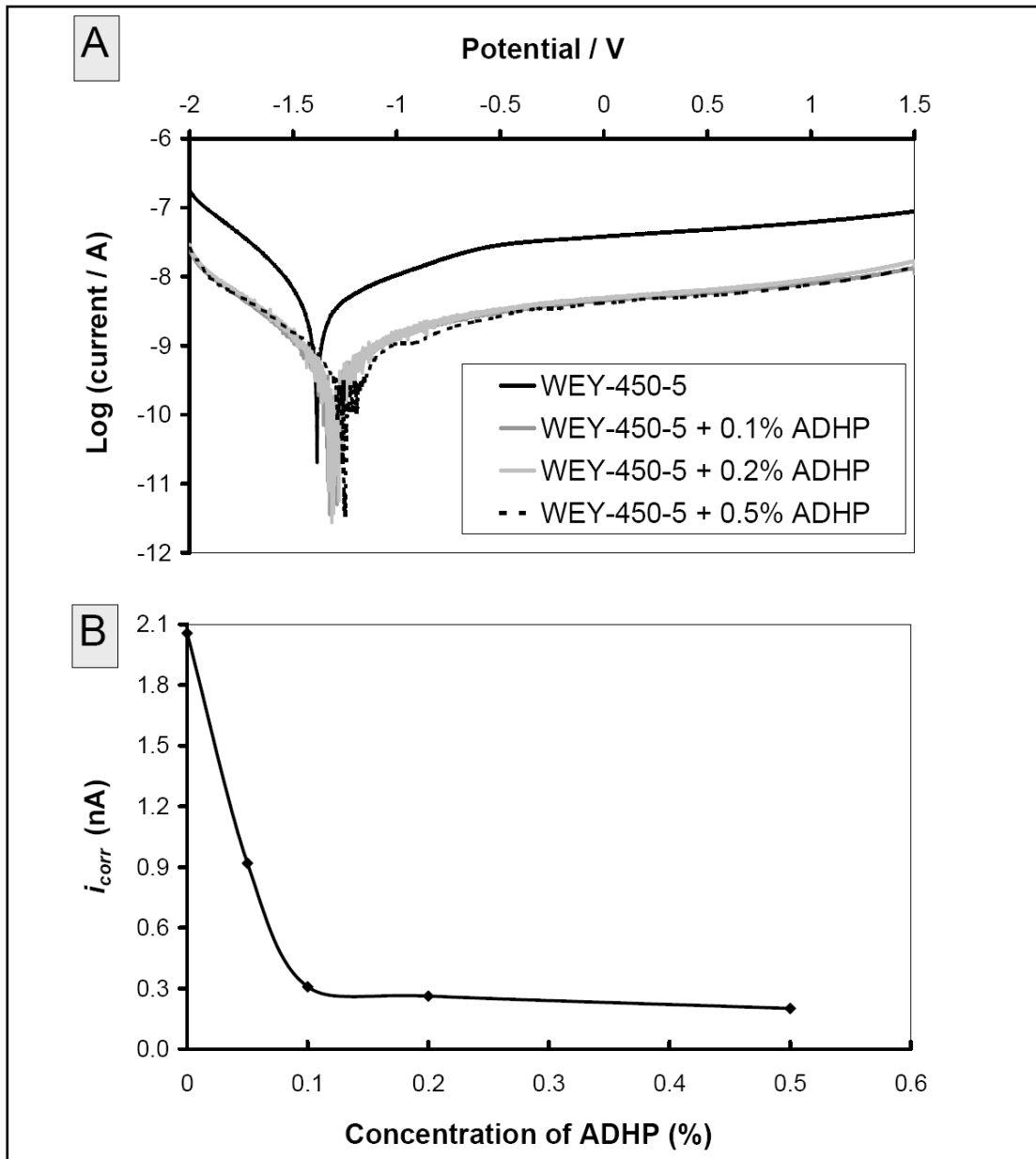
AH and PA are one of the most common inhibitors used in electrolytic capacitors. Previous works,<sup>15-16</sup> presented low flammability electrolytes (with composition similar to WEY-450-5), suggesting 0.7–1.0 % as optimum concentration of PA;<sup>15</sup> and 0–0.2 % as optimum concentration of AH inhibitor.<sup>16</sup> Therefore, these concentration values show good agreement with the optimum concentrations obtained from the Tafel plot results in Figures 2 and 3.

