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A PITZER THEORY APPROACH TO ASSIGNMENT OF pH TO STANDARD BUFFER SOLUTIONS

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Abstract

The quantity pH=lg a_H is immeasurable, as it involves a single ion activity. The IUPAC recommendations for the pH scale for aqueous solutions are based on the Bates-Guggenheim convention for the calculation of the chloride ion activity coefficient. The idea of this convention, intended to be applied to ionic strength not higher than 0.1 mol kg^{-1}, was to impart pH with as much fundamental meaning as possible while recognising that it is conventionally based.

The Pitzer theory, involving ionic specific interactions, may be applied in the calculation of single ion activity coefficients at ionic strengths higher than 0.1 mol kg^{-1}. This approach has the merit that all possible known buffers, with or without background electrolyte, and those yet to be developed, can be assigned pH values.

Key Words: Standard buffer solution; pH; Pitzer coefficients.

Introduction

The quantity pH cannot be assigned without recourse to a non-thermodynamic convention. In an attempt to reconcile several different approaches to this problem, Bates and Guggenheim [1] proposed a convention for the single ion activity coefficient of the chloride ion, γ_{Cl}, that is based on the Debye-Hückel equation, with an assumed value for the ion size parameter, a,

$$lg \, \gamma_{Cl} = (A/\sqrt{I})/(1+Ba\sqrt{I}) \qquad (1)$$

where I is the ionic strength, A and B are the Debye-Hückel parameters and Ba=1.5. This convention is valid for solutions with ionic strength not higher than 0.1 mol kg^{-1}. Recently the Pitzer theory [2] of ionic specific interactions has been proposed for the evaluation of the chloride ion activity coefficient in the standard buffer solutions [3], which enables the establishment of a self-consistent system of aqueous pH standards, not limited to 0.1 mol kg^{-1} in ionic strength. In this work, the

application of the Pitzer model to the phosphate buffer systems is discussed. Also, the chloride ion activity coefficient was calculated for several pH buffers and compared with the values obtained if the Bates-Guggenheim convention were used. It is shown that the difference, in pH, is smaller than 0.01 for buffers with ionic strength lower than 0.1 mol kg^{-1}.

Definition and measurement of pH

The concept of pH was first introduced by Sorenson in 1909 [4], as

$$pH = - \lg \left(\frac{c_H}{c^0} \right) \qquad (2)$$

where c_H is the hydrogen ion concentration, in mol dm^{-3}, and c^0 is a standard state where $c^0 = 1$ mol dm^{-3}. As it has been accepted that it is more satisfactory to define pH in terms of the activity of hidrogen ions in solution, a_H, it was later reformulated to

$$pH = - \lg a_H \quad \text{or} \quad pH = - \lg \left(\frac{m_H \gamma_H}{m^0} \right) \qquad (3)$$

where $m^0 = 1$ mol kg^{-1}. This is the notional definition of pH, but this quantity is immeasurable, as it involves a single ion activity.

According to the International Union of Pure and Applied Chemistry (IUPAC) recommendations [5] the pH of a solution, X, is related to the pH of a standard reference solution, S, by means of the equation

$$pH(X) = pH(S) + \frac{E(S) - E(X)}{(RT/F) \ln 10} \qquad (4)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant and E(S) and E(X) are, respectively, the electromotive forces of the cells

$$\text{Reference} \left| \begin{array}{c} \text{KCl} \\ \text{Electrode} \end{array} \right| \begin{array}{c} \text{KCl} \\ m \geq 3.5 \text{ mol kg}^{-1} \end{array} \left| \right| \text{Solution S} \left| H_2 \right| \text{Pt} \qquad (I)$$

and

$$\text{Reference} \left| \begin{array}{c} \text{KCl} \\ \text{Electrode} \end{array} \right| \begin{array}{c} \text{KCl} \\ m \geq 3.5 \text{ mol kg}^{-1} \end{array} \left| \right| \text{Solution X} \left| H_2 \right| \text{Pt} \qquad (II)$$

