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

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Electromotive force (emf) measurements of the cell Pt–Pd|H_2|$C_8H_5O_4K$ (m) + MCl (m_1)|AgCl|Ag, where M represents K or Na, at 298.15 K have been carried out, with the molality of potasssium hydrogen *o*-phthalate ($C_8H_5O_4K$), m, ranging from 0.01 to 0.1 mol kg^{-1}, m_1(KCl) from 0.01 to 2 mol kg^{-1}, and m_1(NaCl) = 1 mol kg^{-1}. From emf data, pH values have been calculated for these solutions, using an approximation method based on Pitzer's system for single-ion activity coefficients at high ionic strengths. Differences between these values and operational pH values obtained from conventional measurements using combination pH glass electrodes were attributed to liquid junction potential contributions. pH was constant at 3.704 ± 0.004 when the molality of $C_8H_5O_4K$ was in the range 0.03–0.1 mol kg^{-1} for the solutions containing 1 mol kg^{-1} KCl. For 1 mol kg^{-1} NaCl solutions, pH was constant at 3.680 ± 0.004 when the molality of $C_8H_5O_4K$ was between 0.02 and 0.1 mol kg^{-1}.

Introduction

Application of Pitzer's system (*1–3*) of equations to describe mean ionic activity coefficients in mixtures at moderate to very high ionic concentrations has been useful in the treatment of both solubility and electromotive force (emf) data (*4–7*). Recent interests have been to apply the Pitzer system of equations to obtain single-ion activity coefficients (*4, 8–10*) for ionic species in sea water as well as pH. Covington and Ferra (*11*) have proposed that a self-consistent system of aqueous pH standards be established with values assigned using a convention based on Pitzer's system of equations for single-ion activity coefficients. There is a need for pH standards at ionic strengths greater than 0.1 mol kg^{-1} to be established since generally accepted pH standards (IUPAC, NIST) are dilute buffer solutions. The pH values of these dilute buffers are *conventionally* (*12*) based on the Bates–Guggenheim (B-G) single-ion molal activity coefficient equation (*13*) which was used to evaluate the single-ion activity coefficient of the chloride ion with its molality approaching zero in the buffer solutions and on emf measurements of the hydrogen–Ag|AgCl cell (without liquid junction) containing these solutions to which low concentrations of a soluble chloride had been added.

The Bates–Guggenheim equation is assumed to be adequate for low ionic strengths, generally 0.1 mol kg^{-1} and lower. No single system of equations for the calculation of single-ion activities has been formally adopted to assign standards conventionally for pH determination in media of higher ionic concentrations. An aqueous solution of 0.05 mol kg^{-1} potassium hydrogen *o*-phthalate is the IUPAC Reference Value pH Standard (*12*), but there is a lack of information on the pH behavior of solution mixtures containing this substance at ionic strengths higher than 0.1 mol kg^{-1} and, for that matter, how meaningful pH numbers can be determined for solutions at higher ionic strengths. It would be useful to assign pH numbers for solutions of this substance at higher ionic concentrations on the basis of a self-consistent system of equations for describing single-ion activities. Since potassium hydrogen *o*-phthalate (abbreviated to KHPh in this work for convenience, where Ph represents *o*-phthalate) is only moderately soluble at 298.15 K [10.23 g/100 g of water or 0.501 mol kg^{-1} (*14*)], addition of other more soluble salts to its solutions is necessary to study its behavior at higher ionic strengths. This paper reports precise emf data for the following hydrogen–AgCl|Ag cell (abbreviated to H-cell) at 298.15 K: Pt–Pd|H_2(g, 101 325 Pa)|KHPh (m) + MCl (m_1)|AgCl|Ag, where M represents K or Na and m and m_1 are the molalities of the respective electrolytes. The following types of mixtures were used: (A) KHPh (m = 0.05 mol kg^{-1}) + KCl (m_1 = 0.01, 0.05, 0.1, 0.5, 1, or 2 mol kg^{-1}), (B) KHPh (m = 0.01, 0.02, 0.03, 0.05, or 0.1 mol kg^{-1}) + KCl (m_1 = 1 mol kg^{-1}), and (C) KHPh (m = 0.01, 0.02, 0.03, 0.05, 0.07, or 0.1 mol kg^{-1}) + NaCl (m_1 = 1 mol kg^{-1}).

In theory, from the emf data obtained for these cell solution mixtures, the pH could be calculated using eq 1, where $k = (RT/F)\ \ln 10$, E and $E°$(AgCl|Ag) are the experimentally determined emf of the cell and the standard electrode potential of the silver–silver chloride electrode, respectively, $\gamma(\mathrm{Cl}^-)$ is the single-ion molal activity coefficient of the chloride ion, T is the thermodynamic temperature, R is the gas constant, and F is the Faraday constant. The calculated pH will depend on the convention used in the computation of log $\gamma(\mathrm{Cl}^-)$ for the solution mixtures considered here. It is also implicitly assumed that pH is given by (*12*)

$$\mathrm{pH} = [E - E°(\mathrm{AgCl|Ag})]/k + \log m_1 + \log \gamma(\mathrm{Cl}^-) \qquad (1)$$

$$\mathrm{pH} = -\log a(\mathrm{H}^+) = -\log(m(\mathrm{H}^+)\gamma(\mathrm{H}^+)/m°) \qquad (2)$$

where $m°$ is arbitrarily chosen to be 1 mol kg^{-1}, representing the ideal standard state, and $a(\mathrm{H}^+)$, $m(\mathrm{H}^+)$, and $\gamma(\mathrm{H}^+)$ are, respectively, the single-ion activity, molality, and molal activity coefficient of the hydrogen ion as a single ionic species. Both eqs 1 and 2 also assume acceptance of the concept of single-ion activities and activity coefficients that can be calculated on the basis of extrathermodynamic assumptions which cannot be proven absolutely (*15*).

