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pH Standardization of 0.05 mol·kg^{-1} Tetraoxalate Buffer at Temperatures from (5 to 45) °C with Added KCl Molality up to 1.0 mol·kg^{-1}

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The standard pH of 0.05 mol·kg^{-1} potassium tetraoxalate was determined using the calculation method recommended by IUPAC (*Pure Appl. Chem.* **2002**, *74*, 2169−2200) at various temperatures from new Harned cell data and literature data. New data were obtained for 0.05 mol·kg^{-1} potassium tetraoxalate solution containing up to 1 mol·kg^{-1} KCl at temperatures of (5, 15, 25, 35, and 45) °C. One step in the calculation method of IUPAC is a linear extrapolation of the experimental quantity p[a(H$^+$)γ(Cl$^-$)], where a refers to the activity and γ refers to the activity coefficient, to zero molality of KCl. The possibilities of using more concentrated KCl solutions in this determination with nonlinear extrapolations were also investigated.

Introduction

The Bates−Guggenheim[1] convention has been used as an assumption required to calculate the activity coefficient for chloride ion at zero added chloride molality in the standardization of pH buffers.[2] It is often asserted in the literature (see, for example, ref 3) that this assumption is only valid up to an ionic strength of about 0.1 mol·kg^{-1}. Nowadays, several studies are available where the speciation of buffer solutions was determined by using either Pitzer[4−9] or Hückel[8−12] equations for the activity coefficients of ions. The pH values of the IUPAC buffers obtained (based on Bates−Guggenheim convention) usually checks within 0.01 with these other activity coefficient equations.

The pH values recommended by IUPAC[13] for the 0.05 mol·kg^{-1} potassium tetraoxalate dihydrate solution were based on the extensive experimental data of Bower et al.[14] for Harned cells in mixed solutions of this electrolyte with KCl at temperatures from (0 to 60) °C. The recommended pH value of this solution at 25 °C is 1.68. Later, Barriada et al.[15] measured with Harned cells aqueous mixtures of these salts at 25 °C, analyzing their data by using Pitzer equations, and obtained at this temperature a value of 1.650 for the 0.05 mol·kg^{-1} potassium tetraoxalate solution significantly smaller than that recommended by IUPAC (also if a slight error that resulted from the use of Bates−Guggenheim convention is taken into account). This casts some doubt on the experimental data of Bower et al.[14] For this reason in the present study, new data from these aqueous mixtures were measured with Harned cells at temperatures from (5 to 45) °C at intervals of 10 °C. These data were analyzed together with the literature data using the calculation method recommended by IUPAC. Calculation methods are also suggested here for stronger KCl solutions in the determination of pH values of the tetroxalate buffer at the various temperatures.

Experimental Section

The 0.05 mol·kg^{-1} potassium tetroxalate solution was prepared from crystalline potassium tetroxalate dihydrate ($KH_3C_4O_8 \cdot 2H_2O$, Merck, certipur), without drying, and added to reverse-osmosis cleaned water (Millipore). Potassium chloride (pro analysi, Riedel-de Haën) was used after 2 h drying at 110 °C. The solutions used in the measurements were prepared from the solution and KCl by weighing to an accuracy of 0.1 mg with the molalities of those shown in Table 1. Cell potential differences (cpd) of these solutions were measured using the Harned cell:

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|KH_3C_4O_8(aq,}\ m_b\mathrm{),\ KCl\ (aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \quad (1)$$

where f is fugacity of hydrogen. The hydrogen electrode and silver−silver chloride electrode were prepared, handled, and checked in a similar way to that described in ref 16. Additionally, the condition of the electrodes and the cell function was checked a few times between the measurements by measuring the cpd of the 0.01 mol·kg^{-1} HCl solution at 25 °C. The $E°$ values (i.e., the standard cell potential differences) obtained in these checks were always within 0.2 mV of that suggested in ref 17 (222.53 mV).

The cpd values of the tetroxalate solutions were measured with a Keithley 192 programmable digital multimeter. Air was removed from these solutions by bubbling nitrogen slowly through the solution about 20 min in the cell before measurements were commenced. The cell was immersed in the water of a water bath, and the temperature of this bath was controlled within 0.1 °C and measured by using mercury thermometers (for temperatures of (25 and 35) °C, a thermometer with a precision of 0.01 °C was used; for the other temperatures, a thermometer with a precision of 0.1 °C was used). Air pressure was measured by a Lambrecht mercury barometer. Hydrogen gas was purified (with a Saes getters PS11-MC1-H purifier), and the gas flow was controlled using a mass flow controller device. The flow rate was 20 cm^3·min^{-1}. The gas was passed through a ceramic filter into Millipore water and then into the measuring solution below the platinum plate of the hydrogen electrode.

