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-NO_2 compound is the least effective inhibitor in this series. This may be attributed to the coplanarity of the p-NO_2 group with the phenyl ring which imparts maximum electron withdrawal. Also, the NO_2 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 ($pH \leq 7$).

3.2 **alkalinity:** Presence of an excess of hydroxyl ions over hydrogen ions ($pH \geq 7$).

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.

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3.30 electronegative: Qualification applied to a metallic electrode to indicate that its potential is negative with respect to another metallic electrode in the system. [It is interesting that the document does not attempt to define "electropositive"].

3.33 galvanic action: Spontaneous chemical reaction which occurs in a system comprising a cathode and an anode in electrical contact and with an intervening electrolyte, resulting in corrosion of the anode.

3.34 galvanic anode (see also sacrificial anode): Anode that provides cathodic protection current by virtue of its reactivity and when connected to a structure preferentially corrodes and protects the structure from corrosion. [Note that the document had previously defined "anodic area"].

3.39 ion: Atom, or group of atoms, carrying a charge of positive or negative electricity.

3.42 passivity: Condition of low surface activity or resistance to corrosion of a metal, normally as a result of protective film formation.

3.43 pH value: Logarithmic scale used to indicate the concentration of hydrogen ions in an electrolyte.

3.44 polarization: Change in the potential of an electrode as the result of current flow to or from that electrode.

3.45 potential gradient: Difference in potential between two separate points in the same electric field.

3.51 resistivity: Resistivity of an electrolyte is the resistance of a conductor of the electrolyte of uniform cross section. Usually expressed in ohm-metres. The resistivity depends, amongst other things, upon the amount of dissolved salts in the electrolyte.

3.52 sacrificial anode: Anode used to provide cathodic protection by means of galvanic action. The anode is consumed or sacrificed in the process of providing protection to the structure.

3.56 solution potential: Voltage difference between a submerged metallic structure and the electrolyte which is measured with a reference electrode in contact with the electrolyte.

3.57 standard hydrogen electrode: Reference electrode consisting of an electro-positive metal, such as platinum, in an electrolyte containing hydrogen ions at unit activity and saturated with hydrogen gas at one standard atmosphere.

4.1 The nature of metallic corrosion

When a metal corrodes in contact with an electrolyte neutral atoms pass into solution by forming positively charged ions and excess electrons are left in the metal. The process for iron may be expressed as

$$Fe \rightarrow Fe^{++} + 2e^- \qquad (1)$$

……….

The following equations show the most common reactions that occur at cathodes:

$$\underset{\text{oxygen}}{O_2} + \underset{\text{water}}{2\,H_2O} + \underset{\text{electrons}}{4e^-} \rightarrow \underset{\text{hydroxyl ions}}{4\,OH^-} \qquad (2)$$

$$\underset{\text{hydrogen ions ions}}{2\,H^+} + \underset{\text{electrons}}{2e^-} \rightarrow \underset{\text{hydrogen gas}}{H_2\uparrow} \qquad (3)$$

$$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \qquad (4)$$

[Here, they did not say $H_2\uparrow$]

The first of these reactions occurs in the presence of dissolved oxygen and near neutral conditions.

The second is favoured by acidity (excess of hydrogen ions) while the third is dominant at pH values greater than neutral.

It is obvious that for writing documents as the above the assistance of electrochemists with a clear knowledge of fundamental principles would be very helpful. Our commission CT-43 was supposed to comment the document, eventually suggesting specific corrections. I was of the opinion that it is difficult to propose specific alterations in a document so inadequately written. Actually I think that the whole philosophy of writing documents of this nature must be reanalysed. In fact I think that these documents should presuppose that the reader knows elementary principles of basic science and therefore there is no need to "define" concepts such as *ion*, *pH*, *acidity*, *conductor*, *electrolyte*, *gradient*, etc. One may even ask: if the document even "defines" *ion*, why not define *atom*, *molecule*, *electron*, etc. ? Then concepts like *molecule* cannot be properly defined and indeed need not to be. Trying to define *molecule* would be like trying to define *table* or *chair*. Everybody has the adequate concept of the meaning of *table* or *chair* but it would be very difficult to "define" them. And such a "definition" would hardly be of any use !

Indeed, there are situations where it may be useful that a certain standard defines some basic concept just for the objective of that specific standard, but such definition should be consistent with the general meaning of the term. Certainly, it is not the situation of document prEN 12473.

Concerning the proposed alterations from the Portuguese commission CT-43 to document prEN 12473 and despite my reluctance to try to "fix" such type of writing, the commission suggested "corrections" such as

pH value: a parameter used to indicate the acidity or alkalinity of a solution.

In fact there is a widespread misunderstanding for the meaning of pH. Sorensen's 1909 definition [2] relating pH with the hydrogenionic concentration ($pH = \log 1 / [H^+]$) soon give rise to another involving the hydrogenionic activity rather than the concentration. But we cannot measure the activity of a single ion and so IUPAC [3] proposes the following operational definition.

For a solution X the emf E(X) of the galvanic cell

$$\begin{array}{r|l l|l|l} \text{reference} & \text{KCl(aq,} & \parallel \text{solution X} & \text{H}_2\text{(g)} & \text{Pt} \\ \text{electrode} & m > 3.5\ \text{mol kg}^{-1}) & \parallel & & \end{array}$$

is measured, and likewise the emf E(S) of the cell that differs only by the replacement of the solution X of unknown pH(X) by the solution S of standard pH(S). The unknown pH is then given by

$$pH(X) = pH(S) + (E_S - E_X)F / (RT \ln 10)$$

Thus defined, pH is dimensionless. Values of pH(S) for several standard solutions and temperatures are listed in [4]. The reference value pH standard is an aqueous solution of potassium hydrogen phthalate at a molality of exactly 0.05 mol kg^{-1}: at 25 °C (298.15 K) this has a pH of 4.005.