Pitzer's system of equations (*1–3, 9, 10*) has been used in this work for the representation of the necessary single-ion activity coefficients for the various ionic species in the mixtures (A, B, C) considered, which were also complicated

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by the fact that the acid dissociation equilibria for *o*-phthalic acid (or 1,2-benzenedicarboxylic acid) had to be taken into account. A major problem encountered was that values for the Pitzer parameters for specific interactions of HPh^- and Ph^{2-} with other ions, especially those in the solutions considered here, have not been established experimentally. However, it will be seen that, in the presence of high molalities of the added electrolytes (KCl, NaCl), the value of log $\gamma(Cl^-)$ was largely dependent on the terms involving the various Pitzer parameters for the interaction of Cl^- with H^+, K^+, and Na^+, whose values had already been established independently (*2, 6*). To distinguish between pH values obtained with eq 1 and those obtained with eq 2, the term pH(H-cell) was used for the former and pH(P) for the latter. The manner in which they were determined will be outlined in the following sections, but first, let mixtures of the type HCl + NaCl + KCl, which are not complicated by acid dissociation equilibria, be considered to test the self-consistency of pH values calculated using the Pitzer system. Precise H-cell emf data and values of the required Pitzer interaction parameters are available (*2, 6*) from which pH(H-cell) values can be obtained for aqueous mixtures of HCl (0.01 mol kg^{-1}) + NaCl + KCl at a constant total ionic strength of 1 mol kg^{-1} at 298.15 K. pH(P) values for the same solutions can also be obtained, the Pitzer system being used to calculate the single-ion activity coefficients for the H^+ ion. pH values from these two approaches are compared in Table 1. Calculated pH(P) values were all higher than the corresponding pH(H-cell) values, but by only 0.003 unit or less when the published values (*6*) of $\theta_{H,K} = 0.0074$ mol^{-1} kg and $\theta_{H,Na} = 0.0279$ mol^{-1} kg were used, and by 0.001 or less when small adjustments were made to these parameters as shown in Table 1. The adjustments to the θ values had a negligible effect on the pH(H-cell) values, and the self-consistency of the Pitzer system is thus evident, at least for most practical purposes. Regression analysis yielded the linear relation pH(H-cell) = 2.08207 − 0.02343*X*, where $X = [m(Na^+)/\{m(Na^+) + m(K^+)\}]$. The regression coefficient was 0.999, and the standard deviations were 0.000 58 for the intercept and 0.000 73 for the gradient, respectively. This empirical equation holds only for the aqueous mixture HCl (0.01 mol kg^{-1}) + NaCl + KCl, at a constant total ionic strength of 1 mol kg^{-1} at 298.15 K, and clearly, the intercept should give the pH of the mixture HCl (0.01 mol kg^{-1}) + KCl (0.09 mol kg^{-1}).

Pitzer's Equations for Single-Ion Activity Coefficients. The Pitzer system of general equations for single-ion activity coefficients for cations and anions as well as those for the ionic interaction parameters have been described by Pitzer and co-workers (*1–3, 5*) and by Krumgalz and Millero (*9, 10*). On the basis of this system and using symbols and summation terms which carry meanings similar to those used in Pitzer's work (*5*), and used as well by Krumgalz and Millero (*9, 10*), eqs 3–6 give the single-ion activity coefficients of the ions H^+, Cl^-, HPh^-, and Ph^{2-} in the aqueous solution mixture KHPh (*m*) + MCl (m_1), where M = K or Na.

$$\begin{aligned}\ln \gamma(H^+) = {} & f^{\gamma} + 2[B_{H,Cl}m_1 + B_{H,HPh}m(HPh^-) + B_{H,Ph}m(Ph^{2-})] \\ & + M(c,a)[C_{H,Cl}m_1 + C_{H,HPh}m(HPh^-) + C_{H,Ph}m(Ph^{2-})] + F(c,a) \\ & + m[2\theta_{H,K} + m_1\Psi_{H,K,Cl} + m(HPh^-)\Psi_{H,K,HPh} + m(Ph^{2-})\Psi_{H,K,Ph}] \\ & + m_1[2\theta_{H,M} + m_1\Psi_{H,M,Cl} + m(HPh^-)\Psi_{H,M,HPh} + m(Ph^{2-})\Psi_{H,M,Ph}] \\ & + m_1m(HPh^-)\Psi_{H,Cl,HPh} + m_1m(Ph^{2-})\Psi_{H,Cl,Ph} + m(HPh^-)m(Ph^{2-})\Psi_{H,HPh,Ph} \end{aligned} \qquad (3)$$

$$\begin{aligned}\ln \gamma(Cl^-) = {} & f^{\gamma} + 2[B_{H,Cl}m(H^+) + B_{K,Cl}m + B_{M,Cl}m_1] \\ & + M(c,a)[C_{H,Cl}m(H^+) + C_{K,Cl}m + C_{M,Cl}m_1] + F(c,a) \\ & + m(HPh^-)[2\theta_{Cl,HPh} + m(H^+)\Psi_{H,Cl,HPh} + m_1\Psi_{M,Cl,HPh} + m\Psi_{K,Cl,HPh}] \\ & + m(Ph^{2-})[2\theta_{Cl,Ph} + m(H^+)\Psi_{H,Cl,Ph} + m_1\Psi_{M,Cl,Ph} + m\psi_{K,Cl,Ph}] \\ & + m(H^+)m_1\Psi_{H,M,Cl} + m(H^+)m\psi_{H,K,Cl} + mm_1\Psi_{M,K,Cl} \end{aligned} \qquad (4)$$

$$\begin{aligned}\ln \gamma(HPh^-) = {} & f^{\gamma} + 2[B_{H,HPh}m(H^+) + B_{K,HPh}m + B_{M,HPh}m_1] \\ & + M(c,a)[C_{H,HPh}m(H^+) + C_{K,HPh}m + C_{M,HPh}m_1] + F(c,a) \\ & + m_1[2\theta_{HPh,Cl} + m(H^+)\Psi_{H,Cl,HPh} + m\Psi_{K,Cl,HPh} + m_1\Psi_{M,Cl,HPh}] \\ & + m(Ph^{2-})[2\theta_{HPh,Ph} + m(H^+)\Psi_{H,HPh,Ph} + m\Psi_{K,HPh,Ph} + m_1\Psi_{M,HPh,Ph}] \\ & + m(H^+)m_1\Psi_{H,M,HPh} + mm(H^+)\Psi_{H,K,HPh} + m_1m\psi_{M,K,HPh} \end{aligned} \qquad (5)$$