In most practical measurements, a single glass electrode is transferred between the two cells and the residual liquid junction potential is assumed to be zero. The variation of the liquid junction potentials between solutions and the deviations from the ideal nernstian response of the electrodes are minimised by the use of two standards, S_1 and S_2, with $E(S_1)$ and $E(S_2)$ values on either side of E(X) and as close as possible to this value. Then the pH of the solution X is obtained by

$$\frac{pH(X) - pH(S_1)}{pH(S_2) - pH(S_1)} = \frac{E(X) - E(S_1)}{E(S_2) - E(S_1)} \qquad (5)$$

assuming linearity between pH and E.

There is some criticism to this procedure [6] with the indication that more than two standard solutions should be used when high precision is required.

Conventionally assigned pH values'

The assignment of pH to the standard solutions is based on the electromotive force measurements (e.m.f.) on the Harned cell, without liquid junction,

$$\text{Pt} \left| H_2 \right| \text{Solution S, Cl}^- \left| \text{Ag} \right| \text{AgCl} \qquad (III)$$

where the hydrogen and silver, silver chloride electrodes are immersed in suitable buffer solutions with added chloride at known molalities [7]. There are four steps in the assignment of the standard values:

- Determination of $p(a_H \gamma_{Cl})$ for three or more portions of the buffer solution with known small amounts of chloride. The $p(a_H \gamma_{Cl})$ is obtained from the measured e.m.f., E, using the Nernst equation

$$p(a_H \gamma_{Cl}) = \frac{(E - E^0) F}{RT \ln 10} + \lg m_{Cl} \qquad (6)$$

where E^0 is the standard potential of the silver, silver chloride electrode that can be determined from measurements on the cell

$$\text{Pt} \left| H_2 \right| \text{HCl} \left| \text{Ag} \right| \text{AgCl} \qquad (IV)$$

- Evaluation of $p(a_H \gamma_{Cl})^0$, the limit of $p(a_H \gamma_{Cl})$ as the molality of the added chloride in the buffer solution approaches zero.
- Computation of pa_H from $p(a_H \gamma_{Cl})^0$ by introduction of a conventional individual ionic activity coefficient:

$$pa_H = p(a_H \gamma_{Cl})^0 + \lg \gamma_{Cl} \qquad (7)$$

The Bates-Guggenheim convention [1], Ba = 1.5, is used to calculate $\lg \gamma_{Cl}$, by means of the equation (1).

- Identification of the pa_H of certain selected buffer solutions with pH(S).

The primary standards have been chosen for their reproducibility, stability, buffer capacity and ease of preparation. For these solutions,

$$pH(S) \equiv pa_H \qquad (8)$$

The standards cover the range 3.5 to 10.0 and their ionic strength, I, is not higher than 0.1 mol kg^{-1}, in order to be applied the Bates-Guggenheim convention. In spite of this, it has been used

in the clinical ($I \cong 0.15$ mol kg^{-1}) and sea water ($I \cong 0.7$ mol kg^{-1}) media. Therefore, pH standard solutions of higher ionic molalities are needed in order to match those existing in the environment, so that the residual liquid junction potential remains negligible. The Pitzer theory of electrolytes [2] seems to be adequate, in this situation.

Pitzer model for electrolytes

According to the Pitzer theory, the equation for the excess Gibbs energy, G^{ex}, is:

$$\frac{G^{ex}}{w_w RT} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \ldots \ldots \quad (9)$$

where w_w is the number of kilograms of water and m_i, m_j, ... are the molalities of all soluble species. The first term includes the Debye-Hückel limiting law. The quantity $\lambda_{ij}(I)$ represents the short range interactions between particles i and j, it is the second virial coefficient and depends on the ionic strength. The quantity μ_{ijk} represents the third virial coefficient.

