

## EVALUATION OF THE IONIC STRENGTH OF pH REFERENCE BUFFER SOLUTIONS

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### Abstract

In this work, the various methods that have been used for the calculation of ionic strength are discussed. An iterative process is introduced where, instead of traditional approximations, calculation of ionic strengths through complete equations derived from the acidity constants is performed. Concentrations of the various species involved in the conventional assignment of pH, their distribution and activity coefficients are also obtained. The process proves particularly useful for polyprotic acids with overlapping acidity constants (e.g.  $H_3Cit$ :  $k_1 = 7.447 \times 10^{-4}$ ;  $k_2 = 1.734 \times 10^{-5}$ ;  $k_3 = 4.018 \times 10^{-7}$  at 25°C).

Finally and as a consequence, conventionally assigned pH values of reference buffer solutions are recalculated and corrections are introduced whenever required.

### Introduction

pH defined as the negative decimal logarithm of hydrogen ion activity is ultimately associated with the species concentration. Its measurement and control is often required in diverse fields

from fundamental research to industrial processes; commercially available pH meters allowing readings of 0.001 pH unit can be found in most laboratories where chemical analysis are performed. The pH of unknown solutions is the result of comparison, through the operational definition, with the conventionally assigned [1] pH of standard reference buffer solutions pH(S). Sets of these solutions lead to the establishment of pH scales where internal consistency is a prime requirement; universal agreement on a pH scale guarantees compatibility of readings.

The development associated to pH meters, electrodes and experimental methodology, which leads to better reproducibility of results has not been followed by the progress concerning the fundamental meaning of values, since the complexity of ionic interactions in electrolyte solutions has not allowed the exact knowledge of activity coefficients.

Current projects on problems related to pH determination are paying particular attention to this aspect.

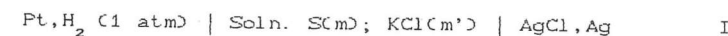
The current assessment of the ionic strengths of solutions is of the utmost importance since the calculation of activity coefficients depends on its knowledge.

In this work, published conventional pH values will be reanalysed up to the third decimal place, as well as the ionic strengths that allow the definition of activity coefficients. The various methods that have been used for the calculation of ionic strength are discussed. An iterative method is developed and used in which the acidity constants lead to the concentration of the various species, their distribution, the ionic strength and the activity coefficients of the species involved in the conventional

assignment of pH.

### Conventional Assignment of pH(S)

Standard pH values are calculated from emf values,  $E(1)$ , of Harned type cells I

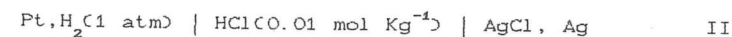


with reference buffer solutions S, with added KCl, for which

$$E = E_{\text{Ag,AgCl}}^{\circ} - \frac{RT}{F} \ln 10 \log m_{\text{H}} m'_{\text{Cl}} \gamma_{\text{H}} \gamma_{\text{Cl}} \quad (1)$$

where the letters have the usual meanings.

The standard potential  $E_{\text{Ag,AgCl}}^{\circ}$  is calculated from emf readings of cell II



by means of equation (1), where  $\gamma_{\text{H}} \gamma_{\text{Cl}} = \gamma_{\pm}^2$ ,  $\gamma_{\pm}$  being the mean ionic activity coefficient for 0.01 mol Kg<sup>-1</sup> HCl.