$$\begin{aligned}\ln \gamma(Ph^{2-}) = {} & 4f^{\gamma} + 2[B_{H,Ph}m(H^+) + B_{K,Ph}m + B_{M,Ph}m_1] \\ & + M(c,a)[C_{H,Ph}m(H^+) + C_{K,Ph}m + C_{M,Ph}m_1] \\ & + 2m(H^+)\Sigma_a[2B'_{H,a} + C_{H,a}]m_a + 2m\Sigma_a[2B'_{K,a} + C_{K,a}]m_a + 2m_1\Sigma_a[2B'_{M,a} + C_{M,a}]m_a \\ & + m_1[2\theta_{Cl,Ph} + m(H^+)\Psi_{H,Cl,Ph} + m\Psi_{K,Cl,Ph} + m_1\Psi_{M,Cl,Ph}] \\ & + m(HPh^-)[2\theta_{HPh,Ph} + m(H^+)\Psi_{H,HPh,Ph} + m\Psi_{K,HPh,Ph} + m_1\Psi_{M,HPh,Ph}] \\ & + m(H^+)m_1\Psi_{H,M,Ph} + mm(H^+)\Psi_{H,K,Ph} + m_1m\psi_{M,K,Ph} \end{aligned} \qquad (6)$$

$$f^{\gamma} = -A^{\phi}I^{1/2}/[(1 + bI^{1/2}) + 2b^{-1}\ln(1 + bI^{1/2})] \qquad (7)$$

$$\begin{aligned}F(c,a) = {} & m(H^+)\Sigma_a[B'_{H,a} + C_{H,a}]m_a + \\ & m\Sigma_a[B'_{K,a} + C_{K,a}]m_a + m_1\Sigma_a[B'_{M,a} + C_{M,a}]m_a \end{aligned} \qquad (8)$$

$$M(c,a) = [2m_1 + m + m(H^+) + m(HPh^-) + 2m(Ph^{2-})] \qquad (9)$$

In the above equations, c and a represent cations and anions, respectively, $A^{\phi} = 0.392$ mol$^{-1/2}$ kg$^{1/2}$ at 298.15 K, $b = 1.2$, and $\alpha = 2.0$ mol$^{-1/2}$ kg$^{1/2}$ (*1–3*). Values of $B_{c,a}$ and

Table 1. pH in Aqueous Mixtures of HCl (0.01 mol kg^{-1}) + NaCl + KCl at a Constant Total Ionic Strength of 1.0000 mol kg^{-1} at 298.15 K, Based on Emf Data (*6*) and Pitzer's System of Equations ($E°$(AgCl|Ag) = 0.222 50 V (*6*), m(H$^+$) = 0.010 000 mol kg^{-1})

E/V	X^a	log γ(Cl$^-$)	pH(H-cell)	ΔpH^{b,c}	ΔpH^{b,d}
0.358 58	0	−0.218 66	2.0817	0.0030	0.0013
0.357 75	0.250 00	−0.209 87	2.0764	0.0024	0.0005
0.356 91	0.500 00	−0.200 99	2.0711	0.0019	−0.0003
0.355 96	0.750 00	−0.192 01	2.0640	0.0032	0.0007
0.355 10	1.000 00	−0.182 93	2.0586	0.0027	0.0001

[a] $X = [m(\mathrm{Na^+})/\{m(\mathrm{Na^+}) + m(\mathrm{K^+})\}]$. [b] $\Delta\mathrm{pH} = \mathrm{pH(P)} - \mathrm{pH(H\text{-}cell)}$. [c] $\theta_{\mathrm{H,K}}/(\mathrm{mol^{-1}\,kg}) = 0.0074$, $\theta_{\mathrm{H,Na}}/(\mathrm{mol^{-1}\,kg}) = 0.0279$. [d] $\theta_{\mathrm{H,K}}/(\mathrm{mol^{-1}\,kg}) = 0.0094$, $\theta_{\mathrm{H,Na}}/(\mathrm{mol^{-1}\,kg}) = 0.0310$.

$B'_{\mathrm{c,a}}$ were calculated from the corresponding $\beta^{(0)}{}_{\mathrm{c,a}}$ and $\beta^{(1)}{}_{\mathrm{c,a}}$ values using the relevant equations (*1*−*3*). Interaction terms related to higher-order unsymmetrical electrostatic mixing effects (*18*) have been omitted as their contributions are expected to be negligible in the solutions considered here. For 1−1, 2−1, 3−1 , and 4−1 electrolytes (1−3, 9) the B and B' terms are given by

$$B_{\mathrm{ca}} = \beta^{(0)}{}_{\mathrm{ca}} + (2\beta^{(1)}{}_{\mathrm{ca}}/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \qquad (10)$$

$$B'_{\mathrm{ca}} = (2\beta^{(1)}{}_{\mathrm{ca}}/\alpha^2 I^2)[-1 + (1 + \alpha I^{1/2} + 0.5\alpha^2 I) \times \exp(-\alpha I^{1/2})] \qquad (11)$$

and

$$C_{\mathrm{ca}} = C^{\phi}{}_{\mathrm{ca}}/(2|z_{\mathrm{c}}z_{\mathrm{a}}|^{1/2}) \qquad (12)$$

Values of the $\beta^{(0)}{}_{\mathrm{ca}}$, $\beta^{(1)}{}_{\mathrm{ca}}$, and $C^{\phi}{}_{\mathrm{ca}}$ parameters for many single electrolytes and those for θ_{ij} and Ψ_{ijk}, the mixing parameters (second and third virial coefficients), for mixtures at 298.15 K have been tabulated quite extensively by Pitzer and his co-workers (*1*−*3*). Unfortunately, in addition to the complexities of the equations involved, too many of the Pitzer parameters for the interactions of HPh$^-$ and Ph^{2-} with other ions involved in eqs 3−12 have unknown values to allow these parameters to be solved readily by procedures based on normal least-squares regression analysis. The manner in which tentative values were assigned to these parameters, in order that eqs 3−12 could be useful, will be discussed.

Calculations of Single-ion Molalities and Ionic Strengths. To calculate the molality of hydrogen ions in an aqueous mixture of KHPh (molality m) + MCl (molality m_1), the following ionic equilibria are relevant:

$$\mathrm{H_2Ph} \rightleftharpoons \mathrm{H^+} + \mathrm{HPh^-}\ (\mathrm{K_1})$$

$$\mathrm{HPh^-} \rightleftharpoons \mathrm{H^+} + \mathrm{Ph^{2-}}\ (K_2)$$

From considerations (*16*) of charge and mass balances, and assuming that the presence of OH$^-$ ions could be neglected and that the activity coefficient of the uncharged species H$_2$Ph could be approximated to unity, the following equations were obtained:

$$m(\mathrm{HPh^-}) = m - m(\mathrm{H_2Ph}) - m(\mathrm{Ph^{2-}}) \qquad (13)$$

$$m(\mathrm{H^+})^2 = [K_1K_2/\gamma(\mathrm{H^+})^2\gamma(\mathrm{Ph^{2-}})Q] \qquad (14)$$

where $Q = \{1 + K_1/(m(\mathrm{HPh^-})\gamma(\mathrm{H^+})\gamma(\mathrm{HPh^-}))\}$, $m(i)$ = molality of species i, $\gamma(i)$ is the single-ion activity coefficient of species i, and K_1 and K_2 are the first and second thermodynamic dissociation constants of *o*-phthalic acid.