The convenient derivation of this equation leads to the activity coefficient of the species i:

$$\ln \gamma_i = \frac{\partial (G^{ex} / w_w RT)}{\partial m_i} \quad (10)$$

In a solution of HA, NaA, NaCl, where A is the weak acid anion, the chloride ion activity coefficient is given by

$$\ln \gamma_{Cl} = f^\gamma + 2 m_{Na}\left[B_{NaCl} + m\, C_{NaCl}\right] + 2 m_H\left[B_{HCl} + m\, C_{HCl}\right] + 2 m_A\, \theta_{Cl,A} +$$
$$+ 2 m_{OH}\, \theta_{Cl,OH} + m_{Na}\, m_A\left[B'_{NaA} + C_{NaA} + \psi_{Cl,Na,A}\right] +$$
$$+ m_{Na}\, m_{Cl}\left[B'_{NaCl} + C_{NaCl}\right] + m_{Na}\, m_{OH}\left[B'_{NaOH} + C_{NaOH} + \psi_{Cl,Na,OH}\right] +$$
$$+ m_H\, m_A\left[B'_{HA} + C_{HA} + \psi_{Cl,H,A}\right] + m_H\, m_{Cl}\left[B'_{HCl} + C_{HCl}\right] +$$
$$+ m_{Na}\, m_H\, \psi_{Cl,Na,H} + 2 m_{HA}\, \lambda_{Cl,HA} \quad (11)$$

where $m = m_{Na} + m_H = m_A + m_{HA} + m_{OH}$, B and C are the second and third virial coefficients for single electrolytes, θ is the second virial coefficient for like charged ions and ψ refers to the triple interactions. The parameter λ arises from interactions between the ion and the neutral molecule and B' is the derivative of B with respect to the ionic strength.

For a weak acid, $B_{HA}=0$ and so $B'_{HA}=0$ [8], and for relatively dilute solutions ($I<2$ mol kg^{-1}) [2], the third virial coefficients appear to be very small.

The quantities f', B and B' are functions of the ionic strength and their expressions are:

$$f^\gamma = -A^\phi\left[\sqrt{I} / (1+1.2\sqrt{I}) + (2/1.2) \ln (1+1.2\sqrt{I})\right] \quad (12)$$

$$B = \beta^0 + \beta^1\left[1/(2I)\right]\left[1 - (1+2\sqrt{I}) \exp(-2\sqrt{I})\right] \quad (13)$$

$$B' = \beta^1\left[1/(2I^2)\right]\left[-1 + (1+2\sqrt{I}+2I) \exp(-2\sqrt{I})\right] \quad (14)$$

where A^ϕ is the Debye-Hückel coefficient for the osmotic function.

Phosphate buffer solutions

In phosphate buffer solutions the important equilibrium is

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

which corresponds to the second dissociation of the phosphoric acid and the equilibrium constant, K_2, is given by

$$K_2 = \frac{m_{HPO_4}\, m_H}{m_{H_2PO_4}} \frac{\gamma_{HPO_4}\, \gamma_H}{\gamma_{H_2PO_4}} \quad (15)$$

The cell from which pK_2 is obtained is the Harned cell

$$\text{Pt, } H_2 \mid KH_2PO_4, Na_2HPO_4, KCl \mid Ag \mid AgCl \quad (V)$$

and it is given by

$$pK_2 = \frac{(E - E^0) F}{RT \ln 10} + \lg \frac{m_{H_2PO_4}\, m_{Cl}}{m_{HPO_4}} + \lg \frac{\gamma_{H_2PO_4}\, \gamma_{Cl}}{\gamma_{HPO_4}} \quad (16)$$

where E and E^0 are the e.m.f. reading and the silver, silver chloride standard potential, respectively.

