pH Standardization of 0.05 mol·kg^{-1} Tetraoxalate Buffer: Application of the Pitzer Formalism

José L. Barriada,[§] Isabel Brandariz,[§] Ritu Kataky,[†] Arthur K. Covington,[†,‡] and Manuel E. Sastre de Vicente*,[§]

Departamento de Química Física e Enxeñería Química I Facultade de Ciencias, Universidade da Coruña, Campus da Zapateira 15071 A Coruña, Spain, Department of Chemistry, University of Durham, Durham DH1 3LE, U.K., and Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K.

With the aim to surpass the concentration limit imposed by the Bates-Guggenheim convention, the Pitzer formalism has been applied to the analysis of the standardization of the pH buffer, potassium tetraoxalate dihydrate. Following the same procedure that has been conventionally applied to other pH buffers, hydrogen electrodes have been used to measure the potential differences of Harned cells, which contained 0.05 mol·kg^{-1} potassium tetraoxalate and up to 1 mol·kg^{-1} KCl, at 25 °C. A value of pH = 1.650 has been calculated. Another simpler model for activity coefficients, the Guggenheim specific interaction theory, has been found to be inadequate to model this complex system.

Introduction

The Bates-Guggenheim convention (BGC) has been used as an assumption in order to calculate the activity coefficient for chloride ion at zero added chloride in the standardization of pH buffers.[1−4] Although it is assumed that BGC is valid only if the ionic strength of the buffer solution, I, is 0.1 mol·kg^{-1} or less,[1,5,6] pH measurements are carried out on samples where I exceeds this value, such as seawater and blood.[7]

A few years ago, a new procedure for pH buffer standardization was suggested using the Pitzer equations, which are valid over a wider range of ionic strength[8] than the BGC, to calculate[7,9−13] the pH values of several standard solutions at higher ionic strengths ($I \gg 0.1$ mol·kg^{-1}), by addition of an inert electrolyte.

The main problem in the application of the Pitzer formalism consists of the lack of values for some interaction parameters. Most of the tabulated values are for inorganic ions, and few parameters for organic species are known.[8] Few systematic studies on the dependence of stoichiometric equilibrium constants on the ionic strength are available[14] (and references therein). Such studies allow calculation of the speciation in buffer solutions.

New results for the buffer system potassium tetraoxalate 0.05 mol·kg^{-1} dihydrate + KCl have been analyzed using the Pitzer equations. Since stoichiometric equilibrium constants of oxalic acid in KCl solutions are not available, the ionic strength dependence of pK'_1 values has been determined.

Experimental Section

(a) Stoichiometric Equilibrium Constant. Determination of pK'_1 (at 25.0 ± 0.1 °C) as a function of I was done using a combination glass electrode (Radiometer pHC2401), following the procedure described elsewhere.[15−18] Since interest was focused on the tetraoxalate buffer, only the determination of the first equilibrium constant of oxalic acid was required. Excess of inert electrolyte, KCl (BDH AnalaR), was used to adjust the ionic strength of the solutions studied. Potassium 0.005 mol·L^{-1} tetraoxalate dihydrate (BDH AnalaR) solutions were titrated with a solution of 0.1 mol·L^{-1} HCl, standardized with sodium tetraborate decahydrate (Aldrich ACS reagent). HCl solution was prepared by dilution of a solution of constant boiling point HCl.[19] Measurements were made using a digital pH meter titrimeter (Molspin, Newcastle upon Tyne), and titration data were fitted using Superquad.[20] Low concentrations of potassium tetraoxalate were used to avoid large changes in the ionic strength of the solution during titration as well as in the liquid junction potential.

(b) pH Measurements. Potential differences (±0.03 mV) of Harned cells[2,21] were measured using a Keithley 2000 multimeter. Solutions were prepared by mass (±0.0001 g) with potassium tetraoxalate dihydrate (Merck secondary reference material) and KCl (Merck p.a. and Suprapur). No difference was observed between solutions prepared with the two grades of KCl. Thermoelectrolytic Ag/AgCl electrodes and platinum electrodes were prepared as described.[1] Plating of the platinum electrodes was done with lead acetate (Aldrich) added to the hexachloroplatinic acid (Merck p.s.). Best quality reagents were used in the preparation of electrodes. High purity hydrogen (99.999%) from a cylinder, without further purification, was bubbled through the cells. Potential difference measurements were corrected to 101325 Pa.[1,4] All experiments were done at 25.00 ± 0.02 °C.

