J. Chem. Eng. Data **2005,** *50,* 497−507

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

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, University of Newcastle,
Newcastle upon Tyne NE1 7RU, U.K.

Equations were determined for the calculation of stoichiometric (molality-scale) dissociation constants, K_m, of monoprotic aliphatic carboxylic acids in buffer solutions containing formic acid, acetic acid, or some other weak acids of this kind and potassium chloride from the thermodynamic dissociation constants, K_a, of the acids and the molalities of the components in the solutions. These equations apply for formic acid to temperatures from (0 to 60) °C and were based on the single-ion activity-coefficient equations of the Hückel type. The parameters of formic acid species for these equations and the thermodynamic dissociation constants of this acid at various temperatures were determined from the Harned cell data of Harned and Embree (1934). All calculations from these data were revised, and the final parameter values obtained are independent of the temperature. The interaction parameters between hydrogen and chloride ions were taken from the results of a previous HCl paper (2002). The parameters that resulted from interactions between hydrogen and potassium ions and between potassium and chloride ions were determined from the Harned cell data of Harned and Hamer (1933) in HCl and KCl solutions. The resulting simple equations for formic acid were tested, in addition to the revised data used in the estimation, with the existing literature data sets measured on galvanic cells with and without a liquid junction at various temperatures. The new equations predict well the data used in the tests. The new equations were used to predict pH and p(m_H) values of the formate buffers that contain equal molalities of (0.01 or 0.1) mol kg^{-1} of formic acid and potassium formate at temperatures from (0 to 60) °C. The p(m_H) values, calculated by these equations, were also tabulated for buffer solutions containing KCl as the major component and formate species as minor components for the calibration of a glass electrode cell in such a way that it measures, directly after calibration, the molality of hydrogen ions. The Hückel equations were also applied to a re-evaluation of the activity parameters of acetate species from the literature data obtained from Harned cells for aqueous mixtures of acetic acid and KCl. The resulting values agree quite well with those obtained here for formate species. It is also shown that the resulting parameter values apply well to species from acetic, formic, propionic (propanoic), butyric (butanoic), 2-methylpropanoic, pentanoic, 2,2-dimethylpropanoic, hexanoic, 4-methylpentanoic, and heptanoic acids from the quinhydrone electrode data of Larsson and Adell (1931) measured in aqueous KCl solutions at 18 °C.

Introduction

Solutions of acetic acid and sodium, or potassium, acetate have been used for a long time as standard solutions for pH measurements (see, e.g., Hitchcock and Taylor,[1] MacInnes et al.,[2] Bates and Gary,[3] Covington et al.,[4] Covington and Rebelo,[5] Camoes et al.,[6] and Buck et al.[7]), and therefore, solutions of acetic acid have been intensively studied at various temperatures (especially in the presence of NaCl, see ref 8 and references therein). Harned and coworkers have also studied intensively, using Harned cells, dilute solutions of formic acid, potassium formate, and KCl,[9] of propionic acid, sodium propionate, and NaCl,[10] and of butyric acid, sodium butyrate, and NaCl[11] at temperatures from (0 to 60) °C. The last two of these studies were considered in detail in a recent study[12] where the thermodynamics of several monoprotic aliphatic carboxylic acids in NaCl solutions were considered. In the present study, KCl solutions are treated, and thus, the formic acid study of Harned and Embree[9] is considered here. Prue and Read[13] investigated at 25 °C formic acid, sodium formate, and NaCl solutions using Harned cells (see ref 12), and Harned and Owen[14] investigated formic acid and NaCl or KCl solutions. Harned and Robinson[15] at 25 °C and Harned and Murphy[16] at (20 to 30) °C measured data using Harned cells in acetic acid and NaCl or KCl solutions. Also, Harned and Hickey treated acetic acid and NaCl solutions[17] in the temperature range (0 to 40) °C (see ref 8) and acetic acid and KCl solutions[18] at 25 °C. Larsson and Adell[19,20] used quinhydrone electrode cells to study several aliphatic carboxylic acids in NaCl or KCl solutions at 18 °C. The NaCl data from these studies were considered in ref 12, and the KCl data are considered here.

For formic acid,[21] acetic acid,[22] propionic acid,[23] and butyric acid,[24] equations have been given for the calculation of the molality-scale stoichiometric dissociation constant, K_m, in aqueous NaCl and KCl solutions at 25 °C from the

---

* 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/je040013i CCC: $30.25

ionic strength of the solutions. The values calculated with these equations apply to less dilute solutions only when the salt effectively determines the ionic strength of the solution. The NaCl results of these equations were considered in refs 8 (acetic acid) and 12 (the other acids), and the KCl results for formic acid are considered here. The parameters for these equations were partially determined from the potentiometric titration data.

In the present study, a new and more versatile method than those presented earlier is given for the calculation of the K_m and pH values for aqueous mixtures of formic acid, potassium formate, and KCl from the composition variables of the solutions, and this method applies to temperatures from (0 to 60) °C and probably up to ionic strengths of $\sim$2.0 mol kg^{-1}. The method is based on the single-ion activity-coefficient equations of the Hückel type. In the parameter estimations of these equations, the previous results[25] from activity coefficients of HCl in pure hydrochloric acid solutions and new results calculated from the data of Harned and Hamer,[26] measured for aqueous mixtures of HCl and KCl, were used. The parameters for the formate species were estimated at various temperatures from (0 to 60) °C from the Harned cell data measured by Harned and Embree.[9] In this parameter estimation, revised data were used, in addition to the original data. The original data were revised so that a probable systematic error in the concentrations of the points was corrected. The resulting equations were tested with all reliable cell potential data existing in the literature for KCl solutions for this temperature range. Also, several monoprotic carboxylic acids other than formic acid were used in the tests, and the resulting parameter values of the formate species apply well to dilute solutions of formic acid, as well as to the other acids used in the tests.

By using the K_m values predicted by the new model, the speciation of, for example, a formic acid solution can be determined and the molality of hydrogen ions can be calculated. The $m(\mathrm{H}^+)$ values obtained in this way were used here, with a reasonable extra assumption, to predict pH values of the formate buffers where the molalities of formic acid and potassium formate are both (0.01 or 0.1) mol kg^{-1} at temperatures from (0 to 60) °C. It has been suggested[27–29] that $m(\mathrm{H}^+)$ values (or $\mathrm{p}[m(\mathrm{H}^+)] = -\log[m(\mathrm{H}^+)/(\mathrm{mol\ kg}^{-1})]$ values) 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 $\mathrm{p}[m(\mathrm{H}^+)]$ values, calculated in this way by using the new Hückel model for formic acid in KCl solutions, were tabulated below for the calibration solutions of this kind. 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 activity coefficients, γ, on the molality scale of species in solutions of a monoprotic weak acid (HA), its potassium salt (KA), and potassium chloride

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

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

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

$$\ln \gamma_{\mathrm{HA}} = \lambda_{\mathrm{HA,K}}(m_{\mathrm{K}}/m^\circ) \tag{4}$$

where $m^\circ = 1$ mol kg^{-1} and where the following symbols are used: $\mathrm{H} = \mathrm{H}^+$, $\mathrm{Cl} = \mathrm{Cl}^-$, $\mathrm{K} = \mathrm{K}^+$, HA = RCOOH, and $\mathrm{A} = \mathrm{RCOO}^-$, where R refers to an alkyl group. I_m is the ionic strength on the molality scale, α is the Debye–Hückel parameter for which values at various temperatures are given in Table 1,[30] 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 $\lambda_{\mathrm{HA},i}$ is the interaction parameter between neutral molecule HA and ion i.

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

$$b_{\mathrm{H,Cl}} = 0.306\,45 - 0.001\,006(t/^\circ\mathrm{C}) \tag{5}$$

The thermodynamic dissociation constant, K_a, of a monoprotic weak acid is given by

$$K_{\mathrm{a}} = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{A}}m_{\mathrm{H}}m_{\mathrm{A}}}{\gamma_{\mathrm{HA}}m_{\mathrm{HA}}m^\circ} = (\gamma_{\mathrm{H}}\gamma_{\mathrm{A}}/\gamma_{\mathrm{HA}})K_{\mathrm{m}} \tag{6}$$

where the stoichiometric dissociation constant, K_m, is defined by the equation $K_{\mathrm{m}} = m_{\mathrm{H}}m_{\mathrm{A}}/(m_{\mathrm{HA}}m^\circ)$.