The last term of the equation (16) was computed by means of the expressions (17,18,19) using e.m.f. data obtained by Bates and Acree [9, 10] on the cell (V). The Pitzer parameters where taken from the literature [11] and are given in table 1. Also, $\theta_{Cl,HA} = 0.1$ kg mol^{-1}[8].

$$\ln \gamma_{Cl} = f^\gamma + 2 m_H\, B_{HCl} + 2 m_{Na}\, B_{NaCl} + 2 m_K\, B_{KCl} + 2 m_{HA}\, \theta_{Cl,HA} +$$
$$+ 2 m_A\, \theta_{Cl,A} + m_{Na}\, m_{HA}\, B'_{Na,HA} + m_{Na}\, m_A\, B'_{Na,A} + m_{Na}\, m_{Cl}\, B'_{NaCl} +$$
$$+ m_K\, m_{HA}\, B'_{K,HA} + m_K\, m_{Cl}\, B'_{KCl} \quad (17)$$

$$\ln \gamma_{HA} = f^\gamma + 2 m_{Na}\, B_{NaHA} + 2 m_K\, B_{KHA} + 2 m_{Cl}\, \theta_{Cl,HA} + 2 m_A\, \theta_{HA,A} +$$
$$+ m_{Na}\, m_{HA}\, B'_{Na,HA} + m_{Na}\, m_A\, B'_{NaA} + m_{Na}\, m_{Cl}\, B'_{NaCl} \quad (18)$$

$$\ln \gamma_A = 4 f^\gamma + 2 m_{Na}\, B_{Na,A} + 2 m_K\, B_{KA} + 2 m_{Cl}\, \theta_{Cl,A} + 2 m_{HA}\, \theta_{HA,A} +$$
$$+ 4 (m_{Na}\, m_{HA}\, B'_{Na,HA} + m_{Na}\, m_A\, B'_{Na,A} + m_{Na}\, m_{Cl}\, B'_{NaCl} +$$
$$+ m_K\, m_{HA}\, B'_{K,HA} + m_K\, m_A\, B'_{KA} + m_K\, m_{Cl}\, B'_{KCl}) \quad (19)$$

These equations, where $A=HPO_4^{2-}$, were written taking into account the presence of both cations Na$^+$ and K$^+$. The data here used refer to quite dilute solutions and so the third virial coefficients were not considered.

Table 1. Values of Pitzer parameters used in the calculation
of ionic activity coefficients at 25 °C (ref.11)

	KCl	NaCl	KH_2PO_4	K_2HPO_4	NaH_2PO_4	Na_2HPO_4
β^0 (kg mol^{-1})	0.04835	0.0765	-0.0678	0.0247	-0.0533	-0.05827
β^1 (kg mol^{-1})	0.2122	0.2664	-0.1042	1.274	0.0396	1.465

The variation of pK_2 with the ionic strength is shown in figure 1, lower line, for series A [9] for which $m_{H_2PO_4} = m_{HPO_4} = m_{Cl}$. For other series the results were identical. It was not possible to fit the pK_2 cell data satisfactorily using the isopiestically derived values for the parameters.
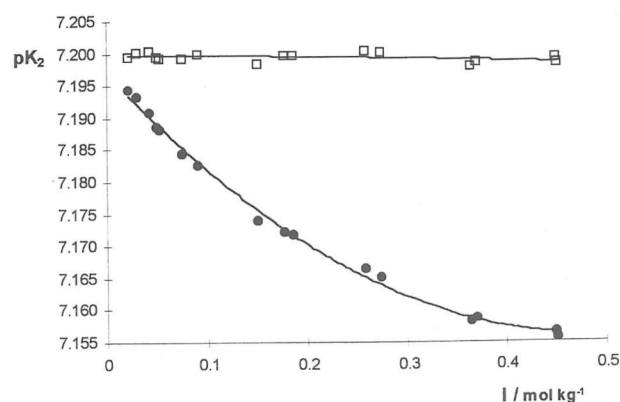

Figure 1. Variation of pK_2 with ionic strength: based on β values for NaH_2PO_4 from ref [11] ($\bullet$) and from ref. [3] ($\square$)

From the comparison of several plots, it was concluded that the parameters for the sodium dihydrogenphosphate had to be changed in order to fit the data. Using the SAS computer programme (SAS Institute Inc., 1990), from linear regression analysis on the published data [8, 9], with various molality ratios, the following values were obtained: $\beta^0_{NaH_2PO_4} = -0.180$ kg mol^{-1} and $\beta^1_{NaH_2PO_4} = 0.608$ kg mol^{-1} as well as $\theta_{Cl,HPO_4} = -0.07$ kg mol^{-1} and $\theta_{H_2PO_4,HPO_4} = -0.53$ kg mol^{-1}. With these parameters, it was then possible to obtain pK_2 independent on the ionic strength, as shown in figure 1, horizontal line. For this series, $pK_2 = 1.9994$ with a standard deviation of 0.0007. However

it should be noted that these results were obtained with dilute solutions, i.e., ionic strength lower than 0.5 kg mol^{-1}, as this was the available potentiometric data.

