Reviews

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

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Equations were determined for the calculation of the second stoichiometric (molality scale) dissociation constant (K_{m2}) of phosphoric acid in buffer solutions containing sodium dihydrogen phosphate, sodium hydrogen phosphate, and sodium chloride and the corresponding systems where mixed potassium and sodium salts were used from the determined thermodynamic values of this dissociation constant (K_{a2}) and the molalities of the components in the solutions. These equations were based on the single-ion activity coefficient equations of the Hückel type. The parameters of the phosphate 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 of Bates and Acree (1943 and 1945), and these data extend at temperatures from (0 to 60) °C up to ionic strengths of about 0.5 mol kg^{-1}. All calculations from these data were completely revised, and all parameters estimated seem to 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 (2002). The parameters resulted from interactions between hydrogen ions and sodium or potassium ions and from interactions between sodium or potassium ions and chloride ions were taken from our recent studies (2003 or 2005) where these parameter values were determined from the Harned cell data measured by Harned (1935) or Harned and Hamer (1933) in HCl solutions with NaCl or KCl, respectively. In the present paper, the resulting simple equations were successfully tested with the data used in the parameter estimation. In the second part of this study, these equations were additionally tested with all reliable data found in the literature from this dissociation reaction in NaCl and KCl solutions.

Introduction

Solutions of sodium or potassium dihydrogen and hydrogen phosphates have for a long time been used as standard solutions for pH measurements (see, for example, Cohn,[1] Guggenheim and Schindler,[2] and Hitchcock and Taylor[3]). The pH values assigned to the phosphate buffers 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. For this purpose, Bates and Acree[4,5] made a large number of measurements from (0 to 60) °C on Harned cells in solutions of NaH_2PO_4 or KH_2PO_4 with Na_2HPO_4 and NaCl. The revised pH scale of 1962 (see Bates[6]) included two phosphate buffer solutions. In one of those (buffer I1), the molalities of KH_2PO_4 and Na_2HPO_4 were both 0.025 mol kg^{-1}, and in the other (buffer I2) they were 0.008695 and 0.03043 mol kg^{-1}, respectively. In this scale, the pH values were recommended for these buffer solutions from (0 to 95) °C (buffer I1) and from (0 to 50) °C (buffer I2) at intervals of 5 °C, and the values at 25 °C for these buffers were 6.865 (I1) and 7.413 (I2). In 1985 and 2002, IUPAC (see Covington et al.[7] and Buck et al.,[8] respectively) also recommended the pH values of the NBS scale as primary pH standards (in the most recent recommendations,[8] however, only up to 50 °C).

The determination of the pH values of standard solutions is, however, a very difficult problem because it is not possible to measure directly the appropriate single-ion activity coefficients associated with this determination. Empirical models for ionic activity coefficients have been given in the literature for calculations of the pH of standard buffer solutions,[9−16] and 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).

For phosphoric acid, empirical Hückel and Pitzer equations were suggested for the calculation of the second

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stoichiometric molality scale dissociation constant (K_{m2}) in aqueous buffer solutions at 25 °C from the ionic strength of the solution.[16] These equations were also applied in that paper to calculate the pH values of phosphate buffer solutions in various compositions. The pH values calculated by these equations for dilute solutions are strongly supported with all existing electrochemical literature data, but the theoretical interpretation of the parameters in some of these equations is limited, and these Hückel and Pitzer equations apply only to 25 °C. In the present study, a new and more versatile method than those mentioned above is given for calculation of the K_{m2} values of phosphoric 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,[17] because very simple and accurate equations resulted from this choice (see below eqs 1−4). The same method has been earlier applied successfully to acetic,[18] propionic,[19] butyric,[19] and formic acid[20] solutions. The necessary Hückel parameters at various temperatures for phosphate species were estimated from the Harned cell data of Bates and Acree.[4,5] The resulting equations were then tested with the data used in the estimation, and a very good agreement was always obtained. In the next part of this study, all other existing reliable literature data were used to test the resulting model, and it applies also well to these data. There, it will be shown that these equations apply at least satisfactorily also to stronger salt solutions than those where the ionic strength (I_m) is 0.5 mol kg^{-1} and in some cases up to I_m of about 3 mol kg^{-1}.

Using the K_{m2} values from the new model, speciation in phosphate buffer solutions can be determined and, for example, the hydrogen ion molality calculated. The pH values obtained by the model with one reasonable extra assumption are used in our companion paper to check the pH values recommended by IUPAC[7,8] for phosphate buffers from (0 to 70) °C. A very satisfactory agreement is obtained in this comparison. It has been suggested[18,21−23] that $m(\mathrm{H}^+)$ values (or $\mathrm{p}[m(\mathrm{H}^+)] = -\log[(m(\mathrm{H}^+)/m°]$ values where $m° = 1$ mol kg^{-1}) calculated by an equation for K_m of buffer solutions containing NaCl or KCl as a major component and weak acid species as minor components can also be used in calibration of a glass electrode cell used in acidity determination. The $\mathrm{p}[m(\mathrm{H}^+)]$ values, calculated in this way using the new Hückel model for phosphate buffers in NaCl and KCl solutions, are tabulated in our companion paper for the calibration solutions of this kind, and the glass electrode cell calibrated with these solutions measures directly the molality of hydrogen ions.