### 3.2.3. Ammonium dihydrogen phosphate (ADHP) and Dibutyl phosphate (DBP).

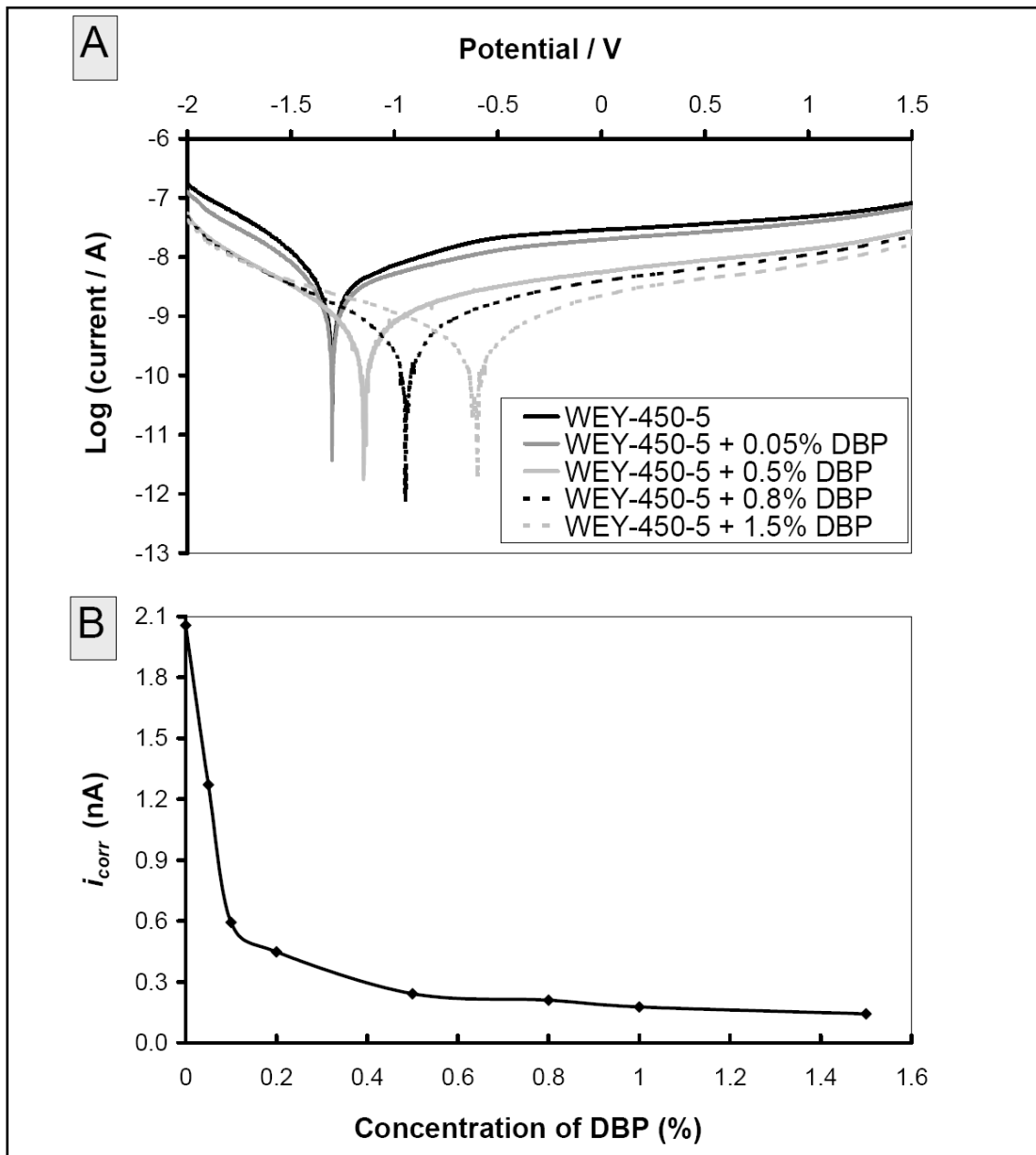
ADHP and DBP were also investigated as corrosion inhibitors (Figures 4(A) and 5(A)). These two inhibitors produced the same trendline observed using AH and PA, *i.e.* the  $E_{corr}$  of WEY-450-5 shifted to less negative potentials, and  $i_{corr}$