Results and Discussion

Determination of the Values of the Parameter $b_{K,Cl} + \theta_{H,K}$. Some of the interaction parameters presented in eqs 1 and 2 can reliably be determined for different temperatures from existing data measured with Harned cells where the electrolyte solution comprises aqueous mixtures of HCl and KCl dilute with respect to HCl. The most important data of this kind are probably the sets measured by Harned and Hamer.[26] In these sets, the data were to (0 to 60) °C, and the cell is represented by

$$\mathrm{Pt(s)}|\mathrm{H_2}(\mathrm{g}, f = 101.325\ \mathrm{kPa})|\mathrm{HCl}(\mathrm{aq}, m_{\mathrm{HCl}} = 0.01\ \mathrm{mol\ kg}^{-1}),\ \mathrm{KCl}(\mathrm{aq}, m_{\mathrm{s}})|\mathrm{AgCl(s)}|\mathrm{Ag(s)} \tag{7}$$

where f is the fugacity. The data for salt molalities of (0 to 2) mol kg^{-1} were used in the parameter estimations. The cell potential difference (CPD = E) for cells of type 7 is given by

$$E = E^\circ - (RT/F)\ln\left[\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}m_{\mathrm{H}}m_{\mathrm{Cl}}}{(m^\circ)^2}\right] \tag{8}$$

where E° is the standard CPD. The following equation can be derived from this equation and from eqs 1 and 2:

$$y_1 = E^\circ - (RT/F)u_{\mathrm{K}}(m_{\mathrm{s}}/m^\circ) \tag{9}$$

where

$$u_{\mathrm{K}} = b_{\mathrm{K,Cl}} + \theta_{\mathrm{H,K}} \tag{10}$$

and where

Table 1. Results of Least-Squares Fitting Using eq 9 from the Data of Harned and Hamer[26] on Cells of Type 7, and the Debye–Hückel Parameter, α, as a Function of the Temperature

t/°C	$\alpha/(m°)^{-1/2}$ [a]	$E°$/mV	$s(E°)$/mV	u_K[b]	$s(u_K)$	s[c]/mV	u_K(pred)[d]
0[e]	1.1293	236.77	0.02	0.0089	0.0011	0.06	0.0094
5[e]	1.1376	234.23	0.03	0.0139	0.0013	0.07	0.0139
10[e]	1.1462	231.54	0.03	0.0182	0.0015	0.08	0.0179
15[e]	1.1552	228.70	0.04	0.0218	0.0018	0.10	0.0214
20[e]	1.1646	225.71	0.04	0.025	0.002	0.11	0.0245
25[e]	1.1744	222.57	0.05	0.027	0.002	0.12	0.0270
30[e]	1.1848	219.27	0.05	0.029	0.002	0.14	0.0292
35[e]	1.1956	215.83	0.06	0.031	0.003	0.15	0.0308
40	1.2068	212.26	0.07	0.032	0.003	0.19	0.0320
45	1.2186	208.51	0.08	0.032	0.003	0.20	0.0327
50	1.2308	204.61	0.08	0.033	0.003	0.21	0.0329
55	1.2436	200.55	0.08	0.033	0.004	0.23	0.0327
60	1.2568	196.34	0.09	0.032	0.004	0.24	0.0319

[a] $m° = 1$ mol kg^{-1}. [b] $u_K = b_{K,Cl} + \theta_{H,K}$ (see eq 10). [c] Standard deviation about the regression. [d] Predicted by eq 12. [e] Points where $m_s = 0.05$ mol kg^{-1} and $E = 0.376\,64$ V ($t = 0$ °C), 0.376 77 V (5 °C), 0.376 75 V (10 °C), 0.376 61 V (15 °C), 0.376 34 V (20 °C), 0.375 95 V (25 °C), 0.375 43 V (30 °C), or 0.374 78 V (35 °C) were omitted.

$$y_1 = E + (RT/F)\ln(m_{HCl}/m°) + (RT/F)\ln[(m_{HCl} + m_s)/m°] - \frac{2(RT/F)\alpha\sqrt{I_m}}{1 + B_H\sqrt{I_m}} + (RT/F)b_{H,Cl}[(2m_{HCl} + m_s)/m°] \quad (11)$$

In eq 11, now I_m is $m_{HCl} + m_s$. Equation 9 represents an equation of the straight line y_1 versus $m_s/m°$. The quantity y_1 in this equation, defined by eq 11, can be directly calculated from the experimental data, and the parameter u_K (defined by eq 10) can be determined from the slope of the resulting straight line. The results from these parameter estimations are shown in Table 1.

The experimental u_K values shown in Table 1 can be correlated to the temperature using the following equation:

$$u_K = 0.009\,44 + 0.000\,938\,9(t/°C) - 0.000\,009\,4(t/°C)^2 \quad (12)$$

The predictions from eq 12 are also shown in Table 1, and they agree well with the experimental values. Predicted values of u_K were used to reproduce the data of Harned and Hamer,[26] and they apply well to these data. Error plots for selected temperatures between (0 and 60) °C are presented in Figure 1, where the deviation, $e_{(E)}$, defined by

$$e_{(E)} = E(\text{observed}) - E(\text{predicted}) \quad (13)$$

is presented at each temperature as a function of the salt molality, and these plots demonstrate the agreement.

The parameter value obtained for u_K at 25 °C (=0.027) agrees well with previous results in the literature for this temperature: First, in a previous study,[31] the following Hückel equation was used for the mean activity coefficient of KCl in pure electrolyte solutions at 25 °C:

$$\ln\gamma_\pm = -\frac{\alpha\sqrt{I_m}}{1 + B_{KCl}\sqrt{I_m}} + b_{KCl}(I_m/m°) \quad (14)$$

The following parameter values were determined in that study from literature data of both CPD and isopiestic measurements: $B_{KCl} = 1.28$ (mol kg^{-1})$^{-1/2}$ and $b_{KCl} = 0.015$. Second, from the Pitzer theory,[32,33] the following equation can be derived for activity coefficients of H$^+$ ions in aqueous mixtures of HCl and KCl:

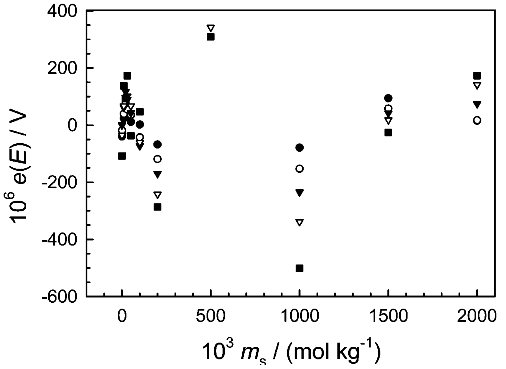

Figure 1. Deviation between the observed and predicted cell potential difference (CPD), $e_{(E)}$ in eq 13, as a function of the salt molality, m_s, in the HCl + KCl sets measured by Harned and Hamer[26] on cell 7 at various temperatures. The predicted CPD was calculated by eqs 1, 2, and 8 with the $E°$ values in Table 1. ●, 0 °C; ○, 10 °C; ▼, 25 °C; ▽, 40 °C; ■, 60 °C.

$$\ln\gamma_H = f^\gamma + 2B_{H,Cl}m_{Cl} + 2\theta_{H,K}(P)m_K + f'(B) \quad (15)$$

where f^γ, B, and $f'(B)$ are functions of the ionic strength of the solution (see ref 33) and where $\theta(P)$ is a parameter related to the interactions between like-charged ions (between H$^+$ and K$^+$ ions in this case). Pitzer and Kim[34] have suggested that $\theta_{H,K}(P)$ is 0.005 at 25 °C. Accordingly, the value of the quantity $b_{KCl} + 2\theta_{H,K}(P) = 0.015 + (2 \times 0.005) = 0.025$ can be compared with the present value of u_K (=0.027). Complete agreement cannot be expected in this comparison because the present B value for hydrogen and chloride ions [i.e., 1.40 (mol kg^{-1})$^{-1/2}$] is close but not identical to the value determined previously for KCl solutions [$B_{KCl} = 1.28$ (mol kg^{-1})$^{-1/2}$]. These results, however, support well the suggested value of u_K at 25 °C.

Determination of the Parameters B_A and $b_{K,A} + \theta_{H,K} - \lambda_{HA,K}$ for Formate Species. Harned and Embree[9] have measured precise data on Harned cells of the following type at temperatures from (0 to 60) °C:

$$\text{Pt(s)}|\text{H}_2(\text{g}, f = 101.325\ \text{kPa})|\text{HA(aq}, m_a), \quad \text{KA(aq}, m_b), \quad \text{KCl(aq}, m_s)|\text{AgCl(s)}|\text{Ag(s)} \quad (16)$$

where A refers to formate ions. The values of the molalities, m_a, m_b, and m_s, are shown at different temperatures in Tables 2–4. The experimental K_m value (see eq 6) for formic acid was obtained from these data for each data point by using the following two equations:

$$\ln(m_H/m°) = \frac{(E° - E)F}{RT} - \ln(\gamma_H\gamma_{Cl}m_{Cl}/m°) \quad (17)$$

$$K_m = \frac{m_H(m_b + m_H)}{(m_a - m_H)m°} \quad (18)$$

In this determination, the $E°$ values obtained previously[25] from the HCl data of Harned and Ehlers[35,36] were used and are shown in Tables 2–4. Equations 1 and 2 were used for the activity coefficients of H$^+$ and Cl$^-$ ions, respectively, and the relevant parameter values for these equations are given above. Iterative calculations were needed in this

Table 2. Experimental 10^4K_m Values for Formic Acid at Temperatures from (0 to 20) °C from Data Measured by Harned and Embree[9] on Cell 16 Where $m_b = m_a/0.7865^a$ and $m_s = m_a/0.9268$, and the Standard Potential of the Silver−Silver Chloride Electrode, $E°$, as a Function of the Temperature

	10^4K_m at the following values of t/°C				
m_a/(mol kg^{-1})	0	5	10	15	20
0.006 451	2.135	2.197	2.244	2.273	2.294
0.012 20	2.279	2.348	2.400	2.433	2.457
0.024 57	2.478	2.557	2.621	2.659	2.683
0.036 60	2.610	2.692	2.760	2.807	2.834
0.048 73	2.710	2.797	2.868	2.921	2.950
0.098 96	2.985	3.073	3.150	3.207	3.246
$E°$ ^{b}/mV	236.64	234.15	231.49	228.63	225.64

[a] This corrected value was used instead of the reported value 0.8021 (see text). [b] Determined previously[25] from the HCl data of Harned and Ehlers.[35,36]

