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. 2. Estimation of Parameters for the Model for the First Dissociation Constant and Tests and Use of the Resulting Activity Coefficient Equations

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.

Previously (in Part 1, *J. Chem. Eng. Data* **2006**, *51*, 777−784), equations were determined for the calculation of the second stoichiometric (molality scale) dissociation constant (K_{m2}) of phthalic acid in buffer solutions containing potassium hydrogen phthalate (KHPh), dipotassium phthalate, and potassium 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 were based on the single-ion activity coefficient equations of the Hückel type. The parameters of phthalate species for these equations and the second thermodynamic dissociation constant of this acid at various temperatures were determined from Harned cell data of Hamer and Acree (*J. Res. Natl. Bur. Stand.* **1945**, *35*, 381−416), and the resulting parameter values were also tested with these data. In the present study, the corresponding equations were determined from the Harned cell data measured by Hamer et al. (*J. Res. Natl. Bur. Stand.* **1945**, *35*, 539−564) in phthalic acid, KHPh, and KCl solutions for the first dissociation constant of this acid at various temperatures, and the resulting equations were also tested. Additionally, the new models for calculation of K_{m1} (determined in this part) and K_{m2} (determined in Part 1) were tested with the plentiful Harned cell data existing in the literature for 0.05 mol·kg^{-1} KHPh solutions containing KCl at temperatures from (0 to 60) °C. The models usually apply well to these data. The new activity coefficient equations were used to evaluate pH values of the phthalate buffer solution (i.e., of the 0.05 mol·kg^{-1} KHPh solution) for comparison with the pH values recommended by IUPAC (*Pure Appl. Chem*. **1985**, *57*, 531−542; **2002**, *74*, 2169−2200) at temperatures from (0 to 60) °C. Values of p(m_H), which give the molality of protons directly, calculated from these equations are also tabulated for these buffers as well as for buffer solutions with KCl and KHPh as the major component and minor component, respectively.

Introduction

In the first part of this study,[1] activity coefficient equations of the Hückel type were presented for the calculation of the second stoichiometric dissociation constant (K_{m2}) of phthalic acid (H_2Ph) in buffer solutions containing potassium hydrogen phthalate (KHPh) with dipotassium phthalate (K_2Ph) and potassium chloride at temperatures from (0 to 60) °C. The activity parameters for these equations for phthalate species and the thermodynamic values of the second dissociation constant (K_{a2}) of phthalic acid at various temperatures were determined from Harned cell data measured by Hamer and Acree[2] in these solutions. The resulting Hückel model has also been tested with good results in Part 1[1] with the data used in the parameter estimations.

In the present study, a new Hückel model was used for calculation of the first dissociation constant (K_{m1}) of H_2Ph in mixed solutions with KHPh and KCl from Harned cell data of Hamer et al.[3] at temperatures from (0 to 60) °C. Also the thermodynamic values of this dissociation constant (K_{a1}) were re-evaluated at various temperatures, and the resulting new model was tested first with the data[3] used in the estimations. Then, the new models for the calculation of K_{m1} (obtained in this part) and K_{m2} (obtained in Part 1) were tested with Harned cell data of Hamer and Acree,[4] Hamer et al.,[5] and Hetzer et al.[6] for 0.05 mol·kg^{-1} KHPh solutions with KCl at temperatures from (0 to 60) °C. Also in these tests similar Harned cell results of Bütikofer and Covington[7] for KHPh and KCl solutions in this temperature range were included and the more recent results of Chan et al.[8] at 25 °C. The new calculation method for phthalic acid solutions usually applies well to the data used in the tests. Therefore, it can be used for many other purposes such as determination of the K_{m1} and K_{m2} values of this acid at various temperatures for KCl solutions where the salt effectively determines the ionic strength. Tables for such K_{m1} and K_{m2} values are presented below. Also, equations are given for calculation of pH and p(m_H) [$= -\log(m_H/m°)$ where $m°$ is 1 mol·kg^{-1}] for 0.05 mol·kg^{-1} KHPh buffer solution, and the resulting pH values are compared to those recommended by IUPAC[9,10] at various temperatures for calibration of glass electrode cells. Calculated p(m_H) values are also tabulated for

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* Corresponding author. Fax: +358 5 621 2199. E-mail: jpartane@lut.fi.
† Lappeenranta University of Technology.
‡ University of Newcastle.

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buffer solutions containing KCl as the major component and KHPh as the minor component for calibration of glass electrode cells for direct measurements of hydrogen ion molality.

Theory

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

$$\ln \gamma_{\mathrm{H}} = -\frac{\alpha\sqrt{I_{\mathrm{m}}}}{1 + B_{\mathrm{H}}\sqrt{I_{\mathrm{m}}}} + b_{\mathrm{H,Cl}}(m_{\mathrm{Cl}}/m^\circ) + \theta_{\mathrm{H,K}}(m_{\mathrm{K}}/m^\circ) \quad (1)$$

$$\ln \gamma_{\mathrm{Cl}} = -\frac{\alpha\sqrt{I_{\mathrm{m}}}}{1 + B_{\mathrm{Cl}}\sqrt{I_{\mathrm{m}}}} + b_{\mathrm{H,Cl}}(m_{\mathrm{H}}/m^\circ) + b_{\mathrm{K,Cl}}(m_{\mathrm{K}}/m^\circ) \quad (2)$$

$$\ln \gamma_{\mathrm{HPh}} = -\frac{\alpha\sqrt{I_{\mathrm{m}}}}{1 + B_{\mathrm{HPh}}\sqrt{I_{\mathrm{m}}}} + b_{\mathrm{K,HPh}}(m_{\mathrm{K}}/m^\circ) + \theta_{\mathrm{HPh,Ph}}(m_{\mathrm{Ph}}/m^\circ) \quad (3)$$

$$\ln \gamma_{\mathrm{Ph}} = -\frac{4\alpha\sqrt{I_{\mathrm{m}}}}{1 + B_{\mathrm{Ph}}\sqrt{I_{\mathrm{m}}}} + b_{\mathrm{K,Ph}}(m_{\mathrm{K}}/m^\circ) + \theta_{\mathrm{HPh,Ph}}(m_{\mathrm{HPh}}/m^\circ) \quad (4)$$

$$\ln \gamma_{\mathrm{H2Ph}} = \lambda_{\mathrm{K,H2Ph}}(m_{\mathrm{K}}/m^\circ) \quad (5)$$

where $m^\circ = 1\ \mathrm{mol{\cdot}kg^{-1}}$ and where the following symbols are used: $\mathrm{H} = \mathrm{H}^+$, $\mathrm{Cl} = \mathrm{Cl}^-$, $\mathrm{K} = \mathrm{K}^+$, $\mathrm{H2Ph} = \mathrm{H_2Ph}$, $\mathrm{HPh} = \mathrm{HPh}^-$, and $\mathrm{Ph} = \mathrm{Ph}^{2-}$. I_{m} in these equations is the ionic strength on the molality scale, α is the Debye−Hückel parameter, and the values of this parameter at various temperatures are given in Tables 1 to 3 of Part 1.[1] B_i is a parameter dependent on ion i, $b_{i,j}$ or $\theta_{i,j}$ are the ion−ion interaction parameters between ions i and j that have opposite or like charges, respectively, and $\lambda_{\mathrm{H2A},i}$ is the interaction parameter between neutral molecule H2A and ion i. The following constant values were given for these equations in Part 1: $B_{\mathrm{H}} = B_{\mathrm{Cl}} = B_{\mathrm{HPh}} = B_{\mathrm{Ph}} = 1.4\ (\mathrm{mol{\cdot}kg^{-1}})^{-1/2}$, and $\theta_{\mathrm{HPh,Ph}} = -0.70$. Additionally, the following results were given in Part 1:

$$b_{\mathrm{H,Cl}} = 0.30645 - 0.001006(t/^\circ\mathrm{C}) \quad (6)$$

$$b_{\mathrm{K,Cl}} + \theta_{\mathrm{H,K}} = 0.00944 + 0.0009389(t/^\circ\mathrm{C}) - 0.0000094(t/^\circ\mathrm{C})^2 \quad (7)$$

$$q_{\mathrm{K2}} = b_{\mathrm{K,Ph}} + \theta_{\mathrm{H,K}} - b_{\mathrm{K,HPh}} = 0.08395 - 0.00146(t/^\circ\mathrm{C}) \quad (8)$$