In practice, a glass electrode is almost always used in place of the $Pt \mid H_2$ electrode. The cell might then take the form

$$\begin{array}{r|l l|l|l|l|l} \text{reference} & \text{KCl(aq,} & \parallel \text{solution X} & \text{glass} & \text{H}^+,\text{Cl}^- & \text{AgCl} & \text{Ag} \\ \text{electrode} & m > 3.5\ \text{mol kg}^{-1}) & \parallel & & & & \end{array}$$

The solution to the right of the glass electrode is usually a buffer solution of KH_2PO_4 and Na_2HPO_4, with 0.1 mol dm^{-3} of NaCl. The reference electrode is usually a calomel electrode, silver/silver chloride electrode, or a thallium amalgam/thallous chloride electrode. The emf of this cell depends on $a(H^+)$ in the solution X in the same way as that of the cell with the $Pt \mid H_2$ electrode, and thus the same procedure is followed.

In the restricted range of dilute aqueous solutions having amount concentrations less than 0.1 mol dm^{-3} and being neither strongly acidic nor strongly alkaline ($2 < pH < 12$) the above definition is such that

$$pH = -\lg[y_\pm c(H^+)/(\text{mol dm}^{-3})] \pm 0.02,$$

$$= -\lg[y_\pm m(H^+)/(\text{mol kg}^{-1})] \pm 0.02,$$

where $c(H^+)$ denotes the amount concentration of hydrogen ion H^+ and $m(H^+)$ the corresponding molality, and $y_\pm$ denotes the mean ionic activity coefficient of a typical uni-univalent electrolyte in the solution on a concentration basis or a molality basis as appropriate. For further information on the definition of pH see [4].

In another words, when we say that a solution has a pH of, say 3.54, what we are saying is that we have measured the emf of a certain electrochemical cell in the specified conditions and obtained a value in volts leading to $pH = 3.54$, according to the above IUPAC convention. But this is far from saying that the hydrogenionic concentration is $10^{-3.54}$, or even that the hydrogenionic activity is $10^{-3.54}$. Only in very diluted solutions (destilled water slightly polluted as the joke goes !) where the ionic strength is very low can we relate the pH with the hydrogenionic concentration with a reasonable degree of approximation.

Therefore, pH is merely a parameter that gives us a certain type of information about the degree of acidity of a solution [5]. It is indeed a very important information, but we must have in mind its relative value. pH information is widely used in situations such as sea waters, human blood, etc., which are very, very far from solutions of low ionic strength. The value may be extremely useful for comparative purposes, but we cannot take any valid conclusion from it about the hydrogenionic activity or concentration of such sea waters, human bloods, etc.

In a standard such as prEN 12473 we could say about pH that, for example, IUPAC definition applies, or that certain standards should be used, or any other objective type of procedure had to be used for the purpose of this standard. And though I agreed that our commission had to suggest something to try to call the attention for such unfortunate pH definition, I think that trying to define pH in a rather vague manner as we eventually suggested, is of no use to anybody.

Similarly for other definitions. It is not easy to "correct" a document that says

3.57 standard hydrogen electrode: Reference electrode consisting of an electro-positive metal, such as platinum, ... [just replacing "electropositive" by "inert", as we suggested, is still not enough].

3.1 acidity: ... ($pH \leq 7$). [We suggested $pH < 7$]

3.2 alkalinity: ... ($pH \geq 7$). [We suggested $pH > 7$, though only at a specific temperature is $K_w = [H^+]\,[OH^-] = 10^{-14}$]

3.51 resistivity: Resistivity of an electrolyte is the resistance of a conductor of the electrolyte of uniform cross section. Usually expressed in ohm-metres. The resistivity depends, amongst other things, upon the amount of dissolved salts in the electrolyte. [The salts are not dissolved in the electrolyte; they are, in principle, the electrolyte dissolved in a solvent, water in this case; also, the wording of this "definition" is rather unfortunate].

There is also widespread confusion about the concept of electrolyte. A recent paper [6] attempts to clarify the situation noting that one thing is the electrolyte, another is the electrolytic solution. In Ref. [6] electrolyte is defined as follows.

"Electrolyte: A substance when dissolved in a given solvent produces a solution with an electric conductivity higher than the solvent conductivity. May be a solid (e.g. sodium chloride), a liquid (e.g. sulphuric acid), or a gas (e.g. hydrochloric acid)."

Recent conventions about writing chemical equations and formulae are not respected. Thus it should be Fe^{2+}, not Fe^{++}, it should be $H_2(g)$, not $H_2\uparrow$. The wording leading to eq. (1) (see section 4.1 in the second page of this paper) is certainly unfortunate. Also, eq. (2) may occur, in principle, at any pH. However, the extension of it is pH dependent, as anyone with a minimum knowledge of fundamental chemistry should understand. Similarly, the last quoted paragraph (section 4.1) is irrelevant and also unfortunate ("pH values *greater* than neutral").

Other indications in prEN 12473 show similar inadequate wording.

Fig. 6 and Table 2 in prEN 12473 do not indicate the units in the proper way [3]. It should be "Potential / V" not "Potential (V)", as is indicated there. In fact, quantities in tables, graphs, figures, etc., should be coherent with the respective numbers. Therefore, if the numbers do not indicate any units (which is the normal case, and the present case of Fig. 6 and Table 2), then the headings on tables or the abscissae of graphs (or plots) must be adimensional, that is, we must divide the symbols (or appropriate wording) by the units in which they are expressed. In the present case, we must divide the quantity "potential" by the units (V).

These situations should encourage electrochemists to give some more collaboration to bodies such ISO, CEN, OIML.

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