Table 3. Experimental 10^4K_m Values for Formic Acid at Temperatures from (25 to 40) °C from Data Measured by Harned and Embree[9] on Cell 16 Where $m_b = m_a/0.7865^a$ and $m_s = m_a/0.9268$, and the Standard Potential of the Silver−Silver Chloride Electrode, $E°$, as a Function of the Temperature

	10^4K_m at the following values of t/°C			
m_a/(mol kg^{-1})	25	30	35	40
0.006 538	2.316	2.315	2.297	2.182^b
0.011 76	2.467	2.467	2.448	2.408
0.024 45	2.706	2.711	2.690	2.659
0.035 75	2.852	2.852	2.839	2.812
0.048 63	2.978	2.977	2.968	2.943
0.098 76	3.269	3.279	3.281	3.265
$E°$ ^{c}/mV	222.53	219.22	215.75	212.12

[a] This corrected value was used instead of the reported value 0.8021 (see text). [b] Omitted from the subsequent considerations as a probable outlier. [c] Determined previously[25] from the HCl data of Harned and Ehlers.[35,36]

Table 4. Experimental 10^4K_m Values for Formic Acid at Temperatures from (45 to 60) °C from Data Measured by Harned and Embree[9] on Cell 16 Where $m_b = m_a/0.7865^a$ and $m_s = m_a/0.9268$, and the Standard Potential of the Silver−Silver Chloride Electrode, $E°$, as a Function of the Temperature

	10^4K_m at the following values of t/°C			
m_a/(mol kg^{-1})	45	50	55	60
0.006 063	2.206	2.166	2.115	2.046
0.012 38	2.390	2.351	2.296	2.225
0.024 28	2.621	2.581	2.522	2.451
0.036 45	2.793	2.741	2.679	2.610
0.049 00	2.918	2.872	2.806	2.739
0.098 95	3.252	3.205	3.135	3.061
$E°$ ^{b}/mV	208.36	204.50	200.46	196.29

[a] This corrected value was used instead of the reported value 0.8021 (see text). [b] Determined previously[25] from the HCl data of Harned and Ehlers.[35,36]

determination because the dissociation of formic acid influences the ionic strength.

The data of Harned and Embree is probably not free from systematic experimental error (see, e.g., Prue and Read[13]). In the present study, these data were corrected by using at all temperatures a value of 0.7865 for the molality ratio of m_a/m_b (see cell 16) instead of the reported value 0.8021. This correction was chosen, since it leads to the value of K_a for formic acid at 25 °C that agrees closely with the value determined by Prue and Read[13] for this quantity using CPD data (1.82×10^{-4}) and with the value determined by Saxton and Darken[37,38] from conductance data. The value reported by Harned and Embree[9] for K_a at 25 °C on the basis of their data is 1.77×10^{-4}. The experimental K_m values, obtained from the corrected data of Harned and Embree, are shown in Tables 2−4. At all temperatures, the experimental K_m values were also solved here from the original data of Harned and Embree without any corrections, and the present parameter estimations were also carried out with these uncorrected K_m values (see below).

Table 5. Results of Least-Squares Fitting Using eq 19 from the Formic Acid Data of Harned and Embree When the K_m Values Were Obtained with the Corrected Value 0.7865 for m_a/m_b (See Tables 2−4)

t/°C	10^4K_a	$-\log K_a$	$s(\log K_a)$	$q_K{}^a$	$s(q_K)^b$	10^3s^c	$10^4K_a(\text{exptl})^d$
0	1.696	3.7707	0.0004	0.084	0.008	1.5	1.697
5	1.744	3.7585	0.0003	0.098	0.006	1.0	1.744
10	1.781	3.7494	0.0003	0.102	0.006	1.1	1.780
15	1.801	3.7445	0.0004	0.093	0.009	1.5	1.801
20	1.813	3.7416	0.0002	0.096	0.004	0.7	1.812
25	1.825	3.7387	0.0003	0.117	0.007	1.2	1.821
30	1.820	3.7399	0.0003	0.122	0.006	1.0	1.815
35	1.800	3.74483	0.00008	0.0984	0.0016	0.3	1.799
40	1.767	3.7528	0.0007	0.066	0.013	2.0	1.772
45	1.734	3.7611	0.0005	0.031	0.010	1.9	1.743
50	1.698	3.7699	0.0003	0.039	0.007	1.2	1.707
55	1.654	3.7816	0.0002	0.053	0.005	0.9	1.660
60	1.597	3.7966	0.0006	0.033	0.013	2.3	1.606

[a] $q_K = b_{K,A} + \theta_{H,K} - \lambda_{HA,K}$. [b] Standard deviation of the parameter q_K. [c] Standard deviation about the regression. [d] The experimental value of K_a determined by using the recommended value $q_K = 0.10$.

The thermodynamic dissociation constant, K_a, and the parameters B_A and q_K ($=b_{K,A} + \theta_{H,K} - \lambda_{HA,K}$) were determined at each temperature from the K_m values presented in Tables 2−4 by the following equation

$$\ln K_m - \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{1}{1 + B_A\sqrt{I_m}}\right) + b_{H,Cl}(m_{Cl}/m°) = y_2 = \ln K_a - (b_{K,A} + \theta_{H,K} - \lambda_{HA,K})(m_K/m°) = \ln K_a - q_K(m_K/m°) \quad (19)$$

For a fixed value of B_A, the quantity y_2 can be calculated from each experimental point, and therefore, eq 19 represents an equation of the straight line y_2 versus $(m_K/m°)$. It was observed that the value $B_A = 1.8$ (mol kg^{-1})$^{-1/2}$, determined previously for acetate ions,[8] can be used in this equation for formate ions at all temperatures. Once the value of the parameter B_A has been fixed, the data presented in Tables 2−4 were used for the regression analysis using eq 19. The results are shown in Table 5, and the parameter values and dissociation constants in this table thus were based on the K_m values obtained with the slightly corrected molalities of potassium formate, m_b (see above). The same quantities as in Table 5 were also calculated directly from the original data of Harned and Embree without corrections, and these are shown in Table 6.

The values for the thermodynamic dissociation constant, K_a, at various temperatures differ significantly in Tables 5 and 6 from each other. Conversely, the values of the parameter q_K at various temperatures in these tables agree rather well with each other, and additionally, the values of this parameter are close to 0.10 at all temperatures. This value is therefore recommended for q_K at all temperatures. It seems that the K_a values in Table 5 are more reliable than those in Table 6, and for this reason, only these values will be considered below. Table 5 also shows the experimental K_a values obtained by using the recommended value of q_K ($=0.10$) at all temperatures.

Table 6. Results of Least-Squares Fitting Using eq 19 from the Formic Acid Data of Harned and Embree When the K_m Values Were Directly Obtained from the Original Data[9] without Corrections

t/°C	10^4K_a	$-\log K_a$	$s(\log K_a)$	$q_K{}^a$	$s(q_K)^b$	10^3s^c
0	1.663	3.7790	0.0004	0.088	0.009	1.6
5	1.711	3.7668	0.0003	0.104	0.006	1.0
10	1.747	3.7578	0.0003	0.104	0.006	1.0
15	1.766	3.7530	0.0004	0.094	0.008	1.4
20	1.778	3.75009	0.00015	0.099	0.003	0.5
25	1.790	3.7471	0.0003	0.120	0.007	1.2
30	1.785	3.7484	0.0003	0.125	0.005	0.9
35	1.765	3.75330	0.00007	0.1013	0.0015	0.3
40	1.733	3.7611	0.0007	0.070	0.012	1.9
45	1.700	3.7694	0.0005	0.034	0.010	1.7
50	1.666	3.7783	0.0003	0.042	0.005	0.9
55	1.621	3.7901	0.0002	0.053	0.005	0.8
60	1.566	3.8051	0.0006	0.035	0.013	2.3

[a] $q_K = b_{K,A} + \theta_{H,K} - \lambda_{HA,K}$. [b] Standard deviation of the parameter q_K. [c] Standard deviation about the regression.

Table 7. Thermodynamic Dissociation Constant, K_a, of Formic Acid as a Function of the Temperature, t

t/°C	10^4K_a(exptl)^a	10^4K_a(recd)^b	10^4K_a(H&E)^c	10^4K_a(R&S)^d
0	1.697	1.702	1.642	1.641
5	1.744	1.743	1.689	1.689
10	1.780	1.775	1.725	1.726
15	1.801	1.799	1.750	1.751
20	1.812	1.813	1.765	1.766
25	1.821	1.818	1.770	1.770
30	1.815	1.814	1.764	1.764
35	1.799	1.800	1.748	1.748
40	1.772	1.778	1.724	1.723
45	1.743	1.746	1.690	1.690
50	1.707	1.706	1.649	1.649
55	1.660	1.659	1.602	1.602
60	1.606	1.604	1.548	1.550

[a] The experimental value (see Table 5). [b] Calculated from eq 20 and recommended in this study. [c] Calculated from eq 21 given by Harned and Embree.[9] [d] Calculated from eq 22 given by Robinson and Stokes.[39]

Determination of the Thermodynamic Dissociation Constant, K_a, for Formic Acid. The logarithms of the K_a values in Table 5 were fitted to a quadratic equation in temperature, and the resulting equation is

$$\ln K_a = -8.678\,41 + 0.005\,227(t/°\mathrm{C}) - 0.000\,103\,6(t/°\mathrm{C})^2 \quad (20)$$

Predicted values from this equation and also experimental K_m values are shown in Table 7, and the predicted values are preferred. In Table 7 are also shown K_a values calculated by using the following equations:

$$\log K_a = -39.061\,23 - 0.028\,039\,7(T/\mathrm{K}) - \frac{173.624\ \mathrm{K}}{T} + 17.883\,48\log(T/\mathrm{K}) \quad (21)$$

$$\log K_a = 5.2743 - 0.015\,168(T/\mathrm{K}) - \frac{1342.85\ \mathrm{K}}{T} \quad (22)$$

where T is the temperature in Kelvin (K). The former equation was used by Harned and Embree[9] and was based on the temperature dependence for the enthalpy of the dissociation reaction being given by $\Delta H = a + bT + cT^2$, where a, b, and c are constants. The latter equation is given in the textbook of Robinson and Stokes.[39] The K_a values calculated by these two equations do not agree with those recommended in Table 7 but agree with those shown in Table 6. This is due to the fact that both of these equations were based on the original data of Harned and Embree. These data are probably not correct (see above), and therefore, the new K_a values seem to be the more reliable ones.