decreased sharply with the increase of the concentration of inhibitor until reaching a point from which  $i_{corr}$  does not decrease anymore, or from which the  $i_{corr}$  decrease is insignificant. In the case of ADHP, this point is ca. 0.1 % ADHP (Figure 4(B)), whereas in the case of DBP it was ca. 0.5 % DBP (Figure 5(B)). The optimum concentration ranges were 0.1 to 0.3 % ADHP, and 0.4 to 0.6 % DBP.

On the other hand, concentrations greater than 0.5 % ADHP were not studied due to electrolyte supersaturation, *i.e.* concentrations of ADHP greater than 0.5 % did not dissolve in WEY-450-5 electrolyte (Figure 4(B)).



**Figure 4.** (A) Tafel plot of aluminium in WEY-450-5. Effect of increasing concentrations of ammonium dihydrogen phosphate (ADHP) in the  $i_{corr}$ . Scan rate: 0.01 V/s. (B)  $i_{corr}$  as a function of the concentration of ADHP.



**Figure 5.** (A) Tafel plot of aluminium in WEY-450-5. Effect of increasing concentrations of dibutyl phosphate (DBP) in the  $i_{corr}$ . Scan rate: 0.01 V/s. (B)  $i_{corr}$  as a function of the concentration of DBP.

#### 3.2.4. Summary of the corrosion inhibitor studies

In electrolyte development, a series of corrosion inhibitors can be selected to study their performance against corrosion. In this work, ammonium hypophosphite (AH); phosphoric acid (PA); ammonium dihydrogen phosphate (ADHP); and dibutyl phosphate (DBP) were selected as corrosion inhibitors for WEY-450-5 electrolyte, showing different optimum concentrations. When a corrosion inhibitor is used, a minimum concentration is required in order to achieve the best or optimum performance. However, there is no further improvement when the concentration of inhibitor is above that optimum value. Furthermore, increasing concentrations of corrosion inhibitor may not only increase the electrolyte costs, but also cause negative effects in the electrolyte parameters (e.g. reduction in conductivity or reduction in breakdown voltage). Table 3 summarises the optimum concentrations of AH, PA, ADHP and DBP in WEY-450-5 electrolyte.



**Table 3.** Summary of the corrosion inhibitor studies.

Corrosion inhibitor in WEY-450-5:	AH	PA	ADHP	DBP
Optimum concentration:	0.15 - 0.25 %	0.75 - 1 %	0.1 - 0.2 %	0.4 - 0.6 %

#### 4. Conclusions

The Tafel plot electrochemical technique has been presented as a useful corrosion test method for electrolyte development in aluminium electrolytic capacitor applications. This technique is thus proposed for the study of the aluminium corrosion caused by electrolytes used in this type of capacitor and for the investigation of the performance of different corrosion inhibitors.