$$K_1 = [m(\mathrm{H^+})m(\mathrm{HPh^-})/m(\mathrm{H_2Ph})][\gamma(\mathrm{H^+})\gamma(\mathrm{HPh^-})/\gamma(\mathrm{H_2Ph})] \qquad (15)$$

$$K_2 = [m(\mathrm{H^+})m(\mathrm{Ph^{2-}})/m(\mathrm{HPh^-})][\gamma(\mathrm{H^+})\gamma(\mathrm{Ph^{2-}})/\gamma(\mathrm{HPh^-})] \qquad (16)$$

The ionic strength I is given by

$$I = 0.5[m + 2m_1 + m(\mathrm{HPh^-}) + m(\mathrm{H^+}) + 4m(\mathrm{Ph^{2-}})] \qquad (17)$$

At 298.15 K, $-\log K_1 = 2.950$ and $-\log K_2 = 5.408$, from the tabulations of Robinson and Stokes (*17*). In this study, a first approximation for m(H$^+$) in each solution was obtained using eq 14 by neglecting m(H$^+$), m(Ph^{2-}), and m(H$_2$Ph) in eqs 13 and 17, and assuming the Pitzer equations for calculating the relevant single-ion activity coefficients with a chosen set of assumed values for those Pitzer interaction parameters that were unknown. Then values of m(H$_2$Ph) and m(Ph^{2-}) were calculated from eqs 15 and 16 using the approximated value of m(H$^+$), followed by a second calculation of m(HPh$^-$) in eq 13. A better value of I having now been obtained (eq 17), the single-ion activity coefficients were computed again to obtain better values of m(H$^+$). This procedure, which was adapted from that described by Butler (*16*), was repeated until successively computed values of the ionic molalities, ionic strength I, ionic activity coefficients, pH(P), pH(H-cell), and E(H-cell, calculated via eq 1) could be obtained, which all remain unchanged up to at least six significant figures, for each solution mixture studied and with each set of values assumed (cf. Tables 3−5) for the various parameters used in the Pitzer equations. A spreadsheet software with a good graphic facility was found to serve this purpose when the worksheets were properly programmed with the relevant formulas. The best set of parameter values assumed was considered that which yielded the smallest differences between pH(P) and pH(H-cell) values, and between calculated and observed emf values for each series of solutions studied.

Experimental Section

All solutions were prepared using doubly-distilled water from all-glass stills. Merck analytical grade potassium hydrogen *o*-phthalate, potassium chloride, and sodium chloride were dried at 383 K before use. Constant-boiling hydrochloric acid prepared from commercial analytical reagent grade reagent was used, after precise gravimetric chloride analysis, to prepare a 0.010 000 mol kg^{-1} HCl solution required for the standardization (*19*) of the AgCl|Ag electrodes. The preparation and use of electrodes and other experimental details pertinent to hydrogen cell emf measurements have been described before (*20*), and all emf readings were corrected to a hydrogen partial pressure of 101 325 Pa. Platinum electrodes lightly coated with palladium (*21*) were used in order to avoid significant reduction of phthalate at the hydrogen electrodes. Emf measurements precise to ±0.02 mV were carried out using a Keithley Model 197 precision digital multimeter. A pair of platinized Pt and a pair of Pd-coated Pt electrodes were used in the standardization of a matched pair of Ag|AgCl electrodes (bias potential <0.02 mV). All solutions were thermostated at (298.15 ± 0.02) K. The combination pH glass electrodes used were a Corning general purpose type (Cat. No. 476530) and a Cole-Palmer type (G05991-91, recommended for solutions with high Na$^+$ content). A Corning Research Model 250 digital pH/ISE meter, with 0.001 pH resolution, was used for the operational pH

Table 2. Emf, log $\gamma(Cl^-)$, and pH Data[a] for the Solution Mixtures at 298.15 K: (A) KHPh (m = 0.05 mol kg^{-1}) + KCl (m_l = 0.01, 0.05, 0.1, 0.5, 1, 2, or 3 mol kg^{-1}), (B) KHPh (m = 0.01, 0.02, 0.03, 0.05, or 0.1 mol kg^{-1}) + KCl (m_l = 1 mol kg^{-1}), (C) KHPh (m = 0.01, 0.02, 0.03, 0.05, 0.07, or 0.1 mol kg^{-1}) + NaCl (m_l = 1 mol kg^{-1})

	m(KHPh)/(mol kg^{-1})	m_l/(mol kg^{-1})	E(H-cell)/V	pH(op)[b]	log $\gamma(Cl^-)$	pH(H-cell)	pH(P)
(A)	0.050 00	0.010 00	0.581 92	3.995	−0.0971	3.980	3.990
	0.050 00	0.050 00	0.539 63	3.947	−0.1161	3.945	3.950
	0.050 00	0.100 00	0.520 50	3.905	−0.1328	3.906	3.914
	0.050 00	0.500 00	0.474 48	3.763	−0.1925	3.767	3.775
	0.050 00	1.000 0	0.454 64	3.682	−0.2212	3.702	3.696
	0.050 00	2.000 0	0.432 32	3.602	−0.2422	3.607	3.617
	0.050 00	3.000 0		3.559	−0.2447		3.578
(B)	0.010 00	1.000 0	0.456 88	3.714	−0.2201	3.743	3.747
	0.020 00	1.000 0	0.455 47	3.690	−0.2204	3.719	3.717
	0.030 00	1.000 0	0.454 76	3.680	−0.2207	3.707	3.706
	0.050 00	1.000 0	0.454 64	3.678	−0.2212	3.702	3.696
	0.070 00	1.000 0		3.679	−0.2217		3.691
	0.100 00	1.000 0	0.454 68	3.680	−0.2225	3.703	3.686
(C)							
	0.010 00	1.000 0	0.453 22	3.623	−0.1844	3.717	3.714
	0.020 00	1.000 0	0.451 36	3.597	−0.1850	3.685	3.692
	0.030 00	1.000 0	0.451 17	3.589	−0.1855	3.681	3.684
	0.050 00	1.000 0	0.451 11	3.579	−0.1866	3.679	3.677
	0.070 00	1.000 0	0.451 00	3.580	−0.1876	3.676	3.673
	0.100 00	1.000 0	0.451 29	3.586	−0.1891	3.679	3.671
	0.050 00	0					4.003

[a] Based on sets X and NE values of Pitzer parameters (cf. Tables 3–5). [b] pH(operational) from measurements with combination pH glass electrodes.

measurements. For two-point calibration of the glass electrode, precision secondary pH standards from Analytical Products Inc. (API), U.S.A., certified to be 4.000 ± 0.002 and 7.000 ± 0.002 at 298.2 K, respectively, and conforming to NIST standards (B-G convention), were used. Each pH(operational) reading presented in Table 2 was the mean value of at least 4 separate measurements with a reproducibility of ±0.002 pH unit, each measurement being preceded by a two-point calibration of the pH electrode.

