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Equations for the Calculation of the pH of Buffer Solutions Containing Potassium Hydrogen Phthalate, Dipotassium Phthalate, and Potassium Chloride at 298.15 K

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Published experimental thermodynamic data at 298.15 K for aqueous mixtures of H_2Ph, KHPh, and KCl, of KHPh, K_2Ph, and KCl, and of KHPh and KCl, where H_2Ph means phthalic acid, KHPh potassium hydrogen phthalate, and K_2Ph dipotassium phthalate, were used to test the methods for calculation of the pH values of phthalate buffer solutions. Equations for ionic activity coefficients are used in these methods. It is shown that all data used, up to an ionic strength of about 0.5 mol kg^{-1}, can be predicted almost within experimental error by two methods. In one of these methods, equations of the modified Guggenheim type are used for ionic activity coefficients, and in the other equations of the Pitzer type are used. Several sets of phthalate buffer solutions are suggested in the pH range 3.8−5.3, e.g., for calibration solutions for glass electrode cells or for constant-pH reaction media where the pH is known. In the recommended sets, the pH values of the buffer solutions have been calculated by the Guggenheim method, and the pH predictions of the Pitzer method agree with those in most cases within 0.01 at least up to ionic strengths of about 0.15 mol kg^{-1}. The recommended pH = 4.005 of the standard reference solution (0.05 mol kg^{-1} KHPh solution) agrees closely with the value suggested in the present study (4.003) for this solution.

Introduction

A 0.05 mol kg^{-1} solution of potassium hydrogen phthalate (KHPh) has for a long time been used as one of the main standard solutions of pH measurements since the pioneering studies of Clark and Lubs (1916), Hitchcock and Taylor (1937), and MacInnes *et al.* (1938). The pH value assigned to this buffer in the early studies was based on electromotive force (emf) measurements on cells containing a liquid junction. Because of the theoretical difficulties associated with the liquid junction in these cells, NIST (NBS at that time) preferred to define the pH scale by means of measurements on cells without a liquid junction. The pH value of the 0.05 mol kg^{-1} KHPh solution (i.e., at 298.15 K, pH = 4.008) was one of the seven reference points that fix the pH scale of the year of 1962, at each temperature at intervals of 5 K from 273.15 to 368.15 K, recommended by NBS [see Bates (1962)]. In the determination of these reference points, the convention of Bates and Guggenheim (1960) was uniformly used for the activity coefficients of chloride ions. For the determination of the pH values for the 0.05 mol kg^{-1} KHPh solution and for other phthalate solutions, Hamer and co-workers made a large number of measurements using Harned cells in solutions of KHPh and KCl (Hamer and Acree, 1944; Hamer *et al.*, 1946), of KHPh, K_2Ph (dipotassium phthalate), and KCl (Hamer and Acree, 1945) and of H_2Ph (phthalic acid), KHPh, and KCl (Hamer *et al.*, 1945) at temperatures from 273.15 to 333.15 K. Later, Hetzer *et al.* (1977) based the determination of the pH values for the 0.05 mol kg^{-1} KHPh solution on new data measured by Harned cells in solutions of KHPh and KCl, and by using the Bates−Guggenheim convention (1960) they obtained at 298.15 K pH = 4.007 for this solution. In 1985, IUPAC [see Covington *et al.* (1985)] recommended the pH values of only this solution as the reference value pH standards [pH(RVS)] at different temperatures from 273.15 to 368.15 K. According to these recommendations, based mainly on the critical evaluations of Bütikofer and Covington (1979), at 298.15 K pH(RVS) = 4.005.

In order to calculate the pH of a solution from the composition variables of the solution, ionic activity coefficients are needed. These quantities are, unfortunately, not accessible by purely thermodynamic methods. Nevertheless, it is possible to suggest equations for them, and these equations can be tested by means of the existing electrolyte data and by means of the few pH standards that fix the pH scale. It should be emphasized, again, that these equations are always hypothetical because there is no direct thermodynamic way to test them. They are, however, useful in dilute electrolyte solutions where the specific interactions between ions are less pronounced, but they become gradually less useful as the concentrations increase. The existing pH scale could not be defined without an equation of this kind, i.e., without the Bates−Guggenheim convention. In the recent literature, at least three such studies are available where equations of this kind have been used to predict the pH values of the standard buffer solutions of the scale: Lito *et al.* (1990) employed a simple equation of the Bates−Guggenheim type for all ions in the calculation of the pH values of the citrate, phthalate, acetate, carbonate, and two phosphate buffers. Covington and Ferra (1994) presented equations based on the Pitzer approach to electrolyte solutions for ions for the calculation of the pH values of the two phosphate buffers and the carbonate buffer, and finally Chan *et al.* (1995) also gave Pitzer equations for aqueous mixtures of potassium hydrogen phthalate and sodium or potassium chloride. The Pitzer parameters of the last-mentioned paper are also further tested below.

Similar hypothetical equations as in these three studies are used in the present study. Two methods are recommended here for the calculation of the pH of phthalate buffer solutions at 298.15 K, and these methods are tested with all reliable emf data found in the literature involving

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the first and second dissociations of phthalic acid. In one of these an equation of the modified Guggenheim type is used for ionic activity coefficients. In previous communications, an activity coefficient model similar to that of this method has been used in weak acid solutions (Partanen *et al.*, 1995a−c). In the other method, the simplified Pitzer equations [see, e.g., Pitzer and Silvester (1976)] are used for the ionic activity coefficients. It is shown below that both of these methods predict well the existing emf data up to ionic strengths of about 0.5 mol kg^{-1}. In addition, it can be shown that these two methods predict almost identical pH values for phthalate buffer solutions of various compositions. Also the conventional pH value of the phthalate buffer recommended by IUPAC can be predicted accurately by these two models. Therefore it is reasonable to suggest the pH predictions of these methods as reference values for such phthalate buffers for which experimental thermodynamic data are available. Values are tabulated for pH predicted by the Guggenheim and Pitzer methods at rounded ionic strengths for several phthalate buffer solutions containing KHPh and possibly also K_2Ph and/or KCl.

Results of Calculations

Equations for Ionic Activity Coefficients. In the modified Guggenheim method, the following equations were used for the activity coefficients on the molality scale (γ) of ions existing in the phthalate solutions studied

$$\ln \gamma_{\mathrm{H}} = -\alpha(I_{\mathrm{m}})^{1/2}/[1 + b_{\mathrm{G}}(I_{\mathrm{m}})^{1/2}] + m_{\mathrm{Cl}}\beta_{\mathrm{G,HCl}}/(m^0) \tag{1}$$

$$\ln \gamma_{\mathrm{Cl}} = -\alpha(I_{\mathrm{m}})^{1/2}/[1 + b_{\mathrm{G}}(I_{\mathrm{m}})^{1/2}] + m_{\mathrm{H}}\beta_{\mathrm{G,HCl}}/(m^0) + m_{\mathrm{K}}\beta_{\mathrm{G,KCl}}/(m^0) + m_{\mathrm{HPh}}\Theta_{\mathrm{G,ClHPh}}/(m^0) + m_{\mathrm{Ph}}\Theta_{\mathrm{G,ClPh}}/(m^0) \tag{2}$$

$$\ln \gamma_{\mathrm{HPh}} = -\alpha(I_{\mathrm{m}})^{1/2}/[1 + b_{\mathrm{G}}(I_{\mathrm{m}})^{1/2}] + m_{\mathrm{K}}\beta_{\mathrm{G,KHPh}}/(m^0) + m_{\mathrm{Cl}}\Theta_{\mathrm{G,ClHPh}}/(m^0) + m_{\mathrm{Ph}}\Theta_{\mathrm{G,HPhPh}}/(m^0) \tag{3}$$

$$\ln \gamma_{\mathrm{Ph}} = -4\alpha(I_{\mathrm{m}})^{1/2}/[1 + b_{\mathrm{G}}(I_{\mathrm{m}})^{1/2}] + m_{\mathrm{K}}\beta_{\mathrm{G,KPh}}/(m^0) + m_{\mathrm{Cl}}\Theta_{\mathrm{G,ClPh}}/(m^0) + m_{\mathrm{HPh}}\Theta_{\mathrm{G,HPhPh}}/(m^0) \tag{4}$$