Results and Discussion

(a) Stoichiometric Equilibrium Constant (pK'_1). Because of a general lack of information on the tetraoxalate system, the first step was the determination of the stoichiometric constant as a function of ionic strength. In previous studies, the Pitzer equations were used to analyze other pH buffers; unlike the case of the tetraoxalate system, the thermodynamic constants of the weak acids or bases

---

* Corresponding author. E-mail: eman@udc.es. Telephone: +34 981 167 000 (ext. 2198). Fax: +34 981 167 065.

[§] Universidade da Coruña.

[†] University of Durham.

[‡] University of Newcastle.

10.1021/je010052j CCC: $20.00

Table 1. pK'_1 vs I for Oxalic Acid in KCl at 25 °C

I/mol·kg^{-1}	pK
0.10	0.93 (0.03)
0.30	0.859 (0.013)
0.51	0.837 (0.009)
0.72	0.824 (0.008)
0.93	0.84 (0.03)

Table 2. Fitting Parameters for Potassium Tetraoxalate Dihydrate Titrations in KCl (Eq 1)

pK	1.147 ± 0.010
H_1	0.21 ± 0.04
H_2	0.09 ± 0.07
σ	0.005

were known as well as the Pitzer interaction parameters.[7,11] Only for the phthalate system were these parameters not known.[10] Instead of using the procedure described in the phthalate study, it was decided to evaluate pK'_1 as a function of I, so speciation in the solutions can be easily calculated.

Data listed in Table 1 collect the pK'_1 as a function of I for the equilibrium between oxalic acid and hydrogen oxalate.

Using the Pitzer equations for the system tetraoxalate + KCl, where KCl is used as supporting electrolyte, at much higher concentration than that of tetraoxalate, the following equation can be obtained:[15]

$$\mathrm{p}K'_1 = \mathrm{p}K + \frac{2}{\ln 10}f^{\gamma} + H_1 I + H_2 g + \frac{2}{\ln 10}\beta^{(1)}_{\mathrm{K,Cl}} I e^{-2\sqrt{I}} \quad (1)$$

where pK'_1 and pK are the stoichiometric and the thermodynamic pK, respectively, and g and f^{γ} are exponential functions of ionic strength:

$$g = 1 - (1 + 2\sqrt{I})\mathrm{e}^{-2\sqrt{I}}$$

$$f^{\gamma} = -0.391\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2}\ln(1 + 1.2\sqrt{I})\right], \quad (2)$$

and $\beta^{(1)}_{\mathrm{K,Cl}}$ is the double interactions parameter between K^+ and Cl^- ions.[8] H_1 and H_2 encompass additions of interaction parameters between other species in solutions,[15] obtained from a linear fitting of the experimental data, together with the thermodynamic pK value.

$$H_1 = \frac{2}{\ln 10}(\beta^{(0)}_{\mathrm{H,Cl}} + \beta^{(0)}_{\mathrm{K,OxH}} - \lambda_{\mathrm{N}})$$

$$H_2 = \frac{1}{\ln 10}(\beta^{(1)}_{\mathrm{H,Cl}} + \beta^{(1)}_{\mathrm{K,OxH}} - \beta^{(1)}_{\mathrm{K,Cl}}) \quad (3)$$

In eq 1 a simplification has been made. Oxalate concentration, Ox^{2-}, has not been considered because titrations were done by adding HCl to a tetraoxalate solution, so the main species are oxalic acid and hydrogen oxalate. The second dissociation constant for oxalic acid is, at least,[22] three orders of manitude lower that the first dissociation constant, so the concentration of oxalate ion can be neglected in the buffered solution of potassium tetraoxalate.

