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p-Substituted Benzoic Acid Derivatives as Corrosion Inhibitors for Aluminium in H₃PO₄

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ABSTRACT

The use of some p-substituted benzoic acid derivatives as low cost inhibitors for the corrosion of aluminium in 60% H₃PO₄ solution was explored by weight loss and galvanostatic polarization measurements. The inhibition efficiency of the compounds increases in the order: p-OH > p-NH₂ > benzoic acid > p-Br > p-NO₂. This order is not affected by the variation in temperature in the range 30-60 °C. Rate of corrosion is affected by both concentration of inhibitors and the temperature of the medium. The reaction rate was found to be proportional to the absolute value of Hammett constant (σ). Some thermodynamic functions were computed and are discussed.

Key words: Corrosion, aluminium, polarization, weight-loss measurements.

INTRODUCTION

The industrial importance of corrosion inhibitors is widespread, ranging from pickling to water-cooled systems. The selection of inhibitor for a given system depends on the corrosive medium, the nature of the metal and the magnitude of the charge at the metal-solution interface. The study of adsorption of organic compounds at electrode-electrolyte interfaces is a subject with pronounced practical significance in view of its relevance to electrochemical energy conversion, electro-organic synthesis and corrosion inhibition. Previous work in this laboratory deals with the effect of heterocyclic quaternary ammonium halide [1] and some 3,3,5-trimethyl azepine N-derivatives [2] on the corrosion of mild steel and aluminium in H₃PO₄. In this investigation, the inhibitive power of some p-substituted benzoic acid derivatives towards aluminium corrosion in 60% H₃PO₄ was investigated.

EXPERIMENTAL

All the chemicals employed in this investigation were reagent grade and the inhibitors were chemically pure substances. The composition of aluminium specimens used was: Al = 99.535, Si = 0.15, Fe = 0.19, Mn = 0.005, Mg = 0.1 and Cu = 0.02%. Aluminium specimens of size 20x20x2 mm were used for weight loss measurements. A cylindrical rod with a surface area of 0.72 cm² was used as an electrode in galvanostatic polarization measurements. The specimens were abraded mechanically with different grades of emery paper, grinded with 4/0 polishing paper, degreased in an alkaline carbonate - phosphate mixture and cleaned as usual [3]. The current-polarization curves were measured using a simple galvanostatic technique in the absence and presence of various concentrations of compounds used. Current densities were calculated on the basis of apparent surface area. The working aluminium anode or cathode was immersed into the electrolyte before polarization measurements were started and the free corrosion potential was measured. Polarization curves were obtained in the absence and in the presence of the added compound. Saturated calomel electrode and a platinum wire counter electrode were used. All experiments were carried out at 30 ± 0.1 °C.

RESULTS AND DISCUSSION

Weight loss measurements: The penetration P (depth of corrosion) was calculated from the weight loss by the relationship:

$$P = \text{weight loss}/(\text{area})(\text{density}) \quad (1)$$

The penetration for different concentrations of H₃PO₄ at 303 K is shown in Figure 1 and is described by the expression:

$$\log P = a + b \log t \quad (2)$$

where t is time and a and b are constants.

When the rate of penetration varies with the amount of penetration, the instantaneous rate of corrosion is:

$$dP/dt = k P^n \quad (3)$$

where k is the rate constant and n is the order of the reaction. Equations 2 and 3 which describe the results of the corrosion of pure iron and mild steel in o-H₃PO₄ were known before [1,4]. These equations can be applied for aluminium also. The integral of the derived differential equation

$$\int_{P=0}^{P=P} P^{-n} dP = k \int_{t=0}^{t=t} dt \quad (4)$$

$$\text{is } P^{1-n} = (1-n) k t \quad (5)$$

which is expressed logarithmically as

$$\log P = \frac{1}{1-n} [\log (1-n) + \log k] + \frac{1}{1-n} \log t \quad (6)$$

