study is a convenient model host, however optically more transparent materials, with similar structural attributes, are being prepared for future studies.

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APPLICATION OF THE PITZER THEORY TO THE STUDY OF THE ACETATE pH STANDARD AT 25º C

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Abstract

The mixing parameters, $\theta_{Cl,Ac}$ and $\psi_{Na,Cl,Ac}$, included in the Pitzer equation to evaluate the chloride ion activity coefficient, were determined from electromotive force data, at 25º C. The ionic strength of the mixed electrolyte, sodium chloride and sodium acetate, varied from 0.05 to 2.5 mol kg^{-1}.

The activity coefficient of the chloride ion, in acetate buffer solutions, was calculated using the Pitzer model and the Debye-Hückel theory, with the Bates-Guggenheim convention, and the difference, in pH, has been discussed.

Key words: Acetate buffer solution; Pitzer equations; pH standard

Introduction

The acetate buffer solution has been used as a standard for pH determination. If the procedure for assignment of pH values to the primary standards [1] were applied to this buffer, the difference, in pH, caused by the application of the Pitzer theory instead of the Bates-Guggenheim convention, would be negligeable up to ionic strength about 0.4 mol kg^{-1}, as described bellow.

The assignment of pH to the primary standards involves the calculation of the chloride ion activity coefficient, γ_{Cl}, in the solution at the limit of zero molality of this ion [1], and this calculation is based on the Debye-Hückel theory, using the equation

$$\lg \gamma_{Cl} = A\, I^{1/2} / (1 + Ba\, I^{1/2}) \qquad (1)$$

where A is the Debye-Hückel parameter, I is the ionic strength and Ba = 1.5, at any pemperature, according to the Bates-Guggenheim convention [2]. This is valid for dilute solutions, that is, ionic strength not higher than 0.1 mol kg^{-1}. If the Pitzer theory [3] is applied, the specific ionic interactions are taken into account and γ_{Cl} may be calculated in solutions of higher concentrations, by means of the following equation

$$\ln \gamma_{Cl} = f^{\gamma} + 2m_{Na}B_{NaCl} + m_{Na}(2m_{Ac}+3m_{Cl})C_{NaCl} + m_{Na}m_{Ac}C_{NaAc} + m_{Na}m_{Cl}B'_{NaCl} +$$
$$+ m_{Na}m_{Ac}B'_{NaAc} + 2m_{Ac}\theta_{Cl,Ac} + m_{Na}m_{Ac}\psi_{Na,Cl,Ac} + 2m_{HAc}\lambda_{HAc,Cl} \qquad (2)$$

$$\lg \gamma_{Cl} = \ln \gamma_{Cl} / 2{,}303$$

$$f^{\gamma} = -A^{\Phi}\left[\, I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})\,\right] \qquad (3)$$

$$B = \beta^{(0)} + \beta^{(1)}(1/\alpha I)\left[\, 1 - (1+\alpha I^{1/2})\exp(-\alpha I^{1/2})\right] \qquad (4)$$

$$B' = \beta^{(1)}(1/\alpha I^2)\left[\, -1 + (\, 1 +\alpha I^{1/2} + (\alpha^2/2)I)\exp(-\alpha I^{1/2})\right] \qquad (5)$$

where B and C are the second and third virial coefficients of the pure electrolytes, B′ is the derivative of B, in order to the ionic strength, A^{Φ} is the Debye-Hückel parameter to the osmotic function, b is a universal parameter with the value 1.2 $kg^{1/2}mol^{-1/2}$, α =2.0 $kg^{1/2}mol^{-1/2}$, for electrolytes of 1:1 type and m is the molality of indicated species.

The parameters relative to the pure salts, sodium chloride and sodium acetate are known [3] at 25° C and their values are shown in table 1. The mixing parameters $\theta_{Cl,Ac}$ and $\psi_{Na,Cl,Ac}$ were determined in this work and their values are close to those obtained by Manohar and Ananthaswamy [4].

Table 1- Pitzer parameters for sodium chloride and sodium acetate

	$\beta(0)$ / kg mol^{-1}	$\beta(1)$ / kg mol^{-1}	$C=C^{\phi}/2$ / kg^2 mol^{-2}
NaCl	0,0765	0,2664	0,000635
NaAc	0,1426	0,3237	-0,003145

The difference in $lg\gamma_{Cl}$, given by equations (1) and (2) correspnds to the difference, in pH, when the procedure recommended for the primary standards is followed [1].