The second thermodynamic dissociation constant (K_{a2}) for phthalic acid is given by

$$K_{\mathrm{a2}} = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ph}}m_{\mathrm{H}}m_{\mathrm{Ph}}}{\gamma_{\mathrm{HPh}}m_{\mathrm{HPh}}m^\circ} = \left(\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ph}}}{\gamma_{\mathrm{HPh}}}\right)K_{\mathrm{m2}} \quad (9)$$

The second stoichiometric dissociation constant K_{m2} in this equation is defined by $K_{\mathrm{m2}} = m_{\mathrm{H}}m_{\mathrm{Ph}}/(m_{\mathrm{HPh}}m^\circ)$. In Part 1,[1] the following equation was determined for the temperature dependence of K_{a2}:

$$\ln K_{\mathrm{a2}} = -12.48488 + 0.006681(t/^\circ\mathrm{C}) - 0.000183(t/^\circ\mathrm{C})^2 \quad (10)$$

The first thermodynamic dissociation constant (K_{a1}) for phthalic acid is given by

$$K_{\mathrm{a1}} = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{HPh}}m_{\mathrm{H}}m_{\mathrm{HPh}}}{\gamma_{\mathrm{H2Ph}}m_{\mathrm{H2Ph}}m^\circ} = \left(\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{HPh}}}{\gamma_{\mathrm{H2Ph}}}\right)K_{\mathrm{m1}} \quad (11)$$

The first stoichiometric dissociation constant K_{m1} in this equation is defined by $K_{\mathrm{m1}} = m_{\mathrm{H}}m_{\mathrm{HPh}}/(m_{\mathrm{H2Ph}}m^\circ)$. Missing parameters for eqs 1, 3, and 5 are here estimated from the data of Hamer et al.[3]

Results and Discussion

Determination of Parameter $\boldsymbol{b_{\mathrm{K,HPh}} + \theta_{\mathrm{H,K}} - \lambda_{\mathrm{K,H2Ph}}}$**.** Hamer et al.[3] gave precise data on Harned cells of the following type at temperatures from (0 to 60) °C:

$$\mathrm{Pd(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|H_2Ph(aq,}\ m_{\mathrm{a}}),\ \mathrm{KHPh(aq,}\ m_{\mathrm{b}}),\ \mathrm{KCl(aq,}\ m_{\mathrm{s}})\mathrm{|AgCl(s)|Ag(s)} \quad (12)$$

where f is the fugacity. The molalities of components in the five series (A−E) measured are shown in Tables 1 and 2. The cell potential difference (cpd = E) for cells of type 12 is given by

$$E = E^\circ - (RT/F)\ln\left[\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}m_{\mathrm{H}}m_{\mathrm{Cl}}}{(m^\circ)^2}\right] \quad (13)$$

where E° is the standard cell potential difference. The experimental K_{m1} values were obtained from these points by

$$\ln(m_{\mathrm{H}}/m^\circ) = \frac{(E^\circ - E)F}{RT} - \ln(\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}m_{\mathrm{Cl}}/m^\circ) \quad (14)$$

$$\ln K_{\mathrm{m2}} = \ln K_{\mathrm{a2}} + \alpha\sqrt{I_{\mathrm{m}}}\left(\frac{1}{1 + B_{\mathrm{H}}\sqrt{I_{\mathrm{m}}}} + \frac{3}{1 + B_{\mathrm{HPh}}\sqrt{I_{\mathrm{m}}}}\right) - \theta_{\mathrm{HPh,Ph}}(m_b/m^\circ) - b_{\mathrm{H,Cl}}(m_{\mathrm{Cl}}/m^\circ) - q_{\mathrm{K2}}(m_{\mathrm{K}}/m^\circ) \quad (15)$$

$$K_{\mathrm{m1}} = \frac{m_{\mathrm{H}}^2(m_{\mathrm{b}} + m_{\mathrm{H}})/m^\circ}{m_{\mathrm{H}}(m_{\mathrm{a}} - m_{\mathrm{H}}) + K_{\mathrm{m2}}m^\circ(2m_{\mathrm{a}} + m_{\mathrm{b}} - m_{\mathrm{H}})} \quad (16)$$

In these determinations, the E° values obtained previously[11] from the HCl data of Harned and Ehlers[12,13] were used, and the values are shown in Tables 1 to 3 of Part 1.[1] Equations 1 and 2 were used for the activity coefficients of H^+ and Cl^- ions, respectively, and the relevant parameters for these equations are given above. Iterative calculations were needed because the dissociation of phthalic acid influences the ionic strength. Equation 16 was obtained by solving K_{m1} from the following equation for the molality of hydrogen ions in the solutions of cell 12 (compare to eq 24 in ref 14):

$$m_{\mathrm{H}}^3 + (K_{\mathrm{m1}}m^\circ + m_{\mathrm{b}})m_{\mathrm{H}}^2 + K_{\mathrm{m1}}m^\circ(K_{\mathrm{m2}}m^\circ - m_{\mathrm{a}})m_{\mathrm{H}} - K_{\mathrm{m1}}K_{\mathrm{m2}}(m^\circ)^2(2m_{\mathrm{a}} + m_{\mathrm{b}}) = 0 \quad (17)$$

Equation 17 was derived in a usual way from the definitions of K_{m1} and K_{m2} (see eqs 11 and 9, respectively), from the mass balance equation for phthalic acid species, and from the electroneutrality equation. The value of K_{m2}, needed in eq 16, can be calculated from eq 15 (which was derived from eqs 1, 3, 4, and 9). For this equation, K_{a2} values can be calculated from eq 10. The experimental K_{m1} values obtained from the data of Hamer et al.[3] are shown in Tables 1 to 6.

The thermodynamic dissociation constant K_{a1} and parameter q_{K1} ($= b_{\mathrm{K,HPh}} + \theta_{\mathrm{H,K}} - \lambda_{\mathrm{K,H2Ph}}$) were determined at each

Table 1. Experimental $10^3\ K_{m1}$ Values at 25 °C for Phthalic Acid from Data Measured by Hamer et al.[3] on Cell 12[a]