Theory

In the present study, the following equations were used for the molality scale activity coefficients (γ) of the ions existing in aqueous buffer solutions resulting from sodium or potassium salts of dihydrogen phosphate, hydrogen phosphate, and chloride ions:

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

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

$$\ln \gamma_{\mathrm{HA}} = -\frac{\alpha\sqrt{I_m}}{1 + B_{\mathrm{HA}}\sqrt{I_m}} + b_{\mathrm{Na,HA}}(m_{\mathrm{Na}}/m°) + b_{\mathrm{K,HA}}(m_{\mathrm{K}}/m°) + \theta_{\mathrm{HA,A}}(m_{\mathrm{A}}/m°) \quad (3)$$

$$\ln \gamma_{\mathrm{A}} = -\frac{4\alpha\sqrt{I_m}}{1 + B_{\mathrm{A}}\sqrt{I_m}} + b_{\mathrm{Na,A}}(m_{\mathrm{Na}}/m°) + b_{\mathrm{K,A}}(m_{\mathrm{K}}/m°) + \theta_{\mathrm{HA,A}}(m_{\mathrm{HA}}/m°) \quad (4)$$

where the following symbols are used: H = H^+, Cl = Cl^-, Na = Na^+, K = K^+, HA = $\mathrm{H_2PO_4}^-$, and A = $\mathrm{HPO_4}^{2-}$. I_m in these equations is the ionic strength on the molality scale, α is the Debye−Hückel parameter for which values at various temperatures are given in Tables 1−3 (see Archer and Wang[24]), 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 $B_{\mathrm{H}} = B_{\mathrm{Cl}}$, $B_{\mathrm{HA}} = B_{\mathrm{A}}$, $\theta_{\mathrm{Cl,HA}} = \theta_{\mathrm{Cl,A}} = 0$, and these two θ parameters have been omitted from eqs 2−4.

From the previous HCl results,[25] a value of $B_{\mathrm{H}} = B_{\mathrm{Cl}} = 1.4$ (mol kg^{-1})$^{-1/2}$ was taken for eqs 1 and 2 for all temperatures considered. The following equation was also taken for the parameter $b_{\mathrm{H,Cl}}$ in these equations from the results of that study:

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

In the previous study from acetic acid in NaCl solutions,[18] the following equation was determined from the Harned cell data of Harned[26] for aqueous mixtures of HCl + NaCl:

$$b_{\mathrm{Na,Cl}} + \theta_{\mathrm{H,Na}} = 0.12175 + 0.001075(t/°\mathrm{C}) - 0.0000104(t/°\mathrm{C})^2 \quad (6)$$

In the recent study from formic acid in KCl solutions,[20] the following equation was determined from the Harned cell data of Harned and Hamer[27] for aqueous mixtures of HCl + KCl:

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

Equations 5−7 were determined for temperatures from (0 to 60) °C, and these equations were also used here. Missing parameters for eqs 1, 3, and 4 were estimated here from the data of Bates and Acree.[4,5]

The second thermodynamic dissociation constant (K_{a2}) of phosphoric acid is given by:

$$K_{a2} = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{A}}m_{\mathrm{H}}m_{\mathrm{A}}}{\gamma_{\mathrm{HA}}m_{\mathrm{HA}}m°} = \left(\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{A}}}{\gamma_{\mathrm{HA}}}\right)K_{m2} \quad (8)$$

The stoichiometric dissociation constant K_{m2} in this equation is defined by $K_{m2} = m_{\mathrm{H}}m_{\mathrm{A}}/(m_{\mathrm{HA}}m°)$.

Results and Discussion

Determination of Parameters B_A, $\theta_{HA,A}$ and $b_{Na,A} + \theta_{H,Na} - b_{Na,HA}$. Bates and Acree[4] have measured precise data on Harned cells of the following type at temperatures from (0 to 60) °C:

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|NaH_2PO_4(aq,}\ m_a\mathrm{),\ Na_2HPO_4(aq,}\ m_b\mathrm{),\ NaCl(aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \quad (9)$$

where f is fugacity. The molalities in the three series measured (denoted as A, B, and C) are shown in Table 1.

Table 1. Experimental 10^8 K_{m2} Values for Phosphoric Acid at (0 and 5) °C from Data Measured by Bates and Acree[4] on Cell 9 Where $m_s = m_a$, and the Standard Potential of Silver−Silver Chloride Electrode ($E°$) and the Debye−Hückel Parameter (α) as a Function of the Temperature

m_a	m_b	I_m		t/°C 10^8K_{m2}	
(mol kg^{-1})	(mol kg^{-1})	(mol kg^{-1})	symbol	0	5
0.004213	0.004137	0.020837	43A1	8.459	9.140
0.005978	0.005870	0.029566	43A2	9.204	9.981
0.008598	0.008442	0.042522	43A3	10.20	11.05
0.010151	0.009968	0.050206	43A4	10.75	11.61
0.010491	0.010354	0.052044	43A5	10.91	11.77
0.015090	0.014818	0.074634	43A6	12.24	13.23
0.018456	0.018122	0.091278	43A7	13.13	14.20
0.03017	0.02977	0.14965	43A8	16.00	17.17
0.03592	0.03527	0.17765	43A9	17.02	18.39
0.03726	0.03678	0.18486	43A10	17.30	18.78
0.05199	0.05105	0.25713	43A11	20.15	21.44
0.05507	0.05435	0.27319	43A12	20.51	22.00
0.07340	0.07245	0.36415	43A13	23.50	25.22
0.07475	0.07340	0.36970	43A14	23.49	25.27
0.09079	0.08915	0.44903	43A15	25.68	27.64
0.09079	0.08961	0.45041	43A16	25.92	27.75
0.005365	0.003420	0.02099	43B1	8.454	9.153
0.007546	0.004811	0.02953	43B2	9.270	10.05
0.009764	0.006226	0.03821	43B3	9.909	10.71
0.014911	0.009507	0.05834	43B4	11.43	12.35
0.02343	0.014937	0.09167	43B5	13.41	14.39
0.03459	0.02205	0.13533	43B6	15.58	16.83
0.05294	0.03375	0.20713	43B7	18.70	20.12
0.07410	0.04725	0.28995	43B8	21.62	23.23
0.09079	0.05789	0.35525	43B9	24.08	26.01
0.0019314	0.002953	0.012722	43C1	7.636	8.244
0.002943	0.004501	0.019389	43C2	8.303	8.971
0.004944	0.007560	0.032568	43C3		10.32
0.007914	0.012102	0.052134	43C4	10.85	11.73
0.011957	0.018283	0.078763	43C5	12.41	13.42
0.02578	0.03943	0.16985	43C6	16.44	17.75
0.04820	0.07371	0.31753	43C7	21.24	22.89
0.06661	0.10185	0.43877	43C8	24.43	26.29
0.09079	0.13882	0.59804	43C9	27.96	30.06
($E°$/mV)[a]				236.64	234.15
[α/($m°$)$^{-1/2}$][b]				1.1293	1.1376