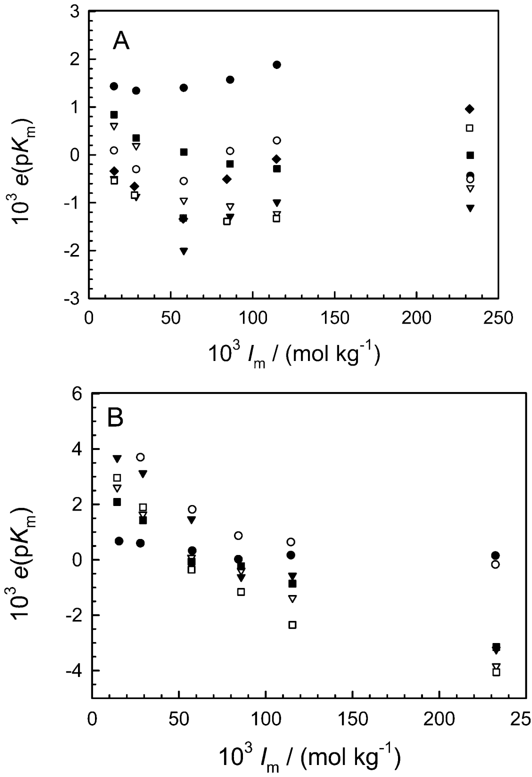

Figure 2. Differences, $e(\mathrm{p}K_m)$ in eq 23, between the experimental $\mathrm{p}K_m$ values obtained from the cell potential data of Harned and Embree[9] for formic acid (see Tables 2−4) and those predicted by the Hückel method as a function of the ionic strength, I_m. The K_m values were predicted from eqs 1, 3, 4, and 6 with the recommended K_a values shown in Table 7 and with the determined parameter values. ●, 0 °C (part A), 35 °C (part 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).

Results with the New Parameter Values from the Data of Harned and Embree. The experimental K_m values given in Tables 2−4 were reproduced by means of the Hückel model. For these calculations, recommended K_a values are given in Table 7, $E°$ values are given in Tables 2−4, $b_{H,Cl}$ values were obtained from eq 5, and the q_K value was 0.10. The results are shown as error plots where the error in $\mathrm{p}K_m$ defined by

$$e(\mathrm{p}K_m) = \mathrm{p}K_m(\text{observed}) - \mathrm{p}K_m(\text{predicted}) \quad (23)$$

is presented as a function of the ionic strength in Figure 2. The results of the data sets for temperatures from (0 to 30) °C are shown in part A and those for the rest (35 °C ≤ t ≤ 60 °C) in part B. The error plots support the suggested model well.

Results with the New Parameter Values from the Harned Cell Data for Mixtures of HCOOH + KCl and of CH₃COOH + KCl. Harned and Owen[14] studied at 25 °C formic acid solutions in cells of the following type:

$$\mathrm{Pt(s)|H_2(g},\ f = 101\ \mathrm{kPa)|HA(aq},\ m_a),\ \mathrm{KCl(aq},\ m_s)\mathrm{|AgCl(s)|Ag(s)} \quad (24)$$

where HA refers to formic acid. In that study, a value of 0.100 31 mol kg^{-1} was used for m_a, and a series of salt solutions were measured where the molality of KCl, m_s,

Table 8. Data Sets Measured by Cells of Type 24 in Acetic Acid Solutions and Used to Test the Present Hückel Model

symbol	t/°C	ref	$m_a/m°$ [a]	N[b]	$m_s/m°$ [a]
HaRo25(0.1)	25[c]	15	0.1005	7	0.05−3.0
HaRo25(0.2)	25[c]	15	0.2001	8	0.05−3.0
HaMu20(0.2)	20[d]	16	0.2	8	0.05−3.0
HaMu25(0.2)	25[c]	16	0.2	8	0.05−3.0
HaMu30(0.2)	30[e]	16	0.2	8	0.05−3.0
HaHi25(0.2)	25[c]	18	0.21	6	0.1−2.0
HaHi25(0.5)	25[c]	18	0.485	4	0.1−2.0

[a] $m° = 1$ mol kg^{-1}. [b] Number of points included. [c] $K_a = 1.756 \times 10^{-5}$ (ref 8). [d] $K_a = 1.756 \times 10^{-5}$ (ref 8). [e] $K_a = 1.748 \times 10^{-5}$ (ref 8).

was varied from (0.05 to 3) mol kg^{-1}. Harned and Robinson,[15] Harned and Murphy,[16] and Harned and Hickey[18] measured cells of type 24 where HA is acetic acid. Some details of these data are shown in Table 8. These data for formic and acetic acids were used to test the suggested Hückel model for formic acid.

Since the solutions in these sets contain a considerable amount of free weak acid, the interactions between weak acid molecules and ions are now more important than earlier in this study. Therefore, the equations of the activity coefficients of $HCOO^-$ and HCOOH (or CH_3COO^- and CH_3COOH) must now be presented as follows (compare with the acetic acid study[8]):

$$\ln \gamma_A = -\frac{\alpha\sqrt{I_m}}{1 + B_A\sqrt{I_m}} + b_{K,A}(m_K/m°) + \lambda_{HA,A}(m_{HA}/m°) \tag{25}$$

$$\ln \gamma_{HA} = \lambda_{HA,K}(m_K/m°) + \lambda_{HA,A}(m_A/m°) \tag{26}$$

Hence, they contain the terms where interactions between formic (or acetic) acid molecules and formate (or acetate) ions are taken into account. In recent studies, a value of −0.27 was determined for $\lambda_{HA,A}$ of formate species[12] and a value of −0.30 for $\lambda_{HA,A}$ of acetate[8] species from Harned cell data of formic and acetic acids in NaCl solutions at 25 °C, and these values are used here. Experimental K_m values obtained (as described above for the data of cell 16) from these data sets were used here to test the present model where $q_K = 0.10$. In the case of acetic acid, the thermodynamic values shown in Table 8 were used for the calculation of the predicted K_m values. The results are shown as pK_m error plots (see eq 23) in part A of Figure 3. The errors in this figure are usually more than 5 times larger than those shown in Figure 2, but also, they support (almost within their experimental precision, that is, probably not better than about 0.01 pK_m units) the suggested Hückel model in all cases at least up to an I_m value of 1.0 mol kg^{-1}. From the acetic acid data sets (see Table 8), the best value of $q_K = 0.15$ can be estimated. The error plots corresponding to this value are shown for the acetic acid sets in part B of this figure. According to this graph, the latter q_K value applies well to all data.

It should be mentioned, additionally, that the inclusion of the value $\lambda_{HA,A} = -0.27$ in the calculation of the formic acid data of Harned and Embree[9] does not significantly affect the results obtained above from these data. This is shown for data at three temperatures, as examples, in Figure 4.

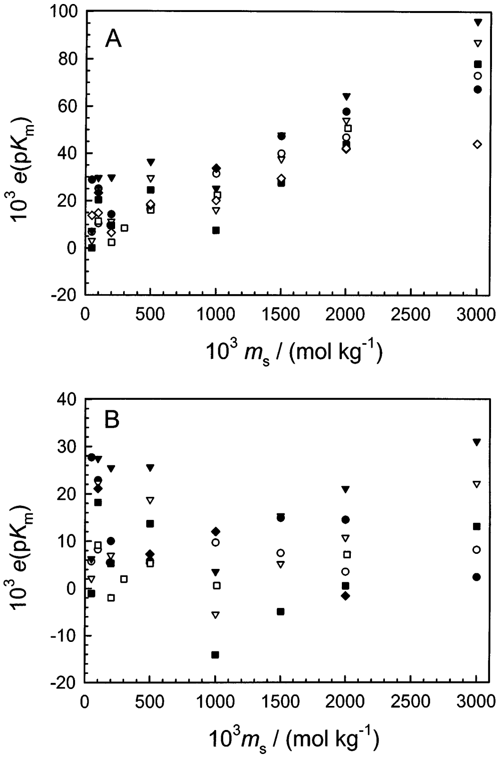

Figure 3. Differences, $e(pK_m)$ in eq 23, between the experimental pK_m values obtained from the cell potential data measured by Harned and Owen[14] on cell 24 for formic acid and by Harned and Robinson,[15] Harned and Murphy,[16] and Harned and Hickey[18] for acetic acid (HA = CH_3COOH, see Table 8) and those predicted by the Hückel method as a function of the salt molality, m_s. The K_m values were predicted from eqs 1, 6, 25, and 26 with the recommended K_a values (for formic acid, $K_a = 1.818 \times 10^{-4}$, and for acetic acid, see Table 8) and with the parameter values suggested in this study. Part A shows the results obtained with the parameter value $q_K = 0.10$ and part B those obtained with the parameter value $q_K = 0.15$ for acetic acid sets (for the symbols of the sets, see Table 8). ●, HaRb25(0.1); ○, HaRb25(0.2); ▼, HaMu20(0.2); ▽, HaMu25(0.2); ■, HaMu30(0.2); □, HaHi25(0.2); ◆, HaHi25(0.5); ◇, formic acid (part A).