Fitting of experimental data is very good, as can be seen in Table 2. However, there is a large difference in the calculated pK from the one that is reported in the literature, which varies considerably depending on the source, between 1.42 and 1.252, as can be seen in a compilation of the thermodynamic constants of oxalic acid.[22]

(b) Standardization of Potassium Tetraoxalate. The Harned cells studied can be represented according to the following scheme:

$$\mathrm{Pt}|\mathrm{H_2}|\text{potassium tetraoxalate } (0.05\ \mathrm{mol{\cdot}kg^{-1}}), \mathrm{KCl(m)}|\mathrm{AgCl}|\mathrm{Ag} \quad (4)$$

Once that stoichiometric equilibrium constant is known, concentrations of all species in the solutions studied with the Harned cells can be determined as follows.

The concentration of hydrogen ion is calculated by solving the following equation

$$m_{\mathrm{H}}^{2} + (m_{\mathrm{KTet}} + K'_1)m_{\mathrm{H}} + K'_1(m_{\mathrm{KTet}} - m_{A_0}) = 0 \quad (5)$$

where K'_1 is initially calculated using eq 1 and an approximate value of ionic strength, $I = m_{\mathrm{KTet}} + m_{\mathrm{KCl}}$; m_i is the molality of species i, the subscript KTet means potassium tetraoxalate, H represents hydrogen ion, and m_{A_0} is the total oxalic concentration, oxalic acid plus hydrogen oxalate concentrations. Equation 5 comes from combination of the stoichiometric equilibrium constant, K'_1, the mass balance equation, and the charge balance equation, as is usual in all calculations of this kind.[3,9,23] The ionic product of water does not need to be taken into account in such acidic solutions.

The ionic strength of the system is given by

$$I = m_{\mathrm{K}} + m_{\mathrm{H}} = m_{\mathrm{KCl}} + m_{\mathrm{KTet}} + m_{\mathrm{H}} \quad (6)$$

and a new, more accurate value of I can be calculated with the hydrogen ion concentration calculated by solving eq 5.

pK'_1 can be calculated again by solving eq 1, with this new value of I. The process is repeated until no difference in I is observed, so the hydrogen ion concentration remains constant. A similar iterative process has been used for acetate buffer,[9,23] where the thermodynamic constant was used, because, for acetate buffer, the Pitzer interaction parameters are known.

When hydrogen ion concentration is constant (usually 6 to 7 iterations are required to reach a constant value), oxalic acid and hydrogen oxalate concentrations are calculated from the mass balance and charge balance equations for the 70 solutions used (see Table 3).

Once all concentrations are known, the next step consists of using the Pitzer equations combined with the Nernst equation applied to each cell. Equation 7 is obtained:

$$\begin{aligned} E - E^{\circ} + \kappa \ln m_{\mathrm{Cl}} + \kappa \ln m_{\mathrm{H}} = {}& \\ -\kappa[2f^{\gamma} + 2B_{\mathrm{H,Cl}}(m_{\mathrm{H}} + m_{\mathrm{Cl}}) + 2mC_{\mathrm{H,Cl}}(m_{\mathrm{Cl}} + m_{\mathrm{H}}) + {}& \\ 2m_{\mathrm{H}}m_{\mathrm{Cl}}B'_{\mathrm{H,Cl}} + 2m_{\mathrm{H}}m_{\mathrm{Cl}}C_{\mathrm{H,Cl}} + 2m_{\mathrm{K}}m_{\mathrm{Cl}}B'_{\mathrm{K,Cl}} + {}& \\ 2m_{\mathrm{K}}m_{\mathrm{Cl}}C_{\mathrm{K,Cl}} + 2m_{\mathrm{K}}\theta_{\mathrm{K,H}} + m_{\mathrm{K}}m_{\mathrm{Cl}}\psi_{\mathrm{H,K,Cl}} + 2m_{\mathrm{K}}B_{\mathrm{K,Cl}} + {}& \\ 2m\,m_{\mathrm{K}}C_{\mathrm{K,Cl}} + 2m_{\mathrm{K}}m_{\mathrm{OxH}}B'_{\mathrm{K,OxH}} + 2m_{\mathrm{K}}m_{\mathrm{OxH}}C_{\mathrm{K,OxH}} + {}& \\ m_{\mathrm{K}}m_{\mathrm{OxH}}\psi_{\mathrm{K,Cl,OxH}} + m_{\mathrm{H}}m_{\mathrm{K}}\psi_{\mathrm{H,K,Cl}} + 2m_{\mathrm{OxH}}\theta_{\mathrm{Cl,OxH}}] \quad (7)& \end{aligned}$$