[a] Determined previously[25] from the HCl data of Harned and Ehlers.[28,29] [b] $m° = 1$ mol kg^{-1}.

Table 2. Experimental 10^8 K_m Values for Phosphoric Acid at Temperatures from (10 to 35) °C from Data Measured by Bates and Acree[4] on Cell 9 Where $m_s = m_a$, and the Standard Potential of Silver−Silver Chloride Electrode ($E°$) and the Debye−Hückel Parameter (α) as a Function of the Temperature

	t/°C $10^8 K_{m2}$					
symbol[a]	10	15	20	25	30	35
43A1	9.794	10.38	10.82	11.24	11.44	11.67
43A2	10.68	11.31	11.81	12.26	12.49	12.75
43A3	11.82	12.52	13.07	13.58	13.88	14.15
43A4	12.42	13.16	13.76	14.32	14.66	14.99
43A5	12.60	13.34	13.98	14.49	14.90	15.18
43A6	14.14	14.99	15.70	16.33	16.76	17.14
43A7	15.20	16.11	16.87	17.51	17.90	18.31
43A8	18.37	19.47	20.42	21.20	21.81	22.24
43A9	19.64	20.80	21.77	22.66	23.21	23.73
43A10	19.96	21.06	22.30	23.03	23.85	24.41
43A11	22.91	24.26	25.47	26.43	26.93	27.65
43A12	23.52	24.92	26.14	27.15	27.93	28.60
43A13	26.95	28.55	29.93	30.97	32.01	32.77
43A14	26.97	28.57	29.86	31.13	31.99	33.05
43A15	29.47	31.14	32.56	33.92	34.82	35.76
43A16	29.61	31.28	32.77	34.05	35.08	35.96
43B1	9.792	10.35	10.84	11.21	11.54	11.72
43B2	10.78	11.42	11.96	12.36		
43B3	11.46	12.11	12.67	13.14		
43B4	13.20	13.99	14.66	15.19	15.66	16.06
43B5	15.40	16.31	17.09	17.72	18.24	18.46
43B6	17.97	19.06	19.96	20.69	21.37	21.79
43B7	21.47	22.75	23.86	24.81	25.65	26.13
43B8	24.80	26.22	27.49	28.59	29.47	30.05
43B9	27.88	29.67	30.87	31.78	32.64	33.29
43C1	8.802	9.294	9.705	10.12	10.23	10.43
43C2	9.593	10.13	10.62	11.01	11.20	11.44
43C3	10.99	11.60	12.14	12.66	12.85	13.07
43C4	12.55	13.29	13.92	14.46		
43C5	14.35	15.18	15.93	16.55	16.95	17.34
43C6	19.01	20.12	21.12	22.03	22.53	23.18
43C7	24.45	25.87	27.21	28.36	29.13	30.12
43C8	28.09	29.70	31.17	32.39	33.28	34.28
43C9	32.07	33.87	35.55	37.14	38.05	39.41
($E°$/mV)[b]	231.49	228.63	225.64	222.53	219.22	215.75
[α/($m°$)$^{-1/2}$][c]	1.1462	1.1552	1.1646	1.1744	1.1848	1.1956

[a] For the symbols of the solutions, see Table 1. [b] Determined previously[25] from the HCl data of Harned and Ehlers.[28,29] [c] $m° = 1$ mol kg^{-1}.

In these series, m_a is always the same as m_s and the molalities m_a and m_b are in these three series approximately related by equations $m_a(A)/m_b(A) = 1.015$, $m_a(B)/m_b(B) = 1.57$, and $m_a(C)/m_b(C) = 0.654$. 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 cpd.

Experimental K_{m2} values were obtained from these data as follows: The observed K_{m2} value was calculated from each experimental point by

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

$$K_{m2} = \frac{m_H(m_b + m_H)}{(m_a - m_H)m°} \tag{12}$$

In this determination, the $E°$ values determined previously[25] from the HCl data of Harned and Ehlers[28,29] were used, and these values are shown in Tables 1−3. Equations 1 and 2, without the terms containing m_K, 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 not needed in this case because the dissociation does not influence significantly on the ionic strength. The experimental K_{m2} values obtained from the data of Bates and Acree[4] are shown in Tables 1−3.

