

Mario Emilio  
Cardinali\*  
Claudio Giomini\*\*  
Giancarlo Marrosu\*\*

## Diluted Solutions of Weak Electrolytes : Simple Approximate Formulae for Accurate pH Calculations

### Introduction

This paper proposes an original method for pH calculations of aqueous solutions of electrolytes characterized by *only one* (acid or basic) ionization constant. It relies upon some simplifying assumptions, but, unlike the method usually employed in general chemistry courses at the first year undergraduate level, can yield quite good results even for the most difficult cases, represented by very diluted solutions of extremely weak electrolytes.

The method can be applied to the solutions of :

- (1) weak monoprotic acids (WMA's) ;
- (2) weak monoprotic bases (WMB's) ;
- (3) salts deriving from strong monoprotic acids (SMA's) and WMB's ; and
- (4) salts deriving from WMA's and strong monoprotic bases (SMB's).

However, the method produces very good results also with the polyprotic acids or bases whose first ionization constant is much larger than the successive ones, and with their normal (improperly, neutral) salts with SMB's and SMA's, respectively. Moreover, the method can be profitably applied both to the acid and to the normal salts of diprotic acids, strong with respect to their 1st ionization ( $S_1DA$ 's), with SMB's (typically,  $NaHSO_4$  and  $Na_2SO_4$ ). Finally, provided some modifications are made, it can be employed also with the  $S_1DA$ 's.

Throughout the whole treatment to follow, it will be assumed that the effect of the internal ionic strength of the electrolytic solutions under examination may be ignored, or anyway thought of as negligible. The theory of the method will be described with reference to the case of a WMA ; subsequently, it will be extended to the other kinds of electrolytes quoted above. Finally, in the appendix, an improvement of the method will be presented, with reference to the case of a WMA.

### Theory

Let  $c_a$  be the analytical concentration of a WMA in a given solution. The mathematically exact equation to calculate the hydrogen-ion concentration  $[H^+]$  is the cubic equation [1-2] :

$$[H^+] = \frac{K_a c_a}{K_a + [H^+]} + \frac{K_w}{[H^+]} \quad (1)$$

where  $K_a$  is the ionization constant of the acid, and  $K_w$  is the autoionization constant of water. Eq (1) can be rewritten as :

$$D = \frac{K_a c_a}{K_a + [H^+]} \quad (2)$$

where  $D$  is the difference between the concentrations of  $H_3O^+$  and  $OH^-$  ions :

$$D = [H^+] - [OH^-] = [H^+] - K_w/[H^+] \quad (3)$$

At the first year undergraduate level, the approach usually employed in solving eq (1) or (2) consists in reducing them to a quadratic equation in the unknown  $[H^+]$  :

$$[H^+] \cong \frac{K_a c_a}{K_a + [H^+]} \quad (4)$$

whence the well-known formula :

$$[H^+] \cong - (K_a/2) + \sqrt{(K_a^2/4) + K_a c_a} \quad (5)$$

\* Chemistry Department, University, via Elce di Sotto, 8, 06100 Perugia (Italy).

\*\* ICMMPM Department, sede Chimica, "La Sapienza" University, via del Castro Laurenziano, 7, 00161 Rome (Italy).

Of course, the assumption underlying eq (4) is :

$$D = [H^+] - [OH^-] \cong [H^+] \quad (6)$$

that amounts to identifying the left-hand member of eq (2), namely D, with the requested quantity, *i.e.*  $[H^+]$ .

The pH values obtained through formula (5) are almost exact if  $[H^+] \gg [OH^-]$ , but whenever these two concentrations are comparable, it yields pH values grossly in excess, and even absurd ( $pH \geq \frac{1}{2} pK_w$ ) when

$$c_a \leq K_w^{1/2} \left( 1 + \frac{K_w^{1/2}}{K_a} \right) \quad (7)$$

For example, let us consider a solution of phenol,  $C_6H_5OH$ , (at 24 °C,  $K_a = 1.02 \cdot 10^{-10}$ ), at a concentration  $c_a = 2.00 \cdot 10^{-5}$  mol/l. Its pH is exactly 6.96, while formula (5) yields  $pH = 7.35$ .

These inadequacies of formula (5) may be ignored for most practical purposes, since the errors they introduce become not negligible only when the solution is extremely diluted and/or the acid extremely weak. Nevertheless, at least from a theoretical point of view, it could appear desirable to have at one's disposal a simple method for pH calculations that can work regardless of how diluted the solution and how weak the acid may be.