where $m = m_{\mathrm{H}} + m_{\mathrm{K}} = I$, E and E° are the potential difference measured and the standard potential difference for the silver/silver chloride electrode, respectively, and $\kappa = RT/F$, where R is the gas constant, T the absolute temperature, and F the Faraday constant. $C_{i,j}$, $\theta_{i,j}$, and $\psi_{i,j,k}$ are Pitzer interaction parameters between the different species in solution, and B and B' are ionic strength functions.[8] B and B' encompass interaction parameters as well, two of them in B and one in B'. All the interaction parameters appearing in eq 7 have been tabulated[8] except those related to hydrogen oxalate interactions. Equation

Table 3. Difference Potentials (±0.03 mV) and Potassium Chloride Concentrations of Solutions Studied[a]

m_{KCl}	E	m_{KCl}	E	m_{KCl}	E
$mol \cdot kg^{-1}$	mV	$mol \cdot kg^{-1}$	mV	$mol \cdot kg^{-1}$	mV
0.002 75	477.80	0.039 31	410.39	0.386 35	353.15
0.002 75	477.85	0.039 31	410.22	0.409 02	352.85
0.003 08	476.08	0.060 1	398.92	0.444 68	350.72
0.003 08	475.65	0.060 1	399.39	0.444 68	350.68
0.006 19	457.13	0.076 77	392.96	0.449 46	349.64
0.006 19	457.29	0.076 77	393.51	0.449 46	350.28
0.007 54	452.00	0.076 77	393.26	0.574 45	344.36
0.007 54	452.59	0.154 2	375.86	0.574 45	344.25
0.007 61	452.45	0.154 2	376.20	0.677 62	339.95
0.007 61	453.07	0.156 7	375.84	0.677 62	339.59
0.007 61	452.52	0.156 7	375.98	0.754 67	337.05
0.015 64	433.76	0.200 33	369.73	0.754 67	336.99
0.015 64	434.00	0.200 33	370.05	0.882 93	332.73
0.016 77	432.13	0.200 33	370.12	0.912 33	331.66
0.016 77	432.28	0.317 59	359.00	0.914 51	331.69
0.029 19	417.24	0.317 59	359.23	0.914 51	331.92
0.029 19	417.49	0.345 4	356.65	0.947 77	330.39
0.029 35	417.22	0.345 4	356.74	0.947 77	330.13
0.029 35	417.35	0.379 64	354.64	1.129 84	326.47
0.035 01	412.74	0.379 64	353.87	1.129 84	326.28
0.035 01	413.01	0.382 67	353.17	1.150 35	325.69
0.035 01	413.26	0.385 58	353.54	1.150 35	325.88
0.036 08	413.18	0.385 58	353.38	1.154 49	325.01
0.036 08	413.16	0.386 35	353.14	1.154 49	325.67

[a] Every solution was 0.05 $mol \cdot kg^{-1}$ in potassium tetraoxalate.

Table 4. Pitzer Interaction Parameters for Hydrogenoxalate in KCl

$\beta^1_{K,OxH}$	0.16 ± 0.10
$\theta_{Cl,OxH}$	0.005 ± 0.013

7 should include the interaction parameters between the neutral molecule and the ions H^+ and Cl^-. Their values are not known, but they are expected to be small,[11,12] so they were not taken into account.[10,13]

Instead of using eq 7, a simplification can be made. Since concentrations were not higher than 1 $mol \cdot kg^{-1}$ in KCl (with 0.05 $mol \cdot kg^{-1}$ in tetraoxalate in each), and lower than 2 $mol \cdot kg^{-1}$, higher order interaction parameters (C and ψ) can be ignored[8] and eq 8 is obtained:

$$\begin{aligned} E - E^\circ + \kappa \ln m_{Cl} + \kappa \ln m_H = \\ -\kappa[2f^\gamma + 2B_{H,Cl}(m_H + m_{Cl}) + 2mC_{H,Cl}(m_{Cl} + m_H) + \\ 2m_H m_{Cl} B'_{H,Cl} + 2m_H m_{Cl} C_{H,Cl} + 2m_K m_{Cl} B'_{K,Cl} + \\ 2m_K m_{Cl} C_{K,Cl} + 2m_K \theta_{K,H} + 2m_K B_{K,Cl} + 2m\,m_K C_{K,Cl} + \\ 2m_K m_{OxH} B'_{K,OxH} + 0.2 m_{OxH} \theta_{Cl,OxH}] \end{aligned} \quad (8)$$