Values of  $(-\log m_{\text{H}} \gamma_{\text{H}} \gamma_{\text{Cl}})$  are obtained from extrapolation of the emf readings  $E$  of cells I plotted against the corresponding  $\log m'_{\text{Cl}}$  values of potassium chloride added to the buffer solutions

$$E = E_{\text{Ag,AgCl}}^{\circ} - \frac{RT}{F} \ln 10 \log m_{\text{H}} \gamma_{\text{H}} \gamma_{\text{Cl}} - \frac{RT}{F} \ln 10 \log m'_{\text{Cl}} \quad (2)$$

Computation of  $\text{p}a_{\text{H}}$  from these limiting values

$$\lim_{m'_{cl} \rightarrow 0} (-\log m_H \gamma_H \gamma_{cl}) = p(a_H \gamma_{cl})^0$$

is made through the introduction of a conventional individual activity coefficient

$$p a_H = p(a_H \gamma_{cl})^0 + \log \gamma_{cl}^0 \quad (3)$$

The limiting value

$$\log \gamma_{cl}^0 = \lim_{m'_{cl} \rightarrow 0} \log \gamma_{cl}$$

is not equal to zero, since for  $m_{cl} = 0$  the ionic strength of the solution is not zero, but it can be assessed by means of the Debye-Hückel equation, introducing the Bates-Guggenheim convention

$$\log \gamma_{\pm} = - \frac{A(Z_+ Z_-) I^{1/2}}{1 + B a I^{1/2}} \quad (4)$$

$$\log \gamma_{cl}^- = - \frac{A I^{1/2}}{1 + 1.5 I^{1/2}} \quad (5)$$

where A and B are the Debye-Hückel parameters depending on the temperature and solvent dielectric constant, a is the ion-size parameter and I is the ionic strength.

Values of  $p a_H$  thus calculated, are conventionally assigned standard pH values, pH(S)

$$p a_H = \text{pH(S)}$$

and the scale based on values obtained for reference buffer

solutions covering a practical range of pH values, is a conventional pH scale [2]. Evaluation of the activity of single ionic species cannot be done without certain assumptions and approximations; those behind the Debye-Hückel model are therefore inherent to pH calculation as described.

Correctness of  $p a_H$  values given by eqn(3) depends on the exact knowledge of  $\gamma_{cl}$  given by eqn(5), which on its turn depends on I.

#### Reanalysis of adopted pH(S) values

A pH scale defined in terms of seven reference buffer solutions selected in 1962 from amongst forty one buffers taken in 1950, for a study of practical pH buffer solutions, has been recommended by the National Bureau of Standards [3]. From then onwards reagents for the preparation of buffer solutions have undergone detailed studies in order to guarantee their quality as standard reference materials (SRM). Also pH values have been critically reviewed at the light of theoretical and practical progress. Nevertheless some inconsistencies can still be found in the assessment of pH values in the practical scale:

i) Values of Debye-Hückel parameters A and B, [4], function of temperature and dielectric constant of the solvent have been recalculated in 1959 after corrections introduced to the dielectric constant of water [5]. Discrepancies which are the result of adoption of molar or molal scale show only on the fourth decimal place.

ii) Ion-size parameter  $a$  has initially been assumed as variable between 4 and 6 Å and the published pH values were the average of values for the extremes of the interval. After Bates-Guggenheim convention (1960) for the calculation of  $\gamma_{Cl}$  a value of  $Ba = 1.5 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$  for all temperatures and ionic strengths below 0.1 is assumed which corresponds to  $a = 4.6 \text{ Å}$  at 25°C, approaching closely the activity coefficient of NaCl in pure aqueous solutions. Comparison of pH values obtained from these two criteria show differences of 0.000 and 0.023 depending on considering the lower - 4Å - or the upper - 6Å - limit of the interval.

After corrections to Debye-Hückel parameters A and B and the Bates-Guggenheim convention, revision of pH values has only been done for the selected seven NBS reference buffers (tetroxalate; tartrate; phthalate; 1:1 phosphate; 1:3.5 phosphate; borax;  $\text{Ca(OH)}_2$ ). Nevertheless it is common to find references in recent literature to other buffers whose pH has not been corrected yet.

iii) The use of Bates-Guggenheim assumption, eq(5), for the calculation of the activity coefficients of chloride ion in solution with  $I < 0.1$  implies the knowledge of this quantity, I.

