Reviews

Re-evaluation of the First and Second Stoichiometric Dissociation Constants of Phthalic Acid at Temperatures from (0 to 60) °C in Aqueous Phthalate Buffer Solutions with or without Potassium Chloride. 1. Estimation of the Parameters for the Hückel Model Activity Coefficient Equations for Calculation of the Second Dissociation Constant

Jaakko I. Partanen*,† and Arthur K. Covington‡

Department of Chemical Technology, Lappeenranta University of Technology, P. O. Box 20, FIN-53851 Lappeenranta, Finland, and Department of Natural Sciences, Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K.

Equations were developed for the calculation of the second stoichiometric (molality scale) dissociation constant (K_{m2}) of phthalic acid in buffer solutions containing potassium dihydrogen phthalate, hydrogen phthalate, and chloride from the determined thermodynamic values of this dissociation constant (K_{a2}) and the molalities of the components in the solutions. These equations apply at temperatures from (0 to 60) °C up to ionic strengths of about 0.5 mol·kg^{-1}, and they are based on the single-ion activity coefficient equations of the Hückel type. The parameters of phthalate ions for these equations and the thermodynamic values of the second dissociation constant of this acid at various temperatures were determined from the Harned cell data measured by Hamer and Acree (*J. Res. Natl. Bur. Stand.* **1945**, *35*, 381−416). In these parameter estimations, the stoichiometric values of the first dissociation constant of phthalic acid were needed, and these values were obtained from the Harned cell results of Hamer et al. (*J. Res. Natl. Bur. Stand.* **1945**, *35*, 539−564) with some reasonable extra approximations. All calculations from the data of Hamer and Acree were completely revised, and all parameters estimated depend in a simple way on the temperature. The interaction parameters between hydrogen and chloride ions were taken from results of a previous HCl paper (Partanen, J. I.; Covington, A. K. *J. Solution Chem.* **2002**, *31*, 197−210). The parameters resulting from interactions between hydrogen and potassium ions and from interactions between potassium and chloride ions were taken from a recent study (Partanen, J. I.; Covington, A. K. *J. Chem. Eng. Data* **2005**, *50*, 497−507), where these parameter values were determined from Harned cell data of Harned and Hamer (*J. Am. Chem. Soc.* **1933**, *55*, 2194−2206) in HCl + KCl solutions. The resulting simple equations for calculation of K_{m2} for phthalic acid were tested with the data from the parameter estimation and apply well to these data. In the second part of this study, these equations will be additionally tested with good results on all reliable data found in the literature from the first and second dissociation reactions of phthalic acid in KCl solutions.

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,[1] Hitchcock and Taylor,[2] and MacInnes et al.[3] The pH values assigned to this buffer in the early studies were based on cell potential difference (cpd) measurements on cells containing a liquid junction. Because of the experimental and 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 (e.g., at 25 °C, pH = 4.008) was one of the seven reference points that fix the NBS[4] pH scale of the year in 1962 at each temperature at intervals of 5 °C from (0 to 60) °C. In the determinations of these reference points, the convention of Bates and Guggenheim[5] was 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;[6] of KHPh, dipotassium phthalate (K_2Ph) and KCl;[7] and of phthalic acid (H_2Ph), KHPh, and KCl[8] at temperatures from (0 to 60) °C. Later, Hetzer et al.[9] based the determination of the pH values of 0.05 mol·kg^{-1} KHPh solution on their new data measured using Harned cells at temperatures from (0 to 60) °C in solutions of KHPh and KCl, and using the Bates−Guggenheim convention[5] they obtained at 25 °C, for example, pH = 4.007 for this solution. At higher temperatures from (60 to 95) °C, Bower and Bates[10] also determined pH values for this buffer from Harned cell data

* To whom correspondence should be addressed. Fax: +358 5 621 2199. E-mail: jpartane@lut.fi.
† Lappeenranta University of Technology.
‡ University of Newcastle.

10.1021/je0504921 CCC: $33.50 © 2006 American Chemical Society
Published on Web 02/25/2006

from solutions of KHPh and KCl. In 1985, IUPAC (see Covington et al.[11]) recommended the pH values of this solution only as reference value pH standards [pH(RVS)] at temperatures from (0 to 95) °C. According to these recommendations (based mainly on the critical evaluations of Bütikofer and Covington[12]) at 25 °C, for example, pH(RVS) is 4.005. In the current IUPAC pH recommendations (see Buck et al.[13]), for the 0.05 mol·kg^{-1} KHPh solution is not given special assignation in the seven standard buffer solutions for pH measurements. Its pH values are given from (0 to 50) °C only, and these values are same as those in the previous IUPAC recommendations.[11]

The evaluation of the pH values of standard solutions is, however, a non-thermodynamic problem because it is not possible to measure directly the appropriate single-ion activity coefficients associated with these determinations. Empirical models for ionic activity coefficients have been given in the literature for calculations of pH of standard buffer solutions.[14−22] These models reproduce, in all cases, the standard values at least satisfactorily. Some of the models were also successfully tested with literature data obtained from activity coefficients of electrolytes (that are experimentally obtainable quantities). From these papers, the one of Chan et al.[16] uses the Pitzer model for solutions of KHPh at 25 °C and was considered earlier in detail in ref 22. Recently, de Mendonça and Juusola[23] have reported Pitzer model parameters and modified Guggenheim model parameters for K_2Ph and KHPh from results of cpd measurements in solutions of these salts and KCl at 25 °C using potassium ion-selective electrodes.

For phthalic acid, both empirical Hückel and Pitzer equations have been suggested[22] for the calculation of the first and second molality-scale stoichiometric dissociation constants, K_{m1} and K_{m2}, respectively, in aqueous buffer solutions at 25 °C from the molalities of the components of the solution. These equations were also applied[22] to calculate the pH values of phthalate buffer solutions in various compositions. The pH values calculated by these equations for dilute solutions are strongly supported with all existing electrochemical data, but the theoretical interpretation of the parameters in these equations is limited because these equations contain a larger number of adjustable parameters than required and apply only to 25 °C.

In the present study, a new and more versatile method than those mentioned above is given for the calculation of the K_{m1} and K_{m2} values for phthalic acid in buffer solutions from the composition variables of the solutions, and this method is applicable to temperatures from (0 to 60) °C and to ionic strengths up to about 0.5 mol·kg^{-1}. The method is based on the single-ion activity coefficient equations of the Hückel type[24] because very simple and accurate equations resulted from this choice (see eqs 1−4). The same method was successfully applied earlier to acetic,[25] propionic,[26] butyric,[26] formic,[27] and phosphoric (K_{m2})[28,29] acid solutions.

The required Hückel parameters at various temperatures for phthalate species were estimated from Harned cell data of Hamer and co-workers.[7,8] In the first part of this study, the results from the parameter estimation are presented for the second dissociation of phthalic acid (see ref 7), and in the second part they will be presented for the first dissociation (see ref 8). The resulting equations were then tested with the data used in the estimations, and very good agreement was always obtained. The test results from the data of Hamer and Acree[7] are shown here and from the data of Hamer et al.[8] in part 2, where, in addition, all other existing reliable literature data from the dissociations of phthalic acid are also successfully used to test the resulting models.

