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Trihexyltetradecylphosphonium bis(Trifluoromethylsulfonyl) imide as inhibitor for 6063 aluminium alloy corrosion in physiological solution

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Aluminium alloys have found extensive use in several industrial, biological and dentistry applications, due to their high resistance towards corrosion in certain environments compared with carbon steels. Moreover, this choice is also related to the relatively low cost of the aluminium alloys. The use of aluminium alloys in the biological and dentistry related applications is of special importance. The addition of inhibitors presents an effective method for the reduction of the corrosion of the aluminium alloys in different environments. In this paper, the corrosion of 6063 aluminium alloy in physiological solution, with and without the addition of trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl) imide has been discussed. The influence of the inhibitor’s concentration on the corrosion rate of the 6063 aluminium alloy in physiological solution at 37°C, was studied using the weight loss and the potentiodynamic polarization techniques. The increase in the concentration of the trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl) imide added resulted in increased resistance of the 6063 aluminium alloy in the studied corrosion environment.

Keywords: Aluminium alloy, Corrosion, Inhibitor, Ionic liquids, Physiological solution, Potentiodynamic polarization method, Weight loss method

Electrochemical corrosion is a continuous destructive attack of a metal as a result of its electrochemical reaction with the surrounding environment, which is associated with deterioration of the physical and mechanical properties of the metal[1]. The study of corrosion of ferrous and nonferrous metals in different electrolytes, such as seawater and saline (Ringer) solution is of interest for various applications. The durability of metallic materials in specific conditions is very important, as it is related not only to economic and environmental effects, but also to the safety of objects produced from them[2, 3].

After steel, aluminium is the most widely used metal due to its mechanical properties and its good resistance to electrochemical corrosion in several corrosion environments. According to Schweitzer[1]the demand for aluminium and aluminium alloys has been increasing from year to year, due to the increase of their application in several engineering fields. The characteristics (physical, mechanical and chemical) of aluminium alloys depend on the composition of the alloy, microstructure, production conditions and thermomechanical processes. These characteristics are then connected to the corrosion susceptibility of aluminium and its alloys. It has been reported that the corrosion susceptibility of the aluminium alloys it is dependent on their heterogeneity, quantitative ratios of composition, crystal structure of the alloy (microstructures), temperature, environment, the stress under which the objects operate[1].

The effective corrosion mitigation of metals in different environments represents a continuous challenge even in the XXI century due in part to the sustainable economic development and the living costs[4]. The attempts to mitigate corrosion are not only connected with the effective use of raw materials and the minimization of economic losses, but also with the prevention and minimization of environmental pollution[2]. Various methods have been employed to protect metals from corrosion, including electrochemical protection (galvanization) and addition to the corrosive environment of low concentrations of substances that slow down the corrosion process (inhibitors). Inhibitors bind to the metal surface by chemical bonding to form stable compounds or by physical bonding to form a layer that isolates the metal from the corrosive environment[5, 6]. In addition to a wide range of organic and inorganic compounds, plant extracts, pharmaceutical drugs, ionic liquids and synthetic compounds, are continuously tested in laboratory conditions regarding their effectiveness as inhibitors for various metals in different corrosion environments[3, 7, 8]. Ionic liquids have been extensively used as corrosion inhibitors, mainly for steel, aluminium, copper and their alloys[9-14]. The use of ionic liquids as a corrosion inhibitor is associated with several advantages related to their physicochemical properties. They are non-toxic, have high conductivity, are non-flammable, have high thermal and chemical resistance, and are non-volatile[9, 15-20].

The ionic salt (4-ethoxybenzyl)-triphenyl–phosphonium bromide has been employed as a green corrosion inhibitor on mild steel in acidic medium[21]. This ionic salt inhibits both the anodic and the cathodic corrosion half recations, by both physical and chemical adsorption on the steel surface.