The thermodynamic dissociation constant K_{a2} and parameters B_A, $\theta_{HA,A}$, and $b_{Na,A} + \theta_{H,Na} - b_{Na,HA}$ were determined at each temperature from the K_{m2} values presented in Tables 1−3 by

$$y_1 = \ln K_{a2} - q_{Na}(m_{Na}/m°) \tag{13}$$

where

$$q_{Na} = b_{Na,A} + \theta_{H,Na} - b_{Na,HA} \tag{14}$$

and

$$y_1 = \ln K_{m2} - \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{3}{1 + B_A\sqrt{I_m}}\right) + b_{H,Cl}(m_{Cl}/m°) + \theta_{HA,A}[(m_a - m_b)/m°] \tag{15}$$

For fixed values of B_A and $\theta_{HA,A}$, quantity y_1 can be calculated from each experimental point; therefore, eq 13 represents in this case an equation of a straight-line y_1 versus ($m_{Na}/m°$). It was observed that a value of −1.0 can be used for parameter $\theta_{HA,A}$. This value is almost the same as that obtained by Covington and Ferra[10] for this quantity

Table 3. Experimental 10^8 K_m Values for Phosphoric Acid at Temperatures from (40 to 60) °C from Data Measured by Bates and Acree[4] on Cell 9 Where $m_s = m_a$, and the Standard Potential of Silver−Silver Chloride Electrode ($E°$) and the Debye−Hückel Parameter (α) as a Function of the Temperature

	t/°C				
	$10^8 K_{m2}$				
symbol[a]	40	45	50	55	60
43A1	11.80	11.88	11.90	11.90	11.78
43A2	12.88	13.00	13.02	13.01	12.87
43A3	14.33	14.45	14.52	14.49	14.36
43A4	15.17	15.31	15.34	15.33	15.15
43A5	15.39	15.54	15.62	15.58	15.46
43A6	17.36	17.56	17.67	17.65	17.53
43A7	18.53	18.73	18.81	18.85	18.71
43A8	22.66	22.87	22.96	22.93	22.79
43A9	24.10	24.44	24.61	24.71	24.66
43A10	24.79	25.12	25.35	25.39	25.29
43A11	28.06	28.51	28.80	28.75	28.66
43A12	29.18	29.50	29.81	29.88	29.78
43A13	33.45	33.91	34.12	34.23	34.12
43A14	33.44	33.88	34.30	34.40	34.34
43A15	36.33	36.89	37.13	37.25	37.30
43A16	36.51	36.98	37.31	37.41	37.37
43B1	11.83	11.90	11.93	11.82	11.76
43B4	16.26	16.43	16.47	16.43	16.34
43B5	18.73	18.98	18.98	18.95	18.84
43B6	22.12	22.42	22.57	22.60	22.52
43B7	26.52	26.87	27.08	27.16	27.22
43B8	31.12	31.40	31.58	31.40	31.50
43B9	33.88	34.36	34.75	34.77	34.75
43C1	10.51	10.55	10.55	10.51	10.42
43C2	11.56	11.62	11.63	11.55	11.42
43C5	17.57	17.73	17.81	17.73	17.48
43C6	23.58	23.67	23.83	23.82	23.68
43C7	30.65	30.88	31.39	31.38	31.15
43C8	34.95	35.26	35.81	35.83	35.79
43C9	39.82	40.34	41.20	41.24	41.20
($E°$/mV)[b]	212.12	208.36	204.50	200.46	196.29
[$\alpha/(m°)^{-1/2}$][c]	1.2068	1.2186	1.2308	1.2436	1.2568

[a] For the symbols of the solutions, see Table 1. [b] Determined previously[25] from the HCl data of Harned and Ehlers.[28,29] [c] $m° = 1$ mol kg^{-1}.

Table 4. Results from Least-Squares Fitting Using Eq 13 from the Phosphoric Acid Data Measured by Bates and Acree on Cell 9 (see Tables 1−3)

t/°C	10^8 K_{a2}	$-\log$ K_{a2}	$s(\log$ $K_{a2})$	(q_{Na})[a]	$s(q_{Na})$[b]	q_{Na} (recd)[c]	(10^3 s)[d]
0	4.905	7.3093	0.0008	−0.229	0.010	−0.217	7.1
5	5.281	7.2773	0.0007	−0.186	0.008	−0.189	5.8
10	5.619	7.2503	0.0006	−0.158	0.008	−0.163	5.6
15	5.917	7.2279	0.0007	−0.133	0.009	−0.139	6.6
20	6.161	7.2103	0.0006	−0.112	0.008	−0.118	5.5
25	6.358	7.1967	0.0005	−0.090	0.006	−0.099	4.1
30	6.464	7.1895	0.0008	−0.080	0.009	−0.082	6.4
35	6.544	7.1842	0.0007	−0.078	0.008	−0.067	5.7
40	6.582	7.1817	0.0008	−0.065	0.009	−0.055	6.3
45	6.590	7.1811	0.0008	−0.048	0.009	−0.045	6.3
50	6.553	7.1836	0.0008	−0.048	0.009	−0.038	6.4
55	6.485	7.1881	0.0008	−0.028	0.010	−0.033	6.7
60	6.376	7.1955	0.0010	−0.020	0.011	−0.030	7.6

[a] $q_{Na} = b_{Na,A} + \theta_{H,Na} - b_{Na,HA}$. [b] Standard deviation of parameter q_{Na} (see footnote *a*). [c] Calculated by eq 16, see footnote *a*. [d] s is the standard deviation about the regression.