where $m^0 = 1$ mol kg^{-1}, $\alpha = 1.1744$ (mol kg^{-1})$^{-1/2}$ (Archer and Wang, 1990), m is the molality, I_{m} is the ionic strength on the molality scale, and the following ion abbreviations are used: H = H$^+$, Cl = Cl$^-$, K = K$^+$, HPh = HPh$^-$ (hydrogen phthalate ion), and Ph = Ph^{2-} (phthalate ion). b_{G} is a parameter associated with the ion-size parameter a^* by the equation $b_{\mathrm{G}} = \beta a^*$ where $\beta = 3.245$ (mol kg^{-1})$^{-1/2}$ nm^{-1}. In the present calculations a value of $b_{\mathrm{G}} = 1.25$ (mol kg^{-1})$^{-1/2}$ was used for all ions existing in phthalate solutions, and this value has been determined for HCl solutions in the previous papers (Partanen 1989, 1991). In the original Guggenheim method a value of $b_{\mathrm{G}} = 1.0$ (mol kg^{-1})$^{-!/2}$ was used (Guggenheim and Turgeon, 1955; Lewis *et al.*, 1961). The β_{G} parameters in eqs 1−4 are interaction parameters between ions oppositely charged, and the Θ_{G} parameters are interaction parameters between ions alike charged. In the original Guggenheim method the interactions between pairs of anions (or pairs of cations) were omitted (Guggenheim and Turgeon, 1955). In the present study, it was observed that good fits cannot be obtained by the Guggenheim method in phthalate solutions without the parameters. Details of the estimation of the β_{G} and Θ_{G} parameters and the resulting values are given below.

According to the convention of Bates and Guggenheim (1960), the activity coefficients of chloride ions can be calculated in buffer solutions where I_{m} is smaller than 0.1 mol kg^{-1} by the following equation:

$$\ln \gamma_{\mathrm{Cl}} = -\alpha(I_{\mathrm{m}})^{1/2}/[1 + 1.5(I_{\mathrm{m}}/m^0)^{1/2}] \tag{5}$$

In the Pitzer model, the following equations can be presented for activity coefficients of ions in dilute aqueous mixtures of H_2Ph, KHPh, K_2Ph, and KCl at 298.15 K [see, e.g., Pitzer and Silvester (1976)]

$$\ln \gamma_{\mathrm{H}} = f^{\gamma} + 2m_{\mathrm{Cl}}B_{\mathrm{HCl}} + 2m_{\mathrm{K}}\Theta_{\mathrm{H,K}}/(m^0) + f(B') \tag{6}$$

$$\ln \gamma_{\mathrm{Cl}} = f^{\gamma} + 2m_{\mathrm{K}}B_{\mathrm{KCl}} + 2m_{\mathrm{H}}B_{\mathrm{HCl}} + 2m_{\mathrm{HPh}}\Theta_{\mathrm{Cl,HPh}}/(m^0) + 2m_{\mathrm{Ph}}\Theta_{\mathrm{Cl,Ph}}/(m^0) + f(B') \tag{7}$$

$$\ln \gamma_{\mathrm{HPh}} = f^{\gamma} + 2m_{\mathrm{K}}B_{\mathrm{KHPh}} + 2m_{\mathrm{Cl}}\Theta_{\mathrm{Cl,HPh}}/(m^0) + 2m_{\mathrm{Ph}}\Theta_{\mathrm{HPh,Ph}}/(m^0) + f(B') \tag{8}$$

$$\ln \gamma_{\mathrm{Ph}} = 4f^{\gamma} + 2m_{\mathrm{K}}B_{\mathrm{KPh}} + 2m_{\mathrm{Cl}}\Theta_{\mathrm{Cl,Ph}}/(m^0) + 2m_{\mathrm{HPh}}\Theta_{\mathrm{HPh,Ph}}/(m^0) + 4f(B') \tag{9}$$

where

$$f(B') = m_{\mathrm{K}}m_{\mathrm{Cl}}B'_{\mathrm{KCl}} + m_{\mathrm{H}}m_{\mathrm{Cl}}B'_{\mathrm{HCl}} + m_{\mathrm{K}}m_{\mathrm{HPh}}B'_{\mathrm{KHPh}} + m_{\mathrm{K}}m_{\mathrm{Ph}}B'_{\mathrm{KPh}} \tag{10}$$

The following symbols have been used in eqs 6−10

$$f^{\gamma} = -\alpha_{\mathrm{P}}\{(I_{\mathrm{m}})^{1/2}/[1 + b_{\mathrm{P}}(I_{\mathrm{m}})^{1/2}] + (2/b_{\mathrm{P}})\ln[1 + b_{\mathrm{P}}(I_{\mathrm{m}})^{1/2}]\} \tag{11}$$

$$B_{\mathrm{MX}} = \beta^0_{\mathrm{MX}}/(m^0) + \beta^1_{\mathrm{MX}}f_2 \tag{12}$$

$$B'_{\mathrm{MX}} = \beta^1_{\mathrm{MX}}f_3 \tag{13}$$

$$f_2 = [1/(2I_{\mathrm{m}})]\{1 - [1 + 2(I_{\mathrm{m}}/m^0)^{1/2}]\exp[-2(I_{\mathrm{m}}/m^0)^{1/2}]\} \tag{14}$$

$$f_3 = [1/(2I^2_{\mathrm{m}})]\{-1 + [1 + 2(I_{\mathrm{m}}/m^0)^{1/2} + 2(I_{\mathrm{m}}/m^0)] \times \exp[-2(I_{\mathrm{m}}/m^0)^{1/2}]\} \tag{15}$$

where M refers to a cation and X to an anion. The general parameters in eq 11 are the following: $\alpha_{\mathrm{P}} = 0.3915$ (mol kg^{-1})$^{-1/2}$ and $b_{\mathrm{P}} = 1.2$ (mol kg^{-1})$^{-1/2}$. Details of the present estimation of Pitzer parameters and the resulting values are given below.

Determination of the Thermodynamic Dissociation Constants for Phthalic Acid. The first and second dissociation reactions of phthalic acid are the following:

$$\mathrm{H_2Ph} \rightleftarrows \mathrm{H^+} + \mathrm{HPh^-} \tag{16}$$

$$\mathrm{HPh^-} \rightleftarrows \mathrm{H^+} + \mathrm{Ph^{2-}} \tag{17}$$

The thermodynamic dissociation constants ($K_{\mathrm{a,1}}$ and $K_{\mathrm{a,2}}$) for these chemical equilibria are given by

$$K_{\mathrm{a,1}} = (\gamma_{\mathrm{H}}\gamma_{\mathrm{HPh}}/\gamma_{\mathrm{H_2Ph}})K_{\mathrm{m,1}} \tag{18}$$

$$K_{\mathrm{a,2}} = (\gamma_{\mathrm{H}}\gamma_{\mathrm{Ph}}/\gamma_{\mathrm{HPh}})K_{\mathrm{m,2}} \tag{19}$$

where it is assumed that $\gamma_{\mathrm{H_2Ph}} = 1$ and the stoichiometric dissociation constants $K_{\mathrm{m,1}}$ and $K_{\mathrm{m,2}}$ are defined by

$$K_{\mathrm{m,1}} = m_{\mathrm{H}}m_{\mathrm{HPh}}/(m_{\mathrm{H_2Ph}}m^0) \tag{20}$$

$$K_{\mathrm{m,2}} = m_{\mathrm{H}}m_{\mathrm{Ph}}/(m_{\mathrm{HPh}}m^0) \tag{21}$$