m_b			I_m		t = 25 °C
mol·kg^{-1}	m_a/m_b	m_s/m_b	mol·kg^{-1}	symbol	$10^3\ K_{m1}$
0.0018357	1.5000	1.0000	0.004587	HPAA1	1.300
0.0019071	1.5000	1.0000	0.004747	HPAA2	1.305
0.0027658	1.5000	1.0000	0.006633	HPAA3	1.335
0.0034165	1.5000	1.0000	0.008035	HPAA4	1.353
0.0039521	1.5000	1.0000	0.009179	HPAA5	1.370
0.0040518	1.5063	1.0000	0.009401	HPAA6	1.383
0.0046056	1.5000	1.0000	0.010564	HPAA7	1.389
0.0047953	1.5000	1.0000	0.010960	HPAA8	1.388
0.0068606	1.5000	1.0000	0.015279	HPAA9	1.437
0.0079547	1.5000	1.0000	0.017546	HPAA10	1.457
0.0081020	1.5000	1.0000	0.017852	HPAA11	1.462
0.011058	1.5063	1.0000	0.023942	HPAA12	1.512
0.011799	1.5063	1.0000	0.025462	HPAA13	1.524
0.011913	1.5063	1.0000	0.025697	HPAA14	1.528
0.012000	1.5000	1.0000	0.025864	HPAA15	1.524
0.0008187	2.0000	1.0000	0.002390	HPAB1	1.262
0.0014005	2.0000	1.0000	0.003805	HPAB2	1.288
0.0014548	2.0000	1.0000	0.003933	HPAB3	1.290
0.0023517	2.0000	1.0000	0.005990	HPAB4	1.325
0.0024641	2.0000	1.0000	0.006241	HPAB5	1.327
0.0031025	2.0000	1.0000	0.007658	HPAB6	1.350
0.0036743	2.0000	1.0000	0.008907	HPAB7	1.365
0.0050000	2.0000	1.0000	0.011757	HPAB8	1.398
0.0071782	2.0000	1.0000	0.016362	HPAB9	1.447
0.0090000	2.0000	1.0000	0.020168	HPAB10	1.482
0.0009423	1.5000	1.5000	0.002878	HPAC1	0.788[b]
0.0016280	1.5000	1.5000	0.004943	HPAC2	1.315
0.0026071	1.5000	1.5000	0.007599	HPAC3	1.344
0.0030788	1.5000	1.5000	0.008860	HPAC4	1.363
0.0036444	1.5000	1.5000	0.010363	HPAC5	1.390
0.0038552	1.5000	1.5000	0.010918	HPAC6	1.396
0.0041264	1.5000	1.5000	0.011630	HPAC7	1.402
0.0044082	1.5000	1.5000	0.012366	HPAC8	1.406
0.0054960	1.5000	1.5000	0.015199	HPAC9	1.430
0.0056467	1.5000	1.5000	0.015593	HPAC10	1.438

[a] More values given in Table 2. [b] Omitted as a probable outlier.

Table 2. Experimental $10^3\ K_{m1}$ Values at 25 °C for Phthalic Acid from Data Measured by Hamer et al.[3] on Cell 12[a]

m_b		m_s	I_m		t = 25 °C
mol·kg^{-1}	m_a/m_b	mol·kg^{-1}	mol·kg^{-1}	symbol	$10^3\ K_{m1}$
0.018	1.0000	0.005	0.024436	HPAD1	1.516
0.018	1.0000	0.0079994	0.027451	HPAD2	1.533
0.018	1.0000	0.010	0.029466	HPAD3	1.550
0.018	1.0000	0.014	0.033483	HPAD4	1.569
0.018	1.0000	0.018	0.037507	HPAD5	1.599
0.009	2.0000	0.003	0.014105	HPAE1	1.428
0.009	2.0000	0.005	0.016132	HPAE2	1.452
0.009	2.0000	0.006985	0.018133	HPAE3	1.465
0.009	2.0000	0.009	0.020169	HPAE4	1.483
0.009	2.0000	0.049305	0.060704	HPAE5	1.690

[a] More values given in Table 1.

Table 3. Experimental $10^3\ K_{m1}$ Values at Temperatures from (0 to 20 and 30) °C for Phthalic Acid from Data Measured by Hamer et al.[3] on Cell 12 as a Function of Temperature[a]

	$10^3\ K_{m1}$ at t/°C					
symbol[b]	0	5	10	15	20	30
HPAA1	1.373	1.371	1.357	1.339	1.320	1.266
HPAA2	1.373	1.377	1.361	1.349	1.324	1.280
HPAA3	1.408	1.408	1.387	1.381	1.356	1.308
HPAA4	1.436	1.429	1.416	1.399	1.380	1.326
HPAA5	1.450	1.441	1.426	1.425	1.390	1.344
HPAA6	1.452	1.440	1.431	1.417	1.397	1.347
HPAA7	1.464	1.453	1.435	1.429	1.412	1.364
HPAA8	1.463	1.466	1.449	1.433	1.414	1.363
HPAA9	1.515	1.505	1.495	1.481	1.460	1.413
HPAA10	1.531	1.532	1.508	1.502	1.482	1.430
HPAA11	1.538	1.528	1.517	1.506	1.482	1.433
HPAA12	1.588	1.580	1.568	1.554	1.534	1.482
HPAA13	1.599	1.589	1.579	1.564	1.545	1.493
HPAA14	1.599	1.591	1.583	1.568	1.545	1.497
HPAA15	1.600	1.592	1.584	1.570	1.550	1.494
HPAB1	1.330	1.328	1.396[c]	1.300	1.283	1.228
HPAB2	1.363	1.351	1.349	1.330	1.317	1.260
HPAB3	1.370	1.360	1.349	1.334	1.315	1.271
HPAB4	1.395	1.395	1.375	1.367	1.349	1.300
HPAB5	1.413	1.401	1.389	1.371	1.350	1.307
HPAB6	1.414	1.421	1.404	1.391	1.370	1.329
HPAB7	1.449	1.433	1.425	1.410	1.388	1.345
HPAB8	1.480	1.471	1.458	1.441	1.420	1.373
HPAB9	1.520	1.517	1.507	1.490	1.473	1.420
HPAB10	1.557	1.548	1.540	1.523	1.504	1.451
HPAC1	1.347	1.341	1.328	1.316	1.294	0.767[c]
HPAC2	1.384	1.377	1.368	1.355	1.330	1.286
HPAC3	1.424	1.422	1.411	1.388	1.374	1.322
HPAC4	1.439	1.431	1.417	1.401	1.387	1.341
HPAC5	1.464	1.457	1.443	1.427	1.401	1.360
HPAC6	1.463	1.459	1.444	1.427	1.415	1.360
HPAC7	1.473	1.463	1.453	1.438	1.417	1.370
HPAC8	1.487	1.483	1.467	1.448	1.434	1.384
HPAC9	1.517	1.500	1.486	1.474	1.459	1.406
HPAC10	1.520	1.502	1.493	1.479	1.460	1.414

[a] More values given in Table 4. [b] See Table 1. [c] Omitted as a probable outlier.

Table 4. Experimental $10^3\ K_{m1}$ Values at Temperatures from (0 to 20 and 30) °C for Phthalic Acid from Data Measured by Hamer et al.[3] on Cell 12 as a Function of Temperature[a]

	$10^3\ K_{m1}$ at t/°C					
symbol[b]	0	5	10	15	20	30
HPAD1	1.598	1.590	1.576	1.559	1.540	1.489
HPAD2	1.618	1.611	1.596	1.580	1.560	1.510
HPAD3	1.632	1.622	1.610	1.593	1.573	1.522
HPAD4	1.657	1.652	1.633	1.617	1.597	1.546
HPAD5	1.678	1.671	1.655	1.642	1.623	1.572
HPAE1	1.507	1.492	1.486	1.474	1.452	1.402
HPAE2	1.523	1.516	1.505	1.493	1.468	1.421
HPAE3	1.540	1.535	1.521	1.429[c]	1.486	1.438
HPAE4	1.558	1.553	1.537	1.526	1.507	1.456
HPAE5	1.767	1.761	1.747	1.731	1.709	1.662

[a] More values given in Table 3. [b] See Table 2. [c] Omitted as a probable outlier.

temperature from the K_{m1} values presented in Tables 1 to 6 using the equation

$$y_2 = \ln K_{a1} - q_{K1}(m_K/m^\circ) \tag{18}$$

where

$$q_{K1} = b_{K,HPh} + \theta_{H,K} - \lambda_{K,H2Ph} \tag{19}$$

and

$$y_2 = \ln K_{m1} - \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{1}{1 + B_{HPh}\sqrt{I_m}}\right) + b_{H,Cl}(m_{Cl}/m^\circ) \tag{20}$$

where it is assumed (as before) that $B_{HPh} = B_{Ph} = 1.4$ (mol·kg^{-1})$^{-1/2}$ and where the I_m values obtained in the determination of K_{m1} values were used at all temperatures (for 25 °C, they are shown in Tables 1 and 2). With these I_m values, quantity y_2 can be calculated for each experimental point, and eq 18 is an equation of a straight-line y_2 versus (m_K/m°). All data in Tables 1 to 6 were used for these regression analyses, and the results are shown in Table 7. The experimental q_{K1} values obtained in these calculations are almost independent of temperature, and the average value of 0.15 can be used at all temperatures. Experimental K_{a1} values obtained in these calcula-