Equation 6 is the same general form as equation 2 when:

$$a = \frac{1}{1-n} [\log (1-n) + \log k] \quad (7)$$

$$\text{or } \log k = a (1-n) - \log (1-n) \quad (8)$$

$$\text{and } b = 1/(1-n) \quad (9)$$

$$\text{or } n = (b-1)/b \quad (10)$$

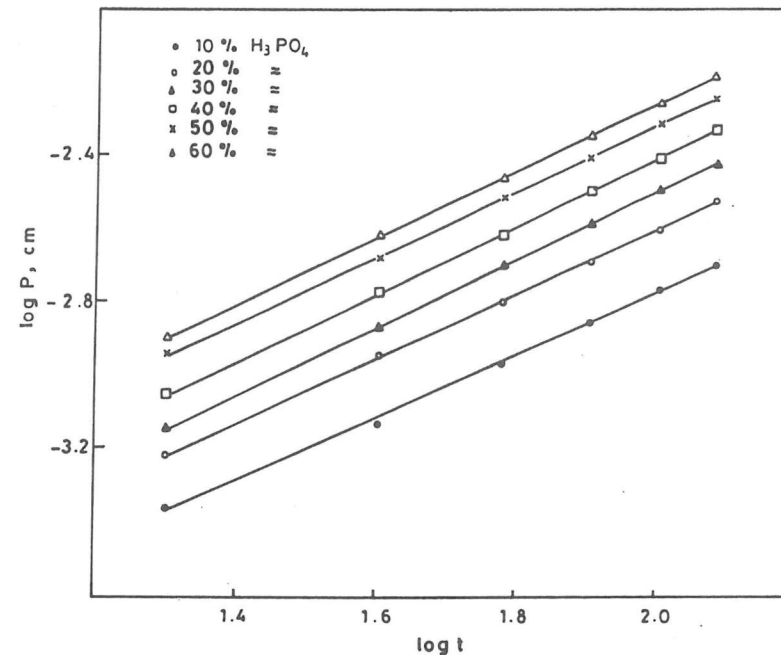


Fig. 1. Corrosion rates of aluminium in H₃PO₄ at 30 °C.

Values of a and b have been computed from Figure 1 and the results of aluminium corrosion in acid solutions of different concentrations are summarized in Table 1.

Table 1. Kinetic parameters for aluminium corrosion in o-phosphoric acid.

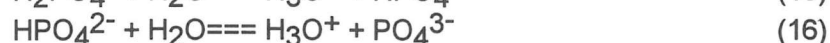
Acid concentration(%)	10	20	30	40	50	60
a	-3.63	-3.49	-3.44	-3.35	-3.23	-3.18
b	0.88	0.87	0.84	0.83	0.82	0.81

The values of b (Table 1) for the tests in 10, 20, 30, 40, 50 and 60% H₃PO₄ were slightly but significantly less than unity, the rate of corrosion decreased as the amount of corrosion increased, indicating that a reaction product had kinetic significance. The small differences from unity of the values of b suggested [4] that the reaction product is either very thin or not firmly adherent to the metal. Moreover, because all values of b are close to unity, equation 10 shows that the values of n are essentially zero. The linearity of the plot in Figure 1 implies that the mechanism of corrosion does not change at least up to corrosion times of the order 3 h.

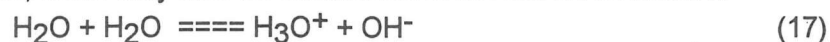
When aluminium dissolves in acid solutions with hydrogen evolution type of attack, the reactions taking place at the aluminium electrode may be represented as:



Phosphoric acid may be assumed to be ionized in aqueous solutions according to the following equilibria:



Further, water may also be considered to be ionized as follows:



Now, both aluminium hydroxide and aluminium phosphate are insoluble in near neutral solutions and, therefore, in case where, due to the corrosion process, the acid becomes depleted of a certain amount of hydrogen ions, there is a probability that a film of oxide (or hydroxide) or

phosphate may be deposited in situ. This would lead to a diminution of attack. The chemical analysis of the deposited film suggested that it was impure aluminium phosphate. On the other hand, where the hydrogen ions are regenerated because of the hydrolysis of the corrosion product or where there is complex formation, there would be an increase in attack.

