

For the two acetate pH standards, 0.01 and 0.1 mol kg<sup>-1</sup>, the change in pH, caused by using the Pitzer model instead of the Bates-Guggenheim convention is 0.000 and -0.001, showing there is no alteration of the published pH values [1].

#### References

1. A.K.Covington, R.G.Bates and R. A.Durst, *Pure Appl. Chem.*, 57, (1985), 531.
2. R.G.Bates and E. A. Guggenheim, *Pure Appl.Chem.*, 1, (1960),163.
3. K.S.Pitzer in K.S.Pitzer (ed), *Activity Coefficients in Electrolyte Solutions*, 2<sup>nd</sup> ed., CRC Press, Boca Raton, London, (1991).
- 4.- S.Manohar and J.Ananthaswamy, *Can. J. Chem.*, 69, (1990),111.
- 5.- R. G. Bates, *Determination of pH. Theory and Practice*, 2<sup>nd</sup> ed., John Willey & Sons Inc., New York, (1973)
- 6.- L. Fernández-Mérida, F. Hernández-Luis, H. R. Galleguillos and M. A. Estes, *Portugaliae Electrochimica Acta*, 11, (1993), 225.
- 7.- K. S. Pitzer and L. F. Silvester, *J. of Sol. Chem.*, 5, (1976), 277.

#### APPLICATION OF THE PITZER THEORY TO THE EVALUATION OF pH OF THE PHTHALATE STANDARD SOLUTION

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**Abstract** - The pH value of the potassium hydrogen phthalate 0.05 mol.kg<sup>-1</sup> has been determined, using the Bates-Guggenheim convention and the Pitzer model for the calculation of the chloride ion activity coefficient. A comparison has been made between the two approaches.

**Key words** - pH; Phthalate buffer; Bates-Guggenheim convention; Pitzer's equations.

#### Introduction

The reference primary standard for pH determination is an aqueous solution of potassium hydrogen phthalate (KHPH) 0.05 mol.kg<sup>-1</sup>, according to the IUPAC recommendations [1]. Its pH value is based on electromotive force (EMF) measurements on the Harned cell, without liquid junction:



where the hydrogen and silver-silver chloride electrodes are immersed in solutions of KHPH 0.05 mol.kg<sup>-1</sup> and KCl of varying molalities. The respective potential, E, is given by

$$E = E^\circ_{\text{Ag,AgCl}} - k \cdot \lg (a_{\text{H}} \cdot a_{\text{Cl}}) \quad (1)$$

where  $E^\circ_{\text{Ag,AgCl}}$  is the standard potential of the silver-silver chloride electrode,  $k = (RT/F) \ln 10$  ( $= 0.059159 \text{ V}$  at 298.15 K), R, T and F are the gas constant, absolute temperature and Faraday constant, respectively, and  $a_{\text{H}}$  and  $a_{\text{Cl}}$  represent the activities of  $\text{H}^+$  and  $\text{Cl}^-$ .

From equation (1) the acidity function,  $p(a_{\text{H}} \gamma_{\text{Cl}})$ , may be calculated:

$$p(a_{\text{H}} \gamma_{\text{Cl}}) = \frac{E - E^\circ}{k} + \lg m_{\text{Cl}} \quad (2)$$

where  $\gamma_{\text{Cl}}$  is the activity coefficient of the chloride ion and  $m_{\text{Cl}}$  is its molality, and the quantity  $p(a_{\text{H}} \gamma_{\text{Cl}})^0$  is obtained from extrapolation to  $m_{\text{Cl}}=0$  of a straight line of  $p(a_{\text{H}} \gamma_{\text{Cl}})$  against  $m_{\text{Cl}}$ . The  $p_{\text{aH}}$  value is then given by

$$p_{\text{aH}} = p(a_{\text{H}} \gamma_{\text{Cl}})^0 + \lg \gamma_{\text{Cl}} \quad (3)$$

The term  $\lg \gamma_{\text{Cl}}$  is calculated by means of the Debye-Hückel theory [2]:

$$\lg \gamma_{\text{Cl}} = - \frac{A \sqrt{I}}{1 + B a \sqrt{I}} \quad (4)$$

where A is a constant ( $A = 0.5108 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  at 298.15 K) and  $Ba = 1.5$  at any temperature, according to the Bates-Guggenheim convention [3], applicable to solutions with ionic strength (I)

not higher than 0.1 mol.kg<sup>-1</sup>. This treatment ignores the short range specific interactions which become significant at higher ionic strengths.