Table 1. List of the Sets Measured on Cell 22 and Used in the Tests of Activity Coefficient Equations

symbol[a]	N[b]	(m_2/m^0)[f]	(m_1/m_2)	(m_3/m_2)	(m_4/m^0)[f]	(E^0/V)[j]
HPA45I	11	0.002−0.012	1.5	0	m_2/m^0	0.222 50
HPA45II	10	0.001−0.009	2	0	m_2/m^0	0.222 50
HPA45III	5	0.018	1	0	0.005−0.018	0.222 50
HPA45IV	5	0.009	2	0	0.003−0.05	0.222 50
HPA45V	9[c]	0.002−0.006	1.5	0	$1.5m_2/m^0$	0.222 50
HA45A	20	0.001−0.108	0	1.0057	$1.0014m_2/m^0$	0.222 24[k]
HA45B	18	0.0005−0.072	0	1.5070	$1.0035m_2/m^0$	0.222 50
HA45C	10[c]	0.003−0.055	0	2.0005	$1.0006m_2/m^0$	0.222 50
HA45D	6[c]	0.014−0.054	0	2.0223	$0.1858m_2/m^0$	0.222 50
HA45E-G	5[c]	0.053−0.108	0	1.0074	*h*	0.222 50
HA45H-K	8	0.025−0.072	0	*g*	*i*	0.222 50
HA44	27	0.05	0	0	0.001−0.05	0.222 50
HPA46	13	0.05	0	0	0.002−0.05	0.222 50
BC79A	18[d]	0.05	0	0	0.01−0.035	0.222 18[k]
BC79B	5[e]	0.05	0	0	0.01−0.03	0.222 57[k]
CEE95A	5	0.05	0	0	0.01−2	0.222 50[l]
CEE95B	5	0.01−0.1	0	0	1	0.222 50[l]

[a] See reference list; e.g., the symbol HPA45 means Hamer, Pinching and Acree, 1945. [b] Number of determinations. [c] Points V1, C1, D4, and G2 (see the original papers) were omitted. [d] Points ($m_4 = 0.020\ 141m^0$, $E = 0.566\ 88$ V), (0.024 749, 0.561 38) and (0.030 167, 0.555 38) were omitted. [e] Results of a set where freshly remade Ag−AgCl electrodes were used (see Table 4 in the original paper). [f] $m^0 = 1$ mol kg^{-1}. [g] In sets H−J (six points) m_3/m_2 is 1.5139 and in set K (two points) 2.0223. [h] In set E (two points) m_4/m_2 is 0.6479, in set F (two points) 0.2777, and in set G (one point) 0.092 57. [i] In set H (two points) m_4/m_2 is 0.6956, in set I (two points) 0.4143, in set J (two points) 0.1392, and in set K (two points) 0.5575. [j] Standard emf given by Harned and Ehlers (1932), see text. [k] Adjusted value of E^0 for the Guggenheim method. It was determined by requiring that sum of all errors in the set considered is zero. [l] See Chan *et al.* (1995).

Emf's of galvanic cells of the following general type

$$\mathrm{Pt(s)\quad or}\quad \mathrm{Pd(s)|H_2(}g, f = 101.325\ \mathrm{kPa)|H_2Ph(aq,}m_1\mathrm{), KHPh(aq,}m_2\mathrm{), K_2Ph(aq,}m_3\mathrm{), KCl(aq,}m_4\mathrm{)|AgCl(s)|Ag(s)} \quad (22)$$

where f is the fugacity were used to estimate new K_a values for phthalic acid and new parameters for the activity coefficient equations and to test these equations. Details of the data measured by cells of this type and used here are given in Table 1. The electromotive force (E) of each point in the sets of Table 1 can be calculated by

$$E = E^0 - (RT/F)\ln[\gamma_H\gamma_{Cl}m_Hm_{Cl}/(m^0)^2] \quad (23)$$

where E^0 is the standard emf. The older emf results (up to 1949) were updated here by multiplying by 1.000 33. For the molality of protons in eq 23, the following polynomial of the third degree can be derived for the solutions of cell 22:

$$m_H^3 + (K_{m,1}m^0 + m_2 + 2m_3)m_H^2 + K_{m,1}m^0(K_{m,2}m^0 + m_3 - m_1)m_H - K_{m,1}K_{m,2}(m^0)^2(2m_1 + m_2) = 0 \quad (24)$$

Sets HPA45I, HPA45II, and HPA45V in Table 1 were used in the determination of $K_{a,1}$ for phthalic acid for the Guggenheim and Pitzer methods. For the extrapolations of this quantity, the following equation was derived from eqs 18, 23, and 2 and 3 (Guggenheim method) or 7 and 8 (Pitzer method):

$$E - E^0 + (RT/F)\ln[m_{Cl}m_{H_2Ph}/(m_{HPh}m^0)] = y_{X,1} = -(RT/F)\ln K_{a,1} + u_X(I_m) \quad (25)$$

where X refers to the Guggenheim method (X = G) or to the Pitzer method (X = P) and where u_X is an unknown function of the ionic strength and has the property that $\lim u_X = 0$ as I_m approaches zero. In the extrapolations using eq 25 it was assumed that $E^0 = 0.222\ 50$ V [see Hamer *et al.* (1945) and Harned and Ehlers (1932); the hydrogen silver−silver chloride cell data ($I_m < 0.1$ mol kg^{-1}) of Harned and Ehlers lead to this value within 0.000 02 V for E^0 by using either of these methods in the extrapolation]. The influence of the second dissociation of phthalic acid cannot be completely omitted from the determination of $K_{a,1}$ from sets HPA45I, HPA45II, and HPA45V. Because of the last term on the left-hand side, therefore, eq 25 does not apply without iterative calculations to this determination. The ratio m_{H_2Ph}/m_{HPh} in this term was determined iteratively using eqs 18, 19, 24, and 1, 3, and 4 (G) or 6, 8, and 9 (P). In these calculations, it was assumed that $K_{a,1} = 1.12 \times 10^{-3}$ (Hamer *et al.*, 1945) and $K_{a,2} = 3.91 \times 10^{-6}$ (Hamer and Acree, 1945) and that the β_G and Θ_G parameters in eqs 1, 3, and 4 are zero as well as the β^0, β^1, and Θ parameters in eqs 6, 8, and 9. When the points of these sets are drawn as suggested in eq 25, they lay strictly on a straight line in the case of both methods. From the intercept of the straight line with the $y_{X,1}$ axis, $K_{a,1}$ can be solved. The results are shown in Table 2. Afterward, some of the extrapolations of eq 25 were also carried out with the final values of the dissociation constants and the activity coefficient equation parameters, and the results do not significantly differ from those shown in Table 2. According to the results of this table, a value of $K_{a,1} = 1.123 \times 10^{-3}$ (p$K_{a,1}$ = 2.9496) can be used for both methods.

Table 2. Results of the Determination of the Thermodynamic Value of the First Dissociation Constant of Phthalic Acid at 298.15 K by Means of Equation 25 from the Electromotive Force Data of Hamer, Pinching, and Acree (1945)

set[a]	$10^3K_{a,1}^G$	$pK_{a,1}^G$	$\Delta(pK_{a,1}^G)$[b]	$10^3K_{a,1}^P$	$pK_{a,1}^P$	$\Delta(pK_{a,1}^P)$[b]
HPA45I	1.122	2.9499	0.0005	1.124	2.9492	0.0005
HPA45II	1.123	2.9497	0.0006	1.124	2.9492	0.0004
HPA45V	1.126	2.9486	0.0022	1.127	2.9479	0.0022

[a] See Table 1. [b] Probable error; given at a level of 0.95.