At the same time another problem is solved. C and ψ (for OxH^-) are multiplied in eq 7, by the same factors, the concentrations of K^+ and OxH^-. Thus, it is impossible to calculate both interaction parameters separately in the fitting process. This fact would be a problem in the last calculation step, but it has been avoided because these parameters have not been taken into account. It is considered that there is no reason to use the full Pitzer equation. It has many parameters, so the fitting could be quite good, but it is well-known in a fitting process that the higher the number of fitting parameters used, the larger are the uncertainties in the parameters.

All terms in eq 8 are known except $\beta^1_{K,OxH}$ and $\theta_{Cl,OxH}$. Linear fitting using this equation and the measured potential differences, together with the concentrations calculated according to the iterative process mentioned above, gave the results in Table 4. Although errors are quite large, the values of the parameters are reasonable.[8]

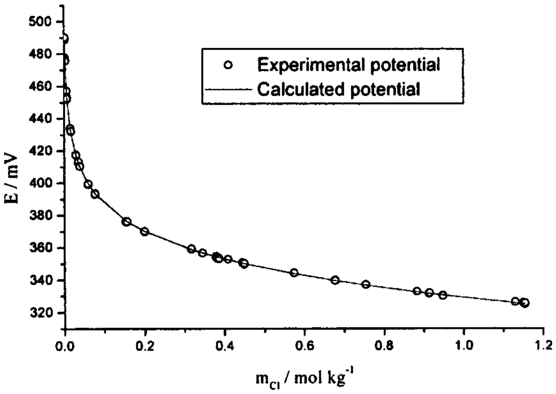

Figure 1. Experimental and calculated potential differences with the Pitzer equations, eq 8, measured on Harned cells with a solution of 0.05 $mol \cdot kg^{-1}$ potassium tetraoxalate and different added concentrations of KCl.

The large error in $\theta_{Cl,OxH}$ can be explained as follows. In the fitting function, eq 8, this parameter is multiplied by m_{OxH}. Although the concentration of hydrogenoxalate changes for different cell compositions, the change is quite small in the buffered solutions. In a linear fitting the change in the dependent variable produced by a change in independent variable is calculated. If the change in the independent variable is not very large, experimental errors will make the error in the fitting parameter increase a lot, because there is almost no relation between the two variables. This happens with $\theta_{Cl,OxH}$, and that is the reason the error is so large.

From eq 8, using the values listed in Table 4, it is possible to calculate the potential difference for the cell. Figure 1 shows the experimental values of potential difference, together with the calculated function. The error in potential difference calculated is

$$\sigma(E) = \sqrt{\frac{\sum_i^n (E_{cal} - E_{exp})^2}{n}} = 0.63 \text{ mV} \quad (9)$$

The concentration of Cl^- is subjected to large experimental errors when it is very low, affecting the potential difference measured. Thus, if experimental data at low Cl^- concentrations are ignored (lower than 8×10^{-3} $mol \cdot kg^{-1}$), the error drops to 0.47 mV.

The final step consists of calculating the pH values. This can be done in two ways. From the Nernst equation for the Harned cell potential, it is possible to solve for pH if the activity coefficient of chloride is known; the activity coefficient of chloride ion can be calculated from the Pitzer equations and the interaction parameters in Table 4. The pH can also be calculated from the definition, pH = $-\log a_H$, because the molality of hydrogen ion is known (from the iterative process) and the activity coefficient is calculated from the Pitzer equations and parameters in Table 4. From the definition of pH the following expression is obtained:

$$\begin{aligned} pH_{def} = -\log(m_H \gamma_H) = \\ -\log m_H - \frac{1}{\ln 10}[f^\gamma + 2m_{Cl} B_{H,Cl} + 2m\,m_{Cl} C_{H,Cl} + \\ m_H m_{Cl} B'_{H,Cl} + m_H m_{Cl} C_{H,Cl} + m_K m_{Cl} B'_{K,Cl} + \\ m_K m_{Cl} C_{K,Cl} + 2m_K \theta_{K,H} + m_K m_{OxH} B'_{K,OxH}] \end{aligned} \quad (10)$$