Table 3. Known and Fixed Values of Pitzer Parameters Used in This Work[a]

interacting ions	$\beta^{(0)}$/ mol^{-1} kg	$\beta^{(1)}$/ mol^{-1} kg	$C_{i,j}$/ (mol^{-2} kg^2)	source
H, Cl	0.177 5	0.2945	0.000 4	ref 2
K, Cl	0.048 35	0.2122	−0.000 42	ref 2
Na, Cl	0.076 5	0.2664	0.000 635	ref 2
H, HPh	0	0	0	assumed
H, Ph	0	0	0	assumed

$\theta_{H,K}$/(mol^{-1} kg) = 0.0074 (*6*)
$\theta_{H,Na}$/(mol^{-1} kg) = 0.0279 (*6*)

$\Psi_{H,K,Cl}$/(mol^{-2} kg^2) = −0.0105 (*6*)
$\Psi_{H,Na,Cl}$/(mol^{-2} kg^2) = 0.0105 (*6*)

[a] All other $C_{i,j}$ and $\Psi_{i,j,k}$ parameters whose values were unknown were approximated with zero values.

Results and Discussion

$E°$(AgCl|Ag) values of 0.222 44 and 0.222 48 V were obtained from the standardization measurements at 298.15 K using Pd-coated Pt electrodes and platinized Pt electrodes in the H-cell, respectively. In each case, the value cited was the mean of four separate determinations obtained with the pair of silver–silver chloride electrodes and a pair of hydrogen electrodes, agreement among readings being ±0.02 mV. These values were in good agreement with previously published $E°$(AgCl|Ag, 298.15 K) values of 0.222 51 V (*22*) and 0.222 50 V (*23*) for thermal-electrolytic AgCl|Ag electrodes prepared and standardized with platinized Pt|H_2 electrodes in this laboratory. The $E°$(AgCl|Ag) value obtained using the Pt–Pd|H_2 electrodes was slightly lower, but it was also obtained with similar precision. Since the Pd-coated Pt electrodes were used for all the measurements involving KHPh, the value of $E°$(AgCl|Ag) = 0.222 44 V was used in eq 1 in the calculation of pH from the emf measurements. The experimental emf and pH results are given in Table 2. pH(H-cell) values were computed using eq 1 with values of log $\gamma(Cl^-)$ = {ln $\gamma(Cl^-)$/ ln 10}, calculated using eq 4. Only the values of Pitzer parameters involving the interactions among H^+, K^+, Na^+, and Cl^- ions were available (*2, 3, 6*), and *reasonable* values of all other unknown parameters in the equation had to be assumed, on a trial-and-error basis, from a consideration of the general range of magnitudes of $\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$, and C^{ϕ}_{ca} parameters for 1−1 and 2−1 single electrolytes, and those for θ_{ij} and Ψ_{ijk} reported by Pitzer et al. (*2, 3*). C^{ϕ}_{ca} and Ψ_{ijk} parameters were generally very small in magnitude, and in this work, all such parameters with unknown values were approximated to zero in eqs 3–8, but those with published known values were retained. In addition, B_{ca} and B'_{ca} terms for weak acids (H−HPh$^-$ and H−Ph^{2-} interactions) were assumed zero, following the procedure used by Pitzer and Silvester (*24*). Different sets of assumed values for the unknown Pitzer parameters were tried, and common to all the sets were the values for the known parameters ($\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$, and C^{ϕ}_{ca} for HCl and KCl, θ_{HK}, and $\Psi_{H,K,Cl}$), as given in Table 3. Representative sets (B–X) of assumed parameter values are given in Table 4. pH(H-cell) values calculated for each solution using the different sets of parameters were within ±0.004 unit of each other. They were therefore only very slightly affected by small changes in the corresponding ln $\gamma(Cl^-)$ values arising from the changes in values assumed for the unknown parameters in eq 4. However, pH(P,calcd) values, computed using eq 2 and Pitzer's system of equations in the procedure described above, show a much greater dependence on the values assumed for the unknown parameters. These observations are summarized in Figures 1–4. The best set of assigned parameter values was arbitrarily chosen as that set which yielded the lowest values for the goodness-of-fit parameters σ(pH) = [{pH(P,calcd) − pH(H-cell)}^{2}/n]$^{1/2}$ and σ(E) = [{E(H-cell,calcd) − E(H-cell,obsd)}^{2}/n]$^{1/2}$, where n is the total number of data points considered and E(H-cell,calcd) = $E°$(AgCl|Ag) + kpH(P) − log m_l − log $\gamma(Cl^-)$. n = 12 for the KCl solutions, and n = 6 for the NaCl solutions.

Table 4. Values of σ(pH) and $\sigma(E)$ Obtained for the KHPh + KCl Mixtures (Series A and B Combined) with Different Selected Sets of Assumed Pitzer Parameters Used with Eqs 3–11[a]