Table 5. Experimental 10^3 K_{m1} Values at Temperatures from (35 to 60) °C for Phthalic Acid from Data Measured by Hamer et al.[3] on Cell 12 as a Function of Temperature[a]

	10^3 K_{m1} at t/°C					
symbol[b]	35	40	45	50	55	60
HPAA1	1.247	1.218	1.197	1.163	1.127	1.091
HPAA2	1.255	1.222	1.201	1.175	1.136	1.107
HPAA3	1.283	1.251	1.233	1.203	1.163	1.127
HPAA4	1.303	1.270	1.251	1.221	1.178	1.147
HPAA5	1.315	1.283	1.265	1.236	1.195	1.159
HPAA6	1.324	1.288	1.272	1.237	1.196	1.162
HPAA7	1.331	1.306	1.277	1.251	1.212	1.174
HPAA8	1.340	1.307	1.285	1.255	1.211	1.174
HPAA9	1.382	1.354	1.326	1.298	1.255	1.217
HPAA10	1.403	1.374	1.348	1.314	1.273	1.234
HPAA11	1.406	1.375	1.350	1.321	1.275	1.238
HPAA12	1.456	1.425	1.399	1.365	1.323	1.283
HPAA13	1.463	1.437	1.405	1.375	1.331	1.294
HPAA14	1.465	1.436	1.409	1.380	1.336	1.298
HPAA15	1.470	1.438	1.413	1.380	1.337	1.299
HPAB1	1.216	1.179	1.221[c]	1.131	1.095	1.044
HPAB2	1.249	1.206	1.189	1.157	1.115	1.078
HPAB3	1.248	1.233	1.192	1.162	1.119	1.077
HPAB4	1.276	1.243	1.221	1.193	1.154	1.129
HPAB5	1.282	1.248	1.228	1.196	1.155	1.119
HPAB6	1.300	1.267	1.242	1.219	1.179	1.144
HPAB7	1.320	1.281	1.260	1.231	1.193	1.156
HPAB8	1.338	1.317	1.292	1.267	1.222	1.181
HPAB9	1.391	1.361	1.335	1.307	1.267	1.228
HPAB10	1.413	1.392	1.371	1.336	1.297	1.257
HPAC1	0.758[c]	1.187	1.171	1.143	1.099	1.066
HPAC2	1.254	1.224	1.215	1.177	1.135	1.099
HPAC3	1.302	1.269	1.242	1.230	1.174	1.138
HPAC4	1.311	1.285	1.259	1.235	1.190	1.148
HPAC5	1.325	1.297	1.277	1.246	1.202	1.168
HPAC6	1.335	1.308	1.284	1.258	1.214	1.180
HPAC7	1.345	1.316	1.291	1.261	1.221	1.184
HPAC8	1.355	1.322	1.297	1.272	1.229	1.192
HPAC9	1.380	1.345	1.326	1.292	1.251	1.215
HPAC10	1.392	1.355	1.336	1.303	1.257	1.221

[a] More values given in Table 6. [b] See Table 1. [c] Omitted as a probable outlier.

Table 6. Experimental 10^3 K_{m1} Values at Temperatures from (35 to 60) °C for Phthalic Acid from Data Measured by Hamer et al.[3] on Cell 12 as a Function of Temperature[a]

	10^3 K_{m1} at t/°C					
symbol[b]	35	40	45	50	55	60
HPAD1	1.465	1.431	1.404	1.375	1.331	1.295
HPAD2	1.483	1.451	1.425	1.391	1.353	1.312
HPAD3	1.499	1.463	1.439	1.404	1.364	1.319
HPAD4	1.521	1.487	1.465	1.423	1.386	1.347
HPAD5	1.544	1.508	1.484	1.450	1.404	1.369
HPAE1	1.374	1.347	1.319	1.288	1.243	1.207
HPAE2	1.428	1.361	1.339	1.305	1.263	1.228
HPAE3	1.409	1.378	1.355	1.322	1.279	1.242
HPAE4	1.427	1.394	1.372	1.338	1.297	1.256
HPAE5	1.641	1.601	1.577	1.546	1.504	1.463

[a] More values given in Table 5. [b] See Table 2.

Table 7. Results from Least-Squares Fitting Using Equation 18 from the Phthalic Acid Data Measured by Hamer et al.[3] on Cell 12 (see Tables 1 to 6)

t/°C	10^3K_{a1}	$-\log K_{a1}$	$s(\log K_{a1})$	(q_{K1})[a]	$s(q_{K1})$[b]	$(10^3\ s)$[c]
0	1.197	2.9218	0.0003	0.10	0.04	2.9
5	1.191	2.9242	0.0003	0.15	0.04	2.5
10	1.179	2.9286	0.0003	0.17	0.04	2.6
15	1.166	2.9335	0.0003	0.18	0.04	2.5
20	1.147	2.9404	0.0002	0.17	0.03	2.2
25	1.127	2.9481	0.0003	0.15	0.04	2.5
30	1.103	2.9573	0.0003	0.14	0.03	2.3
35	1.080	2.9666	0.0004	0.12	0.05	3.6
40	1.052	2.9780	0.0002	0.08	0.03	1.8
45	1.032	2.9861	0.0002	0.14	0.03	2.0
50	1.007	2.9969	0.0003	0.20	0.04	2.7
55	0.970	3.0131	0.0002	0.09	0.02	1.7
60	0.939	3.0274	0.0004	0.07	0.05	3.3

[a] $q_{K1} = b_{K,HPh} + \theta_{H,K} - \lambda_{K,H2Ph}$. [b] Standard deviation of parameter q_{K1} (see footnote *a*). [c] s is the standard deviation about the regression.

Table 8. Thermodynamic Value of the First Dissociation Constant (K_{a1}) of Phthalic Acid as a Function of the Temperature (t)

t/°C	10^3 K_{a1}(exp)[a]	10^3 K_{a1}(recd)[b]	10^3 K_{a1}(HPA)[c]	10^3 K_{a1}(R&S)[d]
0	1.197	1.199	1.190	1.189
5	1.191	1.190	1.182	1.182
10	1.179	1.178	1.171	1.172
15	1.166	1.163	1.157	1.158
20	1.147	1.146	1.141	1.142
25	1.127	1.127	1.123	1.123
30	1.103	1.106	1.102	1.102
35	1.080	1.082	1.078	1.078
40	1.052	1.057	1.053	1.053
45	1.032	1.030	1.027	1.026
50	1.007	1.001	0.998	0.998
55	0.970	0.971	0.968	0.968
60	0.939	0.940	0.937	0.938

[a] The experimental value from data of cell 12, see Table 7. [b] Calculated from eq 21 and recommended in this study. [c] Recommended by Hamer et al.[3] [d] Calculated from eq 22 given by Robinson and Stokes.[15]

tions at various temperatures will be considered in the next subsection.

Determination of First Thermodynamic Dissociation Constant (K_{a1}) for Phthalic Acid. Experimental K_{m1} values from the regression analyses with eq 18 are shown in Table 7, and the logarithms of these values were fitted to a quadratic equation in temperature, with the resultant equation

$$\ln K_{a1} = -6.72604 - 0.001361(t/°\mathrm{C}) - 0.000045(t/°\mathrm{C})^2 \qquad (21)$$

The predictions of this equation as compared to the experimental K_{a1} values are shown in Table 8, and the former are recommended. In Table 8 are also shown the K_{a1} values recommended by Hamer et al.[3] on the basis of the data from cell 12, and those calculated from the following equation:

$$\log K_{a1} = 1.2843 - 0.0078833\,(T/\mathrm{K}) - 561.57\,(\mathrm{K}/T) \qquad (22)$$

where T is the temperature in Kelvin (K). This equation was given by Robinson and Stokes[15] and determined from the K_{a1} values suggested by Hamer et al.[3] as given in Table 8. All K_{a1} values agree well at higher temperatures, but at lower temperatures the new values are slightly larger than those of Hamer et al. The new values seem to be more reliable because they were based on more reliable activity coefficient models than previously.