Using K_{m1} and K_{m2} values calculated from these new models, speciation of phthalate buffer solutions can be determined and, for example, the hydrogen ion molality calculated. The pH values obtained by the model are used in part 2, with one reasonable extra assumption, to check the pH values recommended by IUPAC[11] for the 0.05 mol·kg^{-1} KHPh buffer solution from (0 to 60) °C. Very satisfactory agreement is obtained in this comparison.

It has been suggested[25,30−32] that $m(H^+)$ values (or p[$m(H^+)$] = $-\log[(m(H^+)/m°]$ values where $m° = 1$ mol·kg^{-1}) calculated by an equation for K_m of acetic acid (or other weak acid) in buffer solutions containing NaCl or KCl as a major component and weak acid species as minor components can also be used in the calibration of a glass electrode cell used in acidity determination. The p[$m(H^+)$] values, calculated in this way using the new Hückel models for phthalate buffers in KCl solutions, will be tabulated in part 2 of this study for these calibration solutions, and the glass electrode cell calibrated in this way measures directly the molality of hydrogen ions.

Theory

The following equations are used for the activity coefficients (γ) of the ions existing in aqueous phthalate buffer solutions resulting from potassium salts of hydrogen phthalate, phthalate, and chloride ions:

$$\ln \gamma_{H} = -\frac{\alpha\sqrt{I_m}}{1 + B_H\sqrt{I_m}} + b_{H,Cl}(m_{Cl}/m°) + \theta_{H,K}(m_K/m°) \quad (1)$$

$$\ln \gamma_{Cl} = -\frac{\alpha\sqrt{I_m}}{1 + B_{Cl}\sqrt{I_m}} + b_{H,Cl}(m_H/m°) + b_{K,Cl}(m_K/m°) \quad (2)$$

$$\ln \gamma_{HPh} = -\frac{\alpha\sqrt{I_m}}{1 + B_{HPh}\sqrt{I_m}} + b_{K,HPh}(m_K/m°) + \theta_{HPh,Ph}(m_{Ph}/m°) \quad (3)$$

$$\ln \gamma_{Ph} = -\frac{4\alpha\sqrt{I_m}}{1 + B_{Ph}\sqrt{I_m}} + b_{K,Ph}(m_K/m°) + \theta_{HPh,Ph}(m_{HPh}/m°) \quad (4)$$

where $m° = 1$ mol·kg^{-1} and the following symbols are used: H = H^+, Cl = Cl^-, K = K^+, HPh = HPh^-, and Ph = Ph^{2-}. I_m in these equations is the ionic strength on the molality scale, and α is the Debye−Hückel parameter, and the values of this parameter at various temperatures are given in Tables 1 to 3 (see Archer and Wang[33]). B_i is a parameter that is dependent on ion i, and $b_{i,j}$ or $\theta_{i,j}$ are the ion−ion interaction parameters between ions i and j that have opposite or like charges, respectively. Additionally, in these equations is assumed that $B_H = B_{Cl}$, $B_{HPh} = B_{Ph}$, and $\theta_{Cl,HPh} = \theta_{Cl,Ph} = 0$, and these two θ parameters have been omitted from eqs 2 to 4 (compare with eqs 2 to 4 in the phosphate buffer study[28]).

From the previous HCl results,[34] a value of $B_H = B_{Cl} = 1.4$ (mol·kg^{-1})$^{-1/2}$ was taken in eqs 1 and 2 for all temperatures considered. The following equation was also used for the parameter $b_{H,Cl}$ in these equations from the results of that study:

$$b_{H,Cl} = 0.30645 - 0.001006(t/°C) \quad (5)$$

In the previous study of formic acid,[27] the following equation was determined from the Harned cell data of Harned and Hamer[35] for aqueous mixtures of HCl + KCl:

$$b_{K,Cl} + \theta_{H,K} = 0.00944 + 0.0009389(t/°C) - 0.0000094(t/°C)^2 \quad (6)$$

These equations were also used here.

Table 1. Experimental 10^6 K_{m2} Values at 25 °C for Phthalic Acid from Data Measured by Hamer and Acree[7] on Cell 9, the Standard Potential of Silver−Silver Chloride Electrode ($E°$), the Debye−Hückel Parameter (α), and the Thermodynamic Value of the First Dissociation Constant (K_{a1}) Used in the Calculations for Phthalic Acid at This Temperature

m_b / mol kg^{-1}	m_c / m_b	m_s / m_b	I_m / mol kg^{-1}	symbol	t = 25 °C / $10^6 K_{m2}$	m_b / mol kg^{-1}	m_c / m_b	m_s / m_b	I_m / mol kg^{-1}	symbol	t = 25 °C / $10^6 K_{m2}$
0.0007661	1.0057	1.0014	0.003858	HAA1	5.21	0.034937	1.5070	1.0035	0.22813	HAB16	14.95
0.0014530	1.0057	1.0014	0.007309	HAA2	5.71	0.051843	1.5070	1.0035	0.33853	HAB17	17.33
0.0016690	1.0057	1.0014	0.008394	HAA3	5.82	0.071943	1.5070	1.0035	0.46980	HAB18	19.41
0.0023505	1.0057	1.0014	0.01182	HAA4	6.18	0.071886	1.5139	1.0056	0.47106	HAB19	19.47
0.0031721	1.0057	1.0014	0.01595	HAA5	6.58	0.0012203	2.0005	1.0006	0.009774	HAC1	6.16
0.0034678	1.0057	1.0014	0.01743	HAA6	6.74	0.0026363	2.0005	1.0006	0.02111	HAC2	6.94
0.0036275	1.0057	1.0014	0.01823	HAA7	6.79	0.0044644	2.0005	1.0006	0.03574	HAC3	7.96
0.0048224	1.0057	1.0014	0.02424	HAA8	7.25	0.0087742	2.0005	1.0006	0.07025	HAC4	9.74
0.0049454	1.0057	1.0014	0.02486	HAA9	7.32	0.010675	2.0005	1.0006	0.08546	HAC5	10.41
0.0069349	1.0057	1.0014	0.03485	HAA10	7.99	0.016461	2.0005	1.0006	0.13179	HAC6	12.12
0.0095161	1.0057	1.0014	0.04782	HAA11	8.74	0.022447	2.0005	1.0006	0.17971	HAC7	13.59
0.011319	1.0057	1.0014	0.05688	HAA12	9.19	0.030548	2.0005	1.0006	0.24457	HAC8	15.17
0.014671	1.0057	1.0014	0.07373	HAA13	10.05	0.036014	2.0005	1.0006	0.28833	HAC9	16.20
0.018381	1.0057	1.0014	0.09237	HAA14	10.88	0.042177	2.0005	1.0006	0.33768	HAC10	17.06
0.023770	1.0057	1.0014	0.11946	HAA15	11.89	0.054400	2.0005	1.0006	0.43555	HAC11	18.75
0.026358	1.0057	1.0014	0.13246	HAA16	12.39	0.014013	2.0223	0.1858	0.10168	HAD1	11.02
0.027847	1.0057	1.0014	0.13995	HAA17	12.57	0.023409	2.0223	0.1858	0.16987	HAD2	13.25
0.041527	1.0057	1.0014	0.20871	HAA18	14.68	0.024878	2.0223	0.1858	0.18053	HAD3	13.50
0.062963	1.0057	1.0014	0.31648	HAA19	17.21	0.030089	2.0223	0.1858	0.21834	HAD4	15.06[a]
0.10781	1.0057	1.0014	0.54198	HAA20	20.88	0.042383	2.0223	0.1858	0.30756	HAD5	16.46
0.10803	1.0074	1.0037	0.54389	HAA21	20.93	0.043083	2.0223	0.1858	0.31264	HAD6	16.48
0.0004400	1.5070	1.0035	0.002878	HAB1	5.00	0.053814	2.0223	0.1858	0.39051	HAD7	17.90
0.0006264	1.5070	1.0035	0.004095	HAB2	5.18	0.055730	1.0074	0.6479	0.26069	HAE1	15.89
0.0011836	1.5070	1.0035	0.007733	HAB3	5.72	0.10803	1.0074	0.6479	0.50542	HAE2	20.29
0.0018128	1.5070	1.0035	0.01184	HAB4	6.14	0.053194	1.0074	0.2777	0.22912	HAF1	15.11
0.0023519	1.5070	1.0035	0.01536	HAB5	6.49	0.10803	1.0074	0.2777	0.46540	HAF2	19.61
0.0030064	1.5070	1.0035	0.01963	HAB6	6.84	0.075592	1.0074	0.09257	0.31162	HAG1	16.92
0.0034327	1.5070	1.0035	0.02242	HAB7	7.07	0.10803	1.0074	0.09257	0.44535	HAG2	18.45[a]
0.0035250	1.5070	1.0035	0.02302	HAB8	7.11	0.036174	1.5139	0.6956	0.22581	HAH1	14.84
0.0048817	1.5070	1.0035	0.03188	HAB9	7.73	0.071886	1.5139	0.6956	0.44877	HAH2	19.07
0.0069713	1.5070	1.0035	0.04552	HAB10	8.56	0.024728	1.5139	0.4143	0.14740	HAI1	12.66
0.0087820	1.5070	1.0035	0.05734	HAB11	9.20	0.071886	1.5139	0.4143	0.42854	HAI2	18.70
0.0088235	1.5070	1.0035	0.05761	HAB12	9.23	0.054840	1.5139	0.1392	0.31182	HAJ1	16.65
0.0089534	1.5070	1.0035	0.05846	HAB13	9.23	0.071886	1.5139	0.1392	0.40876	HAJ2	18.30
0.013470	1.5070	1.0035	0.08795	HAB14	10.59	0.026688	2.0223	0.5575	0.20358	HAK1	14.19
0.017045	1.5070	1.0035	0.11129	HAB15	11.47	0.053814	2.0223	0.5575	0.41052	HAK2	18.26
$E°$/mV[b]					222.53						
$\alpha/(m°)^{-1/2}$ [c]					1.1744						
10^3 K_{a1}[d]					1.123						