Sets HA45A, HA45B, and HA45C in Table 1 were used in the determination of $K_{a,2}$ for phthalic acid. For the extrapolation of this quantity for the Guggenheim method, the following equation was derived from eqs 2, 3, 4, 19, and 23:

$$E - E^0 + (RT/F)\ln[m_{Cl}m_{HPh}/(m_{Ph}m^0)] + (2RT/F) \times \alpha(I_m)^{1/2}/[1 + b_G(I_m)^{1/2}] = y_{G,2} = -(RT/F)\ln K_{a,2} + v_G(I_m) \quad (26)$$

For the Pitzer method the corresponding equation is

$$E - E^0 + (RT/F)\ln[m_{Cl}m_{HPh}/(m_{Ph}m^0)] - (2RT/F)f^{\gamma} = y_{P,2} = -(RT/F)\ln K_{a,2} + v_P(I_m) \quad (27)$$

These equations were used in the determination of $K_{a,2}$ in the same way as above eq 25 was used in the determination of $K_{a,1}$ and the functions v_G and v_P in these equations correspond to the functions u_G and u_P in that equation. The results of these determinations are collected in Table 3. In the determinations linear extrapolation was always used, and in this table is also included the number of points that could be taken into account in the extrapolation in each case. As shown in Table 3, $K_{a,2}$ cannot be determined as accurately as $K_{a,1}$ (see Table 2). According to the results of Table 3, a value of $K_{a,2} = 3.935 \times 10^{-6}$ (p$K_{a,2}$ = 5.405) is here suggested, and this value then belongs to the confidence intervals of the $K_{a,2}$ estimates determined from sets

Table 3. Results of the Determination of the Thermodynamic Value of the Second Dissociation Constant of Phthalic Acid at 298.15 K by Means of Equations 26 and 27 from the Electromotive Force Data of Hamer and Acree (1945)

set[a]	$10^6K^G_{a,2}$	$pK^G_{a,2}$	$\Delta(pK^G_{a,2})$[b]	(N^G)[c]	$10^6K^P_{a,2}$	$pK^P_{a,2}$	$\Delta(pK^P_{a,2})$[b]	(N^P)[c]
HA45A	3.968	5.4014	0.0007	18	3.953	5.4031	0.0011	15
HA45B	3.943	5.4041	0.0007	16	3.927	5.4059	0.0008	15
HA45C	3.934	5.4052	0.0009	10	3.901	5.409	0.002	5

[a] See Table 1. [b] Probable error; given at a level of 0.95. [c] Number of points included in the determination; the maximum I_m of the points included in the determination of the $K_{a,2}$ estimates of the Guggenheim method is 0.44 mol kg^{-1} and in those of the Pitzer method is 0.13 mol kg^{-1}.

Table 4. Interaction Parameters for Ionic Activity Coefficient Equations at 298.15 K

	H, Cl	K, Cl	K, HPh	K, Ph	Cl, HPh	Cl, Ph	HPh, Ph	H, K
(β_G)[a]	0.38	0.06	0.1	0.28				
(β^0)[b]	0.1775	0.04835	0.1	0.31				
(β^1)[b]	0.2945	0.2122	0	0.70				
$[\beta^0(\text{Chan})]$[c]	0.1775	0.04835	0.01	0.12				
$[\beta^1(\text{Chan})]$[c]	0.2945	0.2122	−0.03	0.70				
(Θ_G)[a]					0	−0.3	−0.3	
Θ[b]					0	−0.20	−0.25	0.005
$[\Theta(\text{Chan})]$[c]					0.01	−0.008	0.1	0.0074

[a] Guggenheim method (eqs 1−4). [b] Pitzer method of the present study (eqs 6−9). [c] Parameters suggested by Chan *et al.* (1995) for Pitzer method.

HA45B (Guggenheim and Pitzer method) and HA45C (Guggenheim method). In the determination of the $K_{a,2}$ estimates of this table it was again assumed that E^0 = 0.222 50 V. As can be seen in eqs 26 and 27, a different value of E^0 leads to a different $K_{a,2}$ value in these extrapolations. There can be variations of the order of 0.2 mV in the E^0 values of sets measured by cells of type 22 owing to the variation of the standard potential of silver−silver chloride electrodes (e.g., Bates and Macaskill, 1978). This fact can be the reason why the $K_{a,2}$ estimates in Table 3 do not agree within experimental error with each other. In the parameter estimation for the activity coefficient equations from data of cells of type 22, the problems associated with K_a and E^0 values can be overcome by adjusting the quantity $E^0 - (RT/F)\ln K_{a,x}$ where $x = 1$ or 2 (see, e.g., eqs 25 or 26). In the present study, absolute K_a values are needed in the calculation of pH, and the K_a values determined here are probably the most reliable ones that can be obtained from the existing data. Therefore, in this study $K_{a,1}$ and $K_{a,2}$ are fixed and E^0 is adjusted for each set used in the estimations (see below) to avoid the constant-systematic-error problems.

Estimation of Parameters for Guggenheim Method. The following parameter values for eqs 1−4 were taken from the literature: $b_G = 1.25\ (\text{mol kg}^{-1})^{-1/2}$, $\beta_{G,HCl} = 0.38$, and $\beta_{G,KCl} = 0.06$ (Partanen, 1989, 1991). Parameter $\beta_{G,KHPh}$ in eq 3 was estimated from sets HPA45I-V in Table 1 by means of the following equation derived similarly as eq 25:

$$E + (RT/F)\ln K_{a,1} + (RT/F)\ln[m_{Cl}m_{H_2Ph}/(m_{HPh}m^0)] + (RT/F)(\beta_{G,KCl}m_K + \beta_{G,HCl}m_H)/(m^0) = y_{G,3} = E^0 + (RT/F)\beta_{KHPh}m_K/(m^0) \quad (28)$$

This equation is approximative, but it is valid in dilute solutions of sets HPA45I-V. By means of linear regression analysis with the function of $y_{G,3} = y_{G,3}(m_K)$, a result $\beta_{G,KHPh} = 0.1$ was obtained.

Parameter $\beta_{G,KPh}$ in eq 4 was determined from set HA45A in Table 1 by regression analysis using equation

$$E + (RT/F)\ln K_{a,2} + (RT/F)\{\ln[m_{Cl}m_{HPh}/(m_{Ph}m^0)] + 2\alpha(I_m)^{1/2}/[1 + b_G(I_m)^{1/2}]\} + (RT/F)(\beta_{G,KCl}m_K + \beta_{G,HCl}m_H + \beta_{G,KHPh}m_K)/(m^0) + (RT/F)\Theta_{G,ClHPh}(m_{Cl} + m_{HPh})/(m^0) = y_{G,4} = E^0 + (RT/F)\,\beta_{G,KPh}m_K/(m^0) + (RT/F)\,\Theta_{G,ClPh}(m_{Cl} - m_{Ph})/(m^0) + (RT/F)\,\Theta_{G,HPhPh}(m_{HPh} - m_{Ph})/(m^0) \quad (29)$$

In this regression analysis it was additionally assumed that $\Theta_{G,ClHPh} = 0$. In all points of set HA45A, m_{Cl}, m_{HPh}, and m_{Ph} are approximately equal, and therefore $\beta_{G,KPh}$ can be obtained by linear regression analysis from a plot $y_{G,4}$ versus m_K. The result is $\beta_{G,KPh} = 0.28$. When $\beta_{G,KPh}$ has been determined, regression analysis by means of the functions

$$y_{G,4} - (RT/F)\,\beta_{G,KPh}m_K/(m^0) = y_{G,5} = E^0 + (RT/F)(\Theta_{G,ClPh} + \Theta_{G,HPhPh})(m_{Cl} - m_{Ph})/(m^0) \quad (30)$$

and

$$y_{G,5} - (RT/F)(\Theta_{G,ClPh} + \Theta_{G,HPhPh} - \Theta_{G,ClPh})(m_{HPh} - m_{Ph})/(m^0) = y_{G,6} = E^0 + (RT/F)\,\Theta_{G,ClPh}(m_{Cl} - m_{Ph})/(m^0) \quad (31)$$

gives from sets HA45B and HA45C (eq 30) and from sets CEE95A and CEE95B (eq 31) the following results: $\Theta_{G,HPhPh} = -0.3$ and $\Theta_{G,ClPh} = -0.3$. In the derivation of eq 30, the fact that m_{Cl} is almost equal to m_{HPh} in sets HA45B and HA45C has been taken into account. Regression analysis by means of this equation gave a quantity $\Theta_{G,HPhPh} + \Theta_{G,ClPh}$. In the use of eq 31, a few iterative calculations were needed. All parameters used in the calculations of the Guggenheim method are collected in Table 4.