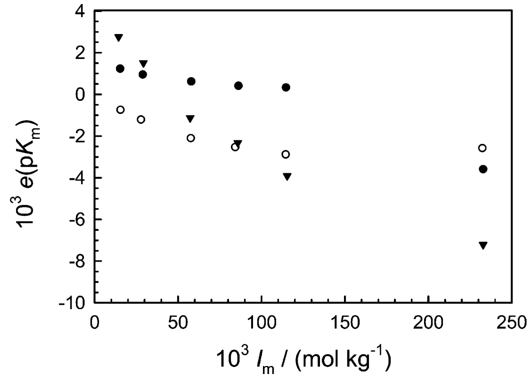

Figure 4. Differences, $e(pK_m)$ in eq 23, between the experimental pK_m values obtained from the cell potential data of Harned and Embree[9] for formic acid (see Tables 2−4) and those predicted by the Hückel method where the $\lambda_{HA,A}$ terms were included as a function of the ionic strength, I_m. The K_m values were predicted from eqs 1, 6, 25, and 26 with the recommended K_a values shown in Table 7 and with the parameter values suggested in this study. ●, 0 °C; ○, 25 °C; ▼, 60 °C.

Results with the New Parameter Values from the K_m Data Measured on Cells Containing a Liquid Junction in KCl Solutions that Are Very Dilute in Weak Acid Species. For aqueous mixtures of HA, KA, and KCl that are very dilute with respect to weak acid species, the following equation is obtained on the basis of the Hückel model:

$$\ln K_{\mathrm{m}} = \ln K_{\mathrm{a}} + \alpha\sqrt{I_{\mathrm{m}}}\left(\frac{1}{1 + B_{\mathrm{H}}\sqrt{I_{\mathrm{m}}}} + \frac{1}{1 + B_{\mathrm{A}}\sqrt{I_{\mathrm{m}}}}\right) - (b_{\mathrm{H,Cl}} + q_{\mathrm{K}})(I_{\mathrm{m}}/m^\circ) \quad (27)$$

The values predicted by this equation for formic acid are given at rounded ionic strengths and various temperatures in Table 9. Values from eq 27 can be compared to K_{m} values obtained from the literature data for all monoprotic aliphatic carboxylic acids in the KCl solutions of this kind.

Larsson and Adell[19,20] measured at 18 °C cell potential differences of quinhydrone (qh) cells of the following type:

$$\mathrm{Hg(l)|Hg_2Cl_2(s)|KCl(aq,}\ c = 3.5\ \mathrm{mol\ dm^{-3})||HA(aq,}\ c_{\mathrm{a}}\mathrm{),}$$
$$\mathrm{NaA(aq,}\ c_{\mathrm{b}}\mathrm{),\ KCl(aq,}\ c_{\mathrm{s}}\mathrm{)|qh(s)|Pt(s)} \quad (28)$$

In the data for each series, the concentrations of HA and NaA were exactly or approximately the same and close to a value of (0.005 or 0.01) mol dm^{-3}. The concentration of KCl varied in each series of measurements from (0 to 3) mol dm^{-3}, and each acid was also measured in NaCl solutions. Larsson and Adell measured using cells of this type many weak acids including several aliphatic carboxylic acids. The experimental data have been reported on the molarity scale. The molarities of salt solutions, c, can be converted into molalities, m, by using the equation of Harned and Owen[40a] for KCl solutions at different temperatures:

$$\frac{cm^\circ}{mc^\circ} = \frac{\rho_0}{\mathrm{g\ cm^{-3}}} - A(m/m^\circ) \quad (29)$$

where $c^\circ = 1$ mol dm^{-3}. A value of 0.0270 was used at 18 °C for the parameter A, and a value of $\rho_0 = \rho(\mathrm{H_2O}) = 0.9986$ g cm^{-3} (see Kell[41]) was used for the density of pure water at this temperature.

The cell potential difference for cells of type 28 is given by

$$E = E^\circ_{\mathrm{QEC}} + (RT/F)\ln(\gamma_{\mathrm{H}} m_{\mathrm{H}}/m^\circ) + E_{\mathrm{corr}} \quad (30)$$

where E°_{QEC} includes the standard qh electrode potential and the potential of the calomel electrode on the left-hand side. The value $E^\circ_{\mathrm{QEC}} = 0.4520$ V, given by Larsson and Adell,[19] was used, but the subsequent treatment is not critically dependent on this choice. The correction term, E_{corr}, is characteristic for a qh electrode cell because the data measured by cells of this kind must be corrected for the salt error of the qh electrode and the diffusion potential associated with the liquid junction in the cell. Larsson and Adell reported the approximate corrections for all experimental points, but their values were not used, as the correction can be evaluated more accurately in the following way (see also refs 12 and 42).

Larsson and Adell[19] also measured potential differences with the quinhydrone electrode cells of type 28 where the weak acid species were replaced by hydrochloric acid. From the CPD data of these cells and the known activity coefficients of HCl in KCl solutions, empirical equations can be determined for the term E_{corr} in eq 30. The activity coefficients of H$^+$ and Cl$^-$ ions can be represented at 18 °C as

$$\ln \gamma_{\mathrm{H}} = \ln \gamma_{\mathrm{Cl}} = -\frac{1.1601\sqrt{I_{\mathrm{m}}/m^\circ}}{1 + 1.25\sqrt{I_{\mathrm{m}}/m^\circ}} + 0.178(I_{\mathrm{m}}/m^\circ) \quad (31)$$

Table 9. Recommended Values of the Stoichiometric Dissociation Constant, 10^4K_{m}, for Formic Acid from eq 27 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

	10^4K_{m} at the following values of I_{m}/m° [a]								
t/°C	0	0.05	0.1	0.2	0.3	0.5	1.0	1.5	2.0
0	1.702	2.42	2.63	2.83	2.92	2.95	2.72	2.37	2.02
5	1.743	2.49	2.70	2.92	3.01	3.04	2.81	2.46	2.11
10	1.775	2.54	2.76	2.99	3.08	3.13	2.90	2.55	2.19
15	1.799	2.58	2.81	3.04	3.15	3.19	2.97	2.62	2.26
18	1.808	2.60	2.83	3.07	3.18	3.23	3.01	2.66	2.29
20	1.813	2.61	2.85	3.09	3.19	3.25	3.03	2.68	2.32
25	1.818	2.63	2.87	3.11	3.23	3.29	3.08	2.73	2.37
30	1.814	2.63	2.88	3.13	3.24	3.31	3.11	2.77	2.41
35	1.800	2.62	2.87	3.12	3.24	3.32	3.13	2.79	2.43
40	1.778	2.60	2.85	3.10	3.23	3.31	3.14	2.81	2.45
45	1.746	2.56	2.81	3.07	3.20	3.28	3.12	2.80	2.46
50	1.706	2.52	2.76	3.02	3.15	3.24	3.10	2.79	2.45
55	1.659	2.46	2.70	2.96	3.09	3.19	3.06	2.76	2.44
60	1.604	2.39	2.63	2.89	3.02	3.12	3.00	2.72	2.41

[a] $m^\circ = 1$ mol kg^{-1}.

Table 10. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where $c_{\mathrm{a}} = c_{\mathrm{b}} = 0.010\ 04$ mol dm^{-3}) for Acetic Acid at 18 °C ($K_{\mathrm{a}} = 1.75 \times 10^{-5}$)[a]

c_{s}/(mol dm^{-3})	m_{s}/(mol kg^{-1})	I_{m}/(mol kg^{-1})	10^5K_{m}
0.1	0.10044	0.11055	2.75
0.2	0.20143	0.21157	3.01
0.5	0.50781	0.51804	3.16
1.0	1.0304	1.0408	2.94
1.5	1.5691	1.5796	2.52
2.0	2.1256	2.1363	2.11
2.5	2.7016	2.7125	1.73
3.0	3.2996	3.3106	1.39

[a] Determined previously[8] from the data of Harned and Ehlers.[35,43]

The estimation of the parameters of this equation was based on the activity-coefficient data in the handbook of Harned and Owen.[40b] The use of eq 31, where the composition variable is the ionic strength, instead of the use of eq 1 for the activity coefficients of hydrogen ions makes the calculations simpler with practically the same results. Using eq 31 for the activity coefficients, the following equation resulted for E_{corr}:

$$\frac{E_{\mathrm{corr}}}{\mathrm{mV}} = 0.54 + 2.305\sqrt{I_{\mathrm{m}}/m^\circ} \quad (32)$$

which is valid up to a molality of 2.0 mol kg^{-1}.