Figure 2 presents the weight loss (mg/cm²) vs. the time of immersion (minutes) for p-OH compound. As expected, increasing the acid concentration increases the corrosion rate at constant inhibitor concentration. As the inhibitor concentration increases the corrosion rate decreases asymptotically. This agrees with the results obtained for the compounds used.

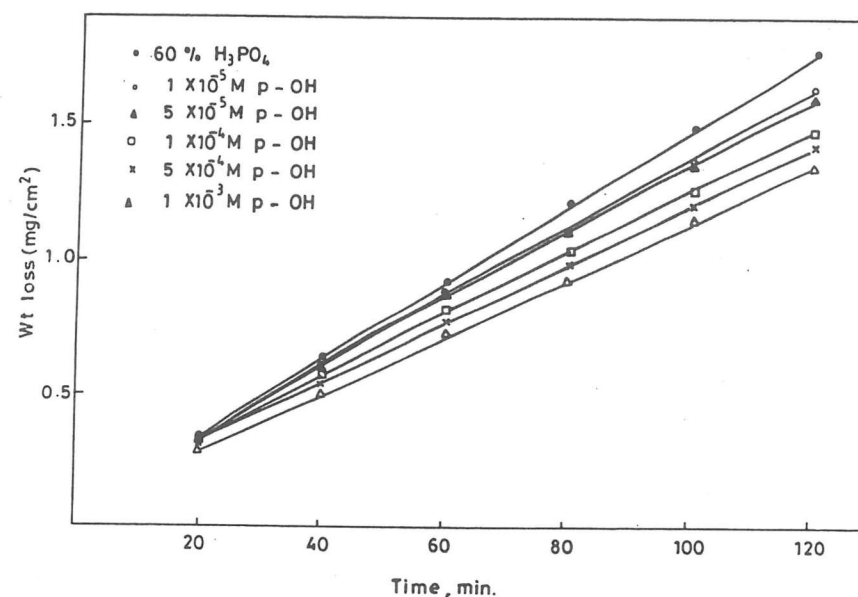


Fig. 2. Weight loss-time curves for aluminium in p-OH compound at 30 °C.

The inhibition efficiency, %P, was calculated by the standard formula:

$$\%P = \frac{w_1 - w_2}{w_1} \times 100 \quad (18)$$

where w_1 = weight loss in 60% H_3PO_4 solution, w_2 = weight loss in inhibited solutions. Figure 3 presents the weight loss - time curves for all compounds used at 5×10^{-4} M. From this Figure, the sequence of decreasing the weight loss and increasing inhibition efficiency is in the order: p-OH > p-NH₂ > benzoic > p-Br > p-NO₂.