The ionic strength of a buffer solution may be increased by adding sodium or potassium chloride or by increasing the molalities of its components. For the equimolal phosphate buffer the variation of lg γ_{Cl}, or pH, with I is shown in figure 2, for the two situations: without chloride and when sodium chloride is added. It is also shown how the same variation would be if the Bates-Guggenheim convention were used even for ionic strength higher than 0.1 mol kg^{-1}.
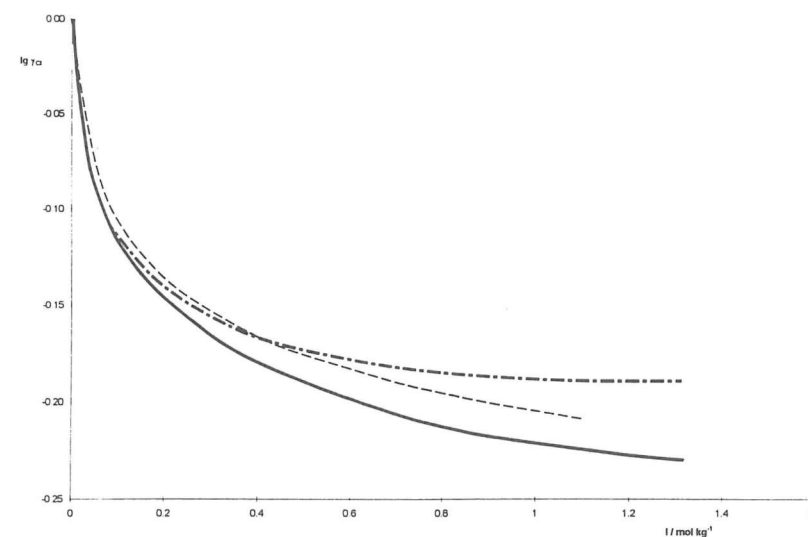

Figure 2. Variation of lg γ_{Cl} with ionic strength: KH_2PO_4 0.025 mol kg^{-1} + Na_2HPO_4 0.025 mol kg^{-1} + NaCl (– - – - –); KH_2PO_4 + Na_2HPO_4 equimolal (——); B-G convention (-----)

Evaluation of pH of some standard solutions

The pH values of the seven primary standards are given in table 2 [5]. They are based on the Bates-Guggenheim convention. The chloride ion activity coefficient was then calculated by means of the equation (17), with $m_{Cl} = 0$, for the two phosphate buffers (A=HPO_4^{2-}) and for the carbonate buffer (A=CO_3^{2-}), using the published Pitzer coefficients [11, 12, 13], leading to slightly lower pH values as shown in table 3. The phthalate buffer solution has been studied by Chan et al. [14] and their data give pH=4.003. The difference, in pH, caused by replacing the Bates-Guggenheim convention by the Pitzer equation in the calculation of the chloride ion activity coefficient is also given in table 2, for those four standard solutions.