The Tafel plot corrosion current,  $i_{corr}$ , was measured and used to characterise a series of glycol-based electrolytes, showing significant differences between electrolytes. These differences in  $i_{corr}$  are due to the different chemical compositions of the electrolytes. Hence, the selection of suitable acids, bases and salts is critical to ensure a suitable capacitor performance. The ability of the Tafel plot technique to study the corrosion caused by electrolytes may become extremely valuable in electrolyte development, since corrosive electrolytes can be easily distinguished from *inert* (or less corrosive) electrolytes. This may be time and cost-effective because further capacitor preparation and test will only involve the less aggressive electrolytes.

In addition, ammonium hypophosphite; phosphoric acid; ammonium dihydrogen phosphate; and dibutyl phosphate were studied as corrosion inhibitors, showing optimum inhibition performance when the concentration of inhibitor is approximately 0.15–0.25 % ammonium hypophosphite; 0.75–1 % phosphoric acid; 0.1–0.2 % ammonium dihydrogen phosphate; and 0.4–0.6 % dibutyl phosphate. It is important to stress that these are the optimum concentrations in this particular test electrolyte and these values may vary for different electrolyte formulations. The optimum concentrations of ammonium hypophosphite and phosphoric acid agree very well with the proposed concentrations found in literature. However, little information was found so far from literature about the optimum concentrations of ammonium dihydrogen phosphate and dibutyl phosphate in ethylene glycol-based electrolytes.

Further works shall involve investigations using different organic solvent-based electrolytes (BLO, co-solvents, etc) as well as using the actual aluminium anode and cathode foils employed in aluminium electrolytic capacitors, and aluminium tabs and inserts. In addition, the effect of temperature (85 – 125 °C) on the Tafel plot corrosion current, shall be studied.

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#### References

- [1]. R. Xue, Y.-Y. Qian, K.-K. Liu, X.-X. Jiang, J.-J. Zhu, J.-R. Zhang. *Corrosion Science*, 2008, 50, 2779-2784.
- [2]. T. Morimoto, Y. Hamatani, M. Yoshitake, H. Yamada. US Patent 4831499, 1979.
- [3]. S.D. Ross, M. Finkelstein. US Patent 5006964, 1990.
- [4]. K. Fukuda, T. Ito. US Patent 4469610, 1984.

- [5]. T. Ebel, F. Stippich, J. Behm, O. Magnussen, S. Lauterborn. US Patent 2004/0004806 A1, 2004.
- [6]. M.-L. Tsai, Y.-F. Lu and J.-S. Do. *J. Power Sources*, 2002, 112, 643-648.
- [7]. (a) Z. Dou, R. Xu, A. Berduque. CARTS Europe 2008, 79-92. (b) R. Xu, A. Berduque, Z. Dou. CARTS USA 2009, 83-94.
- [8]. R. Takaoka, K. Honda, Y. Tsubaki, Y. Sugihara. US Patent 7163643, 2007.
- [9]. B. Melody. CARTS USA 1993, 199-205.
- [10]. C. Vargel, M. Jacques and M.P. Schmidt. *Corrosion of aluminium*. Elsevier, 2004.
- [11]. L.R.B. Holzle, D.S. Azambuja, C.M.S. Piatnicki, G.E. Englert. *Mater. Chem. Phys.*, 2005, 91, 375-380.
- [12]. B.A. Abd-El-Nabey, N. Khalil and E. Khamis. *Corrosion Science*, 1985, 25 (4), 225-232.
- [13]. A. Santos Liu, M.A. Silva Oliveira. *Materials Research*, 2007, 10 (2), 205-209.
- [14]. R.G. Kelly, J.R. Scully, D.W. Shoesmith, R.G. Buchheit. *Electrochemical techniques in corrosion science and engineering*. Marcel Dekker, Inc., 2003.
- [15]. T. Ebel, W. Lauer. US Patent 6707661 B2, 2004.
- [16]. T. Ebel. US Patent 2003/0103321 A1, 2003.