[a] Omitted as a probable outlier. [b] Determined previously[34] from the HCl data of Harned and Ehlers.[36,37] [c] $m° = 1$ mol·kg^{-1}. [d] Determined by Hamer et al.[8]

The first and second thermodynamic dissociation constants (K_{a1} and K_{a2}) of phthalic acid are given by

$$K_{a1} = \frac{\gamma_H \gamma_{HPh} m_H m_{HPh}}{\gamma_{H2Ph} m_{H2Ph} m°} = \left(\frac{\gamma_H \gamma_{HPh}}{\gamma_{H2Ph}}\right) \quad K_{m1} \tag{7}$$

$$K_{a2} = \frac{\gamma_H \gamma_{Ph} m_H m_{Ph}}{\gamma_{HPh} m_{HPh} m°} = \left(\frac{\gamma_H \gamma_{Ph}}{\gamma_{HPh}}\right) \quad K_{m2} \tag{8}$$

where H2Ph refers to H_2Ph, the first stoichiometric dissociation constant K_{m1} is defined by equation $K_{m1} = m_H m_{HPh}/(m_{H2Ph} m°)$, and the second one is defined by equation $K_{m2} = m_H m_{Ph}/(m_{HPh} m°)$. Missing parameters for eqs 1, 3, and 4 were estimated from the data of Hamer and Acree.[7]

Results and Discussion

Determination of Parameters B_{Ph}, $\theta_{HPh,Ph}$, and $b_{K,Ph} + \theta_{H,K} - b_{K,HPh}$. Hamer and Acree[7] measured precise data on Harned cells of the following type at temperatures from (0 to 60) °C:

$$\text{Pd(s)} \mid H_2(\text{g}, f = 101.325 \text{ kPa}) \mid \text{KHPh (aq}, m_b), \; K_2\text{Ph (aq}, m_c), \text{KCl(aq}, m_s) \mid \text{AgCl(s)} \mid \text{Ag(s)} \tag{9}$$

where f is the fugacity. The molalities of components in the 11 series (A−K) measured are shown in Tables 1 to 3. The cell potential difference (cpd = E) for cells of type 9 is given by

$$E = E° - (RT/F) \ln\left[\frac{\gamma_H \gamma_{Cl} m_H m_{Cl}}{(m°)^2}\right] \tag{10}$$

where $E°$ is the standard cell potential difference. The experimental K_{m2} values were obtained from these data as follows (i.e., principally in the same way as that used for phosphate buffer solutions in ref 28). The observed K_{m2} value was calculated from each experimental point by

$$\ln(m_H/m°) = \frac{(E° - E)F}{RT} - \ln(\gamma_H \gamma_{Cl} m_{Cl}/m°) \tag{11}$$

$$\ln K_{m1} = \ln K_{a1} + \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{1}{1 + B_{HPh}\sqrt{I_m}}\right) - b_{H,Cl}(m_{Cl}/m°) - q_{K1}(m_K/m°) \tag{12}$$

$$K_{m2} = \frac{m_H(m_c + m_H)}{(m_b - m_H)m°} + \frac{m_H^{\,2}(m_b + 2m_c + m_H)}{K_{m1}(m_b - m_H)(m°)^2} \tag{13}$$

Table 2. Experimental 10^6 K_{m2} Values at Temperatures (0 to 20 and 30) °C for Phthalic Acid from Data Measured by Hamer and Acree[7] on Cell 9, the Standard Potential of Silver−Silver Chloride Electrode ($E°$), the Debye−Hückel Parameter (α), and the Thermodynamic Value of the First Dissociation Constant (K_{a1}) Used in Calculations for Phthalic Acid as a Function of Temperature