set	$\beta^{(0)}_{K,HPh}$/ (mol^{-1} kg)	$\beta^{(1)}_{K,HPh}$/ (mol^{-1} kg)	$\beta^{(0)}_{K,Ph}$/ (mol^{-1} kg)	$\beta^{(1)}_{K,Ph}$/ (mol^{-1} kg)	$\theta_{HPh,Ph}$/ (mol^{-1} kg)	$\theta_{HPh,Cl}$/ (mol^{-1} kg)	$\theta_{Ph,Cl}$/ (mol^{-1} kg)	σ(pH)	σ(E)/mV
B	0.02	0	0.43	0.7	0	0	0	0.136	8.1
C	0.2	0.33	0.43	0.68	0	0	0	0.127	7.5
D	0	0	0	0	0	0	0	0.126	7.5
E	0.15	0.2	0.2	1	0	0	0	0.0647	3.8
F	0.15	0.2	0.2	1	0	0	−0.05	0.0445	2.6
G	0.15	0.2	0.2	1	0	0.03	−0.25	0.0416	2.5
H	0.15	0.2	0.2	1	−0.01	−0.01	−0.2	0.0212	1.3
I	0.2	0.33	0.43	0.68	0	−0.06	−0.3	0.0124	0.73
J	0.2	0.4	0.43	0.6	0	0	−0.2875	0.0114	0.68
K	0.2	0.4	0.43	0.6	−0.03	0	−0.286	0.0113	0.67
L	0.2	0.33	0.43	0.68	−0.044	0.02	−0.308	0.0109	0.65
M	0.15	0.2	0.2	1	−0.003	−0.005	−0.16	0.0109	0.65
N	−0.075	0	0.12	0.7	0	0	0	0.0109	0.65
O	0.02	0	0.43	0.7	0.1	0.07	−0.306	0.0101	0.60
P	0.2	0.33	0.43	0.68	−0.044	0.02	−0.3	0.0100	0.60
Q	−0.05	0	0.1	0.7	0	0	0	0.0099	0.59
R	0.05	0	0.43	0.7	0.1	0.07	−0.303	0.0100	0.59
S	−0.09	−0.005	0.1	0.7	0	0	0	0.0098	0.59
T	−0.09	−0.005	0.12	0.65	0	0	0	0.0097	0.57
U	−0.075	0	0.12	0.7	0	0	−0.008	0.0096	0.57
V	−0.075	0	0.12	0.7	0.09	0.009	−0.008	0.0095	0.56
W	0.01	−0.03	0.12	0.7	0	0	0	0.0091	0.54
X	0.01	−0.03	0.12	0.7	0.1	0.01	−0.008	0.0085	0.50

[a] $\sigma(\text{pH}) = [\{\text{pH(P)} - \text{pH(H-cell)}\}^2/n\ ]^{1/2}$ and n = number of data points = 12. $\sigma(E) = [\{E(\text{H-cell, calcd}) - E(\text{H-cell,obsd})\}^2/n]^{1/2}$.

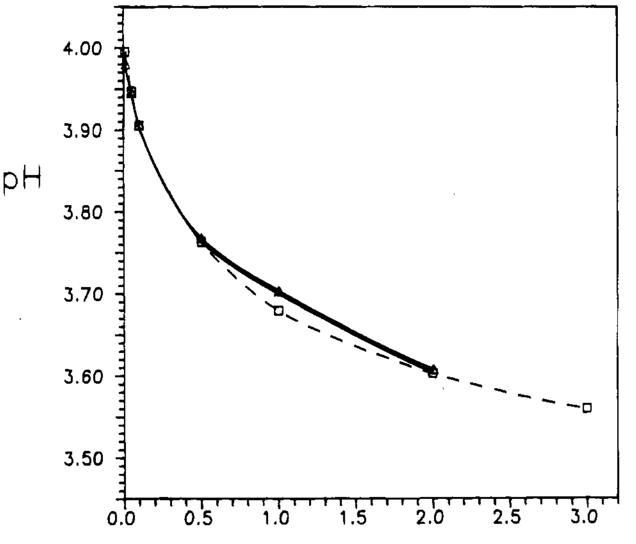

Figure 1. pH(H-cell) values obtained with the different sets of asssumed parameters plotted against the molality of KCl for series A: —, pH(H-cell, sets B–X); △, pH(H-cell, set X); □, pH(operational).

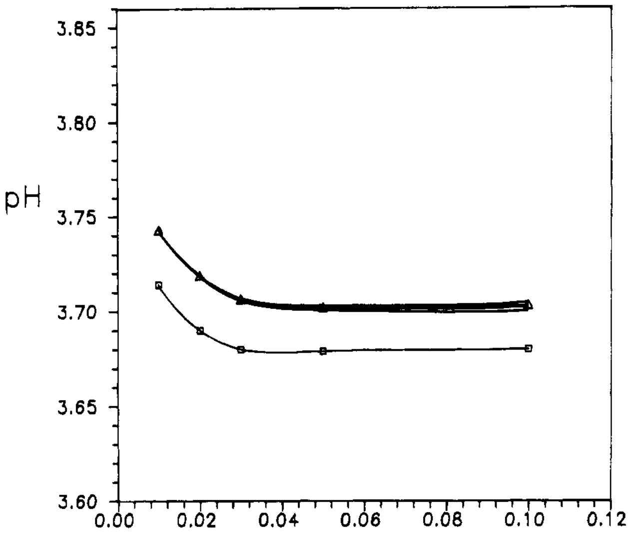

Figure 2. pH(H-cell) values obtained with the different sets of asssumed parameters plotted against the molality of KHPh for series B: △, set X; —, sets B–X; □, pH(operational).

The sets listed in Table 4 are representative of a much larger number of sets tried. Set X resulted in the lowest values for σ(pH) and $\sigma(E)$ for the KCl mixtures. An uncertainty of ±0.004 pH unit was assumed for all the pH(H-cell) values in Table 2, due more to uncertainties in the calculated values of log $\gamma(\text{Cl}^-)$ than experimental uncertainties in the emf measurements. The best result for $\sigma(E)$ at ±0.50 mV corresponded to a larger uncertainty of ±0.0085 in pH. However, this could be expected, largely because the many approximations in the calculation of pH(P) would lead to larger uncertainties in the calculated values of the theoretical emf, E(H-cell,calcd). pH(P) values reported in Table 2 were also based on set X, leading to a value of 4.003 for a pure solution of 0.05 mol kg^{-1} potassium hydrogen phthalate, which was close to the IUPAC pH Reference Value Standard of 4.005 at 298.15 K (*12*, *25*) although the latter was based on the Bates–Guggenheim convention. pH(P) values were also calculated for pure KHPh solutions (0.01–0.1 mol kg^{-1}) at 298.15 K, and there was good agreement with pH(operational) values obtained with combination pH glass electrodes (cf. Figure 6) for these dilute solutions. This observation supported Covington and Ferra's contention (*11*) that pH values for dilute aqueous buffer solutions based on the Pitzer treatment differ by less than 0.01 in pH from those based on the Bates–Guggenheim convention. Set X was then tentatively adopted to treat the data for the NaCl mixtures (C). Table 5 lists the addition parameters required for the NaCl mixtures. Set NE gave the best results of the many sets tried. The observations about how pH(H-cell) and pH(P) values varied with assumed parameter values were similar to those made for the KHPh + KCl solutions, series A and B. $\sigma(E)$ = ±0.3 mV for series C with assumed sets X and NE, and σ(pH) = ±0.005.

