The definition of electrolyte: a comment from a reader and the author's reply

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Summary

A comment from a reader of a paper on the definition of electrolyte and the author's reply is presented.

Key words: electrolyte, solutions.

Shortly after the publication of a paper on the definition of electrolyte in Portugaliae Electrochimica Acta 14, 27-29 (1996), the author had the pleasure, mainly because it shows the journal has prompt readers in far away countries, of receiving a letter from Dr. P. Radhakrishnamurty as follows.

"Dear Prof. Victor M.M. Lobo,

We read with interest your article on "The definition of electrolyte" (Ref: Portugaliae Electrochimica Acta 14 (1996) 27-29.

We agree with the two objections you raised with regard to the definition of "Electrolyte" given by the terminology document CEN/TC 262/SC IN 95 rev. as quoted in your article.

It is of serious concern to us that the document tries to associate "movement of matter" with "flow of electric current". The origin of this problem, viz., association of movement of matter to the flow of electric current, goes back to the model/mechanism of conduction of electric currents through electrochemical cells proposed by Hittorf.

During course of our investigations, we found that Hittorf's model/mechanism suffers from certain drawbacks and needs modification. Therefore, there is an urgent need to have a fresh look at the conductivity problem in ionic media.

It is true, as you have pointed out, that we must distinguish between an electrolyte and electrolyte solution because they are not one and the same.

However, if we define an electrolyte as a substance which when dissolved in a given solvent produces a solution with an electric conductivity higher than the solvent conductivity we would be restricting the scope of the definition, in our opinion, to solutions only. Since an electrolyte need not be a solution (for example molten sodium chloride, molten magnesium chloride etc. are electrolytes that conduct electric current but are not solutions) we should enlarge the scope of the definition, to include molten salts which are not solutions.

The following simple definition, in our opinion, covers all aspects:

"An electrolyte is a substance which conducts electric current through the agency of ionic species (and not electrons)".

If you agree with this you may consider it for publication in Portugaliae Electrochimica Acta either as a letter or note. In any case please write to us your response on the above definition. We have common interests to share.

The author's reply to Dr. Dr. P. Radhakrishnamurty was as follows.

Dear Dr. Radhakrishnamurty,

Thank you for your contribution to the "definition of electrolyte".

You are right when you say that the definition I proposed restricts the scope to solutions only. On that particular case, we were concerned with international standards for the surface treatment industries where electrolytic process involving aqueous solutions are widely used. My initial objections were with the following definition in a proposed standard (prEN 12508):

"**Electrolyte**: A conducting medium in which the flow of current is accompanied by movement of matter. Most often an aqueous solution of acids, bases, or salts, ionized gases, some solids, etc. (ASTM term)".

Also, and because of similar definitions in other standards (e.g. from the USA), the confusion between electrolyte and electrolytic situation was becoming common; I even received a Ph.D. thesis with this confusion all the way through. Therefore, my primary objective was concerned with the clarification of these concepts in the electroplating industry where aqueous electrolytic solutions are used. Before a meeting in London where these matters were going to be discussed, and international standards were going to be approved, a participant in that meeting from another country wrote to me saying, concerning the definition of electrolyte:

"...

Please read the scope, as follows

'It should be understood that the interpretations given are those corresponding to the practical usage in this fields and that they do not necessary coincide with the use in other fields.'

This is indeed an essential statement to the idea of this standard. I hope you can accept this.

It is usual in metal finishing to use 'electrolyte' as a synonym for a 'solution' sometimes called a 'bath' also, to avoid confusion with 'bath' in a bathroom or in medical sense, a lot of people normally say 'electrolyte'.

..."

Eventually, it was agreed in that London meeting to replace the word "electrolyte" by "electrolytic solution", and thus I hope that industry will gradually replace their common use of "electrolyte" by the more correct term (for that case) "electrolytic solution". Now, EN 12508 reads as follows:

"**Electrolytic solution**: A conducting medium in which the flow of current is accompanied by movement of matter. Most often an aqueous solution of acids, bases, or salts."