This result can be readily obtained. Instead of turning eq (2) into eq (4), let us give it a form very similar to (4), but quadratic with respect to D :

$$D \cong \frac{K_a c_a}{K_a + D} \quad (8)$$

by means of the assumption :

$$K_a + [H^+] \cong K_a + [H^+] - [OH^-] \cong K_a + D \quad (9)$$

which is less severe than (6), and amounts to identifying  $K_a + [H^+]$ , the denominator of the right-hand member of eq (2), with the term  $K_a + D$ .

Now, from eq (8),

1) through the formula :

$$D \cong -\frac{K_a}{2} + \sqrt{\frac{K_a^2}{4} + K_a c_a} \quad (10)$$

a value of D is obtained which coincides with the value that formula (5) would yield for  $[H^+]$  ; then :

2) from the above value of D, inserted into eq (3), the corresponding  $[H^+]$  value is calculated by the formula :

$$[H^+] = \frac{D}{2} + \sqrt{\frac{D^2}{4} + K_w} \quad (11)$$

The related pH values, even for the most diluted solutions and the weakest acids, differ by defect from the exact values by less than 1/10 of pH unit, and always correctly fall into the acidic range.

To resume the above example of the phenol solution, the sequence of formulae (10) and (11) yields  $pH = 6.90$ , *vs.* an exact  $pH = 6.96$  value.

Obviously, in practice, it is not necessary to calculate  $[H^+]$  after obtaining D, unless formula (10) yields  $D < 10 \cdot K_w^{1/2}$  (*i.e.*,  $D < 1 \cdot 10^{-6}$ , at 24 °C). Indeed, if D turns out to be higher than (or about equal to)  $10 \cdot K_w^{1/2}$ , then D can be taken equal to  $[H^+]$ , the

difference between them being negligibly small. Therefore, our two-step method does not involve more calculations than the traditional one, except when the latter fails.

## Discussion

In the exact eq (1), the two addends at the right-hand member represent the concentrations of the anion of the acid and the hydroxyl ion, respectively, expressed as functions of the hydrogen-ion concentration. If we designate the acid as HX, and its anion as  $X^-$ , eq (1) can be rewritten as :

$$[H^+] = [X^-] + [OH^-] \quad (12)$$

that expresses the electric neutrality of the solution under examination.

From a chemical standpoint, assumption (6), upon which formula (5) relies, is tantamount to simply neglecting the concentration of  $OH^-$  ion with respect to that of  $X^-$  (and, *a fortiori*, of  $H_3O^+$ ), and, therefore, to identifying  $[H^+]$  with  $[X^-]$ . Thus, whenever  $[X^-] \leq K_w^{1/2}$  (as, for instance, it occurs with the phenol solution of the example), formula (5) yields results absurdly low :  $[H^+] \leq K_w^{1/2}$ . On the contrary, assumption (9) underlying formula (10), does not neglect any concentration term, but just overestimates  $[X^-]$ , setting its value about equal to  $(K_a c_a)/(K_a + D)$ , instead of exactly equal to  $(K_a c_a)/(K_a + [H^+])$ . However, since it is always verified that :

$$D = [X^-] \cong \frac{K_a c_a}{K_a + D} < c_a$$

the value of D (and, hence, of  $[H^+]$ ), though in excess with respect to the exact value, never turns out to be absurdly high.

The chemically sounder base of the "D-method", with respect to the traditional one, can be better realized also by comparison of the limiting  $[H^+]$  values yielded by each of them, respectively, for  $K_a \rightarrow 0$  and  $K_a \rightarrow \infty$  (SMA), and for  $c_a \rightarrow 0$  and  $c_a \rightarrow c$ , where c represents a value of  $c_a$  anyway much higher than the higher<sup>a</sup> between the two values of  $K_w^{1/2}$  and  $K_a$ . From formula (5) (traditional method), the following results are obtained :

$$\lim_{K_a \rightarrow 0} [H^+] = 0 \quad (13)$$

$$\lim_{K_a \rightarrow \infty} [H^+] = c_a \quad (14)$$

$$\lim_{c_a \rightarrow 0} [H^+] = 0 \quad (15)$$

$$\lim_{c_a \rightarrow c_a^*} [H^+] = \sqrt{K_a c_a^*} \quad (16)$$

Of these, only the last is correct. Results (13) and (15) are absurd, since they imply that no auto-ionization of water takes place, and result (14) can apply only to solutions of SMA's whose analytical concentration is much higher than  $K_w^{1/2}$ .