Generally for each solution, the cpd at 25 °C was measured first, then at (15, 5, 25, 35, 45) °C, and finally again at 25 °C.

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Table 1. Cell Potential Differences (E) Measured in the Present Study on Harned Cell of Type 1 for 0.05 mol·kg^{-1} Potassium Tetroxalate Buffer Solutions at Various Temperatures (t) and Salt Molalities (m_s)

m_s	E/V at the following values of t/°C				
mol·kg^{-1}	5	15	25	35	45
0.00305	0.47010	0.47334	0.47610	0.47876	0.48090
0.00732	0.44958	0.45211	0.45400	0.45582	0.45711
0.01528	0.43220	0.43412	0.43552	0.43671	0.43745
0.03487	0.41275	0.41395	0.41467	0.41510	0.41503
0.06928	0.39673	0.39736	0.39755	0.39726	0.39670
0.1531	0.37885	0.37870	0.37826	0.37736	0.37600
0.3016	0.36356	0.36282	0.36177	0.36027	0.35833
0.4957	0.35226	0.35098	0.34942	0.34753	0.34521
0.4996		0.35046	0.34895		
0.6969		0.34270	0.34076	0.33852	0.33601
0.6978			0.34059	0.33821	0.33553
0.9011		0.33613	0.33386	0.33119	0.32842
0.9914		0.33363	0.33127	0.32864	0.32565

Table 2. Results from Least-Squares Fitting Using Equation 3 from the Potassium Tetroxalate Data Measured by Bower et al.[14] on Cell 1 Where m_b = 0.05 mol·kg^{-1}

t/°C	$p(a_H\gamma_{Cl})^0$	$s[p(a_H\gamma_{Cl})^0]$[a]	k	$s(k)$[b]	($10^3\ s$)[c]
0	1.7631	0.0005	0.36	0.04	0.4
5	1.7630	0.0011	0.51	0.11	1.1
10	1.763	0.002	0.7	0.2	1.8
15	1.7676	0.0014	0.52	0.13	1.3
20	1.7713	0.0006	0.48	0.06	0.6
25	1.7771	0.0014	0.33	0.13	1.6
30	1.7818	0.0010	0.35	0.09	1.1
35	1.789	0.002	0.2	0.2	2.4
40	1.7959	0.0014	0.29	0.14	1.5
45	1.8021	0.0013	0.48	0.13	1.5
50	1.810	0.002	0.5	0.2	2.1
55	1.818	0.002	0.5	0.2	2.1
60	1.828	0.003	0.5	0.3	3.3

[a] Standard deviation of parameter $p(a_H\gamma_{Cl})^0$. [b] Standard deviation of parameter k. [c] s is the standard deviation about the regression.

Table 3. Results from Least-Squares Fitting Using Equation 3 from the Potassium Tetroxalate Data Measured in the Present Study (Table 1) and by Barriada et al.[15] on Cell 1 Where m_b = 0.05 mol·kg^{-1}

t/°C	$p(a_H\gamma_{Cl})^0$	$s[p(a_H\gamma_{Cl})^0]$[a]	k	$s(k)$[b]	($10^3\ s$)[c]
5[d]	1.765	0.002	0.28	0.03	4.2
15[d]	1.771	0.003	0.27	0.04	4.7
25[d]	1.776	0.003	0.28	0.04	4.8
25[e]	1.7619	0.0013	0.151	0.012	6.5
25[f]	1.7802	0.0013	0.151	0.012	6.5
35[d]	1.790	0.002	0.26	0.03	3.9
45[d]	1.805	0.002	0.24	0.03	3.7

[a] Standard deviation of parameter $p(a_H\gamma_{Cl})^0$. [b] Standard deviation of parameter k. [c] s is the standard deviation about the regression. [d] Taken from Table 1, and points up to m_s = 0.1531 mol·kg^{-1} were included (number of points was 6). [e] Taken from ref 15, and points up to m_s = 0.31759 mol·kg^{-1} were included (number of points was 40), and a value of $E°$ = 222.53 mV was used (see ref 17). [f] Taken from ref 15, and points up to m_s = 0.31759 mol·kg^{-1} were included (number of points was 40), and a value of $E°$ = 221.45 mV was used (see ref 22).