The corrosion inhibition efficiency of some bis(trifluoromethyl-sulfonyl) imide imidazolium-based ionic liquids for mild steel in hydrochloric acid solution was studied by Murulana *et al.*[22]. The ionic liquids tested are 1-propyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([PMIM][NTf$_2$]), 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([BMIM][NTf$_2$]), 1-hexyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([HMIM][NTf$_2$]), and 1-propyl-2,3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([PDMIM][NTf$_2$]). The inhibition efficiency of these ionic liquids decreased in the order [PDMIM][NTf$_2$] > [HMIM][NTf$_2$] > [BMIM][NTf$_2$] > [PMIM][NTf$_2$].

Several studies reported on the use of ionic liquids as corrosion inhibitiors for aluminium and its alloys in different corrosion environments[7]. The inhibition efficiency of three ionic liquids, i.e. 1-butyl-3-methylimidazoliumchlorides (BMIC), 1-hexyl-3-methylimidazolium chlorides (HMIC) and 1-octyl-3-methylimidazoliumchlorides (OMIC) as corrosion inhibitors for aluminium in 1 M HCl solution was studied by Shetty and Shetty[23], using electrochemical and weight loss methods. The inhibition efficiencies of these ionic liquids increased with increasing their concentration and followed the order: OMIC > HMIC > BMIC. Huang *et al.*[24] studied the behavior of 5083 aluminium alloy in 0.1 M NaCl aqueous environment in the presence of trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) ionic liquid amide. The authors reported that the presence of this ionic liquid leads to a decrease in anodic corrosion kinetics and overall corrosion rate of the aluminium alloy. The corrosion susceptibility of 6061 aluminium alloy in 0.1 M H_2SO_4 solution in the presence of 1,3-bis (2-oxo-2-phenylethyl)-1H-imidazol-3-ium bromide (OPEIB) was reported by Arellanes-Lozada *et al.*[25]. Zhang *et al.*[26] synthesized three ionic liquids, i.e. (poly(1-vinyl-3-dodecyl-imidazolium) (PImC12), poly(1-vinyl-3-octylimidazolium) (PImC8) and poly(1-vinyl-3-butylimidazolium) (PImC4) hexa–fluorophosphate), and tested their inhibition efficiency in the corrosion of 6061 aluminium alloy in 0.1–1.0 M H_2SO_4 solution. The synthesized ionic liquids acted as mixed type inhibitor and their corrosion inhibition efficiencies followed the order: PImC12 > PImC8 > PImC4.

The application of aluminium alloys in biological and implant environments is of particular interest and importance. Therefore, it is of great interest to study the stability of aluminium alloys in physiological solution (Ringer's solution), as reported by[10, 27-29]. To the best of our knowledge no studies have been perfomed on the corrosion protection of 6063 aluminium alloy in Ringer’s solution.

In this paper we report on the corrosion of 6063 aluminium alloy in the physiological solution (Ringer’s solution), in the presence of the ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide. The effect of the ionic liquid’s concentration on the corrosion rate of the aluminium alloy is studied using the weight loss and potentiodynamic polarization techniques at 37°C. The corrosion rate of the 6063 aluminium alloy decreased with the increase of the ionic liquid concentration.

Experimental Section

The ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide (assay $\geq$ 95.0%) was provided by Sigma Aldrich. The chemical structure of this ionic liquid is presented in Figure 1.

The 6063 aluminium alloy samples used in this study have a composition as specified in Table 1.

The samples used in the weight loss method were in parallelepiped shape with dimensions

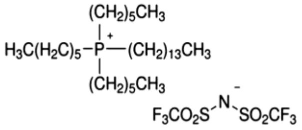

Fig. 1 — Chemical structure of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide.

Table 1 — Chemical composition of the 6063 aluminium alloy samples

Element	Si	Fe	Cu	Mn
Content(%)	0.45–0.42	0.16–0.19	0.0002–0.0007	0.0012–0.0021
Element	Mg	Cr	Zn	Ti
Content(%)	0.47–0.49	0.0005–0.0012	0.019–0.022	0.013–0.018

approximately 45 mm x 10 mm x 10 mm and a diameter of the hanging hole of 4 mm. The 6063 aluminium alloy samples were immersed in the Ringer's solution for 20 days, under stagnant conditions. The solutions were deaerated using with gaseous nitrogen for 15 min before immersion in the samples of the aluminium alloy.