The Pitzer theory [4], widely used in the study of electrolyte solutions, seems to be also appropriate for the calculation of lg γ<sub>Cl</sub> [5], including solutions with ionic strength higher than 0.1 mol.kg<sup>-1</sup>. According to the Pitzer model [4], the equation for the calculation of γ<sub>Cl</sub> in these mixed solutions, when m<sub>Cl</sub>=0, is:

$$\ln \gamma_{Cl} = f1 + m_K m_{HPb} B' + m_K m_{Pb} B'_{Kpb} + m_K m_H \Phi'_{H,K} + m_{HPb} m_{Pb} \Phi'_{HPb,Pb} + m_K (2B_{KCl} + ZC_{KCl}) + m_H (2B_{HCl} + ZC_{HCl}) + m_{Pb} [2\Phi_{Cl,Pb} + (m_K \Psi_{K,Cl,Pb} + m_H \Psi_{H,Cl,Pb})] + m_{HPb} [2\Phi_{Cl,HPb} + (m_K \Psi_{K,Cl,HPb} + m_H \Psi_{H,Cl,HPb})] + m_H m_K \Psi_{H,Cl,K} + m_K m_{HPb} C_{K,HPb} + m_K m_{Pb} C_{K,Pb} + 2m_{H_2Pb} \lambda_{H_2Pb,Cl} \quad (5)$$

where:

$$\Phi_{ij} = \theta_{ij} + {}^E \theta_{ij}(I) \quad (5a)$$

$$\Phi'_{ij} = {}^E \theta'_{ij}(I) \quad (5b)$$

$$B_{ij} = \beta_{ij}^{(0)} + \beta_{ij}^{(1)} \cdot f2 \quad (5c)$$

$$B'_{ij} = \beta_{ij}^{(1)} \cdot f3 \quad (5d)$$

$$f1 = -A_\phi [ I^{1/2} / (1 + 1.2I^{1/2}) + (2 / 1.2) \ln(1 + 1.2I^{1/2}) ] \quad (6)$$

$$f2 = 1 / (2I) [ (1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})) ] \quad (7)$$

$$f3 = 1 / (2I^2) [ -1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2}) ] \quad (8)$$

with:

A<sub>φ</sub> - Debye-Hückel parameter for the osmotic function (A<sub>φ</sub> = 0.915 kg<sup>1/2</sup>.mol<sup>-1/2</sup> at 298.15 K)

m<sub>X</sub> - molality of the ionic species X

Z = Σ m<sub>X</sub> |z<sub>X</sub>|; where z<sub>X</sub> is the electrical charge of the ion X

β<sup>(0)</sup>, β<sup>(1)</sup> - short range interaction parameters relative to pure electrolytes

C<sub>ij</sub> - third virial coefficient for the pure electrolyte

ψ - coefficient relative to triple ion interactions

θ<sub>ij</sub> - term arising from short range forces between ions of like charge

<sup>E</sup>θ<sub>ij</sub>(I) - accounts for electrostatic unsymmetrical mixing effects

<sup>E</sup>θ'<sub>ij</sub>(I) - derivative of <sup>E</sup>θ<sub>ij</sub>(I) with respect to the total ionic strength

From experimental EMF data on the Harned cell (A), p<sub>aH</sub> has been determined using the Bates-Guggenheim convention and the Pitzer equation for the calculation of γ<sub>Cl</sub>.

### Experimental

Potential measurements were taken on cell (A) at 298.15 K, with the hydrogen and silver-silver chloride electrodes in solutions of potassium hydrogenphthalate 0.05 mol.kg<sup>-1</sup> and potassium chloride with molalities 0.005, 0.01, 0.02, 0.04, 0.05 mol.kg<sup>-1</sup>.