The concept of ionic strength, I

$$I = \frac{1}{2} \sum_i m_i Z_i^2 \quad (6)$$

introduced by Lewis [6] prior to Debye-Hückel theory revealed itself important for the study of electrolyte solutions since it quantifies the charges in solution.

In 1950, Bates refers [4] its approximate calculation with the aid of the concentrations of hydrogen and hydroxyl ions derived from the pH of the 41 solutions obtained from cells with liquid junction.

Still before, in 1949, Bates develops a methodology for the introduction of improved ionic strength values restricted nevertheless to solutions of acid salts with  $\text{pH} < 8$  and based on the knowledge of acidity constants and approximate  $m_H$  values [7], table 1.

TABLE 1. Approximated ionic strength values [6] for acid salts

Solution	Ionic strength, I
$\text{MHAC}(m), \text{MCl}(m_2)$ $k_1/k_2 < 500$	$I = m(1 + 0.5x) + 1.5m_H + m_2 \quad (7)$
$\text{MH}_2\text{AC}(m), \text{MCl}(m_2)$ $k_1/k_2 < 500 \quad k_2/k_3 > 1000$	$I = m(1 + 0.5x) + 1.5m_H + m_2 \quad (8)$
$\text{M}_2\text{HAC}(m), \text{MCl}(m_2)$ $k_1/k_2 > 1000 \quad k_2/k_3 < 500$	$I = m(3 + 0.5y) + 2.5m_H + m_2 \quad (9)$
$\text{MH}_2\text{AC}(m), \text{MCl}(m_2)$ $k_1/k_2 < 500 \quad k_2/k_3 < 500$	$I = m(1 + 0.5x) + 1.5m_H + 2.5m_A + m_2 \quad (10)$
$\text{M}_2\text{HAC}(m), \text{MCl}(m_2)$ $k_1/k_2 < 500 \quad k_2/k_3 < 500$	$I = m(3 + 0.5y) + 2.5m_H + 2m_{H_3A} + m_2 \quad (11)$

where

$$x = \frac{2 \left( \frac{k'_2}{k'_1} \right)^{1/2}}{1 + 2 \left( \frac{k'_2}{k'_1} \right)^{1/2}} \quad (12)$$

$$y = \frac{2 \left( \frac{k'_3}{k'_2} \right)^{1/2}}{1 + 2 \left( \frac{k'_3}{k'_2} \right)^{1/2}} \quad (13)$$

$k_1, k_2, k_3$  are the thermodynamic acidity constants

$k'_1, k'_2, k'_3$  are the stoichiometric acidity constants

$$k'_n = k_n / \gamma^{2n}$$

where  $\gamma$  is the molal activity coefficient of a monovalent ionic species, given by the Debye-Hückel equation.

Despite approximations this methodology has the merit of recognizing that the concentrations of the various species may not be calculated with sufficient accuracy from one single equilibrium.

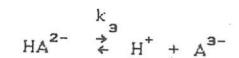
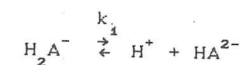
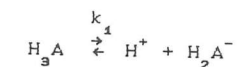
Later, in 1969, when two new buffer standards are proposed [8], Bates regrets the difficulty of not knowing the ionic strength exactly. Nevertheless an iterative process is briefly mentioned, claiming agreement to 0.001 with the one previously described.

#### Development of a method for the evaluation of ionic strength

In this work an iterative process is developed for general application, based on the knowledge of the equilibria in solution.

It is important to distinguish between the stoichiometric composition and the actual distribution of the species.