	10^6 K_{m2} at t/°C							10^6 K_{m2} at t/°C					
symbol[a]	0	5	10	15	20	30	symbol[a]	0	5	10	15	20	30
HAA1	4.85	5.07	5.16	5.24	5.26	5.13	HAB16	13.36	13.93	14.46	14.73	14.89	14.91
HAA2	5.30	5.52	5.66	5.74	5.76	5.63	HAB17	15.31	16.01	16.59	17.00	17.20	17.29
HAA3	5.36	5.60	5.75	5.83	5.86	5.72	HAB18	17.03	17.84	18.46	18.97	19.23	19.40
HAA4	5.78	5.95	6.10	6.18	6.22	6.08	HAB19	17.08	17.90	18.47	19.01	19.33	19.46
HAA5	6.12	6.33	6.50	6.60	6.61	6.51	HAC1	5.52	5.73	5.86	5.94	5.97	5.84
HAA6	6.25	6.49	6.64	6.74	6.77	6.65	HAC2	6.43	6.69	6.86	6.95	7.00	6.83
HAA7	6.30	6.53	6.69	6.79	6.84	6.70	HAC3	7.95[b]	7.62	7.81	7.96	7.98	7.82
HAA8	6.70	6.98	7.13	7.28	7.29	7.20	HAC4	8.89	9.25	9.54	9.69	9.77	9.64
HAA9	6.74	6.97	7.19	7.29	7.32	7.19	HAC5	9.51	9.89	10.12	10.31	10.46	10.33
HAA10	7.34	7.65	7.84	7.97	8.02	7.90	HAC6	10.94	11.42	11.78	12.02	12.11	11.98
HAA11	8.02	8.34	8.56	8.71	8.77	8.67	HAC7	12.20	12.73	13.10	13.38	13.49	13.51
HAA12	8.45	8.77	9.00	9.21	9.28	9.18	HAC8	13.59	14.21	14.66	14.92	15.18	15.14
HAA13	9.16	9.56	9.82	10.00	10.07	9.95	HAC9	14.36	15.05	15.54	15.92	16.15	16.11
HAA14	9.88	10.27	10.56	10.76	10.83	10.76	HAC10	15.17	15.91	16.39	16.74	17.01	17.10
HAA15	10.75	11.19	11.49	11.82	11.92	11.80	HAC11	16.48	17.27	17.85	18.32	18.61	18.73
HAA16	11.14	11.63	12.00	12.22	12.35	12.27	HAD1	10.00	10.42	10.70	10.87	11.02	11.19
HAA17	11.33	11.85	12.14	12.48	12.64	12.48	HAD2	11.95	12.45	12.82	13.08	13.20	13.17
HAA18	13.09	13.67	14.14	14.42	14.57	14.57	HAD3	12.18	12.72	13.11	13.39	13.55	13.46
HAA19	15.17	15.94	16.43	16.88	17.09	17.16	HAD4	13.49[b]	14.07[b]	14.51[b]	14.89[b]	15.02[b]	14.99
HAA20	18.21	19.12	19.79	20.38	20.74	20.91	HAD5	14.66	15.30	15.78	16.12	16.39	16.41
HAA21	18.25	19.16	19.83	20.40	20.75	20.94	HAD6	14.70	15.38	15.81	16.19	16.46	16.46
HAB1	4.69	4.87	4.97	5.04	5.04	4.92	HAD7	15.80	16.51	17.03	17.56	17.76	17.88
HAB2	4.85	5.03	5.13	5.21	5.23	5.10	HAE1	14.16	14.77	15.27	15.62	15.82	15.84
HAB3	5.34	5.54	5.66	5.74	5.75	5.63	HAE2	17.74	18.57	19.26	19.80	20.14	20.30
HAB4	5.73	5.93	6.07	6.16	6.17	6.06	HAF1	13.48	14.10	14.53	14.83	15.03	15.03
HAB5	6.03	6.26	6.41	6.50	6.52	6.41	HAF2	17.19	18.04	18.65	19.15	19.46	19.59
HAB6	6.33	6.58	6.73	6.84	6.86	6.75	HAG1	14.93	15.70	16.17	17.34	16.84	16.88
HAB7	6.54	6.78	6.96	7.07	7.11	6.99	HAG2	16.91	17.70	18.33	18.80	19.09	19.18
HAB8	6.60	6.84	7.00	7.12	7.14	7.03	HAH1	13.31	13.87	14.28	14.59	14.84	14.77
HAB9	7.11	7.39	7.59	7.72	7.75	7.64	HAH2	16.76	17.55	18.12	18.59	18.94	19.04
HAB10	7.84	8.17	8.38	8.53	8.57	8.46	HAI1	11.44	11.93	11.97	12.51	12.41	12.58
HAB11	8.39	8.69	9.00	9.16	9.21	9.09	HAI2	25.47[b]	17.29	17.87	18.32	18.57	18.67
HAB12	8.44	8.75	9.02	9.18	9.23	9.14	HAJ1	14.80	15.45	15.93	16.43	16.58	16.60
HAB13	8.47	8.81	9.04	9.20	9.25	9.15	HAJ2	16.26	16.97	17.51	17.96	18.27	18.29
HAB14	9.61	9.99	10.31	10.47	10.56	10.50	HAK1	12.71	13.27	13.66	13.95	14.13	14.12
HAB15	10.37	10.83	11.14	11.37	11.45	11.38	HAK2	16.11	16.86	17.43	17.84	18.13	18.24
$E°$/mV[c]	236.64	234.15	231.49	228.63	225.64	219.22							
$\alpha/(m°)^{-1/2}$ [d]	1.1293	1.1376	1.1462	1.1552	1.1646	1.1848							
10^3 K_{a1}[e]	1.190	1.182	1.171	1.157	1.141	1.102							

[a] For the symbol, see Table 1. [b] Omitted as a probable outlier. [c] Determined previously[34] from the HCl data of Harned and Ehlers.[36,37] [d] $m° = 1$ mol·kg^{-1}. [e] Determined by Hamer et al.[8]

In eq 12, the parameter q_{K1} is defined by $q_{K1} = b_{K,HPh} + \theta_{H,K} - \lambda_{K,H2Ph}$, and λ in this definition is the interaction parameter between neutral acid molecule and ion (shown, for example, in eq 4 of ref 27). In this determination, the $E°$ values determined previously[34] from the HCl data of Harned and Ehlers[36,37] were used, and these values are shown in Tables 1 to 3. Equations 1 and 2 were used for the activity coefficient of H^+ and Cl^- ions, respectively, and the relevant parameter values for these equations are given above (i.e., $B_H = B_{Cl} = 1.4$ (mol·kg^{-1})$^{-1/2}$, $b_{H,Cl}$ is calculated from eq 5, and $b_{K,Cl} + \theta_{H,K}$ from eq 6). The values of K_{m1} are not needed very accurately in the determination of K_{m2} values with eq 13, and eq 12 is not the full equation that resulted from eqs 1, 3, and 7 with the equation ln $\gamma_{H2A} = \lambda_{K,H2Ph}$ $(m_K/m°)$ (see eq 4 in ref 27), but this equation was observed to be sufficient. In addition in this connection, the values of K_{m1} can be calculated from eq 12 with the values of K_{a1} determined by Hamer et al.[8] (these K_{a1} values are also given Tables 1 to 3), with a value of $B_{HPh} = 1.4$ (mol·kg^{-1})$^{-1/2}$ (how this value was obtained will be described below) and with a constant value of $q_{K1} = 0.15$ at all temperatures. It will be shown in part 2 of this study that this q_{K1} value is the average value from those determined in this study for this quantity for temperatures from (0 to 60) °C, and it is also in a rather close agreement with q_K values obtained previously[27] for aliphatic monoprotic carboxylic acids. Equation 13 was obtained by solving K_{m2} from the following equation for the molality of hydrogen ions in the solutions of cell 9 (compare to eq 24 in ref 22):

$$m_H^{\,3} + (K_{m1}m° + m_b + 2m_c)m_H^{\,2} + K_{m1}m°(K_{m2}m° + m_c)m_H - K_{m1}K_{m2}(m°)^2 \quad m_b = 0 \quad (14)$$

Equation 14 was derived in a usual way from the definitions of K_{m1} and K_{m2} (see eqs 7 and 8), from the mass balance equation for phthalic acid species, and from the electroneutrality equation. The experimental K_{m2} values obtained from the data of Hamer and Acree[7] using eq 13 are shown in Tables 1 to 3. Iterative calculations were needed for each point to obtain the ionic strength correctly, and the resulting I_m values at 25 °C are shown in Table 1.