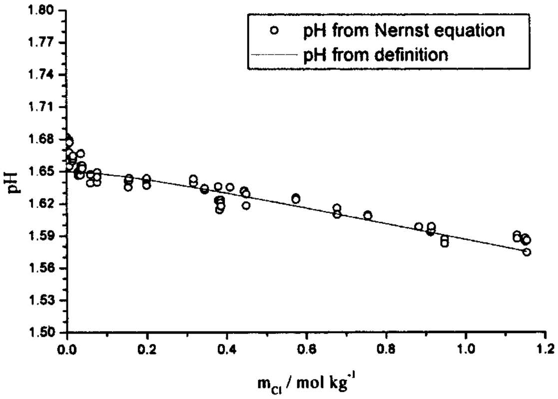

Figure 2. pH from definition and from Nernst equation using the Pitzer equations to describe activities of species in solution.

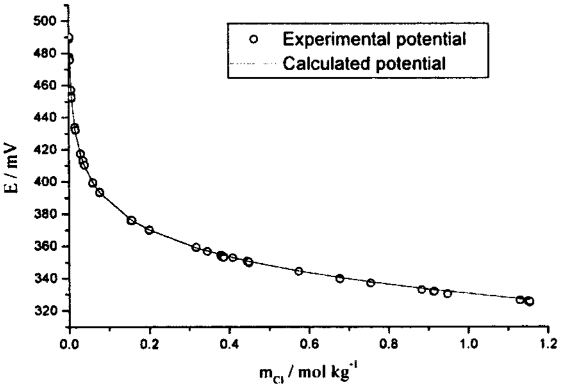

Figure 3. Experimental and calculated potential differences with Guggenheim specific interaction theory, measured on Harned cells with a solution of 0.05 mol·kg^{-1} potassium tetraoxalate and different added concentrations of KCl.

If the Nernst equation is used, the pH can be calculated from eq 11, which includes the experimental values for the potential differences measured:

$$\mathrm{pH_{exp}} = -\log(a_{\mathrm{H}}) = \frac{E - E°}{59.16} + \log m_{\mathrm{Cl}} + \frac{1}{\ln 10}[f' + 2m_{\mathrm{H}}B_{\mathrm{H,Cl}} + 2mm_{\mathrm{H}}C_{\mathrm{H,Cl}} + m_{\mathrm{H}}m_{\mathrm{Cl}}B'_{\mathrm{H,Cl}} + m_{\mathrm{H}}m_{\mathrm{Cl}}C_{\mathrm{H,Cl}} + 2m_{\mathrm{K}}B_{\mathrm{K,Cl}} + m_{\mathrm{K}}m_{\mathrm{Cl}}B'_{\mathrm{K,Cl}} + m_{\mathrm{K}}m_{\mathrm{Cl}}C_{\mathrm{K,Cl}} + 2mm_{\mathrm{K}}C_{\mathrm{K,Cl}} + m_{\mathrm{K}}m_{\mathrm{OxH}}B'_{\mathrm{K,OxH}} + 2m_{\mathrm{OxH}}\theta_{\mathrm{Cl,OxH}}] \quad (11)$$

Figure 2 shows the results obtained by both procedures. The error between experimental and notional pH is

$$\sigma(\mathrm{pH}) = \sqrt{\frac{\sum_i^n(\mathrm{pH_{def}} - \mathrm{pH_{exp}})^2}{n}} = 0.011 \qquad (12)$$

If low chloride concentration points are ignored, as for the potential differences, the error in pH is reduced to 0.008.