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

t/°C	$10^8 K_a$ (exp)[a]	$10^8 K_a$ (recd)[b]	$10^8 K_a$ (B&A)[c]	$10^8 K_a$ (R&S)[d]	$10^8 K_a$ (cell 20)[e]
0	4.91	4.95	4.85	4.87	4.89
5	5.28	5.28	5.24	5.24	5.25
10	5.62	5.59	5.57	5.56	5.59
15	5.92	5.87	5.89	5.85	5.87
20	6.16	6.12	6.12	6.10	6.12
25	6.36	6.32	6.34	6.30	6.32
30	6.46	6.48	6.46	6.45	6.46
35	6.54	6.58	6.53	6.56	6.51
40	6.58	6.64	6.58	6.61	6.57
45	6.59	6.63	6.59	6.61	6.54
50	6.55	6.58	6.55	6.56	6.53
55	6.49	6.47	6.49	6.48	6.42
60	6.38	6.32	6.37	6.35	6.34

[a] The experimental value from the data of cell 9, see Table 4. [b] Calculated from eq 17, and recommended in this study. [c] Recommended by Bates and Acree.[4] [d] Calculated from eq 18 given by Robinson and Stokes.[30] [e] The experimental value from data of cell 20, see Table 9.

for their Pitzer equations. [In ref 10 is given $\theta_{HA,A}$ (in Pitzer formalism) = −0.53, and it should be noted that the present $\theta_{HA,A} = \theta_{HA,A}$(in Hückel formalism) = 2 × $\theta_{HA,A}$ (in Pitzer formalism).] With the value of −1.0 for $\theta_{HA,A}$, a value of 1.3 (mol kg^{-1})$^{-1/2}$ was determined for B_A by searching the value of this parameter that gives with eq 13 the best least-squares fit from the data of Bates and Acree at 25 °C (see Table 2). The determined $\theta_{HA,A}$ and B_A values seem to be independent of the temperature, and these constant values are used here for all temperatures considered.

Once the values of parameters $\theta_{HA,A}$ and B_A have been determined, the data presented in Tables 1−3 were used for the regression analysis with eq 13. The results are shown in Table 4. The experimental q_{Na} values obtained in these linear regression analyses can be correlated with a quadratic equation to temperature giving

$$q_{Na} = -0.2172 + 0.005886(t/°C) - 0.000046(t/°C)^2 \quad (16)$$

Predicted values from eq 16, shown also in Table 4, agree well with the experimental values at all temperatures from (0 to 60) °C. The experimental values, obtained in these calculations, for K_{a2} of phosphoric acid at various temperatures are considered in the next subsection.

Determination of the Second Thermodynamic Dissociation Constant (K_{a2}) for Phosphoric Acid. The experimental K_{a2} values from the regression analysis with eq 13 at temperatures from (0 to 60) °C are shown in Table 4. The logarithms of these values were fitted to a quadratic equation in temperature, and the resulting equation is

$$\ln K_{a2} = -16.82131 + 0.013846(t/°C) - 0.000163(t/°C)^2 \quad (17)$$

The experimental K_{m2} values and the predictions of this equation are shown in Table 5, and these predictions are recommended in the present study. In addition, in Table 5 are shown the K_{a2} values recommended by Bates and Acree[4] on the basis of the data from cell 9, those obtained from data of Bates and Acree[5] on cells of type 20 (see below), and those calculated by the following equation:

$$\log K_{a2} = 5.3541 - 0.019840(T/\mathrm{K}) - \frac{1979.5\mathrm{K}}{T} \quad (18)$$

where T is the temperature in Kelvin (K). This equation is given by Robinson and Stokes,[30] and it was determined from the K_{a2} values recommended by Bates and Acree as given in this table. All K_{a2} values presented in this table agree well.

Results with the New Parameter Values from the Data Measured by Bates and Acree on Cell 9. The experimental K_{m2} values presented in Tables 1−3 were predicted by means of the resulting Hückel model. In the calculations, the recommended K_{a2} values given in Table 5, the $b_{H,Cl}$ values obtained from eq 5, q_{Na} values obtained from eq 16, the $\theta_{HA,A}$ value of −1.00, and the values of B_A