The thermodynamic dissociation constant K_{a2} and parameters B_{Ph}, $\theta_{HPh,Ph}$, and $b_{K,Ph} + \theta_{H,K} - b_{K,HPh}$ were determined at each temperature from K_{m2} values presented in Tables 1 to 3 by the following equation (derived from eqs 1, 3, 4, and 8):

$$y_1 = \ln K_{a2} - q_{K2}(m_K/m°) \quad (15)$$

where

$$q_{K2} = b_{K,Ph} + \theta_{H,K} - b_{K,HPh} \quad (16)$$

Table 3. Experimental $10^6\,K_{m2}$ Values at Temperatures from (35 to 60) °C for Phthalic Acid from Data Measured by Hamer and Acree[7] on Cell 9, the Standard Potential of Silver−Silver Chloride Electrode ($E°$), the Debye−Hückel Parameter (α), and the Thermodynamic Value of the First Dissociation Constant (K_{a1}) Used in Calculations for Phthalic Acid as a Function of Temperature

	$10^6\,K_{m2}$ at t/°C							$10^6\,K_{m2}$ at t/°C					
symbol[a]	35	40	45	50	55	60	symbol[a]	35	40	45	50	55	60
HAA1	5.22[b]	4.84	4.66	4.43	4.18	3.89	HAB16	14.73	14.38	14.00	13.51	12.86	12.23
HAA2	5.52	5.33	5.14	4.89	4.62	4.29	HAB17	17.13	16.78	16.39	15.85	15.11	14.43
HAA3	5.61	5.41	5.22	4.98	4.68	4.38	HAB18	19.27	18.93	18.53	17.96	17.18	16.49
HAA4	5.96	5.76	5.55	5.31	4.99	4.70	HAB19	19.31	18.98	18.57	18.00	17.20	16.42
HAA5	6.37	6.15	5.94	5.68	5.34	5.00	HAC1	5.72	5.53	5.33	5.09	4.77	4.48
HAA6	6.52	6.31	6.09	5.81	5.46	5.13	HAC2	6.70	6.51	6.28	6.00	5.64	5.31
HAA7	6.56	6.36	6.13	5.85	5.51	5.17	HAC3	7.71	7.47	7.25	6.95	6.53	6.16
HAA8	7.04	6.80	6.57	6.31	5.91	5.57	HAC4	9.46	9.26	8.97	8.58	8.10	7.66
HAA9	7.06	6.84	6.65	6.36	5.98	5.63	HAC5	10.15	9.88	9.63	9.21	8.71	8.23
HAA10	7.78	7.52	7.27	6.95	6.55	6.16	HAC6	11.87	11.54	11.24	10.80	10.24	9.72
HAA11	8.52	8.27	8.01	7.65	7.25	6.79	HAC7	13.26	13.02	12.67	12.14	11.49	11.00
HAA12	9.03	8.71	8.43	8.10	7.67	7.22	HAC8	15.00	14.66	14.30	13.81	13.10	12.46
HAA13	9.79	9.55	9.23	8.86	8.41	7.89	HAC9	15.94	15.63	15.22	14.61	14.00	13.32
HAA14	10.57	10.31	10.01	9.60	9.08	8.55	HAC10	16.86	16.61	16.16	15.64	14.83	14.24
HAA15	11.65	11.36	11.01	10.63	10.07	9.47	HAC11	18.52	18.24	17.83	17.15	16.57	15.72
HAA16	12.10	11.77	11.49	11.04	10.45	9.85	HAD1	10.77	10.49	10.16	9.77	9.22	8.73
HAA17	12.40	12.03	11.67	11.30	10.66	10.10	HAD2	13.04	12.72	12.33	11.90	11.27	10.71
HAA18	14.42	14.09	13.73	13.20	12.56	11.89	HAD3	13.27	12.96	12.64	12.25	11.48	10.95
HAA19	16.96	16.57	16.29	15.71	14.97	14.22	HAD4	14.86[b]	14.59[b]	14.09[b]	13.64[b]	12.91[b]	12.30[b]
HAA20	20.77	20.42	20.26	19.52	18.66	17.78	HAD5	16.21	15.90	15.51	14.97	14.22	13.59
HAA21	20.82	20.42	20.07	19.47	18.64	17.83	HAD6	16.29	15.97	15.57	15.08	14.32	13.66
HAB1	4.81	4.64	4.47	4.25	3.99	3.74	HAD7	17.71	17.41	18.23[b]	16.43	15.64	14.95
HAB2	4.98	4.82	4.64	4.41	4.15	3.92	HAE1	15.64	15.31	14.94	14.42	13.72	13.04
HAB3	5.51	5.33	5.13	4.89	4.60	4.32	HAE2	20.16	19.82	19.45	18.77	17.99	17.20
HAB4	5.93	5.74	5.53	5.28	4.97	4.68	HAF1	14.82	14.52	14.19	13.65	12.97	12.29
HAB5	6.27	6.07	5.86	5.59	5.27	4.96	HAF2	19.46	19.05	18.68	18.10	17.29	16.50
HAB6	6.61	6.41	6.19	5.91	5.57	5.24	HAG1	16.66	16.32	15.96	15.40	14.68	13.97
HAB7	6.85	6.63	6.40	6.12	5.77	5.43	HAG2	19.04	18.72	18.32	17.71	16.93	16.16
HAB8	6.89	6.68	6.45	6.16	5.81	5.47	HAH1	14.60	14.25	13.91	13.41	12.73	11.69
HAB9	7.49	7.27	7.03	6.72	6.35	5.98	HAH2	18.89	18.54	18.15	17.62	17.18	16.07
HAB10	8.31	8.07	7.81	7.48	7.07	6.64	HAI1	12.40	12.08	11.76	11.32	10.72	10.14
HAB11	8.91	8.70	8.43	8.07	7.61	7.21	HAI2	18.48	18.17	17.75	17.13	16.40	15.62
HAB12	8.98	8.72	8.45	8.10	7.63	7.21	HAJ1	16.43	16.06	15.69	15.13	14.42	13.73
HAB13	8.99	8.74	8.47	8.11	7.65	7.22	HAJ2	18.13	17.78	17.33	16.75	16.00	15.26
HAB14	10.33	10.06	9.75	9.36	8.87	8.37	HAK1	13.90	13.60	13.26	12.77	12.13	11.53
HAB15	11.21	10.93	10.61	10.20	9.67	9.21	HAK2	18.05	17.73	17.32	16.80	16.06	14.96
$E°$/mV[c]	215.75	212.12	208.36	204.50	200.46	196.29							
$\alpha/(m°)^{-1/2}$ [d]	1.1956	1.2068	1.2186	1.2308	1.2436	1.2568							
$10^3\,K_{a1}$[e]	1.078	1.053	1.027	0.998	0.968	0.937							

[a] For the symbol, see Table 1. [b] Omitted as a probable outlier. [c] Determined previously[34] from the HCl data of Harned and Ehlers.[36,37] [d] $m° = 1\ \mathrm{mol \cdot kg^{-1}}$. [e] Determined by Hamer et al.[8]