Table 2. Values of pH for primary standard solutions at 25 °C [5]

Standard solution	pH(S)	ΔpH (Pitzer)
Potassium hydrogen tartrate (sat. at 25 °C)	3.557	---
Potassium dihydrogen citrate (0.1 mol kg⁻¹)	3.776	---
Potassium hydrogen phthalate (0.05 mol kg⁻¹)	4.005	-0.002
Disodium hydrogen phosphate (0.025 mol kg⁻¹) Potassium dihydrogen phosphate (0.025 mol kg⁻¹)	6.865	-0.007
Disodium hydrogen phosphate (0.03043 mol kg⁻¹) Potassium dihydrogen phosphate (0.008695 mol kg⁻¹)	7.413	-0.009
Disodium tetraborate (0.01 mol kg⁻¹)	9.180	---
Sodium hydrogen carbonate (0.025 mol kg⁻¹) Sodium carbonate (0.025 mol kg⁻¹)	10.012	-0.008

Table 3. Values for pH of phosphate and carbonate buffers at 25 °C

Buffer	- lg γ_{Cl}		pH	
	B-G	Pitzer	B-G	Pitzer
Equimolal Phosphate	0.1095	0.1160[a] 0.1165[b]	6.865	6.868
"Blood" Phosphate	0.1095	0.1183[a] 0.1185[b]	7.413	7.404
Carbonate	0.1095	0.1167	10.012	10.004

[a] Based on β values for NaH_2PO_4 from ref. [11] and [b] from ref. [3].

Conclusions

The pH primary standards have ionic strengths not higher than 0.1 mol kg⁻¹, the validity limit of the Bates-Guggenheim convention, used in the assignment of their pH values, and more concentrated standards should be derived in order to meet the requirements for precise pH measurements. Following the procedure, recommended by IUPAC [5], the assignment of pH values to the standards requires the knowledge of the chloride ion activity coefficient which can only be obtained conventionally, but, in order to impart the pH with as much as fundamental meaning as possible, specific ion interactions must be taken into account.

The Pitzer theory has been widely used in the study of electrolyte solutions and seems to be adequate for the study of the pH buffer systems. Adopting the Pitzer treatment as a convention, instead of the Bates-Guggenheim one, would require a shift of less than 0.01 in pH at 25 °C for the dilute aqueous buffers. However, literature data are still insufficiently extensive to allow the calculation of the required Pitzer coefficients for all buffer standards.

Acknowledgements

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THE INHIBITION EFFECT OF 4(2-PYRIDYL)-1-BENZALEDEHYDE-3-THIOSEMICARBAZONE DERIVATIVES TOWARDS THE IRON CORROSION

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ABSTRACT

The effect of 4(2-pyridyl)-1-benzaldehyde-3-thiosemicarbazone derivatives towards the corrosion of iron in 1M HCl solution at 303K was investigated. Potentiodynamic and weight loss measurements show that compounds under investigation act as effective inhibitors for the corrosion of iron in 1 M HCl. The results show that these compounds behave as mixed type inhibitors. The corrosion rate was found to be a function of the nature and concentration of the inhibitors. The adsorption of the compounds on the iron surface is found to obey Temkin's adsorption isotherm.

Key words: Corrosion, inhibition, iron, potentiodynamic, weight loss.

INTRODUCTION

The inhibition of corrosion of iron in acidic media by different type of organic compounds has been widely studied[1-11]. The existing data show that most organic inhibitors act by adsorption on the iron surface. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte and by the chemical structure of inhibitors. Most organic inhibitors are substances with at least one functional group considered as the reaction centre for the adsorption process. The adsorption of inhibitor is related to the presence of hetero atoms as nitrogen, phosphorus and sulphur as well as triple bond or aromatic ring in their molecular structure. It has also been noted that the molecular area[12] and molecular weight[13] of the inhibitor play an important role.

In previous work, Sym. diphenylcarbazide, thiosemicarbazide and semicarbazide were studied as inhibitors for acid corrosion of aluminium[14] and zinc[15]. Thiosemicarbazone derivatives were used as inhibitors for the corrosion of iron in acidic medium[16]. The aim of the present work is to study the inhibition action of a new class of compounds of 4(2-pyridyl)-1-benzaldehyde-3-thiosemicarbazone derivatives towards the corrosion of iron. The choice of these compounds is based on the presence of an electron cloud on the aromatic ring, the electronegative nitrogen and the easily polarized sulphur which induce greater adsorption of the compounds on the surface of the iron, which can lead to effective inhibition. Compounds used in this study are shown below.