On the contrary, the sequence of (10) and (11) correctly gives :

$$\lim_{K_a \rightarrow 0} [H^+] = K_w^{1/2} \quad (17)$$

$$\lim_{K_a \rightarrow \infty} [H^+] = \frac{c_a}{2} + \sqrt{\frac{c_a^2}{4} + K_w} \quad (18)$$

$$\lim_{c_a \rightarrow 0} [H^+] = K_w^{1/2} \quad (19)$$

$$\lim_{c_a \rightarrow c_a^*} [H^+] = \sqrt{K_a c_a^*} \quad (20)$$

## Extension of the method

As anticipated in the introduction, "D-formula" (10), rewritten in a more general form as :

$$D \cong - (K/2) + \sqrt{(K^2/4) + Kc} \quad (21)$$

is valid for the following classes of "acid-reaction" electrolytes :

1a) WMA's (case extensively treated above), by putting  $K = K_a$  and  $c = c_a$  ;

2a) n-protic acids whose ionization constants are such that :

$K_{a,1} \gg K_{a,2} \gg \dots \gg K_{a,n}$ , by setting  $K = K_{a,1}$  and  $c = c_a$  ;

3a) salts deriving from a SMA and a WMB, by putting  $K = K_w/K_b$  and  $c = c_s$ , where  $K_b$  is the ionization constant of the WMB, and  $c_s$  is the analytical concentration of the salt ;

4a) normal salts deriving from a SMA and a weak n-protic base, whose ionization constants are such that  $K_{b,1} \gg K_{b,2} \gg \dots \gg K_{b,n}$ , by setting  $K = K_w/K_{b,n}$  and  $c = c_s$  ;

5a) acid salts deriving from a  $S_1DA$  and a SMB, by putting  $K = K_{a,2}$  and  $c = c_s$ , where  $K_{a,2}$  is the constant of the second ionization of the acid (obviously,  $K_{a,1} \rightarrow \infty$ ).

Upon inversion of the signs of the right-hand member addends, formula (21) can be rewritten as :

$$D \cong \frac{K}{2} - \sqrt{\frac{K^2}{4} + Kc} \quad (22)$$

which is valid for the following classes of "basic-reaction" electrolytes :

1b) WMB's, by putting  $K = K_b$ , and  $c = c_b$ , where  $K_b$  is the ionization constant of the base, and  $c_b$  its analytical concentration ;

2b) weak n-protic bases of the same kind as those quoted under 4a), by setting  $K = K_{b,1}$  and  $c = c_b$  ;

3b) salts deriving from a SMB and a WMA, by putting  $K = K_w/K_a$  and  $c = c_s$ , where  $K_a$  is the ionization constant of the acid, and  $c_s$  is the analytical concentration of the salt ;

4b) normal salts deriving from a SMB and a n-protic acid of the same kind as those under 2a), by setting  $K = K_w/K_{a,n}$  and  $c = c_s$  ;

5b) normal salts from a  $S_1DA$  and a SMB, by putting  $K = K_w/K_{a,2}$  and  $c = c_s$ , where  $K_{a,2}$  is the constant of the second ionization of the acid, and  $c_s$  is the analytical concentration of the salt.

Finally, a modified "D-formula" can be easily obtained for solutions of  $S_1DA$ 's. For this case, the exact equation is :

$$[H^+] = c_a \cdot \frac{[H^+] + 2K_{a,2}}{[H^+] + K_{a,2}} + \frac{K_w}{[H^+]} \quad (23)$$

or :

$$D = c_a \cdot \frac{[H^+] + 2K_{a,2}}{[H^+] + K_{a,2}} \quad (24)$$

By setting  $[H^+] \cong D$ , eq (24) can be turned into the following equation, quadratic with respect to D :

$$D \cong c_a \cdot \frac{D + 2K_{a,2}}{D + K_{a,2}} \quad (25)$$

From eq (25),

$$D \cong -\frac{1}{2}(K_{a,2} - c_a) + \sqrt{\frac{1}{4}(K_{a,2} - c_a)^2 + 2c_a K_{a,2}} \quad (26)$$

This last formula, *via* (11), yields highly accurate  $[H^+]$  values, even for extremely diluted solutions.

## Appendix

The performances of the two-step method, relying on "D-formula" (10), described in previous sections, can be further improved to give pH values practically exact, however diluted the solution and weak the acid may be.