Concentrations have been taken into account, but through equilibrium constants it is possible to calculate the fractions  $\alpha_i$  of the various species in equilibrium. For polyprotic acid  $H_3A$  it is



$$c_T = m_{H_3A} + m_{H_2A^-} + m_{HA^{2-}} + m_{A^{3-}} \quad (14)$$

$$\alpha_0 = \frac{m_{H_3A}}{c_T} = \frac{a_H^3}{\frac{k_1 k_2 k_3}{\gamma_3} + \frac{k_1 k_2 a_H}{\gamma_2} + \frac{k_1 a_H^2}{\gamma_1} + a_H^3} \quad (15)$$

$$\alpha_1 = \frac{m_{H_2A^-}}{c_T} = \frac{\frac{k_1}{\gamma_1} a_H^2}{\frac{k_1 k_2 k_3}{\gamma_3} + \frac{k_1 k_2 a_H}{\gamma_2} + \frac{k_1 a_H^2}{\gamma_1} + a_H^3} \quad (16)$$

$$\alpha_2 = \frac{m_{HA^{2-}}}{c_T} = \frac{\frac{k_1 k_2}{\gamma_2} a_H}{\frac{k_1 k_2 k_3}{\gamma_3} + \frac{k_1 k_2 a_H}{\gamma_2} + \frac{k_1 a_H^2}{\gamma_1} + a_H^3} \quad (17)$$

$$\alpha_3 = \frac{m_A}{c_T} = \frac{\frac{k_1 k_2 k_3}{\gamma_3}}{\frac{k_1 k_2 k_3}{\gamma_3} + \frac{k_1 k_2 a_H}{\gamma_2} + \frac{k_1 a_H^2}{\gamma_1} + a_H^3} \quad (18)$$

The knowledge of fractions  $\alpha_i$  for the species present in equilibrium allows the calculation of pH with a better approximation.

The various steps used in the calculation of pH and I according to the above description are summarized in Fig. 1.

9. pH calculated in step 8 is the final pH
8. If pH is equal to value calculated in step 2, up to  $1 \times 10^{-6}$  pH units, go to 9., otherwise go back to 3.
7. Calculation of pH, (eq. 3)
6. Calculation of  $\gamma_{Cl}$ , (eq. 5)
5. Calculation of I, (eq. 6)
4. State the concentrations of the various species in solution
3. Determination of  $\alpha_i$  from known  $k_i$  and  $a_H$  calculated in 2, (eqs. 15, 16, 17, 18).
2. Calculation of pH, taking I = formal buffer concentration, (eq. 5)
1. Calculation of  $p_{a_H} \gamma_{Cl}$  from experimental emf values E, (eq. 2).

Fig. 1. Calculation of I and pH for a buffer solution

Calculation of the ionic strength of 0,05 eqm succinate buffer (NaH Succ + Na<sub>2</sub> Succ) can be performed in order to illustrate the effect of the different methodologies:

i) Recently published data [9] for the succinate buffer, 0.05 eqm (Na H Succ + Na<sub>2</sub> Succ) consider

$$I = \frac{1}{2} ( [H.Succ^-] + 4 [Succ^{2-}] + [Na^+] ) = \\ = \frac{1}{2} ( 0.05 + 4 \times 0.05 + 0.15 ) = 0.2$$

ii) If equilibrium constants and an approximate value for  $m_H$  are considered [4] it is, with better approximation  $I = 0.202$ .

iii) If finally,  $\gamma_i$  for each univalent ion is approximated to  $\gamma_{Cl}$  as given by Bates-Guggenheim and for higher charges the valence factor ( $Z_+, Z_-$ ) of eqn(4) is considered, our iterative process leads to the activity coefficient, the concentration of each species and the ionic strength

$$I = \frac{1}{2} ( 0.04265 + 4 \times 0.05504 + 0.15 ) = 0.20641$$

Values of pH and I thus obtained introduce significant corrections to previously published data for systems with overlapping acidity constants. This situation is easily understood if we think that for these systems there is not one single dominating species, but rather a more even distribution.

Table 2 shows some examples of systems for which the calculations have been performed. Comparison is made between

previously published data (pH, I) and the one obtained from the application of the proposed methodology (pH\*, I\*).