The sample used for the potentiodynamic polarisation measurements has a cylindrical shape. The external surface of the sample was ground with polishing paper and then fixed in a teflon tube using epoxy resin. A surface with a 5 mm diameter was exposed to the corrosion environment. Table 1 shows the composition of the 6063 aluminium alloy as specified by the provider.

The physiological solution (Ringer’s solution) was prepared by dissolving in distilled water 6.80 g/L NaCl, 0.40 g/L KCl, 0.20 g/L $CaCl_2$, 0.20 g/L $MgSO_47H_2O$, 0.14 g/L $NaH_2PO_4 \cdot H_2O$, 2.20 g/L $NaHCO_3$, and 1.0 g/L glucose[10]. The *p*H of the Ringer’s solution was *p*H = 7.8. The Ringer’s solution was heated to 37°C and used to perform the measurements. Different volumes of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide were added to the Ringer’s solution and mixed with a magnetic stirrer for 15 min to obtain the desired concentrations, i.e. 0.1, 0.2, 0.3 and 0.4 vol.%. The final volume of the physiological solution was 100 mL. The solutions were deaerated using with gaseous nitrogen for 15 min before immersion in the samples of the aluminium alloy.

The prepared samples for the weight loss method are marked and their surface is polished using emery paper of different grades (120-, 240-, 320-, 600-, 1000-, 1500 and 4000-grit). They are then rinsed with distilled water and dried with warm air pressure. Finally the samples are cleaned in a ultrasonic bath with a 50:50 vol.% mixture of distilled water and acetone for 10 min and then rinsed with distilled water and dried with warm air. The samples were weighed before immersion into the Ringer’s solution for 20 days at 37°C. After removal from the solution the 6063 aluminium alloy samples were rinsed with bidistilled water, immersed in a Na_2CO_3 solution and then dried with warm air pressure. Finally the samples were weighed again and the mass difference before and after immersion was calculated and used to calculate the corrosion rate and the corrosion inhibition efficiency of the ionic liquid.

For the potentiodynamic polarisation measurements was used the same surface preparation procedure as described for the weight loss method. A Tacussel PJT 24-1 type potentiostat equipped with a pilovit for potential scanning was used to polarise the samples with a scanning rate was 6 mV/min. Approximately 15–30 min were allowed for the samples to stabilize in the corrosion environment and the open circuit potential was measured. The working electrode consisted of the 6063 aluminium alloy, while the saturated calomel electrode (SCE) with a luggin capillary and the platinum electrode were used as the reference and the auxiliary electrode, respectively. The potentiodynamic polarization curves obtained are used to determine the corrosion potential and current density values which are then used to calculate the corrosion rate and the corrosion inhibition efficiency of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide.

Results and Discussion

The weight loss tests were performed by immersion of the 6063 aluminium alloy samples in Ringer’s solution for 20 days at 37°C. Four different concentrations of the inhibitor, i.e. 0.1, 0.2, 0.3, and 0.4 vol. % have been tested. The results obtained from the weight loss method are used to calculate the corrosion rate:

in g/m^2h:

$$v_{(g/m^2 hour)} = \frac{\Delta m}{S \cdot t} \qquad \ldots(1)$$

in g/m^2 day:

$$v_{(g/m^2 day)} = v_{(g/m^2 h)} \cdot \frac{24\ h}{day} \qquad \ldots(2)$$

and in mm/year:

$$v_{(mm/year)} = \frac{0.365 \cdot v_{(g/m^2 day)}}{d} \qquad \ldots(3)$$

Δm – weight change (in grams) of the sample before and after exposure to the corrosion environment

Table 2 — Corrosion rates and inhibitor efficiencies for different concentrations of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide added to the Ringer's solution at 37°C, after 20 days of immersion.