Results with the New Activity Parameters from Data of Ref 3 on Cell 12. The experimental K_{m1} values presented in Tables 1 to 6 were predicted using the new Hückel model. The recommended K_{a1} values given in Table 8 together with $b_{H,Cl}$ values obtained from eq 6, q_{K1} value of 0.15, and $B_H = B_{HA} = 1.4\ (\mathrm{mol{\cdot}kg^{-1}})^{-1/2}$ were used in the calculations. The results are shown as error plots where pK_{m1} error is defined by

$$e(\mathrm{p}K_{m1}) = \mathrm{p}K_{m1}(\mathrm{observed}) - \mathrm{p}K_{m1}(\mathrm{predicted}) \qquad (23)$$

and 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 et al.[3] (see Tables 1 and

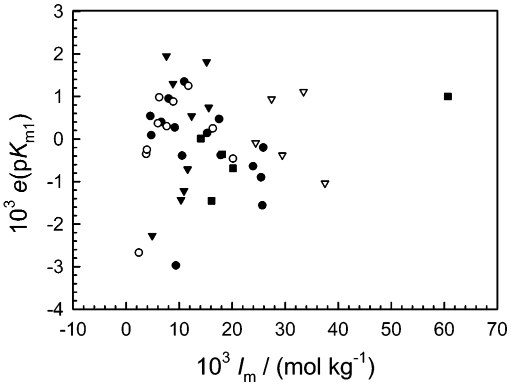

Figure 1. Differences, $e(\mathrm{p}K_{m1})$ in eq 23, between experimental $\mathrm{p}K_{m1}$ values obtained from the cell potential data of Hamer et al.[3] on cell 12 at 25 °C for phthalic acid in KCl solutions (see Tables 1 and 2) and those predicted by the Hückel method as a function of ionic strength I_m. The K_{m1} values were predicted from eqs 1, 3, 5, and 11 with the recommended K_{a1} value of 1.127×10^{-3} (see Table 8) and with parameter values suggested in this study: ●, HPAA (see Table 1); ○, HPAB (Table 1); ▼, HPAC (Table 1); ▽, HPAD (Table 2); ■, HPAE (Table 2).

2) at this temperature. The errors of all series in this figure are almost random. In the four panels of Figure 2 are shown the results for other temperatures but the errors of the different series at each temperature are not shown separately. Panel A shows the errors at temperatures from (0 to 10) °C, panel B at temperatures (20, 30, and 35) °C, panel C at temperatures from (35 to 45) °C, and panel D at temperatures from (50 to 60) °C. The error plots support well the suggested model.

Results with the New Activity Parameters from Harned Cell Data of Ref 6. Hetzer et al.[6] have presented precise data on Harned cells of type

$$\mathrm{Pt(s)} + \mathrm{Pd(s)}|\mathrm{H_2}(\mathrm{g},\ f = 101.325\ \mathrm{kPa})|\mathrm{KHPh}(\mathrm{aq},\ m_b = 0.05\ \mathrm{mol{\cdot}kg^{-1}}),\ \mathrm{KCl}(\mathrm{aq},\ m_s)|\mathrm{AgCl(s)}|\mathrm{Ag(s)} \quad (24)$$

where three molalities of 0.005, 0.010, and 0.015 mol·kg^{-1} were used for m_s at temperatures from (0 to 60) °C at intervals of 5 °C. These data were used by Hetzer et al. to determine the pH values of the 0.05 mol·kg^{-1} KHPh standard buffer solution at various temperatures. At each KCl molality and at each temperature, several replicate determinations were made, and the mean value of these cell potential differences ($= E_{ave}$) and their mean deviation (d_E) were reported. In the present study, these data were used to test the new activity coefficient models for phthalate buffer solutions. The tests were carried out as follows: From each reported E_{ave} value, two cell potential differences (E_1 and E_2) were calculated by equations $E_1 = E_{ave} + d_E$ and $E_2 = E_{ave} - d_E$, and the resulting values were used in the tests. From both values, an experimental $\mathrm{p}m_H$ value [$= \mathrm{p}m_H$(observed)] was calculated by eq 14 where eqs 1 and 2 were used for calculation of γ_H and γ_{Cl}. The $\mathrm{p}m_H$ value predicted by using the new models [i.e., $\mathrm{p}m_H$(predicted)] was obtained for each point numerically (using the Newton−Raphson method) from the following equation derived from eq 17 for solutions of cell 24:

$$m_H^3 + (K_{m1}m^\circ + m_b)m_H^2 + K_{m1}K_{m2}(m^\circ)^2 m_H - K_{m1}K_{m2}(m^\circ)^2 m_b = 0 \quad (25)$$

In eq 25, K_{m1} and K_{m2} were calculated from eqs 11 and 9, respectively. Iterative calculations were needed for these equa-

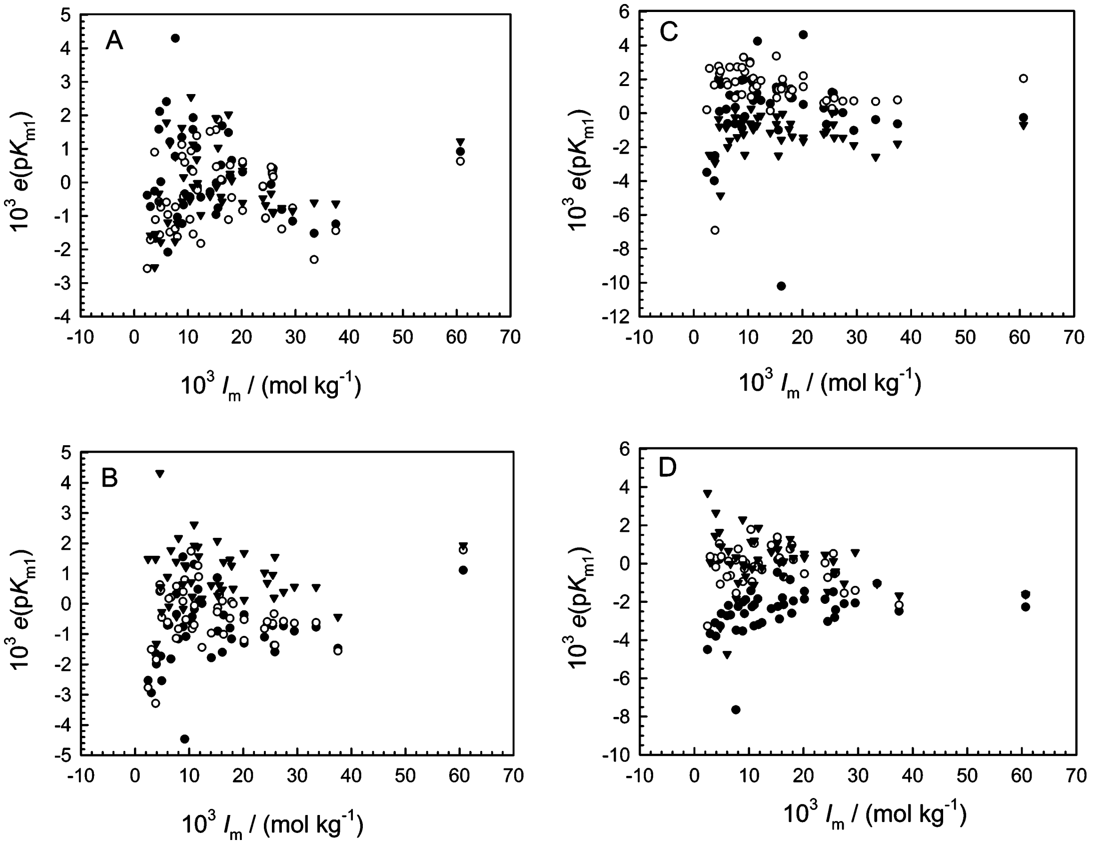

Figure 2. Differences, $e(\mathrm{p}K_{m1})$ in eq 23, between experimental $\mathrm{p}K_{m1}$ values obtained from the cell potential data of Hamer et al.[3] on cell 12 for phthalic acid in KCl solutions (see Tables 3 to 6) and those predicted by the Hückel method as a function of ionic strength I_m. The K_{m1} values were predicted from eqs 1, 3, 5, and 11 with the recommended K_{a1} values shown in Table 8 and with parameter values suggested in this study: ●, 0 °C (A), 15 °C (B), 35 °C (C), 50 °C (D); ○, 5 °C (A), 20 °C (B), 40 °C (C), 55 °C (D); ▼, 10 °C (A), 30 °C (B), 45 °C (C), 60 °C (D).