Experimental

Electromotive force measurements were taken on the galvanic cells :

$$Ag \mid AgCl \mid NaCl\ (m_1) \mid E.S.\ Na^+ \qquad (I)$$

$$Ag \mid AgCl \mid NaCl\ (m_2), NaAc\ (m_3) \mid E.S.\ Na^+ \qquad (II)$$

using a glass Na^+ selective electrode, Metrohm and silver-silver chloride electrodes of the thermo-electrolytic type [5]. Their bias potentials were lower than 0.1 mV.

For the solution preparation, sodium chloride and sodium acetate, both Merck p.a., were dried at 110°C for about 12 hours, and the deionized water had a specific conductivity of about 1.2 μS cm^{-1}.

The cell vessels were immersed in a thermostated bath and the temperature was measured with a thermometer, Hart Scientific, model 1502 and was kept constant within 25 ± 0.05° C.

The potential values were taken with a multimeter, Hewlett-Packard, model HP 3458A. The readings were recorded when the variation was lower than 0.05 mV for at least 5 minutes. Generally this would take around 20 minutes.

Results and Discussion

The readings, E_1 and E_2, were taken on cells (I) and (II), respectively, and the difference, ΔE, is given by

$$\Delta E = E_2 - E_1$$

$$\Delta E = k\ lg\ [\ (m_2+m_3)\ m_2\ \gamma^2_{NaCl}\ /\ (m_1\ \gamma^0_{NaCl})^2\ ] \qquad (6)$$

where m represents the molality of the salt indicated , γ^0_{NaCl} and γ_{NaCl} are the mean activity coefficients of NaCl in the solutions of pure and mixed electrolyte, respectively, k = ln(10)RT/F (k = 59.158 mV at 25°C) and R, T and F are the gas constant, absolute temperature and the Faraday constant. In order to eliminate the assimetry potential, the molality of Na^+ was made approximately equal in cells (I) and (II), for each ionic strength [6], that is, $m_1 = m_2 + m_3$.

From equation (6), $lg\ \gamma_{NaCl}$ (exp) may be calculated

$$lg\ \gamma_{NaCl}\ (exp) = \tfrac{1}{2}\ \{\ \Delta E/\ k\ -lg\ [\ (m_2+m_3)m_2]\ +\ 2lg\ (m_1\gamma^0_{NaCl})\ \} \qquad (7)$$

and the results are shown in table 2. The values in column 4 refer to the ionic strength of the mixed solutions (NaCl + NaAc).

Table 2 - Values of $lg\gamma_{NaCl}$ (exp) in mixed solutions of sodium chloride and sodium acetate

m_1 /mol kg^{-1}	m_2 /mol kg^{-1}	m_3 /mol kg^{-1}	I / mol kg^{-1}	ΔE /mV	$lg\gamma_{NaCl}$
0.0499	0.0300	0.0200	0.0500	-12.66	-0.0826
0.0499	0.0201	0.0300	0.0501	-22.97	-0.0826
0.0994	0.0602	0.0401	0.1003	-12.60	-0.1087
0.0994	0.0399	0.0599	0.0998	-22.97	-0.1064
0.1982	0.1199	0.0798	0.1997	-12.33	-0.1317
0.1982	0.0801	0.1199	0.2000	-22.30	-0.1288
0.2992	0.1999	0.0999	0.2998	-10.49	-0.1519
0.2992	0.0997	0.1995	0.2992	-27.46	-0.1439
0.4013	0.2659	0.1330	0.3989	-10.18	-0.1561
0.4013	0.1999	0.2003	0.4002	-17.22	-0.1542
0.4013	0.1328	0.2661	0.3989	-27.69	-0.1532
0.4988	0.2994	0.2006	0.5000	-12.28	-0.1612
0.4988	0.1982	0.2973	0.4955	-22.57	-0.1565
0.5994	0.3994	0.1997	0.5991	-9.46	-0.1648
0.5994	0.1996	0.3991	0.5987	-26.84	-0.1608
0.7972	0.4985	0.2991	0.7976	-10.81	-0.1694
0.7972	0.2994	0.4990	0.7984	-23.36	-0.1650
0.9986	0.5992	0.4014	1.0006	-12.23	-0.1763
0.9986	0.3981	0.5972	0.9953	-22.16	-0.1703
1.1976	0.7988	0.3993	1.1981	-9.27	-0.1751
1.1976	0.3831	0.7702	1.1533	-27.99	-0.1656
1.4732	0.8959	0.5973	1.4932	-10.86	-0.1703
1.4732	0.5870	0.8804	1.4674	-21.39	-0.1637
1.5979	1.0008	0.5242	1.5250	-11.60	-0.1687
1.5979	0.5110	0.9756	1.4866	-28.55	-0.1604
1.9920	1.1992	0.7995	1.9987	-11.63	-0.1647
2.4951	1.6960	0.7982	2.4942	-7.79	-0.1451
2.4951	0.8005	1.7011	2.5016	-25.58	-0.1331
2.4954	1.6449	0.8476	2.4925	-9.02	-0.1486
2.4954	1.2473	1.2472	2.4945	-15.80	-0.1460