In the above treatment, assumption (9) is mostly questionable when  $[H^+]$  is of the same order of magnitude as  $K_w^{1/2}$ , and  $K_a \ll K_w^{1/2}$ . Indeed, under these circumstances,  $K_a + [H^+] \cong [H^+]$ , and  $[OH^-]$  is comparable with  $K_a + [H^+]$ . But, when  $K_a \ll K_w^{1/2}$ , *a fortiori*  $K_a \ll [H^+]$  ; thus, the exact eq (1) can be turned, with good approximation, into the following equation, quadratic with respect to  $[H^+]$  :

$$[H^+] \cong \frac{K_a c_a}{[H^+]} + \frac{K_w}{[H^+]} \quad (27)$$

whence

$$[H^+] \cong \sqrt{K_a c_a + K_w} \quad (28)$$

If the  $[H^+]$  value yielded by (28) is taken as a zeroth-guess approximation ( $[H^+]_o$ ), and the corresponding  $[OH^-]$  value

$$[OH^-]_o = \frac{K_w}{\sqrt{K_a c_a + K_w}} \quad (29)$$

is inserted into assumption (9) to partially compensate the  $[OH^-]$  term, so that :

$$\begin{aligned} K_a + [H^+] &\cong K_a + [H^+] - \{[OH^-] - [OH^-]_o\} \\ &\cong \{K_a + [OH^-]_o\} + D \\ &\cong \left( K_a + \frac{K_w}{\sqrt{K_a c_a + K_w}} \right) + D \end{aligned} \quad (30)$$

then the following expression, quadratic in D, is obtained from the exact eq (2) :

$$D \cong \frac{K_a c_a}{\left( K_a + \frac{K_w}{\sqrt{K_a c_a + K_w}} \right) + D} \quad (31)$$

which differs from (8) by the presence of a  $K_a$ -corrective, concen-

tration-dependent term in the denominator of the ratio at the right-hand member.

From eq (31), the following formula is obtained for D :

$$D \approx -\frac{1}{2} \left( K_a + \frac{K_w}{\sqrt{K_c + K_w}} \right) + \sqrt{\frac{1}{4} \left( K_a + \frac{K_w}{\sqrt{K_c + K_w}} \right)^2 + K_a c_a} \quad (32)$$

which, through (11), yields pH values which never differ from the exact ones by more than 0.005 pH units, as it can be verified, for instance, for the already-considered phenol solution.

Therefore, it can be concluded that the sequence of formulae (32) and (11) represents a simple alternative to an exact calculation of the pH value, and leads to results that may be considered equivalent to any practical purpose.

The "mechanism" that allows our D-generating eq (31) to work almost as well as the exact eq (2) can be conveniently explained by realizing that the "improved D-formula" (32), through (11), produces its accurate  $[H^+]$  values by operating a weighted average, with automatic tuning of the weight coefficients, between formulae (5) and (28), the former yielding results approximated by defect, the latter by excess.

There is no particular difficulty in extending the improved method, described in this appendix with reference to a WMA, to the other classes of electrolytes quoted in the previous section ; therefore, this task is left to the interested reader.

## References

- [1] Butler J.N., Ionic equilibrium : a mathematical approach, *Addison-Wesley*, Reading, Mass. (USA), 1964.
- [2] Cardinali M.E., Carelli I., *Educ. Chem.*, **1983**, 20, 88-89.

## TPS

Transnational Training Project in Polymer Science and Technology

Forthcoming 5-day Postdoc Courses in 1990 and 1991

Location : University of Maastricht, Netherlands

### Facets of Supramolecular Order in Polymers

August 27 - 31, 1990

Course director : A. Keller, Bristol

### Polymerization Reaction Engineering

September 17 - 21, 1990

Course director : A. Hamielec, Hamilton, Canada

### Polymer Synthesis (Step Polymerization)

October 29 - November 2, 1990

Course director : A. Gandini, Grenoble

### Polymer Synthesis (Chain Polymerization)

November 5 - 9, 1990

Course director : A. Gandini, Grenoble

### Degradation and Stabilization of Polymeric Materials

October 22 - 26, 1990

Course director : G. Camino, Torino

1991 :

### Advanced Analytical Methods for Polymers : Scattering and Polymers

Course directors : J.S. Higgins, London  
and H. Benoit, Strasbourg

### Calorimetry and Thermal Analysis on Polymers

Course director : V.B.F. Mathot, Geleen

### Advanced Materials Science Of Polymers

Course director : H.H. Kausch, Lausanne

For information, please contact

R. Koningsveld, Polymer InstituteΣII

P.O. Box 1043 ; 6160 BA Geleen, Netherlands

Phone (31) (4490) (29772) ; Fax : (31) (4490) (29577)

Change during fall of 1990 :

Phone : (31) (46) (529772) ; Fax : (31) (46) (529577)