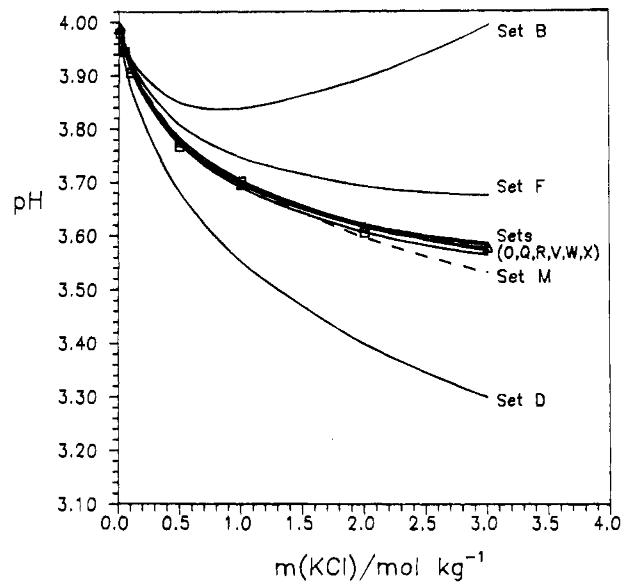

Figure 3. pH(P) values for the different sets of assumed parameters plotted against the molality of KCl for series A: △, pH(P, set X); □, pH(H-cell, set X).

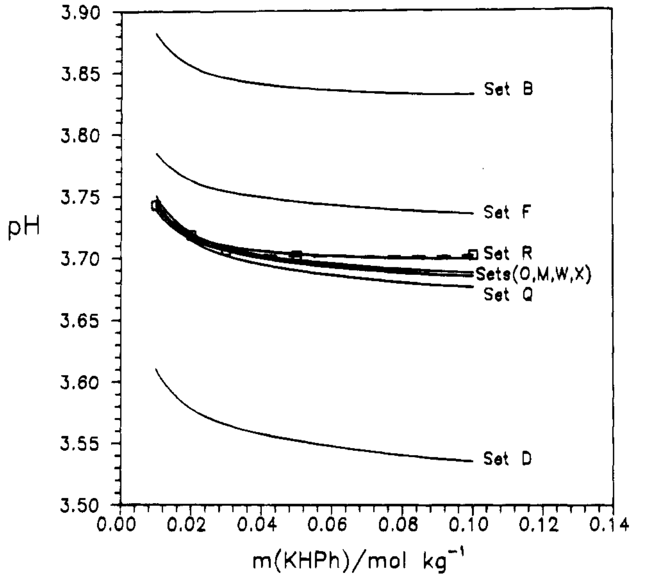

Figure 4. pH(P) values for the different sets of assumed parameters plotted against the molality of KHPh for series B: □, pH(H-cell, set X).

Table 5. Values of σ(pH) and $\sigma(E)$ Obtained for KHPh + NaCl Mixtures (Series C) with Different Selected Sets of Assumed Pitzer Parameters Used with Eqs 3−11, Together with Set X Parameters Given in Table 4[a]

set	$\beta^{(0)}_{Na,HPh}$/ (mol^{-1} kg)	$\beta^{(1)}_{Na,HPh}$/ (mol^{-1} kg)	$\beta^{(0)}_{Na,Ph}$/ (mol^{-1} kg)	$\beta^{(1)}_{Na,Ph}$/ (mol^{-1} kg)	σ(pH)	σ(E)/ mV
NB	0	0	0	0	0.127	7.5
NC	0	0	0.40	−0.20	0.022	1.3
ND	0.1	−0.2	0.44	−0.485	0.0056	0.33
NE	0.01	0.50	0.44	−0.465	0.0050	0.30

[a] $\sigma(\mathrm{pH}) = [\{\mathrm{pH(P)} - \mathrm{pH(H\text{-}cell)}\}^2/n]^{1/2}$ and n = number of data points = 6. $\sigma(E) = [\{E(\mathrm{H\text{-}cell,\ calcd}) - E(\mathrm{H\text{-}cell,obsd})\}^2/n]^{1/2}$.

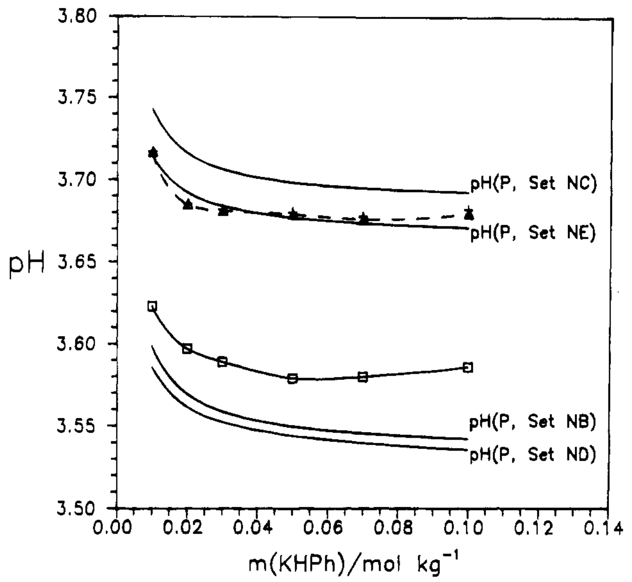

Figure 5. Comparison of plots of pH(P), pH(H-cell), and pH(operational) values for series C solutions, KHPh (m) + NaCl (1 mol kg^{-1}) at 298.15 K: +, pH(H-cell, set NB); △, pH(H-cell, set NE); ○, pH(H-cell, set ND); □, pH(operational).