Table 4. pH Values[a] for the 0.05 mol·kg^{-1} Potassium Tetroxalate Buffer Solution

t/°C	pH(IUPAC)[b]	pH(NBS)[c]	pH(BBS)[d]	pH[e]	(I_m/mol·kg^{-1})[f]
0		1.666	1.671	1.667	0.07685
5	1.67	1.668	1.671	1.666	0.07695
10	1.67	1.670	1.669	1.665	0.07705
15	1.67	1.672	1.674	1.669	0.07684
20	1.68	1.675	1.676	1.672	0.07671
25	1.68	1.679	1.681	1.677	0.07644
30	1.68	1.683	1.685	1.681	0.07625
35		1.688	1.693	1.688	0.07591
40	1.69	1.694	1.697	1.694	0.07559
45		1.700	1.704	1.699	0.07533
50	1.71	1.707	1.712	1.706	0.07497
55		1.715	1.719	1.713	0.07462
60		1.723	1.726	1.722	0.07416

[a] Determined from the experimental data of Bower et al.[14] [b] Recommended by Buck et al.[13] [c] Recommended by Bates.[2] [d] Suggested by Bower et al.[14] [e] Predicted in the present study. [f] The ionic strength of the solution.

The equilibrium at each temperature was achieved normally within about 0.5 h. Cpd values and temperatures were recorded manually, and the number of cpd readings was from 3 to 6 during the measurement of each point. The mean of these values was used in the calculations. The hydrogen pressures were calculated by using atmospheric pressure, vapor pressure of pure water, and hydrogen jet correction (see pp 281−285 in ref 2 and ref 18). The recorded cpd was corrected to the reference pressure of 101.325 kPa of dry hydrogen. The values are shown in Table 1.

Results and Discussion

The standard pH values of the 0.05 mol·kg^{-1} potassium tetroxalate solution were calculated from the new data and from those of refs 14 and 15. The classic method of NIST (formerly NBS; see, e.g., refs 2 and 19) was used for assigning the pH of the buffer solutions, and this method was used in the recent pH recommendations of IUPAC.[13] The method is described here by using the present problem with 0.05 mol·kg^{-1} potassium tetroxalate solution as an example: A value of the acidity function of $p(a_H\gamma_{Cl})$ is calculated from each cpd (= E) measured on the Harned cell containing this buffer solution with KCl and from the standard cpd of this cell (= E^o) at the temperature used in the measurements by

$$p(a_H\gamma_{Cl}) = -\log(m_H\gamma_H\gamma_{Cl}/m^o) = \frac{(E - E^o)F}{RT \ln 10} + \log(m_{Cl}/m^o) \quad (2)$$

where $m°$ is 1 mol·kg^{-1}; a_H is the activity of hydrogen ion; m_H and m_{Cl} are the molalities; and γ_H and γ_{Cl} are the activity coefficients of hydrogen and chloride ions, respectively. In the present calculations, the $E°$ values determined in ref 17 from the Harned cell data of Harned and Ehlers[20,21] [for HCl(aq)] were used for all data. Bower et al.[14] used the values of (0.005, 0.010, and 0.015) mol·kg^{-1} for m_s in cell 1, and at each salt molality at least two replicate determinations were reported. Barriada et al.[15] reported 72 points at 25 °C for salt molalities from (0.00275 to 1.15449) mol·kg^{-1}. Bower et al.[14] observed in small KCl molalities (such as those used in their study) that the quantity $p(a_H\gamma_{Cl})$ depended linearly on m_{Cl} (as was also observed for the other NBS[2] buffer solutions). The value of $p(a_H\gamma_{Cl})$ for the chloride-free buffer solution [i.e., $p(a_H\gamma_{Cl})^0$] was determined for each temperature by extrapolation to zero molality of added KCl. In these dilute solutions, linear regression analysis can be used with the following equation:

$$p(a_H\gamma_{Cl}) = p(a_H\gamma_{Cl})^0 + k(m_{Cl}/m^o) \quad (3)$$

where k is thus an empirical slope parameter. The parameter values obtained in the present study from the data of Bower et al.[14] for various temperatures are shown in Table 2.