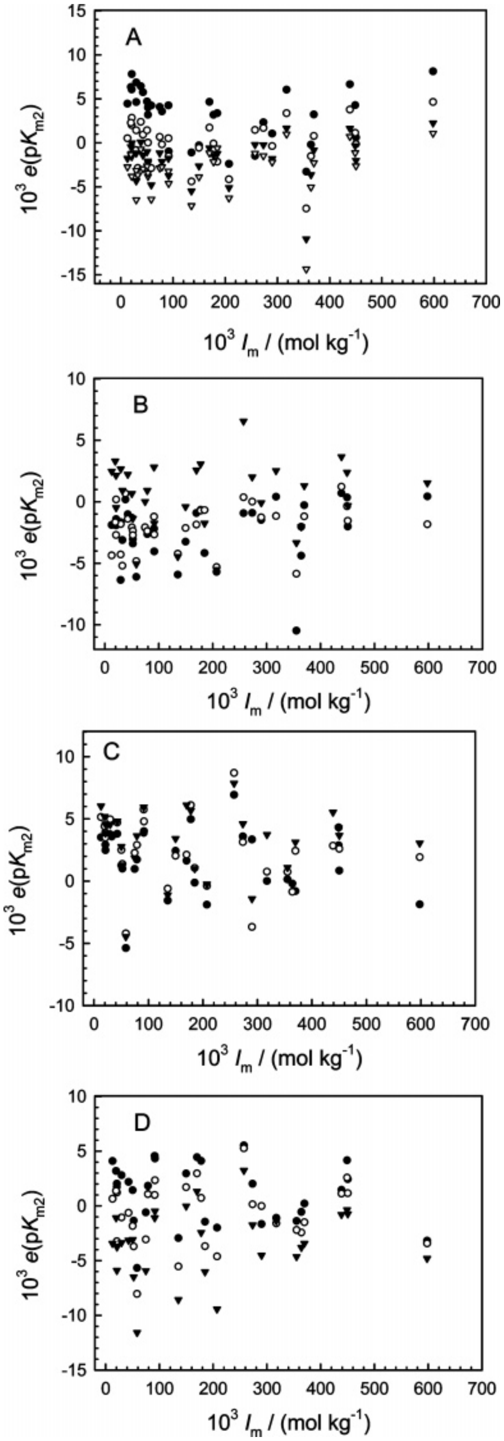

Figure 1. Differences, $e(\mathrm{p}K_{m2})$ in eq 19, between the experimental $\mathrm{p}K_{m2}$ values obtained from the cell potential data of Bates and Acree[4] on cell 9 for phosphoric acid (see Tables 1−3) and those predicted by the Hückel method as a function of the ionic strength I_m. The K_{m2} values were predicted by means of eqs 1, 3, 4, and 8 with the recommended K_{a2} values shown in Table 5 and with the parameter values suggested in this study: ●, 0 °C (A), 20 °C (B), 35 °C (C), 50 °C (D); ○, 5 °C (A), 25 °C (B), 40 °C (C), 55 °C (D); ▼, 10 °C (A), 30 °C (B), 45 °C (C), 60 °C (D); ▽, 15 °C (A).

Table 6. Experimental $10^8\ K_m$ Values for Phosphoric Acid at Temperatures (25 and 0) °C from Data Measured by Bates and Acree[5] on Cell 20 Where $m_b = m_a$

m_a	m_s	I_m		t/°C	
				$10^8\ K_m$	
(mol kg^{-1})	(mol kg^{-1})	(mol kg^{-1})	symbol	25	0
0.004657	0.004660	0.023288	45A1	11.52	8.67
0.007040	0.007043	0.035203	45A2	12.82	9.65
0.007584	0.007591	0.037927	45A3	13.08	9.85
0.009647	0.009651	0.048239	45A4	14.06	10.59
0.012317	0.012328	0.061596	45A5	15.18	11.36
0.013668	0.013672	0.068344	45A6	15.70	
0.018981	0.018999	0.094923	45A7	17.59	13.22
0.019412	0.019422	0.097070	45A8	17.79	13.32
0.02000	0.02000	0.100000	45A9	17.89	
0.02157	0.02158	0.10786	45A10	18.40	
0.02820	0.02822	0.14102	45A11	20.40	15.33
0.02873	0.02875	0.14367	45A12	20.60	15.38
0.03898	0.03898	0.1949	45A13	23.16	
0.06568	0.06568	0.3284	45A14	28.89	
0.019053	0.009921	0.086133	45B1	16.85	12.65
0.03073	0.016003	0.138923	45B2	20.05	14.99
0.05478	0.02853	0.24765	45B3	25.32	19.75
0.09928	0.05170	0.44882	45B4	32.71	24.48
0.02691	0.008411	0.116051	45C1	18.81	14.11
0.05143	0.016069	0.221789	45C2	24.20	18.05
0.09928	0.03087	0.42799	45C3	32.09	24.09
0.010457	0.0012709	0.043099	45D1	13.53	10.16
0.017007	0.002067	0.070095	45D2	15.79	11.84
0.03079	0.003742	0.126902	45D3	19.28	14.43
0.04277	0.005199	0.176279	45D4	22.01	16.47
0.04935	0.005998	0.203398	45D5	23.36	17.41
0.05571	0.006771	0.229611	45D6	24.54	18.28
0.06265	0.007614	0.258214	45D7	25.61	19.14
0.08250	0.010026	0.340026	45D8	28.92	21.58
0.017598	0.0017745	0.072166	45E1	15.91	12.05
0.03802	0.003834	0.155914	45E2	20.97	15.71
0.09928	0.010012	0.407132	45E3	31.17	23.33

Table 7. Experimental $10^8\ K_m$ Values for Phosphoric Acid at Temperatures (5, 10, 15, 20, 30, and 35) °C from Data Measured by Bates and Acree[5] on Cell 20 Where $m_b = m_a$

	t/°C					
	$10^8\ K_{m2}$					
symbol[a]	5	10	15	20	30	35
45A1		10.04		11.13	11.81	
45A2		11.16		12.35	13.18	
45A3	10.62	11.36	12.00	12.57	13.42	13.69
45A4		12.23		13.54	14.49	
45A5	12.25	13.11	13.83	14.50		
45A6	12.74		14.41			16.43
45A7	14.19	15.19	16.05	16.93	18.10	18.50
45A8		15.46		17.13	18.34	
45A10	14.92		16.88			19.42
45A11	16.45	17.65	18.74	19.60	21.09	21.55
45A12		17.88		19.83	21.29	
45A13	18.92		21.29			24.47
45B1	13.61	14.60	15.46	16.15	17.39	17.59
45B2	16.16	17.33	18.35	19.20	20.71	21.04
45B3	20.33	21.78	23.09	24.20	26.12	26.66
45B4	26.31	28.16	29.85	31.24	33.82	34.76
45C1	15.18	16.29	17.23	18.03	19.44	19.72
45C2	19.48	21.05	22.21	23.28	24.93	25.58
45C3	25.86	27.69	29.30	30.71	33.26	33.96
45D1	11.00	11.75	12.42	13.03		
45D2	12.82	13.70	14.50	15.19		
45D3	15.61	16.66	17.64	18.53	19.94	20.41
45D4	17.82	19.04	20.17	21.19	22.68	23.22
45D5	18.83	20.11	21.31	22.43	24.04	24.63
45D6	19.88	21.23	22.48	23.64	25.34	25.98
45D7	20.68	22.13	23.45	24.64	26.47	27.17
45D8	23.31	24.90	26.41	27.77	29.78	30.60
45E1	12.94	13.91	14.73	15.41	16.46	16.87
45E2	16.89	18.11	19.22	20.13	21.69	22.12
45E3	25.12	26.96	28.49	29.89	32.25	33.05

[a] For the symbols of the solutions, see Table 6.