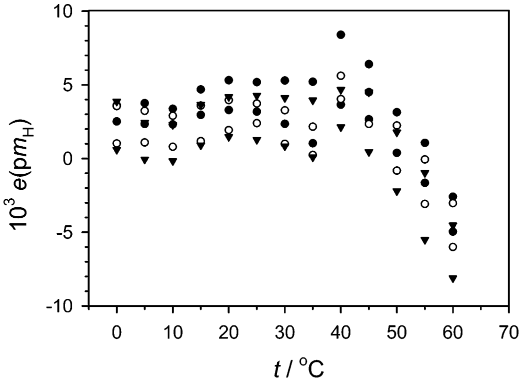

Figure 3. Differences, $e(pm_H)$ in eq 26, between the experimental pm_H values obtained from the cell potential data of Hetzer et al.[6] on cell 24 at various temperatures for the 0.05 mol·kg^{-1} potassium hydrogen phthalate solution with KCl (molality m_s) and those predicted by the Hückel method as a function of the temperature t. The pm_H values were predicted from eq 25 for which the K_{m1} and K_{m2} values were calculated from eqs 1, 3, 4, 5, 9, and 11 with the K_{a1} and K_{a2} values calculated from eqs 21 and 10, respectively, and with the parameter values suggested in this study: ●, m_s = 0.005 mol·kg^{-1}; ○, 0.010 mol·kg^{-1}; ▼, 0.015 mol·kg^{-1}.

tions and for eqs 1 and 2 to obtain the correct ionic strength. The results of these calculations are shown in Figure 3 where the error $e(pm_H)$ is defined by

$$e(pm_H) = pm_H(\text{observed}) - pm_H(\text{predicted}) \qquad (26)$$

and presented as a function of the temperature.

The results support the suggested models well, but a small systematic error of an order of 0.002 occurs below 45 °C. Hetzer et al.[6] reported that their $E°$ values for cell 24 were probably slightly higher than the values usually recommended at various temperatures for hydrogen−silver−silver chloride cells (see Bates and Bower[16]). If a systematic error of 0.15 mV is added to all $E°$ values used in this study for the calculation, complete agreement is obtained in these temperatures. At temperatures higher than 40 °C, a clear trend (that seems to be linear with respect to the temperature of the solution) can be seen in the error pattern.

Results with the New Activity Parameters from Harned Cell Data of Refs 4, 5, 7, and 8. Bütikofer and Covington[7] studied Harned cells of type 24 at temperatures from (0 to 85) °C, and their data up to 60 °C were used here to test the Hückel models. At each temperature measured, many KCl molalities (m_s) from (0.01 to 0.05) mol·kg^{-1} were used in this study. These data were treated similarly to the data of Hetzer et al.[6] above, and the pm_H error plots are shown in Figure 4. Panel A shows the results from (0 to 25) °C, and panel B shows those for the higher temperatures. The results in panel A support the suggested models well, but in panel B at higher temperatures, the errors become gradually more negative.

Hamer and Acree[4] also measured on Harned cells of type 24 at temperatures from (0 to 60) °C, and these data were also used to test the suggested Hückel models. At each temperature, many KCl molalities (m_s) from (0.001 to 0.05) mol·kg^{-1} were used in that study. These data were treated here similarly to those of Hetzer et al.[6] The pm_H error plots are shown in Figure 5. Panel A shows the results from (0 to 30) °C, and panel B shows those from (35 to 60) °C. The results in panel A support the suggested models well, but for the results from the higher temperatures in panel B, the agreement is not so good. All errors in panel B are positive but almost all are smaller than 0.01. This systematic error is slightly higher than the random variation observed in the plots for individual points. A similar systematic error was also observed at the high-temperature data of Bütikofer and Covington (see Figure 4B), but the error in this case was negative.

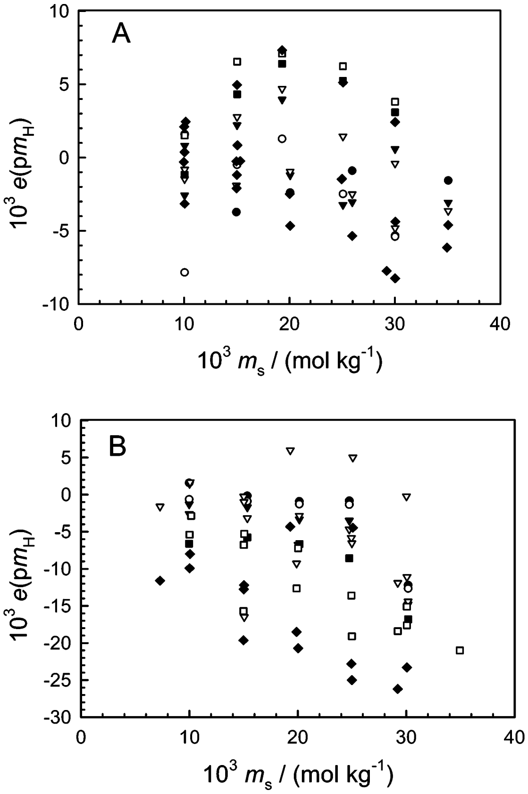

Figure 4. Differences, $e(pm_H)$ in eq 26, between the experimental pm_H values obtained from the cell potential data of Bütikofer and Covington[7] on cell 24 at temperatures from (0 to 25) °C (A) and at temperatures from (30 to 60) °C (B) for the 0.05 mol·kg^{-1} potassium hydrogen phthalate solution with KCl and those predicted by the Hückel method as a function of the KCl molality (m_s). The pm_H values were predicted from eq 25 for which the K_{m1} and K_{m2} values were calculated from eqs 1, 3, 4, 5, 9, and 11 with the K_{a1} and K_{a2} values calculated from eqs 21 and 10, respectively, and with the parameter values suggested in this study: ●, 0 °C (A), 30 °C (B); ○, 0.5 °C (A), 35 °C (B); ▼, 5 °C (A), 40 °C (B); ▽, 10 °C (A), 45 °C (B); ■, 15 °C (A), 50 °C (B); □, 20 °C (A), 55 °C (B); ◆, 25 °C (A), 60 °C (B).

Hamer et al.[5] also gave experimental points for Harned cells of type 24 at temperatures of (0, 15, 25, 35, 45, and 60) °C, and these data were also used to test the Hückel models. At each temperature measured, the KCl molalities (m_s) varied in this case approximately from (0.002 to 0.05) mol·kg^{-1}. These data were treated similarly to those of Hetzer et al.,[6] and pm_H error plots shown in Figure 6 support well the suggested models, but again the low-temperature results are slightly better than the high-temperature results. The same small systematic error for temperatures of (35, 45, and 60) °C was observed as with the data of Hamer and Acree[4] (see Figure 5B).