Table 4. Results from Least-Squares Fitting Using Equation 15 from the Phthalic Acid Data Measured by Hamer and Acree on Cell 9 (see Tables 1 to 3)

t/°C	$10^6\,K_{a2}$	$-\log K_{a2}$	$s(\log K_{a2})$	(q_{K2})[a]	$s(q_{K2})$[b]	q_{K2}(recd)[c]	$(10^3\,s)$[d]
0	3.771	5.4236	0.0006	0.078	0.008	0.084	7.8
5	3.900	5.4090	0.0006	0.075	0.007	0.077	7.7
10	3.978	5.4003	0.0006	0.073	0.008	0.069	8.5
15	4.024	5.3953	0.0007	0.062	0.008	0.062	8.7
20	4.022	5.3955	0.0006	0.058	0.008	0.055	8.1
25	3.988	5.3993	0.0006	0.049	0.008	0.048	8.0
30	3.915	5.4072	0.0006	0.042	0.008	0.040	8.4
35	3.816	5.4184	0.0006	0.037	0.008	0.033	8.3
40	3.676	5.4346	0.0006	0.026	0.007	0.026	7.8
45	3.529	5.4523	0.0006	0.014	0.008	0.018	8.3
50	3.352	5.4747	0.0006	0.013	0.008	0.011	8.3
55	3.135	5.5038	0.0007	−0.001	0.008	0.004	8.7
60	2.928	5.5334	0.0007	−0.003	0.008	−0.004	8.9

[a] $q_{K2} = b_{K,Ph} + \theta_{H,K} - b_{K,HPh}$. [b] Standard deviation of parameter q_{K2} (see footnote *a*). [c] Calculated by eq 18, see footnote *a*. [d] s is the standard deviation about the regression.

and

$$y_1 = \ln K_{m2} - \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{3}{1 + B_{Ph}\sqrt{I_m}}\right) + b_{H,Cl}(m_{Cl}/m°) + \theta_{HPh,Ph}[(m_b - m_c)/m°] \quad (17)$$

Table 5. Thermodynamic Value of the Second Dissociation Constant (K_{a2}) of Phthalic Acid as a Function of the Temperature (t)

t/°C	$10^6\,K_{a2}$(exp)[a]	$10^6\,K_{a2}$(recd)[b]	$10^6\,K_{a2}$(H&A)[c]	$10^6\,K_{a2}$(R&S)[d]
0	3.77	3.78	3.70	3.69
5	3.90	3.89	3.82	3.81
10	3.98	3.97	3.89	3.90
15	4.02	4.01	3.93	3.94
20	4.02	4.02	3.94	3.95
25	3.99	3.99	3.91	3.91
30	3.92	3.92	3.84	3.84
35	3.82	3.82	3.74	3.73
40	3.68	3.69	3.61	3.60
45	3.53	3.53	3.45	3.45
50	3.35	3.34	3.27	3.27
55	3.14	3.14	3.08	3.08
60	2.93	2.92	2.88	2.88

[a] The experimental value from data of cell 9, see Table 4. [b] Calculated from eq 19, and recommended in this study. [c] Recommended by Hamer and Acree.[7] [d] Calculated from eq 20 given by Robinson and Stokes.[38]

In eq 17, it is assumed that $B_{HPh} = B_{Ph}$ and that the approximative value of $I_m = m_b + 3m_c + m_s$ can be used for the ionic strength. For fixed values of B_{Ph} and $\theta_{HPh,Ph}$, the quantity y_1 can be calculated from each experimental point; therefore, eq 15 represents in this case an equation of a straight-line y_1 versus $(m_K/m°)$. For this equation, it was determined the parameter values of $\theta_{HPh,Ph} = -0.70$ and $B_{Ph} = 1.4$ (mol

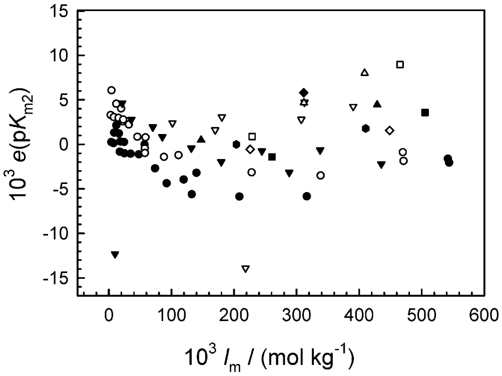

Figure 1. Differences, $e(\mathrm{p}K_{m2})$ in eq 21, between experimental $\mathrm{p}K_{m2}$ values obtained from the cell potential data of Hamer and Acree[7] on cell 9 at 25 °C for phthalic acid in KCl solutions (see Table 1) and those predicted by the Hückel method as a function of ionic strength I_m. The K_{m2} values were predicted from eqs 1, 3, 4, and 8 with the recommended K_{a2} value of 3.99 × 10^{-6} (see Table 5) and with parameter values suggested in this study: ●, HAA (see Table 1); ○, HAB; ▼, HAC; ▽, HAD; ■, HAE; □, HAF; ◆, HAG; ◇, HAH; ▲, HAI; △, HAJ; ⬢, HAK.

kg^{-1})$^{-1/2}$ from the K_{m2} values at 25 °C (see Table 1) by searching the minimum of the standard deviation about regression (s). Additionally, it was observed that these values apply also to all temperatures considered.

Once the values of parameters $\theta_{\mathrm{HPh,Ph}}$ and B_{Ph} have been determined, the data presented in Tables 1 to 3 were used for the regression analyses with eq 15. The results are shown in Table 4. The experimental q_{K2} values obtained in these regression analyses can be correlated to temperature with a linear equation giving

$$q_{K2} = 0.08395 - 0.00146(t/°\mathrm{C}) \qquad (18)$$

Predicted values from eq 18, shown also in Table 4, agree well with the experimental values. The experimental values obtained from these calculations for K_{a2} of phthalic acid at various temperatures will be considered in the next subsection.

Determination of the Second Thermodynamic Dissociation Constant (K_{a2}) for Phthalic Acid. The experimental K_{a2} values from the regression analyses with eq 15 are shown in Table 4, and the logarithms of these values were fitted to a quadratic equation in temperature. The resulting equation is

$$\ln K_{a2} = -12.48488 + 0.006681(t/°\mathrm{C}) - 0.000183(t/°\mathrm{C})^2 \qquad (19)$$

The predictions of this equation and the experimental K_{m2} values are shown in Table 5, and these predictions are recommended in the present study. In Table 5 are also shown the K_{a2} values recommended by Hamer and Acree[7] on the basis of data from cell 9 and those calculated by the following equation:

$$\log K_{a2} = 9.55075 - 0.025694\ (T/\mathrm{K}) - \frac{2175.83\ \mathrm{K}}{T} \qquad (20)$$

where T is the temperature in Kelvin (K). This equation was given by Robinson and Stokes,[38] and it was determined from the K_{a2} values suggested by Hamer and Acree also shown in this table. K_{a2} values presented by Hamer and Acree agree reasonably with the new values in this table but probably not within experimental error. The new values are more reliable because they are based on more reliable activity coefficient models than those given by Hamer and Acree.