Your definition of electrolyte as the "... substance which conducts electric current ..." apparently would not consider, e.g., a crystal of sodium chloride, or the gas hydrogen chloride as being electrolytes (because either of them hardly conducts any current in normal circumstances). But they are considered electrolytes because when added to water they produce a solution (the electrolytic solution) that conducts electric current. Therefore, I would prefer teaching our students 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)."

Just for short, but meaning the above, we could say

"**Electrolyte**: A substance that increases the electrical conductivity of the solvent".

Of course, in mere scientific or teaching terms we need not to worry about "definitions": we only need to understand the concepts and make sure that we use words for those concepts that are not misleading or confusing. That is, as academics we merely need to teach what we mean by electrolytes and electrolytic solutions and then use those words in the appropriate context. Also, we cannot get an adequate definition for "molecule" or for that matter common concepts like "table" or "chair".

It is only when we come to standards to be used by industry, which eventually may end up in a legal court if a disagreement leads the parts involved to seek official justice, that we need to define technical words. They will be used in writing contracts which may involve millions of dollars. This is why we must be very careful when writing and approving national or international standards. We are not making new science but we should, in my opinion, be using the correct scientific concepts when

writing procedures or definitions which eventually may end up in a court. And each standard is only for a particular situation.

Also, your definition is based on the concepts of ions and electrons. I have defended in national and international meetings on standardization (for industry) that the words or concepts we have to define should always be based in observable phenomena, not in theories. We all know that, for example, Prof. Hertz from Karlsruhe, Germany, writes papers and books on electrochemistry without ever having to postulate the concept of the "electron". In another words, the real existence of the electron is a matter of debate.

The definition of electrolyte I proposed is based on observable phenomena: we can measure the electrical conductivity of the solvent, of the solution after adding the substance (we call electrolyte) and now observe that the conductivity is higher.

Fortunately the progress of science is not bound to rigid definitions or words and, fortunately, we discovered solid substances which, by analogy, we name "solid electrolytes", e.g. $RbAg_4I_5$ with which I have worked [1]. However, I do not think that we need to alter definitions in standards merely to accommodate some recent scientific developments irrelevant to the case under discussion. I believe that, in principle, we should only "define" words commonly used in that specific industry and when confusion may occur if such is not done. It is the case of "electrolytic solution", "autocatalytic plating" (formerly "electroless plating"), "sherardizing", etc. But I have defended, e.g. in that London meeting, that terms of basic science should not be defined on those standards, namely in cases where teaching the concepts involves a long story, often with references to its historical development. We should assume, I defended, that the technicians involved should have elementary knowledge of electrochemistry. It was the case of the "definition" of "oxidation" that, in the proposed CEN standard was as follows:

"**Oxidation**: A reaction in which electrons are removed from a reactant. Sometimes, more specifically, the combination of a reactant with oxygen."

I proposed the elimination of this definition (as well as similar ones) from the standard, and this suggestion was accepted by the commission in the London meeting. I proposed that, may be, some kind of a document written not as a standard but as a kind of review article could be published by CEN and/or ISO where all the words and concepts of basic electrochemistry would appear with references to well known text books, dictionaries, encyclopaedias, etc., where an appropriate

explanation of the concept could be found. I will try to find time to outline a draft of such a document.

In conclusion: in academic science we need definitions in mathematical concepts (e.g. circle) but not, generally, in material concepts (e.g. molecule, electrolyte). For standards, which will have legal value in industry, we may have to write definitions for specific purposes. Then, though they need not to be comprehensive, or scientifically totally correct, they must, however, be consistent with the body of scientific knowledge. That was not the case of "electrolyte" in previous national and international standards. I hope that the recently approved standard where electrolyte is replaced by electrolytic solution will gradually contribute to the objectives I pointed out.

Yours sincerely

(Prof. Victor M.M. Lobo)

[1] V.M.M. Lobo (Ionic conductivity of $RbAg_4I_5$ in the microwave range) Portugaliae Electrochimica Acta 3, 203 (1985).

Received: 16 May, 97