Equations 30 and 32 were then used for the calculation of the K_{m} values for the following carboxylic acids from the data of Larsson and Adell:[19,20] acetic, formic, propionic (propanoic), butyric (butanoic), 2-methylpropanoic, pentanoic, 2,2-dimethylpropanoic, hexanoic, 4-methylpentanoic, and heptanoic acids. K_{m} values were calculated from experimental points for these acids by eq 18 and the following equation:

$$\ln(m_{\mathrm{H}}/m^\circ) = \frac{(E - E^\circ_{\mathrm{QEC}} - E_{\mathrm{corr}})F}{RT} - \ln \gamma_{\mathrm{H}} \quad (33)$$

In these calculations, it was assumed that the observed K_{m} value depends only on the ionic strength of the solution and that eq 31 could be used for the activity coefficient of H$^+$ ions. Iterative calculations were needed because the dissociation of the weak acid influences the ionic strength. The results of these calculations are shown in Tables 10 (acetic acid), 11 (formic acid), 12 (propionic acid), 13 (butyric

Table 11. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = 0.004 88 mol dm^{-3} and c_b = 0.004 22 mol dm^{-3}) for Formic Acid at 18 °C (K_a = 1.81 × 10^{-4})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^4K_m
0.10488	0.10534	0.10987	2.91
0.20488	0.20634	0.21092	3.22
0.50488	0.51276	0.51738	3.37
1.0049	1.0354	1.0401	3.13
1.5049	1.5742	1.5789	2.75
2.0049	2.1307	2.1354	2.27
2.5049	2.7068	2.7116	1.89
3.0049	3.3048	3.3096	1.56

[a] Calculated from eq 20.

Table 12. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = c_b = 0.010 20 mol dm^{-3}) for Propionic Acid at 18 °C (K_a = 1.34 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.1	0.10044	0.11071	2.15
0.2	0.20143	0.21173	2.33
0.5	0.50782	0.51820	2.44
1.0	1.0304	1.0409	2.26
1.5	1.5691	1.5798	1.96
2.0	2.1256	2.1364	1.63
2.5	2.7017	2.7127	1.34

[a] Determined previously[12] from the data of Harned and Ehlers.[10]

Table 13. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = 0.010 66 mol dm^{-3} and c_b = 0.010 00 mol dm^{-3}) for Butyric Acid at 18 °C (K_a = 1.53 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.1	0.10044	0.11051	2.46
0.2	0.20143	0.21153	2.68
0.5	0.50781	0.51800	2.83
1.0	1.0304	1.0407	2.61
1.5	1.5691	1.5796	2.23
2.0	2.1256	2.1362	1.88
2.5	2.7016	2.7125	1.58
3.0	3.2996	3.3106	1.27

[a] Determined previously[12] from the data of Harned and Sutherland.[11]

Table 14. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = c_b = 0.010 00 mol dm^{-3}) for 2-Methylpropanoic (Isobutyric) Acid at 18 °C (K_a = 1.44 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.1	0.10044	0.11051	2.30
0.2	0.20143	0.21153	2.54
0.5	0.50781	0.51800	2.66
1.0	1.0304	1.0407	2.50
1.5	1.5691	1.5796	2.21
2.0	2.1256	2.1362	1.88
2.5	2.7016	2.7125	1.56
3.0	3.2996	3.3106	1.27

[a] Determined by Larsson and Adell.[20]

Table 15. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = c_b = 0.011 21 mol dm^{-3}) for Pentanoic (*n*-Valeric) Acid at 18 °C (K_a = 1.51 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.1	0.10044	0.11173	2.43
0.2	0.20144	0.21276	2.64
0.5	0.50783	0.51924	2.77
1.0	1.0304	1.0420	2.60
1.5	1.5692	1.5809	2.26
2.0	2.1257	2.1376	1.88
2.5	2.7018	2.7139	1.56
3.0	3.2997	3.3120	1.27

[a] Determined by Larsson and Adell.[20]

Table 16. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = c_b = 0.010 26 mol dm^{-3}) for 2,2-Dimethylpropanoic (Trimethylacetic) Acid at 18 °C (K_a = 0.94 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.1	0.10044	0.11076	1.53
0.2	0.20143	0.21178	1.68
0.5	0.50782	0.51826	1.81
1.0	1.0304	1.0410	1.74
1.5	1.5691	1.5799	1.58
2.0	2.1256	2.1365	1.36
3.0	3.2996	3.3109	0.95

[a] Determined by Larsson and Adell.[20]

Table 17. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = c_b = 0.005 02 mol dm^{-3}) for Hexanoic (Caproic) Acid at 18 °C (K_a = 1.43 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.10502	0.10548	0.11055	2.29
0.20502	0.20649	0.21157	2.53
0.50502	0.51291	0.51804	2.62
1.0050	1.0356	1.0408	2.45
1.5050	1.5744	1.5796	2.12
2.0050	2.1309	2.1363	1.80
2.5050	2.7071	2.7125	1.47
3.0050	3.3051	3.3106	1.21

[a] Determined by Larsson and Adell.[20]

Table 18. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where c_a = c_b = 0.005 00 mol dm^{-3}) for 4-Methylpentanoic (Isocaproic) Acid at 18 °C (K_a = 1.46 × 10^{-5})[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.10500	0.10546	0.11051	2.34
0.20500	0.20647	0.21153	2.58
0.50500	0.51289	0.51800	2.66
1.0050	1.0355	1.0407	2.48
1.5050	1.5743	1.5796	2.15
2.0050	2.1309	2.1362	1.83
2.5050	2.7070	2.7125	1.51
3.0050	3.3050	3.3106	1.24

[a] Determined by Larsson and Adell.[20]

acid), 14 (2-methylpropanoic acid), 15 (pentanoic acid), 16 (2,2-dimethylpropanoic acid), 17 (hexanoic acid), 18 (4-methylpentanoic acid), and 19 (heptanoic acid).

The experimental K_m values shown in Tables 10−19 were used in tests of the Hückel model with the parameter values B_A = 1.8 (mol kg^{-1})$^{-1/2}$ and q_K = 0.1 for all acids. The results are shown as pK_m error plots (eq 23) in Figures 5 (acetic, formic, propionic, and butyric acids), 6 (2-methylpropanoic, pentanoic, and 2,2-dimethylpropanoic acids), and 7 (hexanoic, 4-methylpentanoic, and heptanoic acids). The values of the thermodynamic dissociation constant, K_a, used in the calculations for all acids are shown in Tables 10−19.

It can be seen in Figures 5−7 that the Hückel model applies very well to these data. All errors in these figures are small and close to the experimental accuracy of the K_m values even at the highest molality used (~3 mol kg^{-1}). The only exception is the data for 2,2-dimethylpropionic acid (see Figure 6), and for the species of this acid, the value q_K = 0.1 does not apply very well. It is consistent with the

Table 19. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 28 Where $c_a = c_b =$ 0.005 01 mol dm^{-3}) for Heptanoic Acid at 18 °C ($K_a = 1.42 \times 10^{-5}$)[a]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	10^5K_m
0.10501	0.10547	0.11053	2.27
0.20501	0.20648	0.21155	2.47
0.50501	0.51290	0.51802	2.62
1.0050	1.0356	1.0407	2.44
1.5050	1.5744	1.5796	2.13
2.0050	2.1309	2.1362	1.76
2.5050	2.7071	2.7125	1.46
3.0050[b]	3.3051	3.3106	1.22

[a] Determined by Larsson and Adell.[20] [b] c_a is 0.004 46 mol dm^{-3} instead of 0.005 01 mol dm^{-3}.

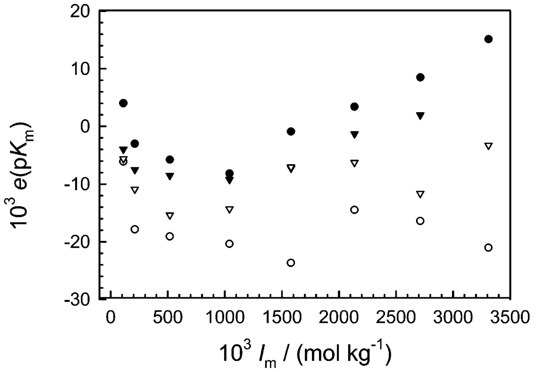

Figure 5. Differences, $e(pK_m)$ in eq 23, between the pK_m values obtained from the cell potential data measured by Larsson and Adell on cell 28 at 18 °C for acetic acid[19] (Table 10), formic acid[20] (Table 11), propionic acid[20] (Table 12), and butyric acid[20] (Table 13) and those predicted by the Hückel method as a function of the ionic strength, I_m. The K_m values were predicted from eq 27 with the K_a values shown in Tables 10−13. ●, acetic acid; ○, formic acid; ▼, propionic acid; ▽, butyric acid.

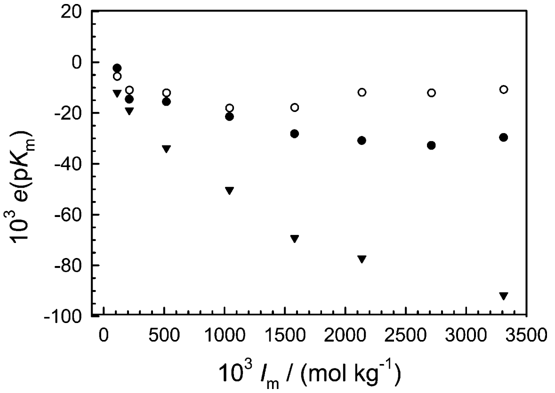

Figure 6. Differences, $e(pK_m)$ in eq 23, between the pK_m values obtained from the cell potential data measured by Larsson and Adell[20] on cell 28 at 18 °C for 2-methylpropanoic acid (Table 14), pentanoic acid (Table 15), and 2,2-dimethylpropanoic acid (Table 16) and those predicted by the Hückel method as a function of the ionic strength, I_m. The K_m values were predicted from eq 27 with the K_a values shown in Tables 14−16. ●, 2-methylpropanoic acid; ○, pentanoic acid; ▼, 2,2-dimethylpropanoic acid.

previous NaCl results[12] that almost all aliphatic carboxylic acids have the same value for the parameter q_K (=0.1) in their Hückel equations.