The Pitzer equation [3] for the calculation of γ_{NaCl} is

$$\ln\gamma_{NaCl} = f' + (m_{Na}+m_{Cl})(B_{NaCl}+m_{Na}C_{NaCl}) + (m_{Na}m_{Cl})(B'_{NaCl}+C_{NaCl}) +$$
$$+ m_{Ac}(B_{NaAc}+m_{Na}B'_{NaAc}+2m_{Na}C_{NaAc}) + m_3\,\theta_{Cl,Ac} + (1/2)\,m_{Ac}(m_{Na}+m_{Cl})\,\psi_{Na,Cl,Ac} \quad (8)$$

where the symbols have the same meaning as before.

Equation (8), excluding the last two terms, is indicated by $\ln\gamma*_{NaCl}$. Therefore the difference $\Delta\ln\gamma_{NaCl}$ gives the terms of equation (8) that include the unknown parameters θ and ψ.

$$\Delta\ln\gamma_{NaCl} = \ln\gamma_{NaCl}\,(exp) - \ln\gamma*_{NaCl} \quad (9)$$

or

$$\Delta\ln\gamma_{NaCl} = m_3\,\theta_{ClAc} + [(1/2)\,m_3\,((m_2+m_3)_++m_2)]\,\psi_{Na,Cl,Ac} \quad (10)$$

The parameters used in the calculation of $\ln\gamma*_{NaCl}$ are given in table 1 [3]. The values of θ and ψ were obtained by multiple linear regression on equation (10), using a computer programme "S A S" (Statiscal Applied System) and are given in table 3. Figure 1 shows the respective residuals and the standard deviation of the fit is 0.005 or 0.26 mV.

Table 3 - Values of the mixing parameters

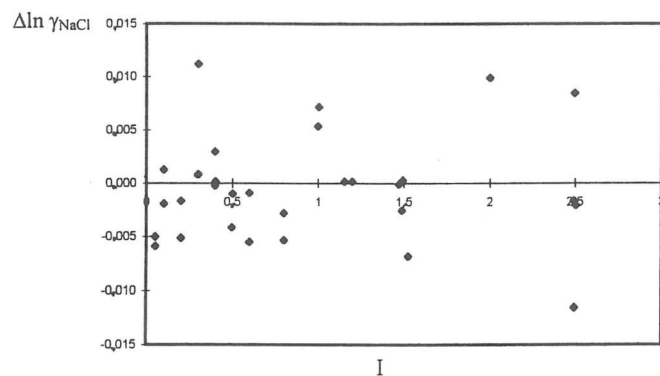| $\theta_{Cl,Ac}$	$\psi_{Na,Cl,Ac}$	
-0.00545	-0.00205	ref [4]
-0.0043	-0.0037	this work

Figure 1 - Difference, $\Delta\ln\gamma$, between experimental and calculated values of $\ln\gamma_{NaCl}$

If the values of ref. [4] were used instead, the standard deviation would also be 0.005 or 0.26 mV, showing a good fit with both sets of parameters.

The last term, in equation (2), for the evaluation of γ_{Cl} involves the interaction between the chloride ion and the neutral molecule. Its value is not known but is expected to be very small. In the

study of the phosphoric acid [7], the equivalent parameter was set to zero. So, the last term of equation (2) was assumed to be negligeable in the following calculations.