In Table 3 are shown the parameter values obtained by linear regression analyses for eq 3 from the new data (see Table 1) and from those of Barriada et al.[15] The new data (see Table 3) gives practically the same values for $p(a_H\gamma_{Cl})^0$ at the temper-

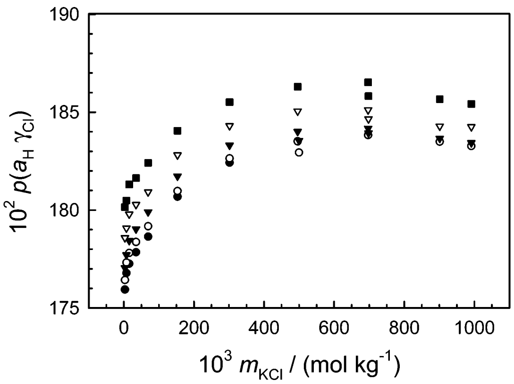

Figure 1. Experimental values of the acidity function $p(a_H\gamma_{Cl})$ (defined in eq 2), obtained from the new Harned cell data (see Table 1) for the 0.05 mol·kg^{-1} tetraoxalate buffer solutions containing also KCl, as a function of the molality of KCl ($=m_{KCl}$): ●, 5 °C; ○, 15 °C; ▼, 25 °C; ▽, 35 °C; ■, 45 °C.

atures in common with the data of Bower et al. (Table 2). The data of Barriada et al.[15] give a value of 1.762 ± 0.003 at 25 °C for this quantity (see Table 3, the confidence interval is given at a probability level of 0.95 as are all confidence intervals given below), which is not in agreement with 1.777 ± 0.003 (Table 2) from the data of Bower et al.[14] In fact the value obtained by Barriada et al. for the standard cpd of cell 1 was 221.45 mV,[22] which was missed out the previous paper.[15] By using in the calculation the value of $E° = 221.45$ mV (instead of 222.53 mV[17]), a $p(a_H\gamma_{Cl})^0$ value of 1.780 ± 0.003 is obtained from the regression analysis with eq 3, and it is in good agreement with the value 1.7771 in Table 2. The results of this fitting are also shown in Table 3. They show, additionally, that the values of other quantities in this fitting were the same as those shown for the value $E° = 222.53$ mV. Thus, the precision of that data is close to that of the new data and in good agreement. A difference between the standard potentials of the silver−silver chloride electrodes is thus possibly due to the disagreement of the $p(a_H\gamma_{Cl})^0$ values from the data of Bower et al.[14] and Barriada et al.[15] From the $p(a_H\gamma_{Cl})^0$ value of the latter study[15] (i.e., from 1.7619 that is shown in Table 3 and calculated with $E° = 0.22253$ mV), the standard pH value of 1.662 was determined by the method suggested by IUPAC[13] (this method is also described below) for 0.05 mol·kg^{-1} potassium tetroxalate buffer solutions. This value differs only 0.012 from that suggested by Barriada et al.[15] on the basis of the Pitzer equations for this pH value (see above). It is thus comparable, for example, to the largest differences between the pH values suggested by IUPAC[3,13] and those calculated on the basis of the Hückel equations (for determination of the speciation of the solutions) for acetate,[10] phosphate,[11] and phthalate buffers.[12]

The final step in the assignment of standard values, pH(S), to the chloride-free 0.05 mol·kg^{-1} potassium tetroxalate buffer solution was the calculation pa_H from $p(a_H\gamma_{Cl})^0$ with the definition

$$\mathrm{pH(S)} = pa_H = p(a_H\gamma_{Cl})^0 + \log \gamma_{Cl} \tag{4}$$

where γ_{Cl} is fixed by the following convention (Bates−Guggenheim convention[1]):

$$\log \gamma_{Cl} = \frac{-A\sqrt{I_m}}{1 + 1.5\sqrt{I_m/m^o}} \tag{5}$$

In eq 5, A is the Debye−Hückel constant at the temperature under consideration [it can be calculated from the tabulated[23] Debye−Hückel parameter for the osmotic coefficient A_ϕ by equation $A = 3A_\phi/\ln(10)$], and I_m is the ionic strength on the molality scale. The ionic strength was iteratively calculated by using the following equations:

Table 5. Results from Least-Squares Fitting Using Equation 8 from the Potassium Tetroxalate Data Measured in the Present Study (Table 1)[a] and in that of Barriada et al.[15] on Cell 1 Where m_b = 0.05 mol·kg^{-1}

t/°C	$[p(a_H\gamma_{Cl})^0]$[b]	$p(a_H\gamma_{Cl})^{0,1}$	$s[p(a_H\gamma_{Cl})^{0,1}]$[c]	k_1	k_2	$(10^3\ s)$[d]
5	1.765	1.765	0.002	0.31	−0.35	4.1
15	1.771	1.771	0.002	0.31	−0.37	4.3
25	1.776	1.776	0.002	0.32	−0.40	4.2
25[e]	1.7802	1.780	0.002	0.18	−0.16	7.3
35	1.790	1.790	0.002	0.29	−0.34	3.6
45	1.805	1.805	0.002	0.27	−0.31	3.4

[a] Points up to $m_s = 0.4996$ mol·kg^{-1} were included. [b] Obtained by using eq 3 (see Table 3). [c] Standard deviation of parameter $p(a_H\gamma_{Cl})^{0,1}$. [d] s is the standard deviation about the regression. [e] Calculated from data of Barriada et al. up to 0.44946 mol·kg^{-1} with $E° = 221.45$ mV.