$= B_{HA} = 1.3$ (mol kg^{-1})$^{-1/2}$ and $B_H = 1.4$ (mol kg^{-1})$^{-1/2}$ were used. The results are shown as error plots where the $\mathrm{p}K_{m2}$ error defined by

$$e(\mathrm{p}K_{m2}) = \mathrm{p}K_{m2}(\text{observed}) - \mathrm{p}K_{m2}(\text{predicted}) \quad (19)$$

is presented as a function of the ionic strength of the solution. The results are shown in four panels of Figure 1. Those for the data sets obtained at temperatures from (0 to 15) °C are shown in panel A, from (20 to 30) °C in panel B, from (35 to 45) °C in panel C, and from (50 to 60) °C in panel D. The error plots support well the suggested model.

Table 8. Experimental $10^8 K_m$ Values for Phosphoric Acid at Temperatures from (40 to 60) °C from Data Measured by Bates and Acree[5] on Cell 20 Where $m_b = m_a$

	t/°C				
	$10^8 K_{m2}$				
symbol[a]	40	45	50	55	60
45A1	12.20		12.30		12.10
45A2	13.63		13.78		13.60
45A3	13.86	14.02	14.00	13.96	13.83
45A4	14.98		15.13		14.94
45A6		16.78		16.78	
45A7	18.73	18.92	19.00	18.99	18.86
45A8	19.04		19.38		19.26
45A10		19.91		20.02	
45A11	21.84	22.03	22.02	21.90	21.84
45A12	22.17		22.58		22.47
45A13		25.13		25.38	
45B1	17.80	17.93	18.01	17.97	17.80
45B2	21.33	21.50	21.61	21.60	21.46
45B3	27.10	27.37	27.59	27.63	27.53
45B4	35.35	35.84	36.25	36.44	36.36
45C1	19.98	20.14	20.24	20.21	20.04
45C2	25.96	26.22	26.35	26.40	26.23
45C3	34.50	34.94	35.22	35.37	35.24
45D3	20.73	20.99	21.13	21.19	21.10
45D4	23.61	23.89	24.09	24.14	24.11
45D5	25.04	25.34	25.55	25.66	25.57
45D6	26.46	26.78	27.03	27.14	27.10
45D7	27.63	27.99	28.25	28.36	28.35
45D8	31.14	31.59	31.93	31.98	31.97
45E1	17.09	17.23	17.31	17.30	17.18
45E2	22.43	22.64	22.75	22.77	22.64
45E3	33.61	34.03	34.32	34.41	34.32

[a] For the symbols of the solutions, see Table 6.

Determination of Parameter $b_{K,A} + \theta_{H,K} - b_{K,HA}$. Bates and Acree[5] have also measured precise data on Harned cells of the following type at temperatures from (0 to 60) °C:

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.325\mathrm{kPa)|KH_2PO_4(aq,}\ m_a\mathrm{),}\\ \mathrm{Na_2HPO_4(aq,}\ m_b\mathrm{), NaCl(aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \quad (20)$$

The molalities in the five series measured (denoted as A−E) are shown in Table 6. In these series, m_a is always the same as m_b, and the molalities m_a and m_s are approximately related by equations $m_a(A)/m_s(A) = 1.000$, $m_a(B)/m_s(B) = 1.92$, $m_a(C)/m_s(C) = 3.21$, $m_a(D)/m_s(D) = 8.23$, and $m_a(E)/m_s(E) = 9.92$. The experimental K_{m2} values were obtained from these data as above the corresponding values from the data of cell 9 (see Tables 1−3). In this determination, full eqs 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. The experimental K_{m2} values obtained from the data of Bates and Acree[5] are shown in Tables 6−8.

Values of parameter $b_{K,A} + \theta_{H,K} - b_{K,HA}$ were determined at each temperature using regression analysis from the K_{m2} values presented in Tables 6−8 by

$$y_2 = \ln K_{a2} - q_K(m_K/m^\circ) \quad (21)$$

where

$$q_K = b_{K,A} + \theta_{H,K} - b_{K,HA} \quad (22)$$

and

$$y_2 = \ln K_{m2} - \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{3}{1 + B_A\sqrt{I_m}}\right) + \\ b_{H,Cl}(m_{Cl}/m^\circ) + \theta_{HA,A}[(m_a - m_b)/m^\circ] + q_{Na}(m_{Na}/m^\circ) \quad (23)$$

where again $q_{Na} = b_{Na,A} + \theta_{H,Na} - b_{Na,HA}$ (eq 14). The values of $\theta_{HA,A} = -1.00$ and $B_A = 1.3$ (mol kg^{-1})$^{-1/2}$ were used in this equation, and the q_{Na} values were calculated from eq 16. Quantity y_2 can thus be calculated from each experimental point, and therefore, eq 21 represents an equation of a straight-line y_2 versus (m_K/m°).