Estimation of Parameters for Pitzer Method. All parameters used in the calculations of the Pitzer method are also collected in Table 4. The literature values for the β parameters of HCl and KCl are given by Pitzer and Mayorga (1973), and the literature value for $\Theta_{H,K}$ is given by Pitzer and Kim (1974). The parameter values determined and recommended by Chan *et al.* (1995) (denoted as the parameter set X in that paper) are also included in this table. The new parameter values for the Pitzer method were estimated in a similar way as those estimated above for the Guggenheim method. In these regression analysis, the following functions were used:

$$E + (RT/F)\ln K_{a,1} + (RT/F)\ln[m_{Cl}m_{H_2Ph}/(m_{HPh}m^0)] + (2RT/F)(B_{KCl}m_K + B_{HCl}m_H) - (2RT/F)\beta^1_{KHPh}f_2\,m_K = y_{P,3} = E^0 + (2RT/F)\beta^0_{KHPh}m_K/(m^0) \quad (32)$$

$$E + (RT/F)\ln K_{a,2} + (RT/F)\{\ln[m_{Cl}m_{HPh}/(m_{Ph}m^0)] - 2f' - 2f'(B)\} + (2RT/F)(B_{KCl}m_K + B_{HCl}m_H + B_{KHPh}m_K) - (2RT/F)\beta^1_{KPh}f_2m_K + (2RT/F)\Theta_{Cl,HPh}(m_{Cl} + m_{HPh})/(m^0) = y_{P,4} = E^0 + (2RT/F)\beta^0_{KPh}m_K/(m^0) + (2RT/F)[\Theta_{Cl,Ph}(m_{Cl} - m_{Ph})/(m^0) + \Theta_{HPh,Ph}(m_{HPh} - m_{Ph})/(m^0)] \quad (33)$$

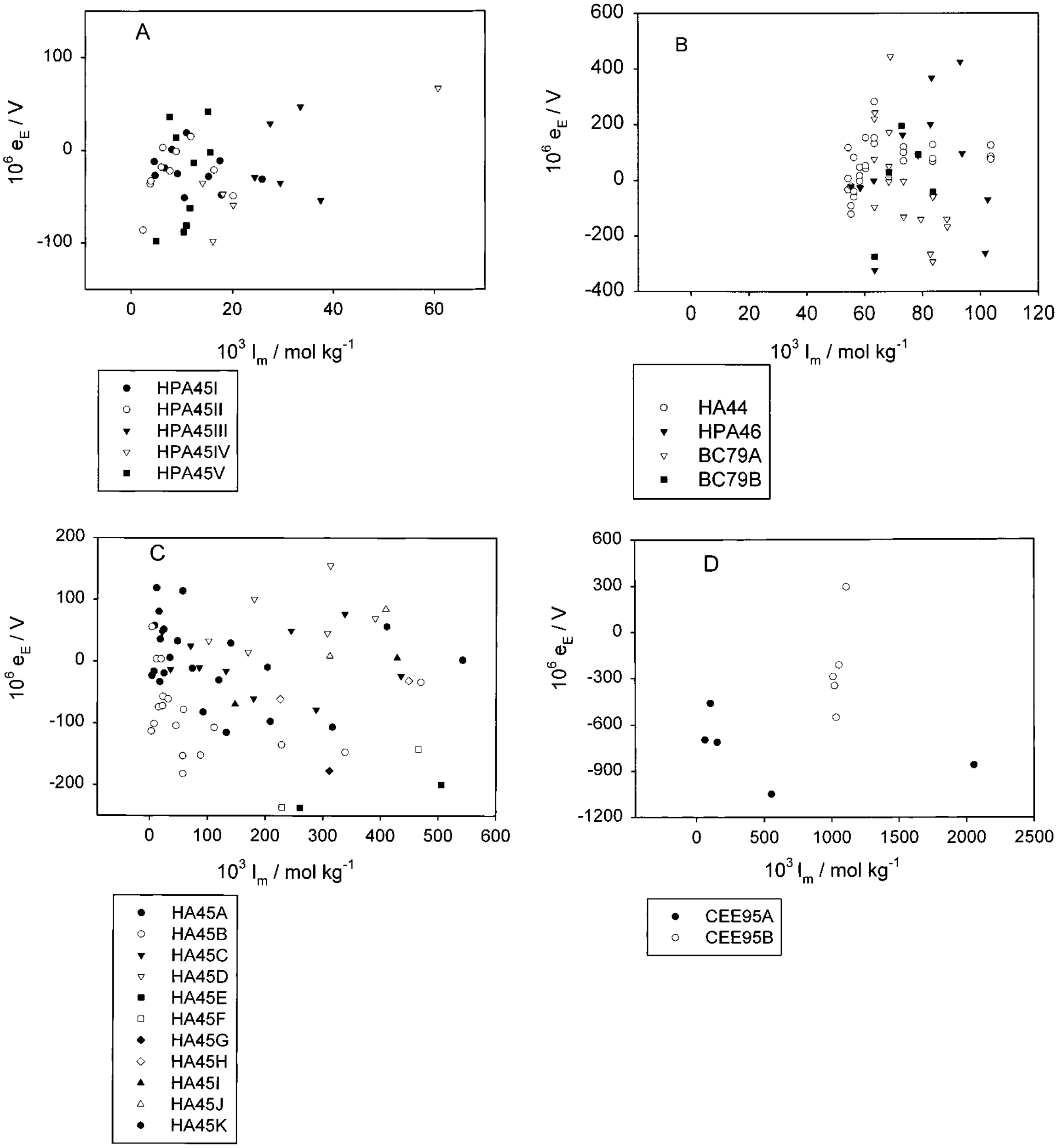

Figure 1. Difference, e_E in eq 36, between the observed emf values and those predicted by the Guggenheim method as a function of the ionic strength, I_m, in the sets measured by Hamer, Bütikofer, and Chan *et al.* on cell 22; see Table 1. The predicted values were calculated by using eqs 1–4 for activity coefficients and the E^0 values given in Table 1. The parameter values needed in the calculation are given in Table 4. The symbols of the different sets of data are given at the legends of the graphs (see also Table 1).

$$y_{P,4} - (2RT/F)\beta^0_{KPh}\, m_K/(m^0) = y_{P,5} = E^0 + (2RT/F)(\Theta_{Cl,Ph} + \Theta_{HPh,Ph})(m_{Cl} - m_{Ph})/(m^0) \quad (34)$$

$$y_{P,5} - (2RT/F)(\Theta_{Cl,Ph} + \Theta_{HPh,Ph} - \Theta_{Cl,Ph})(m_{HPh} - m_{Ph})/(m^0) = y_{P,6} = E^0 + (2RT/F)\,\Theta_{Cl,Ph}(m_{Cl} - m_{Ph})/(m^0) \quad (35)$$

By means of eq 32, a result $\beta^0_{KHPh} = 0.1$ was obtained from sets HPA45I-V. The fit of these sets was not, on the other hand, sensitive to parameter β^1_{KHPh}, and therefore this parameter cannot be determined from these sets. On the basis of the β^1 values for other organic salts (Pitzer and Mayorga, 1973), it is not clear what this value should be. Good results in the other calculations were obtained by assuming that $\beta^1_{KHPh} = 0$. Parameter values $\beta^0_{KPh} = 0.31$ and $\beta^1_{KPh} = 0.7$ were determined by means of eq 33 from set HA45A by assuming that $\Theta_{Cl,HPh} = 0$. Finally parameter values of $\Theta_{Cl,Ph} = -0.20$ and $\Theta_{HPh,Ph} = -0.25$ were determined by eq 34 from sets HA45B and HA45C and by eq 35 from sets CEE95A and CEE95B.