Chan et al.[8] measured on Harned cells of the following type at 25 °C:

$$\mathrm{Pt(s) + Pd(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|KHPh(aq,}\ m_b\mathrm{),}$$
$$\mathrm{KCl(aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \qquad (27)$$

Six points were obtained with m_b = 0.05 mol·kg^{-1} while m_s varied from (0.01 to 2.0) mol·kg^{-1}. Five points were obtained with m_s = 1.0 mol·kg^{-1}, and in this second set m_b was varied from (0.01 to 0.1) mol·kg^{-1}. Only three solutions in these two sets had salt molalities that are of the same order as those considered previously in this study. The other solutions were

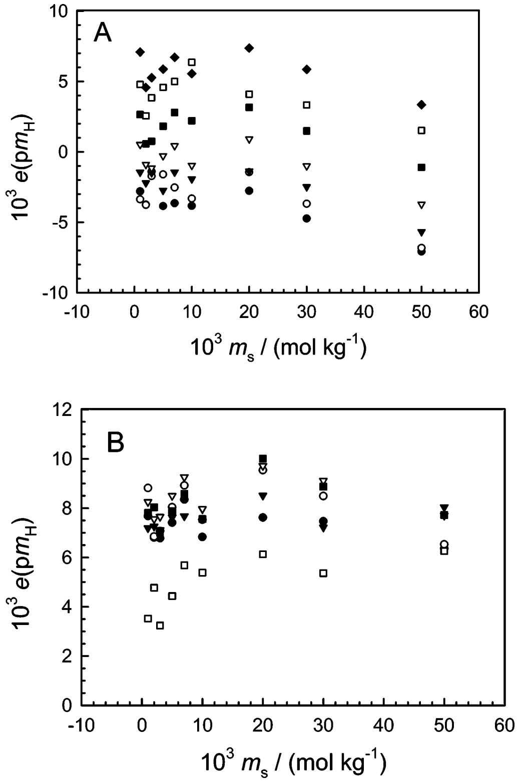

Figure 5. Differences, $e(\mathrm{p}m_\mathrm{H})$ in eq 26, between the experimental $\mathrm{p}m_\mathrm{H}$ values obtained from the cell potential data of Hamer and Acree[4] on cell 24 at temperatures from (0 to 30) °C (A) and at temperatures from (35 to 60) °C (B) for the 0.05 mol·kg^{-1} potassium hydrogen phthalate solution with KCl and those predicted by the Hückel method as a function of the KCl molality (m_s). The $\mathrm{p}m_\mathrm{H}$ values were predicted from eq 25 for which the K_{m1} and K_{m2} values were calculated from eqs 1, 3, 4, 5, 9, and 11 with the K_{a1} and K_{a2} values calculated from eqs 21 and 10, respectively, and with the parameter values suggested in this study. ●, 0 °C (A), 35 °C (B); ○, 5 °C (A), 40 °C (B); ▼, 10 °C (A), 45 °C (B); ▽, 15 °C (A), 50 °C (B); ■, 20 °C (A), 55 °C (B); □, 25 °C (A), 60 °C (B); ◆, 30 °C (A).

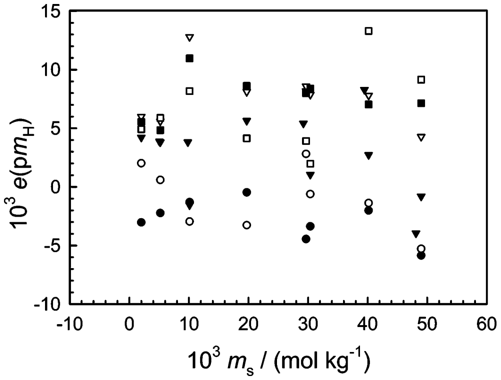

Figure 6. Differences, $e(\mathrm{p}m_\mathrm{H})$ in eq 26, between the experimental $\mathrm{p}m_\mathrm{H}$ values obtained from the cell potential data of Hamer et al.[5] on cell 24 at temperatures from (0 to 60) °C for the 0.05 mol·kg^{-1} potassium hydrogen phthalate solution with KCl and those predicted by the Hückel method as a function of the KCl molality (m_s). The $\mathrm{p}m_\mathrm{H}$ values were predicted from eq 25 for which the K_{m1} and K_{m2} values were calculated from eqs 1, 3, 4, 5, 9, and 11 with the K_{a1} and K_{a2} values calculated from eqs 21 and 10, respectively, and with the parameter values suggested in this study. ●, 0 °C; ○, 15 °C; ▼, 25 °C; ▽, 35 °C; ■, 45 °C; □, 60 °C.

considerably stronger. Despite this, both data sets were used to test the suggested models for phthalate buffer solutions, and $\mathrm{p}m_\mathrm{H}$ error plots are shown in Figure 7. The results from the three points, where the salt molality is less than 0.2 mol·kg^{-1}, support well the suggested model, and the results from the other points (up to m_s = 1.0 mol·kg^{-1}) seem to support the model satisfactorily. All absolute $\mathrm{p}m_\mathrm{H}$ errors for the extrapolated model were in the latter case less than 0.08.

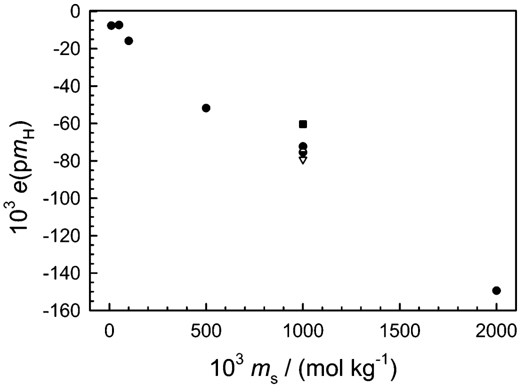

Figure 7. Differences, $e(\mathrm{p}m_\mathrm{H})$ in eq 26, between the experimental $\mathrm{p}m_\mathrm{H}$ values obtained from the cell potential data of Chan et al.[8] on cell 27 at 25 °C for the ○, 0.01 mol·kg^{-1}; ▼, 0.02 mol·kg^{-1}; ▽, 0.03 mol·kg^{-1}; ●, 0.05 mol·kg^{-1}; and ■, 0.1 mol·kg^{-1} potassium hydrogen phthalate solution with KCl and those predicted by the Hückel method as a function of the KCl molality (m_s). The $\mathrm{p}m_\mathrm{H}$ values were predicted from eq 25 for which the K_{m1} and K_{m2} values were calculated from eqs 1, 3, 4, 5, 9, and 11 with the K_{a1} and K_{a2} values calculated from eqs 21 and 10, respectively, and with the parameter values suggested in this study.

Values from the New Models for K_{m1} and K_{m2} of Phthalic Acid in KCl Solutions That Are Very Dilute in Phthalate Species. For aqueous mixtures of H_2Ph, KHPh, K_2Ph, and KCl that are very dilute with respect to the phthalate species, the following equation can be obtained on the basis of the present Hückel model for the first stoichiometric dissociation constant of phthalic acid (K_{m1}):

$$\ln K_{m1} = \ln K_{a1} + \alpha\sqrt{I_m}\left(\frac{1}{1+B_H\sqrt{I_m}} + \frac{1}{1+B_{HPh}\sqrt{I_m}}\right) - (b_{H,Cl} + q_{K1})(I_m/m^\circ) \quad (28)$$

where at all temperatures $q_{K1} = 0.15$. For the second stoichiometric dissociation constant of phthalic acid (K_{m2}) in this case, the following equation is valid:

$$\ln K_{m2} = \ln K_{a2} + \alpha\sqrt{I_m}\left(\frac{1}{1+B_H\sqrt{I_m}} + \frac{3}{1+B_{Ph}\sqrt{I_m}}\right) - (b_{H,Cl} + q_{K2})(I_m/m^\circ) \quad (29)$$

where the value of parameter q_{K2} can be calculated from the temperature by using eq 8. The K_{m1} and K_{m2} values predicted from these two equations are given at rounded ionic strengths and at various temperatures in Tables 9 and 10, respectively.