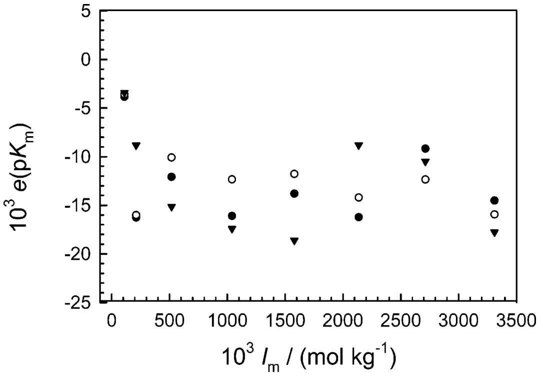

Figure 7. Differences, $e(pK_m)$ in eq 23, between the pK_m values obtained from the cell potential data measured by Larsson and Adell[20] on cell 28 at 18 °C for hexanoic acid (Table 17), 4-methylpentanoic acid (Table 18), and heptanoic acid (Table 19) and those predicted by the Hückel method as a function of the ionic strength, I_m. The K_m values were predicted from eq 27 with the K_a values shown in Tables 17−19. ●, 4-methylpentanoic acid; ○, hexanoic acid; ▼, heptanoic acid.

The recommended K_m values in Table 9 can be compared to the values calculated using equations suggested in the literature for K_m of formic acid. The following three such equations are considered. In ref 21 is given an equation of the following type for formic acid at 25 °C on the basis of potentiometric glass electrode data:

$$\ln K_m = \ln K_a + \frac{\alpha\sqrt{I_m}}{1 + B_H\sqrt{I_m}} + \frac{\alpha\sqrt{I_m}}{1 + B_A\sqrt{I_m}} - (b_{H,KCl} + b_{A,KCl})(I_m/m°) \quad (34)$$

where $K_a = 1.82 \times 10^{-4}$, $B_H = 1.25$ (mol kg^{-1})$^{-1/2}$, $B_A = 1.4$ (mol kg^{-1})$^{-1/2}$, $b_{H,KCl} = 0.178$, and $b_{A,KCl} = 0.308$. This equation is also supported by the Harned cell data in the literature, and it applies usually up to $I_m = 0.5$ mol kg^{-1}.

DeRobertis et al.[44] have suggested on the basis of potentiometric titration data the following general equation for the dissociation constant of monoprotic carboxylic acids in aqueous KCl solutions:

$$\log K_m = \log K_a + \frac{2\sqrt{I_m/m°}}{2 + 3\sqrt{I_m/m°}} - C(I_m/m°) - E(I_m/m°)^2 \quad (35)$$

In the present study, this equation was tested at temperatures of (20, 25, and 30) °C, and the following values of the parameters are given in that paper: $C = 0.1042$ and $E = 0.005\,22$, and they do not depend on the temperature.

Barriada et al.[45] have suggested a Pitzer equation of the following type for the K_m values of monoprotic weak acids in salt solutions:

$$\log K_{m,MCl} = \log K_a - \frac{2}{\ln(10)}f' - \frac{2\beta^1_{MCl}}{\ln(10)}I_m \exp(-2\sqrt{I_m/m°}) - A(I_m/m°) - B[1 - (1 + 2\sqrt{I_m/m°})\exp(-2\sqrt{I_m/m°})] \quad (36)$$

where

$$f' = -(\alpha/3)\left\{\frac{\sqrt{I_m}}{1 + 1.2\sqrt{I_m/m°}} + \frac{2\sqrt{m°}}{1.2}\ln(1 + 1.2\sqrt{I_m/m°})\right\} \quad (37)$$

where in this case MCl is KCl. In eq 36, β^1 is a Pitzer parameter that is dependent on the electrolyte MCl and

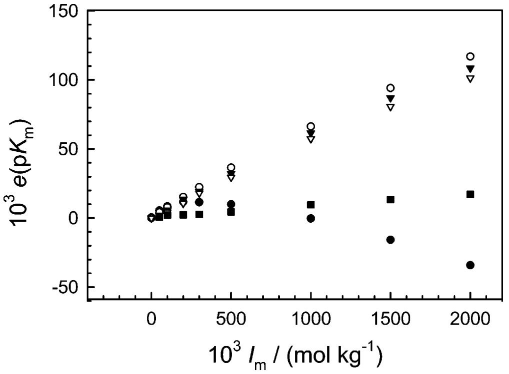

Figure 8. Difference between the recommended pK_m values and the predicted pK_m values, $e(\mathrm{p}K_\mathrm{m})$ = pK_m(recommended) − pK_m(predicted), for formic acid in KCl solutions as a function of the ionic strength, I_m. The recommended K_m values were taken from Table 9, and the K_m values were predicted by means of eqs 34−36. For eq 35, the K_a values recommended here were used. ●, eq 34, 25 °C; ○, eq 35, 20 °C; ▼, eq 35, 25 °C; ▽, eq 35, 30 °C; ■, eq 36, 18 °C.

Table 20. pH Values and p(m_H) Values for the Formate Buffer Solutions, HCOOH(aq, m_a) + HCOOK(aq, m_b), with $m_\mathrm{a} = m_\mathrm{b}$ = 0.01 mol kg^{-1} and with $m_\mathrm{a} = m_\mathrm{b}$ = 0.1 mol kg^{-1}

	$m_\mathrm{a} = m_\mathrm{b}$ = 0.01 mol kg^{-1}		$m_\mathrm{a} = m_\mathrm{b}$ = 0.1 mol kg^{-1}	
t/°C	pH	p(m_H)	pH	p(m_H)
0	3.745	3.701	3.676	3.569
5	3.735	3.691	3.665	3.557
10	3.727	3.683	3.657	3.548
15	3.721	3.676	3.650	3.541
20	3.717	3.672	3.646	3.535
25	3.716	3.671	3.644	3.533
30	3.716	3.671	3.644	3.532
35	3.719	3.673	3.646	3.533
40	3.724	3.678	3.651	3.536
45	3.731	3.684	3.658	3.542
50	3.740	3.693	3.666	3.550
55	3.752	3.704	3.677	3.559
60	3.765	3.717	3.691	3.572

the temperature. The adjustable parameters in this equation are K_a, A, and B. Barriada et al. estimated the parameters for this equation for several acids from the original qh electrode data of Larsson and Adell (see above). For formic acid in KCl solutions, they obtained the following values: pK_a = 3.745, A = 0.215, and B = 0.205. For KCl at 18 °C, the value of β_1 is 0.2047.[45]

In the present study, the three equations (eqs 34−36) were tested with the K_m values that were calculated by the recommended Hückel method and are given in Table 9. In the calculations with eq 35, the K_a values recommended in this study (see eq 20) were used at various temperatures. The results are shown as error plots in Figure 8. These tests show that the predictions of eq 34 agree quite well with the recommended values in Table 9 up to an I_m value of 2.0 mol kg^{-1}. Equation 36 predicts in this case very well the recommended values at all ionic strengths considered. On the other hand, the general equation suggested by DeRobertis et al. (eq 35) applies well in this case only to dilute salt solutions at the three temperatures used in the tests.

Suggestion of the pH and p(m_H) Values for Formate Buffer Solutions. Bates and Gary[3] have suggested p($a_\mathrm{H}\gamma_\mathrm{Cl}$) values for formate buffers with $m_\mathrm{a}/m_\mathrm{b}$ = 0.8021 and $m_\mathrm{a}/m_\mathrm{s}$ = 0.9268 at temperatures from (0 to 60) °C and at rounded ionic strengths from (0.02 to 0.15) mol kg^{-1} on the basis of the original data of Harned and Embree.[9] It seems to us, however, that these values are not theoretically and practically important enough to be recalculated here by using the present Hückel model.

Table 21. p(m_H) Values at Various Temperatures for the Formate Buffer Solutions, HCOOH(aq, m_a) + HCOOK(aq, m_b) + KCl(aq, m_s), with $m_\mathrm{a} = m_\mathrm{b}$ = 0.01 mol kg^{-1} and m_s = 0.2 mol kg^{-1}, with $m_\mathrm{a} = m_\mathrm{b}$ = 0.01 mol kg^{-1} and m_s = 0.5 mol kg^{-1}, and with $m_\mathrm{a} = m_\mathrm{b}$ = 0.01 mol kg^{-1} and m_s = 1.0 mol kg^{-1}

t/°C	m_s = 0.2 mol kg^{-1}	m_s = 0.5 mol kg^{-1}	m_s = 1.0 mol kg^{-1}
0	3.568	3.554	3.588
5	3.556	3.540	3.574
10	3.546	3.530	3.561
15	3.538	3.521	3.551
20	3.533	3.514	3.542
25	3.529	3.509	3.536
30	3.527	3.506	3.532
35	3.528	3.505	3.529
40	3.530	3.506	3.529
45	3.534	3.509	3.531
50	3.541	3.514	3.534
55	3.549	3.521	3.539
60	3.560	3.530	3.547

On the other hand, the following two buffer solutions seem to be important: 0.01 mol kg^{-1} HCOOH + 0.01 mol kg^{-1} HCOOK and 0.1 mol kg^{-1} HCOOH + 0.1 mol kg^{-1} HCOOK. The present Hückel model permits the calculations of the pH values and also the p(m_H) [= −log($m_\mathrm{H}/m°$)] values for these buffer solutions from (0 to 60) °C. For the calculation of the pH values, an extra assumption concerning the value of the parameter $\theta_\mathrm{H,K}$ is needed. The assumed value is ($u_\mathrm{K} - b_\mathrm{KCl}$ = 0.027 − 0.015 =) 0.012 at all temperatures considered (see above and the previous acetic acid study).[8] In the calculation of the p(m_H) values, this assumption is not needed, and therefore, these values can be predicted more reliably than the pH values. The calculated pH and p(m_H) values are shown in Table 20.

p(m_H) values for salt solutions that are dilute with respect to the weak acid species can be used to calibrate a glass electrode cell so that the cell measures directly the molality of hydrogen ions (see, e.g., ref 8). For this purpose, in Table 21 are shown the p(m_H) values for three buffer solutions at various temperatures from (0 to 60) °C: all buffer solutions contain 0.01 mol kg^{-1} formic acid + 0.01 mol kg^{-1} potassium formate, and the molalities of KCl in these are 0.2, 0.5, or 1.0 mol kg^{-1}.