Tests of the Ionic Activity Coefficient Equations by Electrolyte Data. In the present tests, the data shown in Table 1 are predicted by means of the activity coefficient equations of the Guggenheim method (eqs 1–4) and the Pitzer method (eqs 6–9). The results are presented for each data set as error plots. These error plots are shown in four graphs of Figure 1 (Guggenheim method) and Figure 2 (Pitzer method). The error plots for the Pitzer method with the parameter values of Chan *et al.* are shown in two graphs of Figure 3. In Figures 1–3 the emf errors, defined by

$$e_E = E_{obs} - E_{pred} \quad (36)$$

are presented in each set as a function of the ionic strength of the solutions. E_{pred} for each point in the sets was iteratively calculated using eq 23, the ionic activity coefficient equations, and eqs 18, 19, and 24. The E^0 values used in the calculation of the errors of each sets are shown in Table 1. For some sets this value is adjusted; see discussion above.

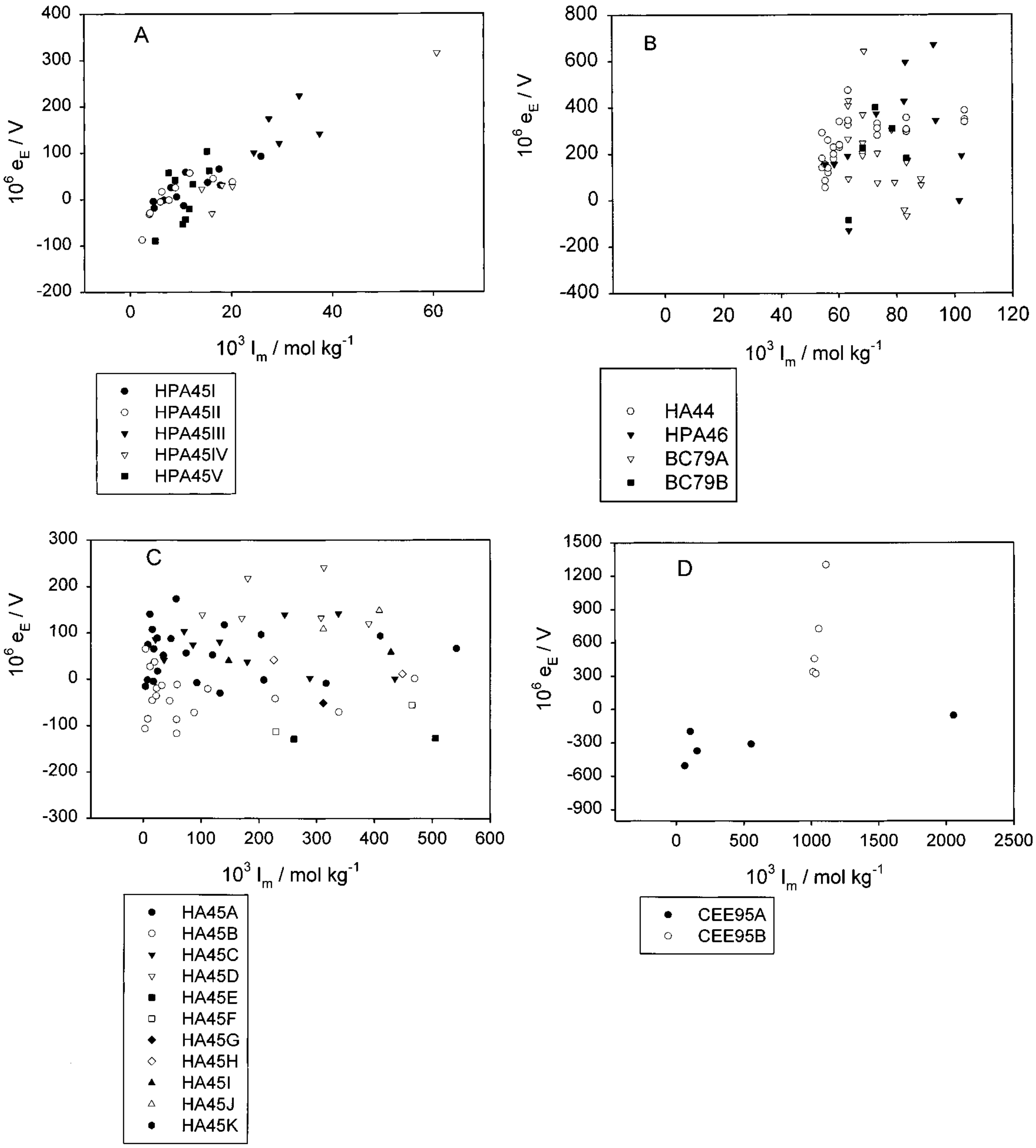

Figure 2. Difference, e_E in eq 36, between the observed emf values and those predicted by the Pitzer method with the new parameter values (see Table 4) as a function of the ionic strength, I_m, in the sets measured by Hamer, Bütikofer, and Chan *et al.* on cell 22; see Table 1. The predicted values were calculated by using eqs 6–9 for activity coefficients and the E^0 values given in Table 1. The symbols of the different sets of data are given at the legends of the graphs (see also Table 1).

Additionally, the Guggenheim and two Pitzer methods were tested with the data of Hetzer *et al.* (1977) measured by cells of type 22. In this set, $m_2 = 0.05$ mol kg^{-1}, $m_1 = m_3 = 0$, and replicate determinations were made at the three different molalities of KCl (m_4). The emf values of this set were predicted by means of the three methods tested, and the results are shown in Table 5.

Calculation of pH for Buffer Solutions. The pH, defined by

$$\mathrm{pH} = -\log(a_H) = -\log(\gamma_H m_H/m^0) \tag{37}$$

where a refers to the activity, can be iteratively calculated by means of the activity coefficient equations of the Guggenheim method (eqs 1–4) or Pitzer method (eqs 6–9) for a buffer solution containing H_2Ph (molality m_1), KHPh (m_2), K_2Ph (m_3), and KCl (m_4), using eqs 18, 19, and 24. Below, the pH calculated by the Guggenheim method and the difference between that and the pH obtained by the Pitzer method are presented at rounded ionic strengths for the following sets of buffer solutions: KHPh solution (Table 6), KHPh + KCl solution where m(KCl) = m(KHPh) (Table 7), KHPh + K_2Ph solution where $m(K_2Ph)$ = m(KHPh) (Table 8), and KHPh + K_2Ph + KCl solution where m(KCl) = $m(K_2Ph)$ = m(KHPh) (Table 9). In addition, the pH is given for the aqueous mixtures of KHPh and KCl at rounded molalities of KCl up to 0.5 mol kg^{-1} in the case where m(KHPh) = 0.05 mol kg^{-1} (Table 10) and at rounded molalities of KHPh up to 0.1 mol kg^{-1} in the case where m(KCl) = 1 mol kg^{-1} (Table 11). On the basis of the Guggenheim (or Pitzer) method it is possible as well to calculate useful pH values for many other phthalate buffers.