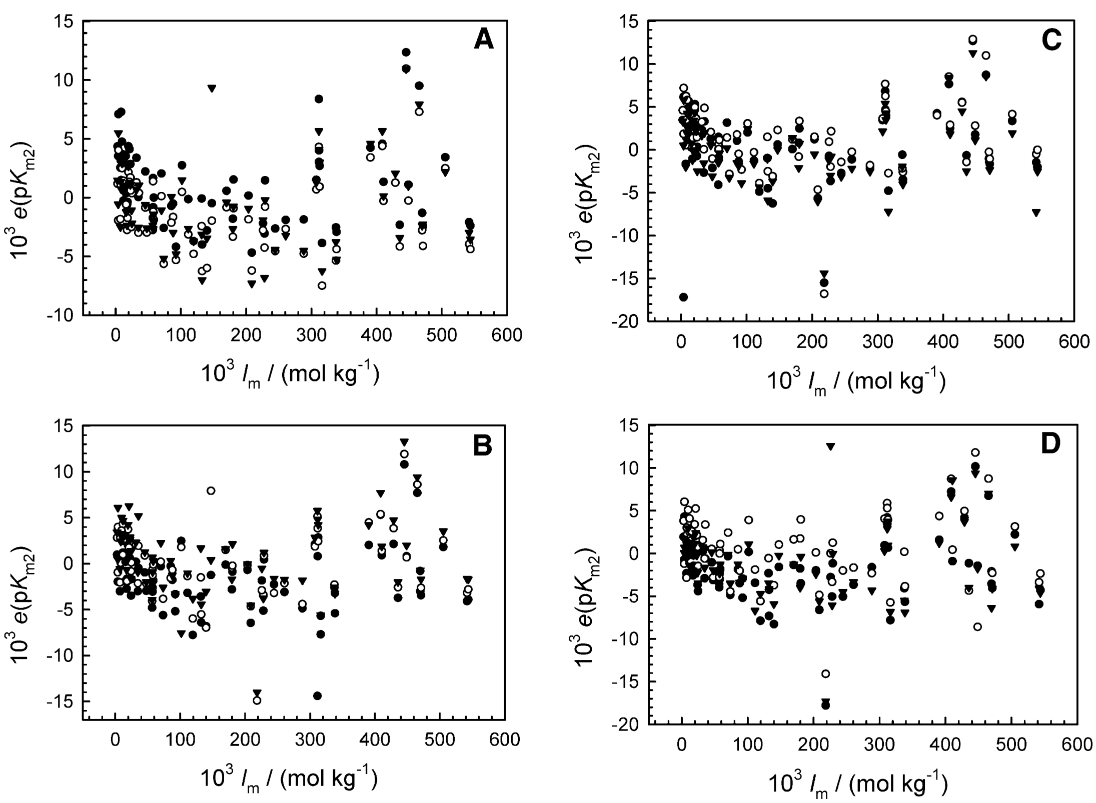

Figure 2. Differences, $e(\mathrm{p}K_{m2})$ in eq 21, between experimental $\mathrm{p}K_{m2}$ values obtained from the cell potential data of Hamer and Acree[7] on cell 9 for phthalic acid in KCl solutions (see Tables 2 and 3) and those predicted by the Hückel method as a function of ionic strength I_m. The K_{m2} values were predicted from eqs 1, 3, 4, and 8 with the recommended K_{a2} values shown in Table 5 and with parameter values suggested in this study: ●, 0 °C (panel A), 15 °C (panel B), 35 °C (panel C), 50 °C (panel D); ○, 5 °C (panel A), 20 °C (panel B), 40 °C (panel C), 55 °C (panel D); ▼, 10 °C (panel A), 30 °C (panel B), 45 °C (panel C), 60 °C (panel D).

Results with the New Parameter Values from the Data Measured by Hamer and Acree on Cell 9. The experimental K_{m2} values presented in Tables 1 to 3 were predicted from the new Hückel model. The recommended K_{a2} values given in Table 5, together with $b_{H,Cl}$ values obtained from eq 5, q_{K2} values from eq 18, $\theta_{HPh,Ph}$ value of -0.70, and $B_H = B_{HPh} = B_{Ph} = 1.4\ (\text{mol·kg}^{-1})^{-1/2}$ were used. The results are shown as error plots where pK_{m2} error defined by

$$e(\mathrm{p}K_{m2}) = \mathrm{p}K_{m2}(\text{observed}) - \mathrm{p}K_{m2}(\text{predicted}) \qquad (21)$$

is presented as a function of the ionic strength of the solution. The results for 25 °C are shown in Figure 1, which shows the errors of all series measured by Hamer and Acree[7] (see Table 1). The errors of all series in this figure are not far from random. In the four panels of Figure 2 are shown the results for other temperatures. The errors of the different series at each temperature are not shown separately in these four panels. In panel A are shown the errors at temperatures from (0 to 10) °C, in panel B are shown the errors at temperatures (15, 20, and 30) °C, in panel C are shown the errors at temperatures from (35 to 45) °C, and in panel D are shown the errors from (50 to 60) °C. The error plots support well the suggested model.

Use of the Suggested Hückel Model. The model used in this study for the calculations of the second stoichiometric dissociation constant of phthalic acid in aqueous KCl solutions seems to be valuable for use in many practical applications, as will be shown in the second part of this study. There, this model will be used first to estimate a corresponding model for the first stoichiometric dissociation constant of phthalic acid from the data of Hamer et al.[8] Then, these two models are tested with all reliable thermodynamic literature data obtained for these dissociations. The models apply equally well to all data. Equations are then given for the calculation of K_{m1} and K_{m2} values for phthalic acid in KCl solutions very dilute in phthalate species. Equations are also given for the calculation of the pH and pm_H [$= -\log(m_H/m°)$] for the phthalate buffer solutions recommended by IUPAC, and the pH values obtained are compared to the recommended pH values. Calculated pm_H values are also tabulated for buffer solutions containing KCl as the major component and phthalate salts as minor components for the calibration of glass electrode cells for direct measurements of hydrogen ion molality.

Literature Cited

(1) Clark, W. M.; Lubs, H. A. Hydrogen electrode potentials of phthalate, phosphate, and borate buffer mixtures. *J. Biol. Chem.* **1916**, *25*, 479−510.

(2) Hitchcock, D. I.; Taylor, A. C. The standardization of hydrogen ion determinations. I. Hydrogen electrode measurements with a liquid junction. *J. Am. Chem. Soc.* **1937**, *59*, 1812−1818.

(3) MacInnes, D. A.; Belcher, D.; Shedlovsky, T. The meaning and standardization of the pH scale. *J. Am. Chem. Soc.* **1938**, *60*, 1094−1099.

(4) Bates, R. G. Revised standard values for pH measurements from 0 to 95 °C. *J. Res. Natl. Bur. Stand., Sect. A* **1962**, *66*, 179−184.

(5) Bates, R. G.; Guggenheim, E. A. Report on the standardization of pH and related terminology. *Pure Appl. Chem.* **1960**, *1*, 163−168.

(6) Hamer, W. J.; Acree, S. F. A method for the determination of the pH of 0.05-molal solutions of acid potassium phthalate with or without potassium chloride. *J. Res. Natl. Bur. Stand.* **1944**, *32*, 215−227.

(7) Hamer, W. J.; Acree, S. F. Second dissociation constant of *o*-phthalic acid and related pH values of phthalate buffers from 0° to 60 °C. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 381−416.

(8) Hamer, W. J.; Pinching, G. D.; Acree, S. F. First dissociation constant of *o*-phthalic acid and related pH values of phthalate buffers from 0° to 60 °C. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 539−564.

(9) Hetzer, H. B.; Durst, R. A.; Robinson, R. A.; Bates, R. G. Standard pH values for the potassium hydrogen phthalate reference buffer solution from 0 to 60 °C. *J. Res. Natl. Bur. Stand., Sect. A* **1977**, *81*, 21−24.