Literature Cited

(1) 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.

(2) MacInnes, D. A.; Belcher, D.; Shedlovsky, T. The Meaning and Standardization of the pH Scale. *J. Am. Chem. Soc.* **1938**, *60*, 1094−1099.

(3) Bates, R. G.; Gary, R. Acidity Functions. Values of the Quantity p($a_\mathrm{H}\gamma_\mathrm{Cl}$) for Buffer Solutions From 0 to 95 °C. *J. Res. Natl. Bur. Stand., Sect. A* **1961**, *65*, 495−505.

(4) 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.

(5) Covington, A. K.; Rebelo, M. J. F. Determination of pH Values over the Temperature Range 5−60 °C for Some Operational Reference Standard Solutions and the Values of the Conventional Residual Liquid-Junction Potentials. *Anal. Chim. Acta* **1987**, *200*, 245−260.

(6) 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.

(7) 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.

(8) 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 (0−60) °C. *J. Chem. Eng. Data* **2003**, *48*, 797−807.

(9) Harned, H. S.; Embree, N. D. The Ionization Constant of Formic Acid from 0 to 60°. *J. Am. Chem. Soc.* **1934**, *56*, 1042−1044.

(10) Harned, H. S.; Ehlers, R. W. The Dissociation Constant of Propionic Acid from 0 to 60°. *J. Am. Chem. Soc.* **1933**, *55*, 2379−2383.

(11) Harned, H. S.; Sutherland, R. O. The Ionization Constant of *n*-Butyric Acid from 0 to 60°. *J. Am. Chem. Soc.* **1934**, *56*, 2039−2041.

(12) 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.

(13) Prue, J. E.; Read, A. J. Acidity Constant of Formic Acid. *Trans. Faraday Soc.* **1966**, *62*, 1271−1274.

(14) Harned, H. S.; Owen, B. B. The Thermodynamic Properties of Weak Acids and Bases in Salt Solutions, and an Exact Method of Determining their Dissociation Constants. *J. Am. Chem. Soc.* **1930**, *52*, 5079−5091.

(15) Harned, H. S.; Robinson, R. A. The Ionic Concentrations and Activity Coefficients of Weak Electrolytes in Certain Salt Solutions. *J. Am. Chem. Soc.* **1928**, *50*, 3157−3178.

(16) Harned, H. S.; Murphy, G. M. The Temperature Coefficient of Dissociation of Acetic Acid in Potassium and Sodium Chloride Solutions. *J. Am. Chem. Soc.* **1931**, *53*, 8−17.

(17) Harned, H. S.; Hickey, F. C. The Ionization of Acetic Acid in Aqueous Sodium Chloride Solutions from 0 to 40 °C. *J. Am. Chem. Soc.* **1937**, *59*, 1284−1288.

(18) Harned, H. S.; Hickey, F. C. Salt Action on the Ionization of Acetic Acid and Hydrolysis of the Acetate Ion. *J. Am. Chem. Soc.* **1937**, *59*, 2303−2304.

(19) Larsson, E.; Adell, B. Die electrolytische Dissoziation von Säuren in Salzlösungen. I. Die Dissoziationskonstante der Essigsäure und die Aktivitätsverhältnisse ihrer Ionen in den Lösungen einiger Alkali- und Erdalkalichloride. *Z. Phys. Chem. A* **1931**, *156*, 352−380.

(20) Larsson, E.; Adell, B. Die electrolytische Dissoziation von Säuren in Salzlösungen. II. Die Dissoziationskonstanten einiger Fettsäuren und die Aktivitätsverhältnisse ihrer Ionen in Natriumchlorid- und Kaliumchloridlösungen. *Z. Phys. Chem. A* **1931**, *156*, 381−396.

(21) Partanen, J. I.; Juusola, P. M. Determination of Stoichiometric Dissociation Constants of Formic Acid in Aqueous Sodium or Potassium Chloride Solutions at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 110−115.

(22) Partanen, J. I. Determination of Stoichiometric Dissociation Constants for Formic, Acetic, Glycolic and Lactic Acids in Dilute Aqueous Potassium, Sodium or Lithium Chloride Solutions at 298.15 K. *Acta Chem. Scand.* **1998**, *52*, 985−994.

(23) Partanen, J. I.; Juusola, P. M.; Minkkinen, P. O. Determination of Stoichiometric Dissociation Constants for Propionic Acid in Aqueous Sodium or Potassium Chloride Solutions at 298.15 K. *Acta Chem. Scand.* **1999**, *53*, 547−556.

(24) Partanen, J. I.; Juusola, P. M. Determination of Stoichiometric Dissociation Constant of *n*-Butyric Acid in Aqueous Sodium or Potassium Chloride Solutions at 298.15 K. *Fluid Phase Equilib.* **2000**, *173*, 135−148.

(25) Partanen, J. I.; Covington A. K. Re-evaluation of the Activity Coefficients of Aqueous Hydrochloric Acid Solutions up to a Molality of 2.0 mol kg^{-1} Using Two-Parameter Hückel and Pitzer Equations. Part II. Results from 0 to 95 °C. *J. Solution Chem.* **2002**, *31*, 197−210.

(26) 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.

(27) McBryde, W. A. E. The pH Meter as a Hydrogen Concentration Probe. *Analyst* **1969**, *94*, 337−346; **1971**, *96*, 739−740.

(28) 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.

(29) 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.

(30) 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.

(31) Partanen, J. I.; Minkkinen P. O. Thermodynamic Activity Quantities in Aqueous Sodium and Potassium Chloride Solutions at 298.15 K up to a Molality of 2.0 mol kg^{-1}. *Acta Chem. Scand.* **1993**, *47*, 768−776.

(32) Pitzer, K. S., Ed. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.

(33) Partanen, J. I.; Juusola, P. M.; Minkkinen, P. O. Determination of the Glass Electrode Parameters by Means of Potentiometric Titration of Acetic Acid in Aqueous Sodium or Potassium Chloride Solutions at 25 °C. *J. Solution Chem.* **1999**, *28*, 413−433.

(34) Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(35) Harned, H. S.; Ehlers, R. W. The Dissociation Constant of Acetic Acid from 0 to 35° Centigrade. *J. Am. Chem. Soc.* **1932**, *54*, 1350−1357.

(36) 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.

(37) Saxton, B.; Darken, L. S. The Ionization Constants of Weak Acids at 25° from Conductance Measurements. A Method of Extrapolating the Data. *J. Am. Chem. Soc.* **1940**, *62*, 846−852.

(38) Partanen, J. I. Determination of the Molality Scale Dissociation Constants of Formic, Propionic and *n*-Butyric Acids in Aqueous Sodium Chloride Solutions at 298.15 K. *Acta Chem. Scand.* **1996**, *50*, 492−498.

(39) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth Scientific Publications: London, 1959; App. 12.1.

(40) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold Publishing Corporation: New York, 1958; pp 725(a) and 748(b).

(41) Kell, G. S. Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150 °C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. *J. Chem. Eng. Data* **1975**, *20*, 97−105.

(42) Partanen, J. I.; Juusola, P. M.; Minkkinen, P. O. Determination of Stoichiometric Dissociation Constants of Lactic Acid in Aqueous Salt Solutions at 291.15 and at 298.15 K. *Fluid Phase Equilib.* **2003**, *204*, 245−266.

(43) Harned, H. S.; Ehlers, R. W. The Dissociation Constant of Acetic Acid from 0 to 60° Centigrade. *J. Am. Chem. Soc.* **1933**, *55*, 652−656.

(44) DeRobertis, A.; DeStefano, C.; Foti, C. Medium Effects on Protonation of Carboxylic Acids at Different Temperatures. *J. Chem. Eng. Data* **1999**, *44*, 262−270.

(45) Barriada, J. L.; Brandariz, I.; Sastre de Vicente, M. E. Acid−Base Equilibria on Monocarboxylic Acids in Various Saline Media: Analysis of Data Using Pitzer Equations. *J. Chem. Eng. Data* **2000**, *45*, 1173−1178.

Received for review August 25, 2004. Accepted October 13, 2004. J.I.P. is indebted to the Research Foundation of Lappeenranta University of Technology (the Lahja and Lauri Hotinen's Fund) for financial support.

JE040013I