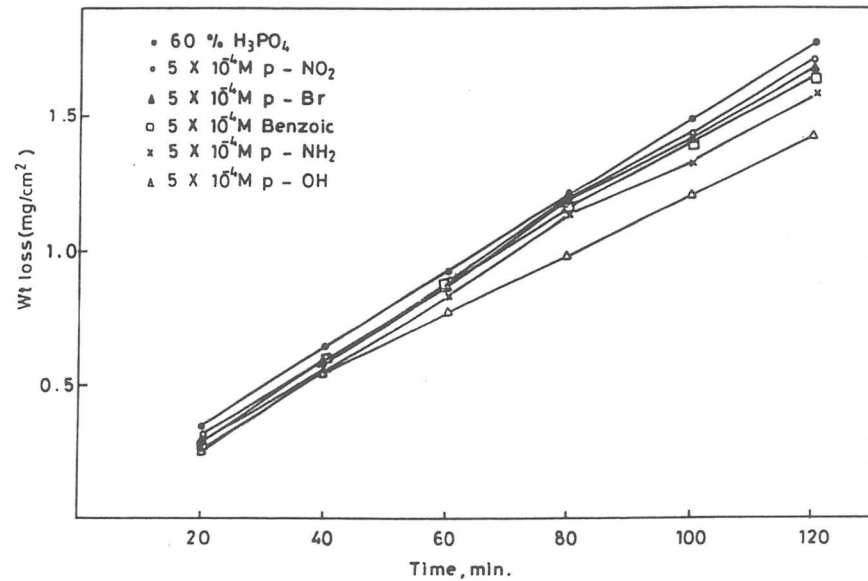


Fig. 3. Weight loss-time curves for aluminium in 5×10^{-4} M solutions of different compounds at 30 °C.

Polarization measurements: The polarization curves for the system involving p-OH compound are shown in Figure 4 and the electrochemical parameters in these media are given in Table 2. The corrosion current density for aluminium in 60% H_3PO_4 is: $i_{corr} = 184.93 \mu A cm^{-2}$. Addition of inhibitor molecules causes a decrease in i_{corr} . The decrease in i_{corr} and the increase in θ with increasing concentration in the range 10^{-5} - 10^{-3} M demonstrate the efficiency of the additive compounds as corrosion inhibitors of aluminium. Also, the slopes of anodic and cathodic Tafel lines are approximately constant, independent

of the concentration of inhibitor. This indicates that the inhibition of the dissolution process takes place without affecting the mechanism.

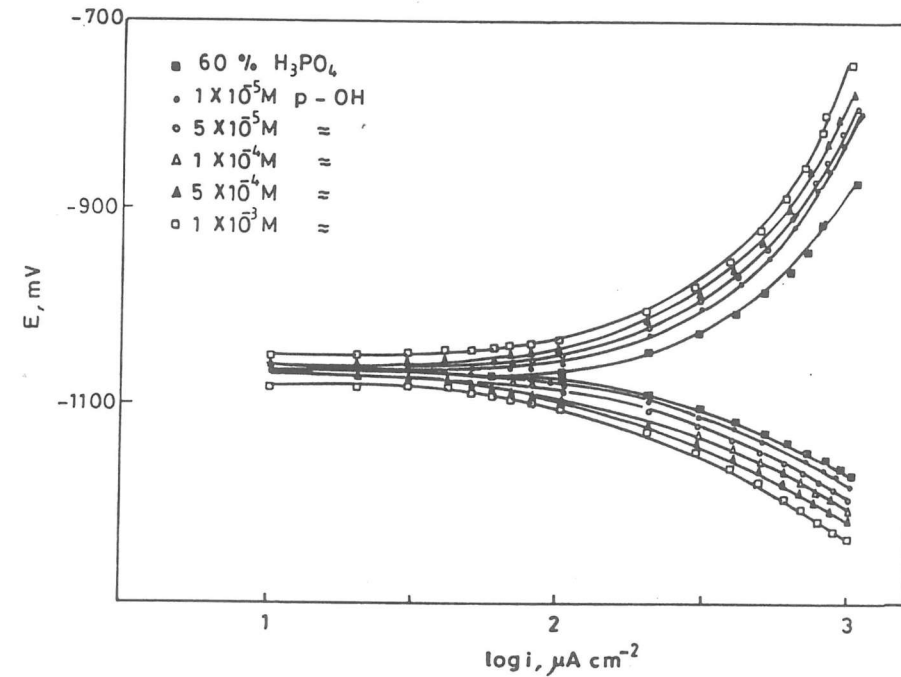


Fig. 4. Polarization curves of aluminium in 60% H_3PO_5 in the presence of different concentration of p-OH compound.