Discussion

According to Figure 1, the Guggenheim method proposed probably reproduces within experimental error the data presented in Table 1. Sets HA45D-K, HA44, HPA46, BC79A, and BC79B in this table were not used at all in the parameter estimation of the Guggenheim (or Pitzer)

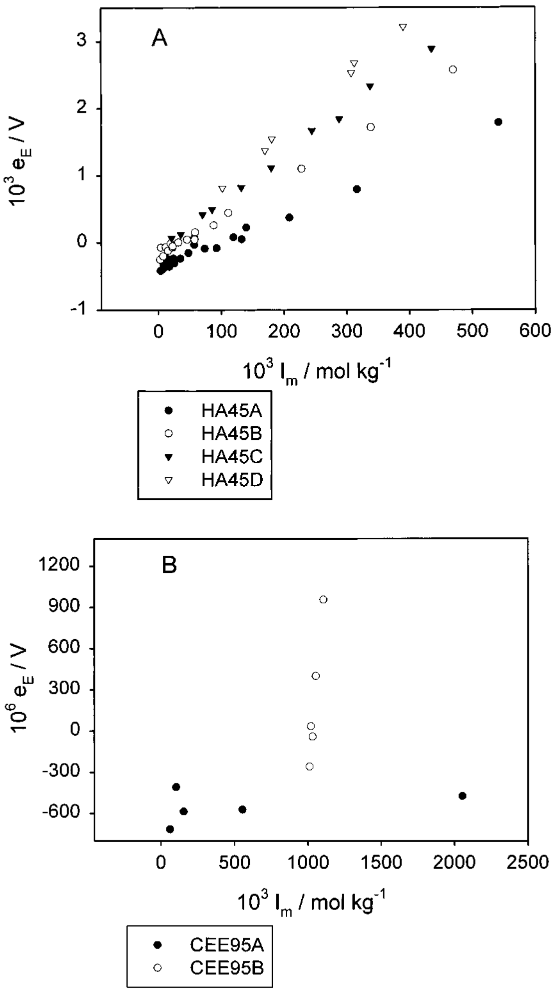

Figure 3. Difference, e_E in eq 36, between the observed emf values and those predicted by the Pitzer method with the parameter values given by Chan *et al.* (1995) (see Table 4), as a function of the ionic strength, I_m, in the sets measured by Hamer and Acree (1945) and Chan *et al.* on cell 22; see Table 1. The predicted values were calculated by using eqs 6−9 for activity coefficients and a value of $E^0 = 0.222\ 50$ V. The symbols of the different sets of data are given at the legends of the graphs (see also Table 1).

Table 5. Results of the Comparison of the Electromotive Forces Measured by Hetzer, Durst, Robinson, and Bates (1977) on Cell 22 ($m_2 = 0.05$ mol kg^{-1}, $m_1 = m_3 = 0$, and $E^0 = 0.222\ 44$ V) with Those Predicted by the Guggenheim and Pitzer Methods

m_4/(mol kg^{-1})	N^a	E_{obs}/V	(ΔE_{obs}/V)^b	(E_G/V)^c	(E_P/V)^d	[E_P(Chan)/V]^e
0.005	12	0.600 60	0.000 06	0.600 55	0.600 36	0.600 58
0.01	12	0.582 57	0.000 04	0.582 56	0.582 36	0.582 58
0.015	17	0.571 99	0.000 09	0.571 97	0.571 76	0.571 98

[a] Number of determinations. [b] Mean deviation from the mean value of E. [c] Calculated by the Guggenheim method. [d] Calculated by the present Pitzer method. [e] Calculated by the Pitzer parameters suggested by Chan *et al.* (1995); see Table 4.

method. As can be seen in Figure 2, the new Pitzer parameters also apply very well to the experimental data described in this table. All errors in the graphs of this figure are small despite the fact that a constant systematic error appears in the error plot of some sets in Table 1. These errors are most apparent in the sets shown in graph B (and also in the results of this method in Table 5), and there they result from a small real difference between the two methods used in predicting the experimental data. The Pitzer parameters presented by Chan *et al.* (1995) do apply well to their own data (see graph B in Figure 3) but not to those of Hamer and Acree (1945) (see graph A in this figure).

Table 6. pH Values at 298.15 K for the Buffer Solutions Which Contain Potassium Hydrogen Phthalate (KHPh)

(m_{KHPh}/m^0)^a	I_m/m^0	pH^c	(pH − pH$_p$)^d
0.009 33	0.01	4.120	0.001
0.01^b	0.010 71^b	4.116	0.001
0.018 73	0.02	4.074	0.002
0.02^b	0.021 35^b	4.069	0.002
0.028 11	0.03	4.046	0.003
0.03^b	0.032 01^b	4.041	0.003
0.037 48	0.04	4.025	0.003
0.046 84 (−0.000 01)	0.05	4.008	0.004
0.05^b	0.053 38 (+0.000 01)^b	4.003	0.004
0.056 19 (−0.000 01)	0.06	3.994	0.005
0.065 52 (−0.000 02)	0.07	3.981	0.005
0.074 85 (−0.000 02)	0.08	3.971	0.006
0.084 18 (−0.000 03)	0.09	3.961	0.006
0.093 49 (−0.000 04)	0.100	3.952	0.007
0.1^b	0.107 0 (+0.000 1)^b	3.946	0.007
0.140 0 (−0.000 1)	0.15	3.915	0.010

[a] Calculated by the Guggenheim method for the I_m given in the next column. The difference between the m_{KHPh} values calculated by the Guggenheim and Pitzer methods is given in parentheses when significant. $m^0 = 1$ mol kg^{-1}. [b] m_{KHPh} is fixed, and I_m is calculated by the Guggenheim method (see also footnote *a*). [c] Calculated by the Guggenheim method. [d] The difference between the pH values calculated by the Guggenheim and Pitzer methods.

Table 7. pH Values at 298.15 K for the Buffer Solutions Which Contain Potassium Hydrogen Phthalate (KHPh) and Potassium Chloride and in Which *m*(KCl) = *m*(KHPh)

(m_{KHPh}/m^0)^a	I_m/m^0	pH^b	(pH − pH$_P$)^c	$p(\gamma^G_{Cl})^d$	(Δ^P)^e	(Δ^{B-G})^f
0.004 80	0.01	4.148	0.001	0.045	0	0.001
0.009 64	0.02	4.090	0.001	0.061	−0.001	0.001
0.014 48	0.03	4.057	0.002	0.072	−0.001	0.002
0.019 31	0.04	4.034	0.003	0.081	−0.001	0.002
0.024 14	0.05	4.016	0.003	0.088	−0.001	0.003
0.028 97	0.06	4.000	0.004	0.094	−0.001	0.003
0.033 80	0.07	3.987	0.005	0.100	−0.001	0.003
0.038 62	0.08	3.976	0.005	0.105	−0.002	0.004
0.043 45	0.09	3.965	0.006	0.109	−0.002	0.004
0.048 27 (−0.000 01)	0.10	3.956	0.006	0.113	−0.002	0.004
0.072 35 (−0.000 02)	0.15	3.918	0.009	0.130	−0.003	
0.096 39 (−0.000 04)	0.20	3.890	0.011	0.142	−0.004	

[a] See footnote *a* in Table 6. [b] See footnote *c* in Table 6. [c] See footnote *d* in Table 6. [d] $p(\gamma_{Cl}) = -\log \gamma_{Cl}$ calculated by the Guggenheim method. [e] $\Delta^P = p(\gamma^G_{Cl}) - p(\gamma^P_{Cl})$ where γ^P_{Cl} was calculated by the Pitzer method; see also footnote *d*. [f] $\Delta^{B-G} = p(\gamma^G_{Cl}) - p(\gamma^{B-G}_{Cl})$ where γ^{B-G}_{Cl} was calculated by the Bates−Guggenheim equation (eq 5); see also footnote *d*.

Table 8. pH Values at 298.15 K for the Buffer Solutions Which Contain Potassium Hydrogen Phthalate (KHPh) and Potassium Phthalate (K_2 Ph) and in Which *m*(K_2Ph) = *m*(KHPh)

(m_{KHPh}/m^0)^a	I_m/m^0	pH^b	(pH − pH$_P$)^c
0.002 50	0.01	5.277	0.001
0.004 99	0.02	5.229	0.002
0.007 49	0.03	5.196	0.003
0.009 98	0.04	5.170	0.004
0.012 48	0.05	5.148	0.005
0.014 98	0.06	5.129	0.005
0.017 47	0.07	5.112	0.006
0.019 97	0.08	5.098	0.007
0.022 46	0.09	5.084	0.007
0.024 96	0.10	5.072	0.008
0.037 44	0.15	5.023	0.011
0.049 92	0.20	4.987	0.013

[a] See footnote *a* in Table 6. [b] See footnote *c* in Table 6. [c] See footnote *d* in Table 6.