The difference of $lg\gamma_{Cl}$, given by equations (1) and (2), corresponds to the difference, in pH, when the Bates-Guggenheim convention [2] is replaced by the Pitzer model for the same solutions. Figure 2 shows the variation of $lg\gamma_{Cl}$ with the ionic strength for acetate buffer solutions containing no chloride. The difference, between the two approaches, is smaller than 0.01 for molalities $m_{HAc} = m_{NaAc}$ lower than 0.4 mol kg^{-1}, indicating a very small change in pH.
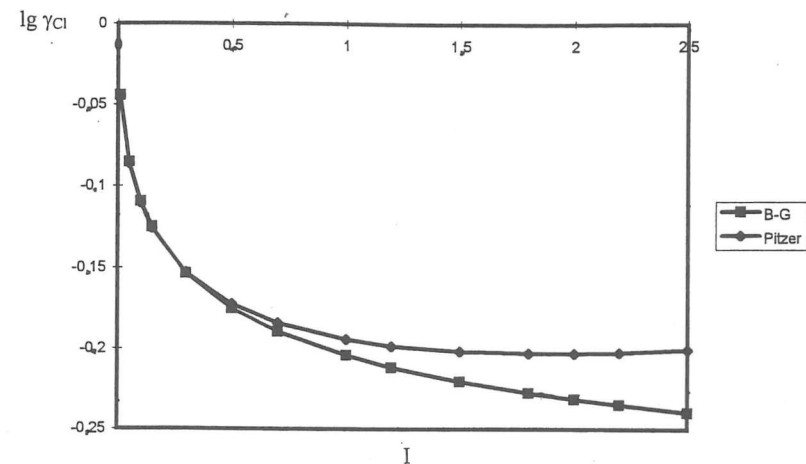

Figure 2 - Variation of $lg\gamma_{Cl}$ with the ionic strength of buffer solutions containing no chloride

But, if the ionic strength is increased by adding NaCl, that variation is quite different, as shown in figure 3, where the molalities of acid and sodium acetate are 0.1 mol kg^{-1}.
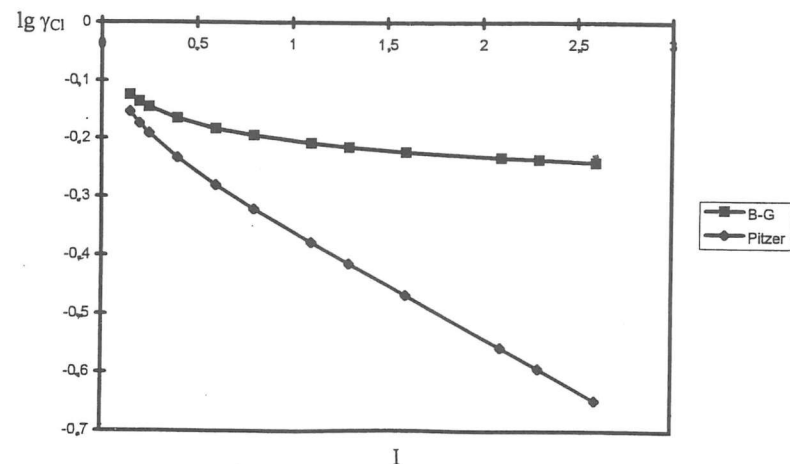

Figure 3 - Variation of $lg\gamma_{Cl}$ with the molality of NaCl

For the two acetate pH standards, 0.01 and 0.1 mol kg^{-1}, 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].

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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^{-1} 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^{-1}, according to the IUPAC recommendations [1]. Its pH value is based on electromotive force (EMF) measurements on the Harned cell, without liquid junction:

$$Pt(Pd) \mid H_2 \text{ (p=101325 Pa)} \mid KHPh, KCl \mid AgCl \mid Ag \qquad (A)$$

where the hydrogen and silver-silver chloride electrodes are immersed in solutions of KHPh 0.05 mol.kg^{-1} and KCl of varying molalities. The respective potential, E, is given by

$$E = E°_{Ag,AgCl} - k.lg(a_H.a_{Cl}) \qquad (1)$$

where $E°_{Ag,AgCl}$ is the standard potential of the silver-silver chloride electrode, k= (RT/F)ln10 (=0.059159 V at 298.15 K), R, T and F are the gas constant, absolute temperature and Faraday constant, respectively, and a_H and a_{Cl} represent the activities of H^+ and Cl^- .

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

$$p(a_H\gamma_{Cl}) = \frac{E - E°}{k} + lg\, m_{Cl} \qquad (2)$$

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

$$pa_H = p(a_H\gamma_{Cl})^0 + lg\, \gamma_{Cl} \qquad (3)$$

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

$$lg\gamma_{Cl} = -\frac{A\sqrt{I}}{1 + Ba\sqrt{I}} \qquad (4)$$

where A is a constant (A= 0.5108 kg$^{1/2}$. 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)