The inhibition efficiency (%P) and the surface coverage were calculated using the formulae:

$$\%P = \frac{I - I'}{I} \times 100 \quad \text{and} \quad \theta = \frac{I - I'}{I} \quad (19,20)$$

where I and I' are the corrosion current without and with inhibitor, respectively.

Figure 5 presents the anodic and cathodic polarization measurements on aluminium in 60% H_3PO_4 containing 5×10^{-4} M of different compounds used. As follows from this Figure, the sequence of increasing inhibition efficiency is in the order: pOH > pNH₂ > benzoic > p-Br > p-NO₂.

Table 2. The effect of p-OH compound on corrosion behaviour for aluminium in 60% H₃PO₄ at 30 °C.

Conc./ /M	-E _{corr} / /mV	i _{corr} / /μA cm ²	%P	b _a / mV/decade	b _c / mV/decade	θ
60% H ₃ PO ₄	1140	184.93	-	242.8	130.0	-
1x10 ⁻⁵	1142	100.00	45.93	133.3	111.4	0.459
5x10 ⁻⁵	1141	73.45	60.28	118.2	120.8	0.603
1x10 ⁻⁴	1139	58.48	68.38	125.0	120.7	0.684
5x10 ⁻⁴	1140	46.45	74.88	127.5	111.8	0.749
1x10 ⁻³	1138	39.72	78.52	120.0	121.2	0.785

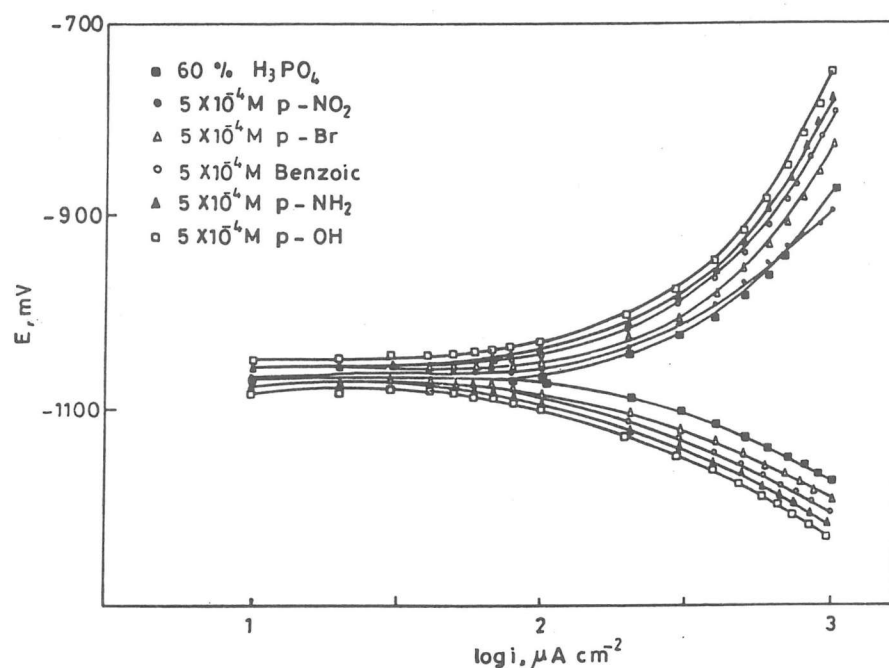


Fig. 5. Polarization curves of aluminium in 60% H₃PO₄ in the presence of 5x10⁻⁴ M different compounds at 30 °C.