Table 9. pH Values at 298.15 K for the Buffer Solutions Which Contain Potassium Hydrogen Phthalate (KHPh), Potassium Phthalate (K_2 Ph), and Potassium Chloride and in Which $m(K_2Ph) = m(KCl) = m(KHPh)$

(m_{KHPh}/m^0)	I_m/m^0	pH^b	$(pH - pH_P)^c$	$p(\gamma^G_{Cl})^d$	$(\Delta^P)^e$	$(\Delta^{B-G})^f$
0.002 00	0.01	5.277	0.001	0.045	−0.001	0.001
0.003 99	0.02	5.229	0.002	0.061	−0.001	0.002
0.005 99	0.03	5.196	0.002	0.073	−0.002	0.003
0.007 99	0.04	5.169	0.003	0.082	−0.002	0.003
0.009 99	0.05	5.147	0.004	0.089	−0.003	0.004
0.011 98	0.06	5.128	0.004	0.096	−0.003	0.005
0.013 98	0.07	5.111	0.005	0.102	−0.004	0.005
0.015 98	0.08	5.096	0.005	0.107	−0.004	0.006
0.017 98	0.09	5.082	0.006	0.112	−0.005	0.006
0.019 97	0.10	5.070	0.007	0.116	−0.005	0.007
0.029 96	0.15	5.020	0.009	0.134	−0.007	
0.039 94	0.20	4.982	0.011	0.147	−0.009	
0.049 93	0.25	4.953	0.013	0.158	−0.011	
0.059 90	0.30	4.928	0.015	0.167	−0.013	

[a] See footnote *a* in Table 6. [b] See footnote *c* in Table 6. [c] See footnote *d* in Table 6. [d−f] See footnotes in Table 7.

Table 10. pH Values at 298.15 K for the Buffer Solutions Containing a Molality of 0.05 mol kg^{-1} Potassium Hydrogen Phthalate (KHPh) and Potassium Chloride

$(m_{KCl}/m^0)^a$	$(I_m/m^0)^b$	pH_G^c	pH_P^d	pH_P^e(Chan)
0.1	0.1538 (+0.0001)	3.918	3.910	3.915
0.2	0.2540 (+0.0001)	3.872	3.859	3.864
0.3	0.3542 (+0.0001)	3.839	3.823	3.828
0.4	0.4543 (+0.0001)	3.814	3.794	3.800
0.5	0.5544	3.793	3.770	3.776

[a] $m^0 = 1$ mol kg^{-1}. [b] Calculated by the Guggenheim method. The difference between the I_m values calculated by the Guggenheim method and the Pitzer method is given in parentheses when significant. [c] Calculated by the Guggenheim method. [d] Calculated by the present Pitzer method. [e] Calculated by means of the Pitzer parameters suggested by Chan *et al.* (1995); see Table 4.

Table 11. pH Values at 298.15 K for the Buffer Solutions Containing Potassium Hydrogen Phthalate (KHPh) and a Molality of 1.0 mol kg^{-1} Potassium Chloride

$(m_{KHPh}/m^0)^a$	$(I_m/m^0)^b$	pH_G^c	pH_P^d	pH_P^e(Chan)
0.01	1.011	3.766	3.737	3.747
0.03	1.033	3.733	3.700	3.707
0.05	1.055	3.725	3.690	3.697
0.1	1.110 (+0.001)	3.715	3.678	3.687

[a−e] See footnotes in Table 10.

The calculation methods considered were additionally tested with the emf data of Hetzer *et al.* (1977); see Table 5. According to this table, these data support well the methods (for the new Pitzer method results, see, however, the previous paragraph). Hetzer *et al.* suggest pH = 4.007 for the 0.05 mol kg^{-1} KHPh solution at 298.15 K. In the determination of this value they used the standard method recommended by NBS for buffer solutions: From a plot where the experimental values of $p(a_H\gamma_{Cl})$ [obtained from the emf data (see Table 5)] are presented as a function of m_{Cl}, they determined by linear extrapolation a value of 4.0946 ± 0.0012 (the confidence interval is given at a level of 0.95) for $p(a_H\gamma_{Cl})$ in the chloride-free buffer solution. To calculate the pH from this value, the convention of Bates and Guggenheim (eq 5) was used for the activity coefficient of chloride ions. The uncertainty associated with this convention in the KHPh solution increases the error of this pH value; see below. The equation recommended by Hetzer *et al.* for the temperature dependence of pH gives pH = 4.0058. IUPAC [see Covington *et al.* (1985)] recommended for this solution pH = 4.005. According to Table 6 the Guggenheim method suggests a value of 4.003 for this solution, and the Pitzer methods suggest the values of 4.003 (Chan *et al.*) and 3.999 (this study). Therefore, the differences between the pH values obtained by the methods considered here and the pH standard have practical significance only in very rare occasions.

For phthalate buffer solutions containing Cl^- ions, the uncertainty of the pH calculated by the present methods can be studied by means of the equation

$$pH = (E - E^0)F/[\ln(10)RT] + \log(m_{Cl}/m^0) + \log \gamma_{Cl} \tag{38}$$

where E is the emf measured by cells of type 22 for the buffer solution considered. In the calculation of pH by this equation, the main sources of errors are quantities E, E^0, and γ_{Cl}. An error of 0.1 mV in the value of E (or E^0) results in an error of about 0.002 for pH. The error resulted from the uncertainty of the activity coefficients of Cl^- is more difficult to estimate. By means of eq 2 (Guggenheim method), eq 7 (Pitzer method), and the Bates−Guggenheim equation (eq 5), however, some understanding of the magnitude of this error is possible to achieve. For this purpose in Tables 7 and 9 are also included the $p(\gamma_{Cl})$ values $[p(\gamma_{Cl}) = -\log(\gamma_{Cl})]$ that have been calculated by these three equations. Below an ionic strength of 0.1 mol kg^{-1}, the difference $|p(\gamma^G_{Cl}) - p(\gamma^P_{Cl})|$ is according to these tables smaller than 0.005, but the difference $|p(\gamma^G_{Cl}) - p(\gamma^{B-G}_{Cl})|$ or $|p(\gamma^P_{Cl}) - p(\gamma^{B-G}_{Cl})|$ can be as high as 0.012. According to the experimental evidence shown in Figures 1 and 2, the values of $p(\gamma^G_{Cl})$ or $p(\gamma^P_{Cl})$ seem to be slightly more useful in this connection than those of $p(\gamma^{B-G}_{Cl})$. On the basis of the former values, it is reasonable to believe that the pH values suggested, e.g., in Tables 6−9 can be useful with a precision of ±0.005 in most cases below an ionic strength of 0.1 mol kg^{-1}.

In the present study, all reliable literature data involving the first and second dissociations of phthalic acid at 298.15 K have been used to test two methods. In one of these methods the equations of the modified Guggenheim type are used for ionic activity coefficients and in the other the simplified equations of the Pitzer type. It has been shown that both of these methods predict accurately these data up to I_m of about 0.5 mol kg^{-1} (see Figures 1 and 2). Also the pH value of the standard phthalate buffer solution recommended by IUPAC [see Covington *et al.* (1985)] can be well predicted by both of these methods (see above). As shown in Tables 6−10, the pH predictions of these two methods agree in most cases within 0.01 at least up to I_m of about 0.15 mol kg^{-1}. The differences between these two methods are, therefore, not significant in practical work where a pH precision higher than 0.01 is only seldom possible to achieve owing to the calibration difficulties with glass electrode cells. Therefore, it seems to be that the Guggenheim (or Pitzer) method gives the best pH estimate determined so far for dilute aqueous solutions containing KHPh, K_2Ph, and KCl at various compositions at 298.15 K. We believe that the ability to calculate the pH of phthalate buffers opens new possibilities for the use of glass electrode cells, e.g., in high-precision analytical and thermodynamic applications. Above an ionic strength of about 0.5 mol kg^{-1} and in some cases above 0.1 mol kg^{-1}, the parameters for the ionic activity coefficient equations cannot at the moment be estimated with a sufficient precision because of the lack of experimental data. We believe that this is one of the main reasons, in addition to the reason of the different conventions used to define the pH scale, why the pH predictions of the methods differ significantly from each other in these cases (see, e.g., Table 11).

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