Suggested pH and p(m_H) Values for Phthalate Buffer Solutions. IUPAC[9,10] suggested pH values for the 0.05 mol·kg^{-1} KHPh buffer solution, and in the most recent recommendations,[10] pH values for this buffer are reported at temperatures from (0 to 50) °C. Use of the Hückel model permits the calculation of the values of $\mathrm{p}(m_\mathrm{H})$ [$= -\log(m_\mathrm{H}/m^\circ)$] for this phthalate buffer solution, and, additionally with an extra assumption concerning the values of parameter $\theta_{H,K}$, the calculation of pH values for this buffer and the comparison of resulting pH values with IUPAC values. The assumption that $\theta_{H,K} = 0.012$ (see ref 17) at all temperatures considered was made here. This assumption is not needed in the calculation of the $\mathrm{p}(m_\mathrm{H})$ values, and thus these values can be predicted more reliably than pH values. The results of comparison of pH values

Table 9. Recommended Values of the First Stoichiometric Dissociation Constant (10^3 K_{m1}) for Phthalic Acid from Equation 28 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous KCl Solution When the KCl Molality Effectively Determines the Ionic Strength

	$10^3 K_{m1}$ at I_m/mol·kg^{-1}						
t/°C	0	0.02	0.05	0.1	0.15	0.2	0.3
0	1.199	1.55	1.72	1.88	1.97	2.04	2.11
5	1.190	1.54	1.71	1.87	1.97	2.03	2.10
10	1.178	1.53	1.70	1.86	1.96	2.02	2.10
15	1.163	1.51	1.69	1.85	1.94	2.01	2.09
20	1.146	1.50	1.67	1.83	1.93	1.99	2.07
25	1.127	1.47	1.65	1.81	1.91	1.97	2.05
30	1.106	1.45	1.62	1.78	1.88	1.95	2.03
35	1.082	1.42	1.59	1.75	1.85	1.92	2.00
40	1.057	1.39	1.56	1.72	1.82	1.89	1.97
45	1.030	1.36	1.53	1.69	1.79	1.85	1.94
50	1.001	1.33	1.49	1.65	1.75	1.82	1.90
55	0.971	1.29	1.45	1.61	1.71	1.78	1.86
60	0.940	1.25	1.41	1.57	1.67	1.73	1.82

Table 10. Recommended Values of the Second Stoichiometric Dissociation Constant (10^6 K_{m2}) for Phthalic Acid from Equation 29 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous KCl Solution When the KCl Molality Effectively Determines the Ionic Strength

	$10^6 K_{m2}$ at I_m/mol·kg^{-1}								
t/°C	0	0.02	0.05	0.1	0.15	0.2	0.3	0.5	1.0
0	3.78	6.4	8.0	9.8	11.1	12.1	13.7	15.5	16.8
5	3.89	6.6	8.3	10.2	11.5	12.6	14.2	16.2	17.8
10	3.97	6.8	8.5	10.5	11.9	13.0	14.7	16.9	18.6
15	4.01	6.9	8.7	10.7	12.1	13.3	15.1	17.4	19.3
20	4.02	6.9	8.7	10.8	12.3	13.5	15.4	17.7	19.9
25	3.99	6.9	8.7	10.8	12.4	13.6	15.5	18.0	20.3
30	3.92	6.8	8.7	10.7	12.3	13.6	15.5	18.0	20.6
35	3.82	6.7	8.5	10.6	12.1	13.4	15.4	18.0	20.7
40	3.69	6.5	8.3	10.3	11.9	13.1	15.1	17.7	20.6
45	3.53	6.2	8.0	10.0	11.5	12.7	14.7	17.3	20.3
50	3.34	5.9	7.6	9.6	11.1	12.3	14.2	16.8	19.9
55	3.14	5.6	7.2	9.1	10.5	11.7	13.6	16.2	19.3
60	2.92	5.3	6.8	8.6	10.0	11.1	12.9	15.4	18.6

Table 11. pH Values and p(m_H) Values for the 0.05 mol·kg^{-1} Potassium Hydrogen Phthalate Buffer Solution

t/°C	pH(IUPAC)[a]	pH[b]	p(m_H)[b]	t/°C	pH(IUPAC)[a]	pH[b]	p(m_H)[b]
0	4.000	4.005	3.920	35	4.018	4.014	3.924
5	3.998	3.999	3.914	40	4.027	4.025	3.934
10	3.997	3.996	3.909	45	4.038[c]	4.038	3.946
15	3.998	3.995	3.908	50	4.050	4.054	3.961
20	4.000	3.996	3.908	55	4.064[c]	4.072	3.978
25	4.005	3.999	3.911	60	4.080[c]	4.093	3.998
30	4.011	4.006	3.916				

[a] Recommended by Buck et al.[10] [b] Predicted in the present study. [c] Recommended by Covington et al.[9]

recommended by IUPAC with those predicted by the Hückel method are shown in Table 11 where the agreement is always within 0.01.

p(m_H) values in salt solutions dilute with respect to weak acid species can be used to calibrate glass electrode cells, particularly for titrimetry, so that the cells measure directly the molality of hydrogen ions.[18] Such p(m_H) values are shown in Table 12 for the following two phthalate buffer solutions at temperatures from (0 to 60) °C: 0.005 mol·kg^{-1} KHPh + 0.1 mol·kg^{-1} KCl and 0.005 mol·kg^{-1} KHPh + 0.2 mol·kg^{-1} KCl. The results in Table 12 are analogous to the results in Table 14 in the previous acetic acid study[18] and can be used similarly.

Table 12. p(m_H) Values at Various Temperatures for the Phthalate Buffer Solutions, KHPh(aq, m_b) + KCl(aq, m_s), with m_b = 0.005 mol·kg^{-1} and m_s = 0.1 mol·kg^{-1} and with m_b = 0.005 mol·kg^{-1} and m_s = 0.2 mol·kg^{-1}

	p(m_H) at m_s/mol·kg^{-1}			p(m_H) at m_s/mol·kg^{-1}	
t/°C	0.1	0.2	t/°C	0.1	0.2
0	3.940	3.884	35	3.934	3.872
5	3.932	3.876	40	3.942	3.879
10	3.927	3.870	45	3.952	3.887
15	3.924	3.866	50	3.965	3.899
20	3.923	3.864	55	3.979	3.912
25	3.924	3.865	60	3.996	3.928
30	3.928	3.867			

Summary of the Main Results and Conclusions. In the first part of this study,[1] the activity coefficient equations of the Hückel type were determined for the calculations of K_{m2} of phthalic acid in solutions of K_2Ph, KHPh, and KCl from the Harned cell data measured by Hamer and Acree[2] at temperatures from (0 to 60) °C. In the present part, the corresponding Hückel equations were determined for the calculations of K_{m1} of this acid in solutions of H_2Ph, KHPh, and KCl from the Harned cell data measured by Hamer et al.[3] at the same temperatures. The resulting equations were thoroughly tested with the data used in the parameter estimations, and these data support those well (see Figures 1 and 2 in Part 1[1] and Figures 1 and 2 in this part). Additionally in the present part, the Hückel equations were tested with the plentiful Harned cell data existing in the literature for 0.05 mol·kg^{-1} KHPh solutions containing KCl, and these equations apply well also to these pH buffer solution data (see Figures 3 to 6). The new Hückel equations were then used to evaluate pH values of the phthalate buffer solution (i.e., of the 0.05 mol·kg^{-1} KHPh solution) for comparison with the pH values recommended IUPAC[9,10] at temperatures from (0 to 60) °C. The agreement in this comparison is always within 0.01 (see Table 11).

The single-ion activity coefficient equations of the Hückel type used in this study have proved to be very useful in thermodynamic considerations of weak acid solutions. Previously, the equations of this type have been estimated for acetic,[18] propionic,[19] butyric,[19] formic,[17] and phosphoric (K_{m2})[20,21] acid solutions. In all cases, the existing thermodynamic data can be reproduced almost within experimental error with the resulting equations. Therefore, we have good reasons to believe that the equations of this type will be very useful in the future in thermodynamic treatments of various weak acid solutions.

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