A correlation between θ and log c of adsorbate is given by Temkin adsorption isotherm. The experimental results (Fig. 6) are in good agreement with the following equations:

$$\theta = \text{const.} + (2.303/f) \cdot \log c \quad (21)$$

$$f = (1/RT) \cdot d(\Delta G_{ads}^{\circ})/d\theta \quad (22)$$

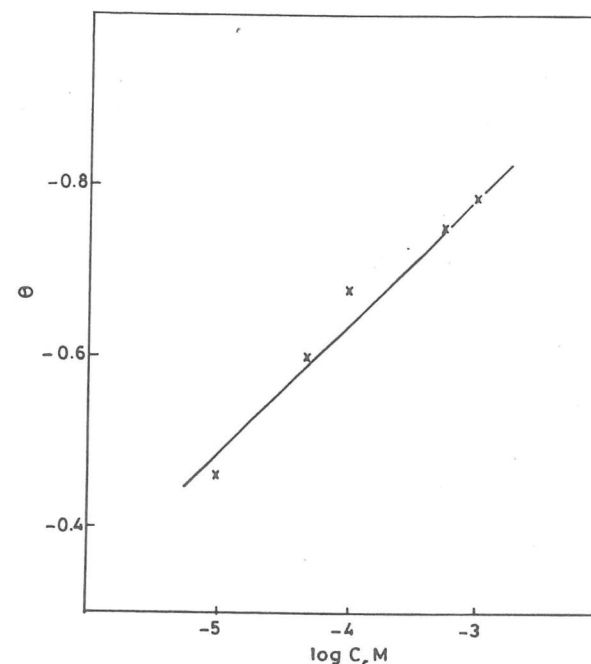


Fig. 6. Dependence of degree of surface coverage on logarithm of concentration of p-OH compound.

The effect of temperature on the rate of dissolution of aluminium in 60% H₃PO₄ was studied by galvanostatic polarization technique in the temperature range of 30-60 °C. For all p-substituted benzoic acid derivatives, the logarithm of log i_{corr} is a linear function of $\frac{1}{T}$ (Fig. 7). The activation energy values E_a^{*} (Table 3) increase with increasing the inhibition efficiency of the compounds. The p-OH compound which gives maximum inhibition efficiency yields the highest activation energy and the opposite is true for p-NO₂ compound. Also, an increase in the

concentration of inhibitors increases the activation energy. The values of free energy of adsorption ΔG_{ads}° , were calculated at 30 °C (Table 3).

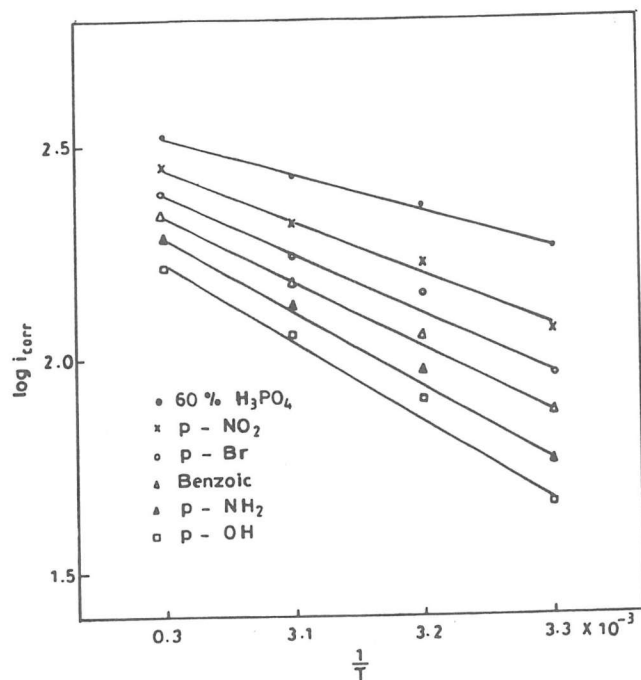


Fig. 7. Log i_{corr} vs. $\frac{1}{T}$ curves for aluminium dissolution in the presence and absence of inhibitors.

Table 3. Inhibition efficiency, the activation energy and the free energy of adsorption of inhibitors at concentration of 5×10^{-4} M.