Table 6. Results from Least-Squares Fitting Using Equation 9 from the Potassium Tetroxalate Data Measured in the Present Study (Table 1) and in that of Barriada et al.[15] on Cell 1 Where m_b = 0.05 mol·kg^{-1}

t/°C	$[p(a_H\gamma_{Cl})^0]$[a]	$p(a_H\gamma_{Cl})^{0,2}$	$s[p(a_H\gamma_{Cl})^{0,2}]$[b]	k_{21}	k_{22}	k_{23}	$(10^3\ s)$[c]
15	1.771	1.771	0.002	0.30	−0.44	0.21	5.2
25	1.776	1.777	0.002	0.31	−0.48	0.23	4.1
25[d]	1.7802	1.7794	0.0014	0.19	−0.23	0.08	7.2
35	1.790	1.790	0.002	0.30	−0.47	0.22	3.7
45	1.805	1.805	0.002	0.28	−0.42	0.19	3.2

[a] Obtained by using eq 3 (see Table 3). [b] Standard deviation of parameter $p(a_H\gamma_{Cl})^{0,2}$. [c] s is the standard deviation about the regression. [d] Calculated from all data of Barriada et al. with $E° = 221.45$ mV.

$$I_m = m_b + m_H \tag{6}$$

$$-\log(m_H/m^o) = p(a_H\gamma_{Cl})^0 - \frac{2A\sqrt{I_m}}{1 + 1.5\sqrt{I_m/m^o}} \tag{7}$$

The standard pH values were calculated from eqs 4 to 7 from each $p(a_H\gamma_{Cl})^0$ value shown in Table 2 and are shown in Table 4 together with the values suggested by Bower et al.,[14] NBS,[2] and IUPAC.[13] Also the ionic strengths of the buffer solution at each temperature are given in the table. The agreement in this table is good because the NBS[2] and IUPAC[13] values were based on these same data. The slight difference of the order of 0.005 between the new values and those of Bower et al.[14] could result from the different values used for the standard potential of silver−silver chloride electrode and from the different activity coefficient equation used for chloride ions in the calculations. According to IUPAC recommendations,[13] the typical uncertainty in standard pH values of buffer solutions is about 0.004.

It will be next considered how all data in Table 1 and in the set of Barriada et al.[15] with the value of $E° = 221.45$ mV (see above) are used in the determination of pH values for 0.05 mol·kg^{-1} potassium tetroxalate buffer. The experimental $p(a_H\gamma_{Cl})$ values are shown as a function of the KCl molality in Figure 1 for the new data (see Table 1). The plots of the different temperatures show clearly the nonlinear behavior above a molality of 0.15 mol·kg^{-1}. The determination of pH values can be based with these more-concentrated points on the extrapolations with the following two nonlinear equations (compare to eq 3):

$$p(a_H\gamma_{Cl}) = p(a_H\gamma_{Cl})^{0,1} + k_1(m_{Cl}/m^o) + k_2(m_{Cl}/m^o)^2 \tag{8}$$

$$p(a_H\gamma_{Cl}) = p(a_H\gamma_{Cl})^{0,2} + k_{21}(m_{Cl}/m^o) + k_{22}(m_{Cl}/m^o)^2 + k_{23}(m_{Cl}/m^o)^3 \quad (9)$$

The results from the least-squares analysis of the experimental data in Table 1 with eqs 8 and 9 are shown in Tables 5 (eq 8) and 6 (eq 9). These results show that the more complex calculation methods using data from more concentrated solutions lead to almost the same values (always within ± 0.001) for quantity $p(a_H\ \gamma_{Cl})^0$ as those obtained by using the linear model (see Table 3). The equation containing a quadratic term (eq 8) applies well up to KCl molality of 0.5 mol·kg^{-1}, and the equation containing additionally a cubic term (eq 9) applies to all data (i.e., up to m_{KCl} of about 1 mol·kg^{-1}).

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