Inhibitor concentration(vol.%)	Corrosion rate(g/m^2h)	Corrosion rate (mm/year)	Inhibitor efficiency(%)
0.0	0.0041	0.0134	-
0.1	0.0033	0.0108	19.1
0.2	0.0022	0.0070	47.6
0.3	0.0016	0.0051	61.9
0.4	0.0007	0.0022	83.3

S – sample's surface (in m^2)

t – exposure time in the corrosion environment (in hours)

d – density of the aluminium alloy (2.7 g/cm^3)

The protection efficiency of the trihexyl–tetradecylphosphonium bis(trifluoromethylsulfonyl) imide is calculated using the formula:

$$IE(\%) = \frac{v^0_{corr} - v_{corr}}{v^0_{corr}} \cdot 100 \qquad \ldots(4)$$

IE (%) – corrosion inhibition efficiency

v^0_{corr} – corrosion rate without inhibitor addition

v_{corr} – corrosion rate with inhibitor addition

Table 2 summarizes the corrosion rates in g/m^2h and mm/year and the respective corrosion efficiency values calculated according to formulas 1–4, for all inhibitor-acid combinations investigated. The lowest corrosion rate (0.0007 g/m^2h) was obtained at 37 °C using the highest concentration of trihexyltetradecylphosphonium bis(trifluoromethyl–sulfonyl) imide (i.e. 0.4 vol.%). Table 2 shows that the corrosion rate decreases with the increase of inhibitor concentration. Moreover, the corrosion inhibition efficiency of the trihexyl–tetradecyl–phosphonium bis(trifluoromethylsulfonyl) imide increase with increasing the ionic liquid concentration. The highest corrosion inhibition efficiency (83.33%) was achieved when 0.4 vol.% of the ionic liquid is added to the Ringer's solution.

The data obtained from the potentiodynamic polarization are represented in polarization curves, as shown in Figure 2. The values of the potential are measured versus the saturated calomel electrode.

Figure 2 presents the potentiodynamic polarization curves for the 6063 aluminium alloy samples immersed in the Ringer's solution, with and without the addition of the inhibitor. The corrosion current density values obtained from the potentiodynamic polarization curves are employed to evaluate the corrosion rate and corrosion inhibition effectiveness according to equations (5-7):

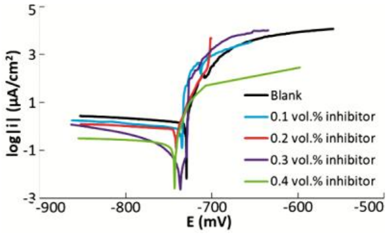

Fig. 2 — Potentiodynamic polarisation curves of the 6063 aluminium alloy immersed in Ringer's solution with and without addition of 0.1–0.4 vol.% of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide.

$$IE(\%) = \frac{i^{\circ}_{corr} - i_{corr}}{i^{\circ}_{corr}} \cdot 100 \qquad \ldots(5)$$

$$v_{g/m^2h} = \frac{E \cdot 3600}{96500} \cdot i_{corr} \qquad \ldots(6)$$

$$v_{(\mathrm{mm/year})} = \frac{8.76 \cdot v_{(g/m^2h)}}{d_{(g/cm^3)}} \qquad \ldots(7)$$

IE(%) - corrosion inhibition efficiency;

i^0_{corr} – corrosion current density without inhibitor addition (μA/cm^2);

i_{corr} – corrosion current density with inhibitor addition (μA/cm^2);

E – equivalent weight of Al^{3+};

d – density of the aluminium alloy (2.7 g/cm^3).

Table 3 presents the corrosion potential, corrosion current density and the respective corrosion inhibition efficiency values of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide obtained from the potentiodynamic curves in Figure 2. The corrosion potential of the aluminium alloy samples is shifted to more negative potentials upon addition of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide (Table 3). In accordance with the weight loss results, the highest inhibition efficiency (86.5%) was achieved for the highest concentration of inhibitor added (i.e. 0.4 vol.%).