The hydrogen electrode bases consist of a 1cm<sup>2</sup> square of platinum foil that were coated with palladium. The silver-silver chloride electrodes were of the thermal electrolyte type [6]. Potential differences among the electrodes were measured several times, between runs of experiments, and were always lower than 0.06 mV.

Both salts, KHPb and KCl p.a. Merck, were dried at 110 °C for at least 4 hours and cooled in a desiccator over blue gel before weighing. The necessary amounts of the solids were weighted for each buffer solution.

The conductivity of the water used in the preparation of the solutions was measured on several occasions and was always around 0.2 μS.cm<sup>-1</sup> at room temperature. Carbon dioxide was removed from the water by bubbling nitrogen gas for at least 30 minutes before the solution preparation.

Five cells were placed in a water bath and the temperature was controlled by means of an immersion thermostat, "GRANT TD". The temperature was kept constant within ±0.03 °C and was measured with a thermometer, "HART SCIENTIFIC", model 1502, and probe with platinum sensor, "STS 5P".

The potential was measured by means of a multimeter, "HEWLETT-PACKARD", 34401 A, connected to a system for data acquisition, "MOLSPIN LTD", that took readings at 5 minute intervals. These were taken as steady when the variation was lower than 0.05 mV during 5 minutes.

The atmospheric pressure was measured at the end of each set of readings, using a barometer, "FORTIN F.D. & CO LTD", Watford. The readings were all corrected to the hydrogen partial pressure of 760 mmHg [6].

### Results and discussion

The standard potential of the silver-silver chloride electrodes, E<sup>o</sup><sub>Ag/AgCl</sub>, is given by the equation:

$$E_{Ag/AgCl}^o = E + 2k \log m_{HCl} + 2k \lg \gamma_{\pm} \quad (9)$$

where m<sub>HCl</sub> and γ<sub>±</sub> are the molality and mean activity coefficient of HCl, respectively, and E is the potential measured on cell (A) with HCl 0.01 mol.kg<sup>-1</sup> as the electrolyte solution. The value of γ<sub>±</sub> was calculated using the Pitzer equation:

$$\ln \gamma_{\pm} = f1 + I(2\beta_{HCl}^{(0)} + \beta_{HCl}^{(1)} \cdot f2) + I^2 \cdot C_{HCl} \quad (10)$$

where the symbols have the same meaning as in equation (5).

From 24 measurements, the mean of the standard potential was 222.35 mV and the standard deviation was 0.066 mV.

The EMF readings on cell (A) and p(a<sub>H</sub>γ<sub>Cl</sub>), calculated from equation (2), are shown in table 1.

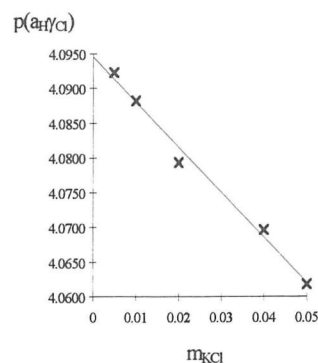
Table 1-EMF readings on cell (A) and  $p(a_H\gamma_{Cl})$  values.

$m_{KCl}$	run1		run2		run3	
	FEM / mV	$p(a_H\gamma_{Cl})$	FEM / mV	$p(a_H\gamma_{Cl})$	FEM / mV	$p(a_H\gamma_{Cl})$
0.005	600.77	4.0959	600.48	4.0910	600.42	4.0900
0.01	582.51	4.0882	582.47	4.0876	582.55	4.0889
0.02	564.26	4.0808	564.16	4.0791	564.12	4.0784
0.04	545.82	4.0701	545.78	4.0694	545.78	4.0694
0.05	539.60	4.0618				

The determination of the acidity function at zero KCl molality was done by linear regression analysis on the equation:

$$p(a_H\gamma_{Cl}) = p(a_H\gamma_{Cl})^0 + b m_{KCl} \quad (11)$$

and the intercept and slope were 4.0945 and -0.647, respectively. Figure 1 shows the variation of  $p(a_H\gamma_{Cl})$  with  $m_{KCl}$ .