(10) Bower, V. E.; Bates, R. G. Standards for pH measurements from 60° to 95 °C. *J. Res. Natl. Bur. Stand.* **1957**, *59*, 261−264.

(11) Covington, A. K.; Bates, R. G.; Durst, R. A. Definition of pH scales, standard reference values, measurements of pH and related terminology. *Pure Appl. Chem.* **1985**, *57*, 531−542.

(12) Bütikofer, H. P.; Covington, A. K. Redetermination of the standard pH values for potassium hydrogenphthalate reference buffer solution from 0 to 85 °C. *Anal. Chim. Acta* **1979**, *108*, 179−191.

(13) Buck, R. P.; Rondinini, S.; Covington, A. K.; Baucke, F. G. K.; Brett, C. M. A.; Camoes, M. F.; Milton, M. J. T.; Mussini, T.; Naumann, R.; Pratt, K. W.; Spitzer, P.; Wilson, G. S. The measurement of pH. Definition, standards, and procedures. *Pure Appl. Chem.* **2002**, *74*, 2169−2200.

(14) Lito, M. J. G.; Camões, M. F. G.; Ferra, M. I. A.; Covington, A. K. Calculation of the reference pH values for standard solutions from the corresponding acid dissociation constants. *Anal. Chim. Acta* **1990**, *239*, 129−137.

(15) Covington, A. K.; Ferra, M. I. A. A Pitzer mixed electrolyte solution theory approach to assignment of pH to standard buffer solution. *J. Solution Chem.* **1994**, *23*, 1−10.

(16) Chan, C. Y.; Eng, Y. W.; Eu, K. S. Pitzer single-ion activity coefficients and pH for aqueous solutions of potassium hydrogen phthalate in mixtures with KCl and with NaCl at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 685−691.

(17) Camoes, M. F.; Lito, M. J. G.; Ferra, M. I. A.; Covington, A. K. Consistency of pH standard values with the corresponding thermodynamic acid dissociation constants. *Pure Appl. Chem.* **1997**, *69*, 1325−1333.

(18) de Mendonça, A. J. G.; Ferra, M. I. A. Application of the Pitzer theory to the evaluation of pH of the phthalate standard solution. *Port. Electrochim. Acta* **1997**, *15*, 245−249.

(19) Ferra, M. I. A. A Pitzer theory approach to assignment of pH to standard buffer solutions. *Port. Electrochim. Acta* **1998**, *16*, 133−142.

(20) Partanen, J. I.; Minkkinen, P. O. Redetermination of the second dissociation constant of phosphoric acid and calculation of the pH values of the pH standards based on solutions of dihydrogen and hydrogen phosphate ions at 298.15 K. *Acta Chem. Scand.* **1996**, *50*, 1081−1086,

(21) Partanen, J. I.; Minkkinen, P. O. Equations for calculation of the pH of buffer solutions containing sodium or potassium dihydrogen phosphate, sodium hydrogen phosphate, and sodium chloride at 25 °C. *J. Solution Chem*. **1997**, *26*, 709−727.

(22) Partanen, J. I.; Minkkinen, P. O. Equations for the calculation of the pH of buffer solutions containing potassium hydrogen phthalate, dipotassium phthalate, and potassium chloride at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 805−813.

(23) de Mendonça, A. J. G.; Juusola, P. M. Activity coefficients of dipotassium phthalate and potassium hydrogen phthalate in water at 298.15 K. *Fluid Phase Equilib.* **2005**, *231*, 114−124.

(24) Hückel, E. Zur Theorie konzentrierterer wässeriger Lösungen starker Elektrolyte. *Physik. Z.* **1925**, *26*, 93−147.

(25) Partanen, J. I.; Covington, A. K. Determination of stoichiometric dissociation constants of acetic acid in aqueous solutions containing acetic acid, sodium acetate and sodium chloride at (0 to 60) °C. *J. Chem. Eng. Data* **2003**, *48*, 797−807.

(26) Partanen, J. I.; Covington, A. K. Re-evaluation of stoichiometric dissociation constants from electrochemical cell data for propionic and *n*-butyric acids at (0 to 60) °C and for some other aliphatic carboxylic acids at (18 or 25) °C in aqueous sodium chloride solutions. *J. Chem. Eng. Data* **2004**, *49*, 394−406.

(27) Partanen, J. I.; Covington, A. K. Re-evaluation of stoichiometric dissociation constants from electrochemical cell data for formic acid at temperatures from (0 to 60) °C and for some other aliphatic carboxylic acids at (18 or 25) °C in aqueous potassium chloride solutions. *J. Chem. Eng. Data* **2005**, *50*, 497−507.

(28) Partanen, J. I.; Covington, A. K. Re-evaluation of the second stoichiometric dissociation constants of phosphoric acid at temperatures from (0 to 60) °C in aqueous buffer solutions with or without NaCl or KCl. 1. Estimation of the parameters for the Hückel model activity coefficient equations. *J. Chem. Eng. Data* **2005**, *50*, 1502−1509.

(29) Partanen, J. I.; Covington, A. K. Re-evaluation of the second stoichiometric dissociation constants of phosphoric acid at temperatures from (0 to 60) °C in aqueous buffer solutions with or without NaCl or KCl. 2. Tests and use of the resulting Hückel model equations. *J. Chem. Eng. Data* **2005**, *50*, 2065−2073.

(30) McBryde, W. A. E. The pH meter as a hydrogen concentration probe. *Analyst* **1969**, *94*, 337−346; **1971**, *96*, 739−740.

(31) Hedwig G. R.; Powell, H. K. J. Direct potentiometric measurement of hydrogen ion concentrations in sodium chloride solutions of fixed ionic strength. *Anal. Chem.* **1971**, *43*, 1206−1212.

(32) Partanen, J. I. Calculation of stoichiometric dissociation constants of monoprotic carboxylic acids in dilute aqueous sodium or potassium chloride solutions and p[m(H^+)] values for acetate and formate buffers at 25 °C. *Talanta* **2000**, *52*, 863−871.

(33) Archer, D. G.; Wang, P. The dielectric constant of water and Debye−Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371−411.

(34) Partanen, J. I.; Covington, A. K. Re-evaluation of the activity coefficients of aqueous hydrochloric acid solutions up to a molality of 2.0 using two-parameter Hückel and Pitzer equations. Part II. Results from 0 to 95 °C. *J. Solution Chem.* **2002**, *31*, 197−210.

(35) Harned, H. S.; Hamer, W. J. The ionization constant of water and the dissociation of water in potassium chloride solutions from electromotive forces of cells without liquid junction. *J. Am. Chem. Soc.* **1933**, *55*, 2194−2206.

(36) Harned, H. S.; Ehlers, R. W. The dissociation constant of acetic acid from 0 to 35 °C. *J. Am. Chem. Soc.* **1932**, *54*, 1350−1357.

(37) Harned, H. S.; Ehlers, R. W. The thermodynamics of aqueous hydrochloric acid solutions from electromotive force measurements. *J. Am. Chem. Soc.* **1933**, *55*, 2179−2193.

(38) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth Scientific Publications: London, 1959; p 520.

Received for review November 22, 2005. Accepted January 20, 2006. J.I.P. is indebted to the Research Foundation of Lappeenranta University of Technology (the Lahja and Lauri Hotinen's Fund) for financial support.

JE0504921