The comparison of the polarization curves (with and without addition of the inhibitor)

Table 3 — Corrosion potential and corrosion current density of the 6063 aluminium samples immersed in the Ringer's solution at 37 °C, with and without addition of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide. The respective corrosion rates and the inhibition efficiencies are calculated according to equation (5–7).

Inhibitor concentration (vol. %)	E_{corr} (mV)	i_{corr} (μA/cm^2)	Corrosion rate (g/m^{2}h)	Corrosion rate (mm/year)	Inhibitor efficiency (%)
0.00	–729	1.48	0.0050	0.0161	-
0.10	–757	1.00	0.0034	0.0110	32.4
0.20	–739	0.76	0.0026	0.0083	48.6
0.30	–775	0.50	0.0017	0.0054	66.2
0.40	–741	0.20	0.0007	0.0022	86.5

clearly shows that trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide influences both the cathodic and the anodic corrosion reactions, behaving as a mixed type inhibitor, with a more pronounced effect on the anodic part of the curve.

According to Caporali *et al.*[30] this behavior of the aluminium alloy may be related to the surface change due to the degradation of the thin layer of Al_2O_3 present on the surface of the sample. This layer is atacked by the chloride ions present in the solution, according to equation (8):

$$Al^{3+}_{(\text{in the alumina crystal lattice})} + 2Cl^- + 2OH^- \rightarrow Al(OH)_2Cl_2^- \quad ...(8)$$

Abdel-Gaber *et al.*[31] reported that the in basic environments aluminium is subjected to pitting corrosion.

Equations (9–11) show the formation of three corrosion products, respectively $Al(OH)_2Cl$, $Al(OH)Cl_2$ and $AlCl_3$.

$$Al(OH)_3 + Cl^- \rightarrow Al(OH)_2Cl + OH^- \quad ... (9)$$

$$Al(OH)_2Cl + Cl^- \rightarrow Al(OH)Cl_2 + OH^- \quad ...(10)$$

$$Al(OH)Cl_2 + Cl^- \rightarrow AlCl_3 + OH^- \quad ...(11)$$

The aluminium chloride formed in equation (11) is soluble in the chloride environment forming $AlCl_4^-$ according to equation (12).

$$AlCl_3 + Cl^- \rightarrow AlCl_4^- \quad …(12)$$

The thickeness of the oxide layer is dependent from the *p*H of the solution Armstrong *et al.*[32]. The cathodic corrosion reaction in weak basic environment is the reduction of water shown in equation (13).

$$2e^- + H_2O = 2H_2 + 2OH^- \quad ...(13)$$

The anodic corrosion reaction (Equation 14) occurs at a low rate due to the formation of the above mentioned compounds on the surface of the working electrode (Equations 9–12).

$$Al + 4OH^- = Al(OH)_4^- + 3e^- \quad ...(14)$$

Conclusion

The corrosion inhibition efficiency of trihexyltetradecylphosphonium bis(trifluoromethyl–sulfonyl) imide in the corrosion of the 6063 aluminium alloy in the Ringer's solution at 37°C was studied in this paper, using the weight loss and potentiodynamic polarization techniques. Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide presents optimal protective (inhibitory) effect against the corrosion of 6063 aluminium alloy in the Ringer's solution at 37°C. The corrosion inhibition efficiency increased with the increase of inhibitor concentration. The lowest corrosion rate according to the weight loss method was found to be 0.0007 g/m^{2}h (or 0.0022 mm/year) and 0.00067 g/m^{2}h (or 0.00217 mm/year) from the potentiodynamic polarization method. The maximum value of the inhibition effectiveness (for 0.4 vol.% trihexyltetradecyl–phosphonium bis (trifluoromethylsulfonyl) added) was found to be 86.5% from the potentiodynamic polarization method and 83.33% from the weight loss method.

From the potentiodynamic polarization curves it was observed that under the studied conditions, trihexyltetradecylphosphonium bis (trifluoromethyl–sulfonyl) imide behaves as a mixed type inhibitor with a more pronounced anodic effect.

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