Equation 10 permits calculation of pH at zero chloride. The result is 1.650, 0.029 in pH lower than the BGC assigned value. The difference is significant, and shows the same behavior as that observed in the buffers already analyzed,[9] for which the Pitzer equations give values of extrapolated pH lower than the assigned values obtained with the BGC.[9]

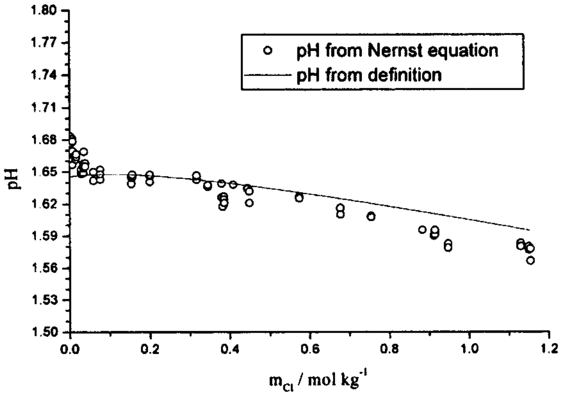

Figure 4. pH from definition and from Nernst equation using Guggenheim specific interaction theory to calculate activities of species in solution.

Guggenheim specific interaction theory has been used to analyze the system in the same way, since Guggenheim, Scatchard, or Pitzer analysis applied to carboxylic acids[15] and other substances[24−27] gives equivalent results.

Following the same procedure described for the Pitzer analysis, the potential difference values calculated with Guggenheim specific interaction theory are shown in Figure 3. The error in potential difference was $\sigma(E) = 0.95$ mV, higher than that with the Pitzer analysis, but the fit is still quite good. The big difference comes in the pH values, Figure 4. Not only is the fitting poor at low concentrations of $\mathrm{Cl^-}$ but it is also poor at high concentrations. In this case $\sigma(\mathrm{pH}) = 0.016$ compared with 0.011, and the pH at zero chloride concentration is 1.645. Thus, the Guggenheim model is poor for describing properly the system studied.

Acknowledgment

J.L.B. thanks R.K. for providing facilities in Durham

Literature Cited

(1) Bates, R. G. *Determination of pH; theory and practice*, 2nd ed.; Wiley: New York, 1973.
(2) Kristensen, H. B.; Salomon, A.; Kokholm, G. International pH Scales and Certification of pH. *Anal. Chem.* **1991**, *63*, A 885−891.
(3) Serjeant, E. P. *Potentiometry and Potentiometric Titrations*; Wiley: New York, 1984; Vol. 69.
(4) Baucke, F. G. K.; Naumann, R.; Alexander-Weber, C. Multiple-Point Calibration with Linear Regression as a Proposed Standardization Procedure for High-Precision pH Measurements. *Anal. Chem.* **1993**, *65*, 3244−3251.
(5) Covington, A. K. Recent Developments in pH Standardisation and Measurement for Dilute Aqueous Solutions. *Anal. Chim. Acta* **1981**, *127*, 1−21.
(6) Covington, A. K.; Bates, R. G.; Durst, R. A. Definition of pH scales, standard reference values, measurements of pH and related terminology. *Pure Appl. Chem.* **1985**, *57*, 531−542.
(7) Covington, A. K.; Ferra, M. I. A. A Pitzer Mixed Electrolyte Solution Theory Approach to Assignment of pH to Standard Buffer Solutions. *J. Solution Chem.* **1994**, *23*, 1−10.
(8) Pitzer, K. S. *Activity coefficients in electrolyte solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.
(9) Camoes, M. F.; Lito, M. J. G.; Ferra, M. I. A.; Covington, A. K. Consistency of pH standard values with the corresponding thermodynamic acid dissociation constants (Technical Report). *Pure Appl. Chem.* **1997**, *69*, 1325−1333.
(10) Chan, C.; Eng, Y.; Eu, K. Pitzer Single-Ion Activity Coefficients and pH for Aqueous Solutions of Potassium Hydrogen Phthalate in Mixtures with KCl and with NaCl at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 685−691.
(11) Nunes, M. H. S. B.; Ferra, M. I. A. Application of the Pitzer Theory to the Study of the Acetate pH Standard at 25 C. *Portug. Electrochim. Acta* **1997**, *15*, 239−244.
(12) de Mendonca, J. G.; Ferra, M. I. A. Application of the Pitzer Theory to the Evaluation of pH of the Phthalate Standard Solution. *Portug. Electrochim. Acta* **1997**, *15*, 245−249.