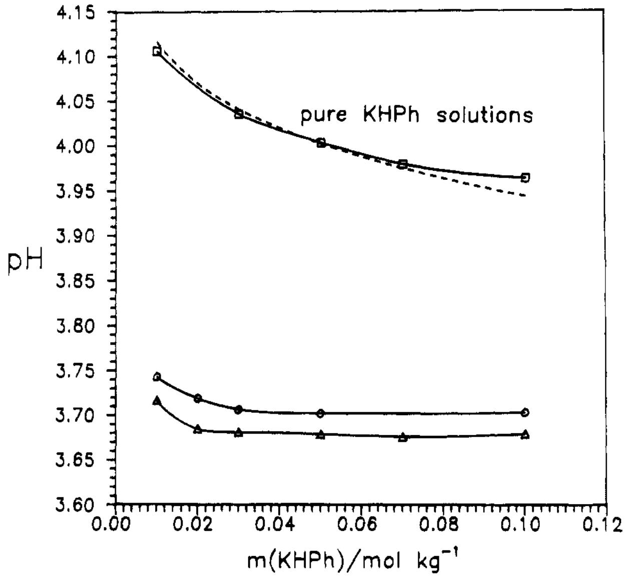

Figure 6. pH versus m(KHPh) plots for pure KHPh solutions and those containing 1 mol kg^{-1} KCl, or NaCl, at 298.15 K: □, pH(operational); △, pH(H-cell) in NaCl solutions; ○, pH(H-cell) in KCl solutions; - - -, pH(P), calculated with set X parameters.

Measured pH(operational) values were about 0.02−0.03 unit lower than the corresponding pH(H-cell) values for series B solutions (cf. Figure 2) containing 1 mol kg^{-1} KCl and could largely be attributed to residual liquid junction potential differences on the order of 1.2−1.8 mV, arising from the use of the combination pH glass electrode in the usual conventional manner, if the difference in conventions (Pitzer versus B-G) involved was not a significant factor. They were about 0.09−0.10 unit lower than the corresponding pH(H-cell) values for series C solutions (cf. Figure 5) containing 1 mol kg^{-1} NaCl, attributable to residual liquid junction potential differences of about 5.3−5.9 mV. In the presence of 1 mol kg^{-1} KCl, the pH(H-cell) of solutions containing KHPh in the molality range 0.03−0.1 mol kg^{-1} remained constant at 3.704 ± 0.004, and in the presence of 1 mol kg^{-1} NaCl, the pH remained constant to within ±0.004 of the mean pH(H-cell) value of 3.680 over the molality range 0.02− 0.1 mol kg^{-1} KHPh.

It was concluded that adding 1 mol kg^{-1} KCl, or NaCl, to a pure KHPh solution lowered its pH by about 0.3−0.4 unit, depending on the molality of KHPh. The solution mixtures containing NaCl were slightly lower in pH, generally by about 0.02 unit, than the corresponding solution mixtures containing 1 mol kg^{-1} KCl. In Figure 7, the calculated values of −log $m(\mathrm{H}^+)$ were plotted against

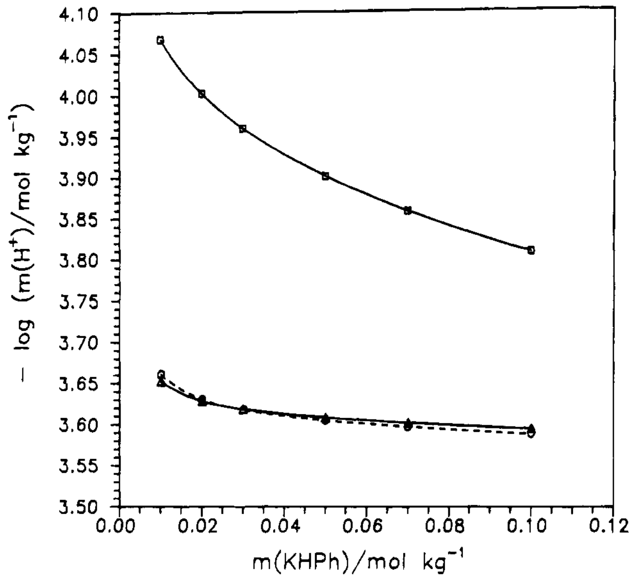

Figure 7. $-\log m(H^+)$ versus m(KHPh) for pure KHPh solutions and those containing 1 mol kg^{-1} KCl, or NaCl, at 298.15 K: □, pure KHPh solutions; ○, in KCl solutions; △, in NaCl solutions.

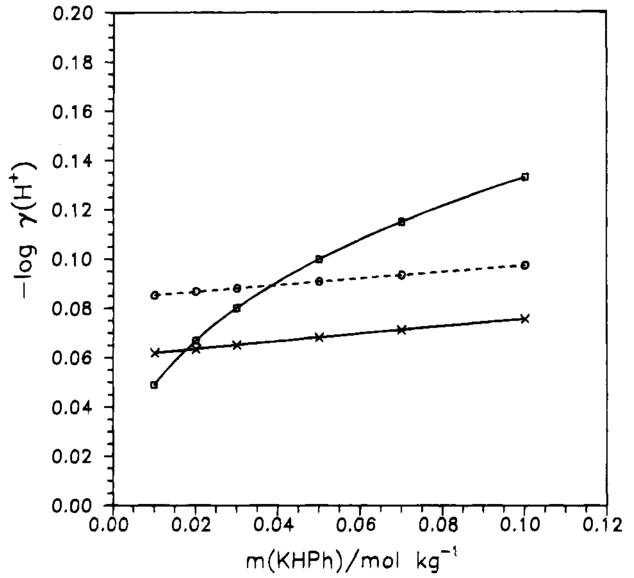

Figure 8. $-\log \gamma(H^+)$ versus m(KHPh) for pure KHPh solutions and those containing 1 mol kg^{-1} KCl, or NaCl, at 298.15 K: □, pure KHPh solutions; ○, in KCl solutions; ×, in NaCl solutions.

the molality of KHPh for pure solutions, for the solutions containing 1 mol kg^{-1} KCl and those containing 1 mol kg^{-1} NaCl, and in Figure 8 calculated values of $-\log \gamma(H^+)$ were plotted. These plots indicated that the lower pH values obtained for the KHPh solutions containing the added salts were largely due to the increases in hydrogen ion molalities in the presence of the salts. At a fixed KHPh molality, there was little difference in molality $m(H^+)$ between the solution containing KCl and that containing NaCl, certainly less than 0.01 in log $m(H^+)$ values. But there was a relatively constant difference of about 0.02 unit in $-\log \gamma(H^+)$ values, lower for NaCl solutions than for KCl solutions, which was the main cause of the slightly lower pH values observed for the former. The Pitzer system of equations for single-ion activity coefficients is sufficiently self-consistent and potentially useful in the estimation of pH for solutions of known composition over a wide range of ionic strengths, thus its advantage over the Bates–Guggenheim convention which is limited to low ionic strengths only. The main problem is the lack of precise experimental data for the calculation of the Pitzer parameters, especially for the buffer substances used in the preparation of primary pH standards over a sufficiently wide range of temperatures.

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