**Legends of the tables**

**Table 1.** Approximated ionic strength. Values [6] for acid salts

**Table 2.** Comparison with literature data of pH and I values evaluated with the proposed methodology in this work.

**TABLE 2.**

*Comparison with literature data of pH and I value evaluated with the proposed methodology in this work (\*) (25°C)*

Buffer solution	Acidity Constant	I	Ref.	pH	Ref pH	I*	pH*
0,05m potassium tetroxalate	$K_1 = 5,358 \times 10^{-2}$ $K_2 = 5,420 \times 10^{-5}$	0,0760	[11]	1.679	[3]	0.7697	1.680
0,0341m potassium hydrogen tartrate	$K_1 = 9,204 \times 10^{-4}$ $K_2 = 4,305 \times 10^{-5}$	0,036	[4]	3.557	[3]	0.04049	3.558
0,05m potassium dihydrogen citrate	$K_1 = 7,447 \times 10^{-4}$ $K_2 = 1,734 \times 10^{-5}$ $K_3 = 4,018 \times 10^{-7}$	0,0526	[8]	3.776	[8]	0.05699	3.773
0,1m potassium dihydrogen citrate	$K_1 = 7,447 \times 10^{-4}$ $K_2 = 1,734 \times 10^{-5}$ $K_3 = 4,018 \times 10^{-7}$	0,115	[4]	3.717	[4]	0.11510	3.713
0,05m potassium acid phthalate	$K_1 = 1,123 \times 10^{-3}$ $K_2 = 3,906 \times 10^{-6}$	0,053	[11]	4.006	[2]	0.05328	4.008
0,05m sodium acid succinate 0,05m sodium succ.	$K_1 = 6,17 \times 10^{-5}$ $K_2 = 2,29 \times 10^{-6}$	0,202	[4]	5.343	[4]	0.2064	5.337
0,025m sodium acid succinate 0,025m sodium succ.	$K_1 = 6,17 \times 10^{-5}$ $K_2 = 2,29 \times 10^{-6}$	0,101	[4]	5.403	[4]	0.10243	5.399
0,025m potassium dihydrogen phosphate 0,025m disodium hydrogen phosphate	$K_1 = 7,112 \times 10^{-3}$ $K_2 = 6,334 \times 10^{-8}$ $K_3 = 4,213 \times 10^{-8}$	0,100	[11]	6.863	[2]	0.09978	6.865
0,01m trisodium phosphate	$K_1 = 7,112 \times 10^{-3}$ $K_2 = 6,334 \times 10^{-8}$ $K_3 = 4,213 \times 10^{-8}$	0,047	[4]	11.719	[4]	0.04625	11.717

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( Received, 2 Februari, 1993  
x Revised form, 13 April 1993 )

## THE POLAROGRAPHIC INVESTIGATION OF 4-NITRO-2'-HYDROXY-5'-TERT-BUTYLAZOBENZENE

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### ABSTRACT

The polarographic reduction of the azo dye 4-nitro-2'-hydroxy-5'-tert-butylazobenzene in Britton Robinson Buffer with pH range of 2 and 12 at room temperature has been investigated in aqueous-ethanol solution of ratio 1:1. Two straight lines were obtained from the  $E_{1/2}$ -pH plots for the compound. Diffusion controlled reduction behaviour was observed in acid and alkaline media. In addition, a polarographic determination method for the analysis of 4-nitro-2'-hydroxy-5'-tert-butylazobenzene has been developed. The detection limit was 50 ppb for this medium.

### INTRODUCTION

Azo dyes are the largest group of organic dyes and constitute more than 35% of the global production of all dyes and thus are used widely by human beings in their living and natural environments. However, azo dyes have toxicological properties and therefore require sensitive, selective methods to determine their physicochemical characteristics (1-3).

Carcinogenic azo dyes have been used for many years in producing liver tumors in rats (4). Because of the suspect that the derivatives of azobenzenes are chemical