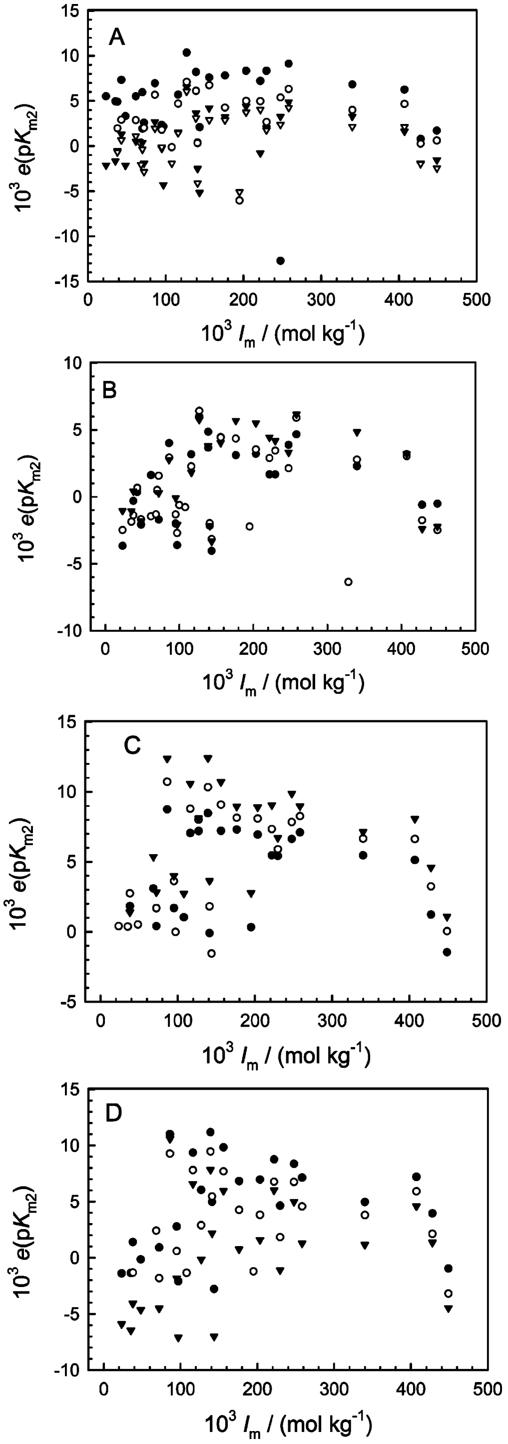

Figure 2. Differences, $e(pK_{m2})$ in eq 19, between the experimental pK_{m2} values obtained from the cell potential data of Bates and Acree[5] on cell 20 for phosphoric acid (see Tables 6−8) and those predicted by the Hückel method as a function of the ionic strength I_m. The K_{m2} values were predicted by means of eqs 1, 3, 4, and 8 with the recommended K_{a2} values shown in Table 5 and with the parameter values suggested in this study. ●, 0 °C (A), 20 °C (B), 35 °C (C), 50 °C (D); ○, 5 °C (A), 25 °C (B), 40 °C (C), 55 °C (D); ▼, 10 °C (A), 30 °C (B), 45 °C (C), 60 °C (D); ▽, 15 °C (A).

The results are shown in Table 9. The resulting q_K values do not depend on the temperature and are close to 0.40.

Table 9. Results from Least-Squares Fitting Using Eq 21 from the Phosphoric Acid Data Measured by Bates and Acree[5] on Cell 20 (see Tables 6−8)

t/°C	$10^8 K_{a2}$	$-\log K_{a2}$	$s(\log K_{a2})$	$(q_K)^a$	$s(q_K)^b$	$(10^3\, s)^c$
0	4.890	7.3107	0.0014	0.37	0.07	10.0
5	5.245	7.2802	0.0011	0.41	0.05	6.8
10	5.592	7.2525	0.0009	0.45	0.05	6.7
15	5.867	7.2316	0.0010	0.42	0.05	6.5
20	6.123	7.2130	0.0009	0.47	0.04	6.6
25	6.323	7.1991	0.0009	0.44	0.04	7.0
30	6.460	7.1898	0.0011	0.46	0.05	7.2
35	6.510	7.1864	0.0013	0.38	0.06	7.6
40	6.572	7.1823	0.0014	0.46	0.06	8.8
45	6.537	7.1846	0.0015	0.40	0.06	8.3
50	6.534	7.1848	0.0015	0.48	0.07	10.0
55	6.418	7.1926	0.0016	0.40	0.07	8.8
60	6.343	7.1977	0.0018	0.51	0.08	11.6

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

Therefore, this value is here recommended for each temperature. The K_{a2} values obtained in these regressions are shown in this table and also in Table 5. It can be seen in Table 5 that they agree well at low temperatures with K_{a2} values recommended above. At higher temperatures, the agreement is only satisfactory but the recommended values seem to be in these cases more reliable. The recommended K_{a2} values are used in the present study in all subsequent calculations.

Results with the New Parameter Values from the Data Measures by Bates and Acree on Cell 20. The experimental K_{m2} values presented in Tables 6−8 were predicted by means of the resulting Hückel model. In these calculations, the value of $q_K = 0.40$ was used together with the parameter values used above for the calculations of the error plots in Figure 1. The results are shown as pK_{m2} error plots in the four panels of Figure 2, which exactly correspond to the panels of Figure 1. The results for the data sets obtained at temperatures from (0 to 15) °C are shown in panel A, from (20 to 30) °C in panel B, from (35 to 45) °C in panel C, and from (50 to 60) °C in panel D. The error plots in these panels support well the suggested model.

Use of the Resulting Hückel Model. The model obtained in this study for the calculations of the second stoichiometric dissociation constant of phosphoric acid in aqueous NaCl and KCl solutions seems to be very useful for many practical applications. This is shown in the second part of this study (a companion paper). There, this model is first tested with almost all reliable thermodynamic data obtained from this dissociation in the literature. This model applies usually very well to these data. Then, equations are given for the calculation of K_{m2} values for phosphoric acid in such NaCl and KCl solutions that are very dilute in phosphate salts. Also equations are given in the second part of this study for the calculation of the pH and pm_H [$= -\log(m_H/m°)$] for phosphate buffer solutions recommended by IUPAC, and the pH values obtained by the equations are compared to the recommended pH values. Calculated pm_H values are also tabulated for buffer solutions containing NaCl or KCl as the major component and phosphate salts as minor components for calibration glass electrode cells for direct measurements of hydrogen ion molality.

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