Inhibitor	% Inhibition (%P)		E_a^* / /KJ mol ⁻¹	$-\Delta G_{ads}^\circ$ / /KJ mol ⁻¹
	weight loss	polarization		

The results show that p-OH compound gives maximum efficiency, exhibits the highest negative ΔG_{ads}° indicating that it is strongly adsorbed on the aluminium surface, i.e., acting as a metal protecting agent. In general, the negative values of ΔG_{ads}° indicate that the adsorption of the inhibitors on the metal surface is spontaneous [5,6].

Table 4 collects the corrosion rate (i_{corr}) values and the inhibiting efficiency percentages calculated from polarization measurements. From these data, it is evident that the order of the lowest corrosion rates in the examined temperature ranges is: p-OH > p-NH₂ > benzoic > p-Br > p-NO₂.

Table 4. Corrosion rate (i_{corr}) of aluminium in the presence of 60% H₃PO₄ and 5×10^{-4} M various inhibitors and corresponding percent inhibition efficiency (%P) at different temperatures.

Inhibitor	30 °C		40 °C		50 °C		60 °C	
	i_{corr}	%P	i_{corr}	%P	i_{corr}	%P	i_{corr}	%P
60% H ₃ PO ₄	184.93	-	232.27	-	271.02	-	328.85	-
p-NO ₂	116.42	37.05	171.00	26.38	207.49	23.44	281.19	14.49
p-Br	92.68	49.88	146.89	36.76	177.42	34.55	250.61	23.79
Benzoic	76.38	58.69	125.93	45.93	152.41	43.76	223.35	32.08
p-NH ₂	58.48	68.38	107.89	53.55	135.83	49.88	199.07	39.46
p-OH	46.45	74.88	88.92	61.72	116.68	56.95	164.82	49.87

Differences in the inhibition efficiency for aluminium corrosion in 60% H₃PO₄ as indicated by the above order arise from the substituents in the p-position of benzoic acid. It is evident that the nucleophilic character of these substituents plays a determining role in imparting inhibition efficiency. Therefore, increase in the electron-donating ability of substituents is expected to increase the inhibition efficiency.

The p-OH compound is the most efficient inhibitor. This may be attributed to the higher electron donating character of -OH compared to the other substituents. On the other hand, p-NO₂ compound is the least effective inhibitor in this series. This may be attributed to the coplanarity of the p-NO₂ group with the phenyl ring which imparts maximum electron withdrawal. Also, the NO₂ group is easily reduced in acid medium and this process is exothermic, the evolved heat aids the desorption of the compound on aluminium surface [7,8].

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Electrochemistry in International Standards

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Summary

Basic concepts of electrochemistry are not yet properly understood in areas related with technical aspects where this science is fundamental, such as corrosion. Examples of this are given here with the objective of alerting electrochemists for the need to give their collaboration in technical bodies (e.g. ISO, CEN, OIML [1]) where it is useful to complement the very important technical knowledge of applied experts on the relevant field (e.g. corrosion) with fundamental knowledge of electrochemistry.

Key words: electrochemistry, corrosion, electrolytes, pH

One example of the above is the European Standard "draft prEN 12473" entitled "General principles of cathodic protection in sea water", dated July 1996, which was sent for discussion in the Portuguese technical commission entitled "CT-43 Metallic Corrosion", of which I am a member. The document proposes a number of definitions, among them the following:

- 3.1 **acidity**: Presence of an excess of hydrogen ions over hydroxyl ions ($\text{pH} \leq 7$).
- 3.2 **alkalinity**: Presence of an excess of hydroxyl ions over hydrogen ions ($\text{pH} \geq 7$).
- 3.4 **anodic area**: That part of a metal surface which acts as an anode.
- 3.10 **cathodic protection**: Means of reduction corrosion by causing direct current to flow from its electrolyte environment into the entire metal surface.
- 3.18 **conductor**: Substance in which electric current flows.
- 3.24 **depolarization**: Removal of factors resisting the flow of current in a cell.
- 3.29 **electrolyte**: Liquid, or the liquid component in a composite material such as soil, in which electric current flows by the movement of ions.