(13) Ferra, M. I. A. A Pitzer Theory Approach to Assignment of pH to Standard Buffer Solutions. *Port. Electrochim. Acta* **1998**, *16*, 133−142.
(14) Sastre de Vicente, M. E. Ionic strength effects on acid−base equilibria. A review. *Curr. Top. Solution Chem.* **1997**, *2*, 157−181.
(15) Barriada, J. L.; Brandariz, I.; Sastre de Vicente, M. E. Acid−Base Equilibria of Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations. *J. Chem. Eng. Data* **2000**, *45*, 1173−1178.
(16) Alonso, P.; Barriada, J. L.; Rodriguez, P.; Brandariz, I.; Sastre de Vicente, M. E. Acid−base equilibrium constants for glycine in NaClO4, KCl, and KBr at 298 K. Dependence on ionic strength. *J. Chem. Eng. Data* **1998**, *43*, 876−879.
(17) Brandariz, I.; Vilariño, T.; Alonso, P.; Herrero, R.; Fiol, S.; Sastre de Vicente, M. E. Effect of ionic strength on the formal potential of the glass electrode in various saline media. *Talanta* **1998**, *46*, 1469−1477.
(18) Brandariz, I.; Fiol, S.; Sastre de Vicente, M. E. Study of the Influence of Ionic-Strength on the Ionic Product of Water in Saline Media at 25-Degrees-C Using the Pitzer Equations. *Ber. Bunsen-Ges. Phys. Chem* **1995**, *99*, 749−752.
(19) Vogel, A. I. *Vogel's textbook of quantitative chemical analysis*, 5th ed.; Longman Scientific & Technical: Harlow, 1989.
(20) Gans, P.; Sabatini, A.; Vacca, A. Superquad—An improved general program for computation of formation-constants from potentiometric data. *J. Chem. Soc., Dalton Trans* **1985**, *6*, 1195−1200.
(21) Bezboruah, C. P.; Camoes, M. F. G. F. C.; Covington, A. K.; Dobson, J. V. Enthalpy of Ionization of Water from Electromotive Force Measurements. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 949−962.
(22) Kettler, R. M.; Wesolowski, D. J.; Palmer, D. A. Dissociation Constants of Oxalic Acid in Aqueous Sodium Chloride and Sodium Trifluoromethanesulfonate Media to 175 °C. *J. Chem. Eng. Data* **1998**, *43*, 337−350.
(23) Lito, M. J. G. H. M.; Camoes, M. F. G. F. C.; Ferra, M. I. A.; Covington, A. K. Calculation of reference pH values for standard solutions from the corresponding acid dissociation constants. *Anal. Chim. Acta* **1990**, *239*, 129−137.
(24) Brandariz, I.; Fiol, S.; Herrero, R.; Vilariño, T.; Sastre de Vicente, M. E. Protonation constants of α-alanine, γ-aminobutyric acid, and ϵ-aminocaproic acid. *J. Chem. Eng. Data* **1993**, *38*, 531−533.
(25) Brandariz, I.; Arce, F.; Armesto, X. L.; Penedo, F.; Sastre de Vicente, M. E. Dependence of Equilibrium-Constants of L-Valine on Ionic-Strength According to Guggenheim, Scatchard and Pitzer Models. *Monatsh. Chem.* **1993**, *124*, 249−257.
(26) Brandariz, I.; Herrero, R.; Sastre de Vicente, M. E. Application of Pitzer and Guggenheim Formalisms to Acid−Base Equilibria of Triethanolamine and L-Valine in Mixtures of Electrolytes. *J. Chim. Phys. Phys.-Chim. Biol.* **1993**, *90*, 63−77.
(27) Vilariño, T.; Fiol, S.; Brandariz, I.; Herrero, R.; Sastre de Vicente, M. E. Acid−base equilibria of cysteine in artificial seawater: Effect of ionic strength on the basis of Specific Interaction Theory. *J. Chem. Res., Synop.* **1997**, 222−223.

Received for review February 15, 2001. Accepted June 5, 2001. The authors want to thank Xunta de Galicia for the financial support received through Projects XUGA 10310B97 and PGIDT00PXI-10308PR. J.L.B. thanks M. E. C. and Universidad de La Coruña for the fellowships granted.

JE010052J