Figure 1. Variation of  $p(a_H\gamma_{Cl})$  with  $m_{KCl}$ 

The value of  $\lg \gamma_{Cl}$  was calculated using the equation (4), with  $I=0.0533 \text{ mol.kg}^{-1}$ . The result was  $\lg \gamma_{Cl} = -0.0876$  and  $p_{a_H} = 4.0069$  with the uncertainty of 0.0024.

The value of  $\log \gamma_{Cl}$  was also calculated using the equation (5). The parameters used in this calculation are given in table 2.

Table 2 - Parameters for Pitzer's model (equation 5).

	KCl [4]	KHPh [8]	$K_2Ph$ [8]
$\beta^{(0)}$	0.04835	0.01	0.12
$\beta^{(1)}$	0.01	-0.03	0.7
C	-0.00042	-----	-----
		$\theta_{Cl,Ph} = -0.008$	$\theta_{Cl,HPH} = 0.01$

In order to apply the Pitzer model, the ionic strength as well as the molalities of all species in the solution were calculated by iteration following the procedure described in reference [7].

In the work of Chan and his collaborators [8], the higher order electrostatic terms were not taken into account. So they were not included in the calculation of  $\gamma_{Cl}$  (equation 5). The third virial coefficients relative to the pure salts ( $C_{K,HPH}$  and  $C_{K,Ph}$ ) and to the mixture ( $\Psi_{K,Cl,HPH}$  and  $\Psi_{K,Cl,Ph}$ ) were neglected due to the low concentration of the solution. The last term, in equation (5) involves the parameter  $\lambda_{H_2Ph,Cl}$  relative to the interaction between the chloride ion and the neutral molecule which is not known but expected to be small and the product  $m_{H_2Ph} \cdot \lambda_{H_2Ph,Cl}$  may be neglected for this solution. This way, the quantities  $\lg \gamma_{Cl} = -0.0912$  and  $p_{a_H} = 4.004$  were obtained. This value is 0.003 lower than the  $p_{a_H}$  obtained when the Bates-Guggenheim is used, and this difference is only slightly higher than the uncertainty found for the experimental determination of the acidity function  $p(a_H\gamma_{Cl})^0$ , but it is expected to be greater for more concentrated solutions, since the specific ionic interactions, included in the Pitzer equations, will become more important.

If the higher order electrostatic terms,  ${}^E\theta$  and  ${}^E\theta'$ , were included,  $\lg \gamma_{Cl} = -0.1129$  and  $p_{a_H} = 3.982$ , keeping the same value for the mixing parameter  $\theta_{Cl,Ph}$ . However, the inclusion of those terms would certainly change the value of  $\theta$  and a redetermination of the mixing parameters should be done in order to study in more detail the implications of including the higher order electrostatic terms.

#### References

- [1] A. K. Covington, R. G. Bates e R. A. Durst, *Pure Appl. Chem.*, **57**, (1985), 531.
- [2] P. Debye e E. Hückel, *Physic. Z.*, **24**, (1923), 185.
- [3] R. G. Bates e E. A. Guggenheim, *Pure Appl. Chem.*, **1**, (1960), 163.
- [4] K. S. Pitzer in K. S. Pitzer (ed.), "Activity Coefficients in Electrolyte Solutions", pg 75-147, 2nd edn. CRC Press, Boca Raton, Florida (1991).
- [5] A. K. Covington e M. I. A. Ferra, *J. Solution Chem.*, **23**, (1994), 1.
- [6] R. G. Bates "Determination of pH- theory and practice", pg 330-334, 2nd edn., John Wiley & Sons, New York (1973).
- [7] M. J. G. Lito, M. F. C. Camões, M. I. Ferra e A. K. Covington, *Analytica Chimica Acta*, **239**, (1990), 129.
- [8] C.-Y. Chan, Y.-W. Eng, K.-S. Eu, *J. Chem. Eng. Data*, **40**, (1995), 685.