Reviews

Determination of Stoichiometric Dissociation Constants of Acetic Acid in Aqueous Solutions Containing Acetic Acid, Sodium Acetate, and Sodium Chloride at (0 to 60) °C

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Equations were determined for calculation of stoichiometric (molality scale) dissociation constants K_m of acetic acid in buffer solutions containing acetic acid, sodium acetate, and sodium chloride from determined thermodynamic dissociation constants K_a of this acid at temperatures from (0 to 60) °C, and molalities of components in solution. These equations were based on single-ion activity coefficients obtained by Hückel-type equations. The thermodynamic dissociation constants and acetate parameters required were determined from the Harned cell data of Harned and Ehlers. The interaction parameter between neutral acetic acid molecules and acetate ions was determined from Harned cell data for unbuffered aqueous mixtures of acetic acid and NaCl at 25 °C, and the resulting value applied to all temperatures. The interaction parameters between hydrogen ions and chloride ions were taken from the recent data reassessment by Partanen and Covington. The parameters resulted from interactions between hydrogen ions and sodium ions and between sodium and chloride ions were determined from the Harned cell data measured by Harned for aqueous mixtures of HCl and NaCl. The resulting equations were tested with literature data for cells both with and without a liquid junction at various temperatures. The new equations predict well the literature data used in the tests. The new parametric equations were used to check the pH values of 0.01 molal acetate and 0.1 molal acetate buffers recommended by IUPAC for temperatures from (0 to 60) °C, and agreement was usually found to be within ±0.005. Calculated p(m_H) values are also tabulated for buffer solutions containing NaCl as the major component and acetate species as minor components for calibration glass electrode cells for direct measurement, particularly in potentiometric titrimetry, of hydrogen ion molality.

Introduction

Solutions of acetic acid and sodium or potassium acetate have been used for many years as standard solutions for pH measurements (see, e.g., refs 1−9). 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. Empirical models for ionic activity coefficients have been given for the calculations of pH of standard buffer solutions,[7,10−17] and these models reproduce the standard values at least satisfactorily. Some of the models were also tested successfully with literature data measured of activity coefficients of electrolytes. For acetic acid, equations were suggested for the calculation of the molality-scale stoichiometric dissociation constant, K_m, in aqueous NaCl and KCl solutions at 25 °C from the ionic strength of the solutions.[18] The values calculated by these equations apply in less dilute solutions only when salt effectively determines the ionic strength of the solution.

In the present study, a new and more versatile method, than those mentioned above, is given for the calculation of the K_m and pH values for acetic acid 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 2.0 mol kg^{-1}. The method is based on the single-ion activity coefficient equations of the Hückel type,[19] because very simple and accurate equations resulted from this choice (see eqs 1−4). The necessary Hückel parameters at different temperatures for acetate species were mainly estimated from the Harned cell data of Harned and Ehlers.[20,21] The resulting equations were tested with reliable cell potential data from the literature. Using the K_m values from the new model, speciation in acetic acid solutions can be determined and hydrogen ion molality can be calculated. The m_H values (H refers to H$^+$ ions) obtained were here used, with one reasonable extra assumption, to check the pH values recommended by IUPAC[5,9] for acetate buffers from (0 to 60) °C. It is shown below that a good agreement was obtained in this comparison.

It has been recently[22] suggested that m_H values, or p(m_H) $= -\lg(m_H/m°)$ values ($m° = 1$ mol kg^{-1}), calculated from K_m for buffer solutions containing NaCl as the major component and acetate species as minor components, can

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Table 1. Results of Least-Squares Fitting Using Equation 8 from the Data of Harned[25] on Cells of Type 6, and Values of the Debye−Hückel Parameter (α) as a Function of the Temperature

t/°C	$[\alpha/(m°)^{-1/2}]^a$	$E°$/mV	$s(E°)$/mV	$(u_{Na})^b$	$s(u_{Na})$	$(s/\mathrm{mV})^c$	$u_{Na}(\mathrm{pred})^d$
0	1.1293	236.86	0.07	0.121	0.004	0.17	0.1218
5	1.1376	234.32	0.07	0.127	0.004	0.17	0.1269
10	1.1462	231.63	0.07	0.132	0.004	0.17	0.1315
15	1.1552	228.78	0.06	0.136	0.003	0.16	0.1355
20	1.1646	225.79	0.06	0.139	0.003	0.15	0.1391
25	1.1744	222.63	0.06	0.142	0.003	0.15	0.1421
30	1.1848	219.33	0.05	0.145	0.003	0.14	0.1447
35	1.1956	215.87	0.05	0.147	0.002	0.13	0.1467
40	1.2068	212.25	0.05	0.148	0.002	0.11	0.1481
45	1.2186	208.48	0.04	0.149	0.002	0.10	0.1491
50	1.2308	204.55	0.04	0.149	0.002	0.10	0.1495
55	1.2436	200.47	0.04	0.149	0.002	0.09	0.1494
60	1.2568	196.23	0.04	0.149	0.002	0.09	0.1488

[a] $m° = 1$ mol kg^{-1}. [b] $u_{Na} = b_{Na,Cl} + \theta_{H,Na}$. [c] Standard deviation about the regression, see eq 9. [d] Predicted by eq 10.

be used in the calibration of glass electrode cells used in acidity determination. These p(m_H) values, calculated using the new Hückel model, are tabulated below for such calibration solutions, and the glass electrode cells calibrated thereby measure, after calibration, directly hydrogen ion molality.

Theory

The following equations were used for activity coefficients (γ) on the molality scale of species in solutions of acetic acid (HA), sodium acetate (NaA), and sodium chloride:

$$\ln \gamma_H = -\frac{\alpha\sqrt{I_m}}{1 + B_H\sqrt{I_m}} + b_{H,Cl}(m_{Cl}/m°) + \theta_{H,Na}(m_{Na}/m°) \tag{1}$$

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

$$\ln \gamma_A = -\frac{\alpha\sqrt{I_m}}{1 + B_A\sqrt{I_m}} + b_{Na,A}(m_{Na}/m°) + \lambda_{HA,A}(m_{HA}/m°) \tag{3}$$

$$\ln \gamma_{HA} = \lambda_{HA,A}(m_A/m°) + \lambda_{HA,Na}(m_{Na}/m°) \tag{4}$$

where the following symbols are used: H = H$^+$, Cl = Cl$^-$, Na = Na$^+$, HA = CH_3COOH, and A = CH_3COO^-. I_m is the ionic strength on the molality scale, α is the Debye−Hückel parameter for which values at different temperatures are given in Table 1,[23] 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 $\lambda_{HA,i}$ is the interaction parameter between neutral molecule HA and ion i.

From the HCl results of a previous paper,[24] the value of $B_H = B_{Cl} = 1.4$ (mol kg^{-1})$^{-1/2}$ is taken for eqs 1 and 2 for all temperatures under consideration. By assuming in pure HCl solutions that $\gamma_H = \gamma_{Cl} = \gamma_\pm$, the following equation can also be used in these equations for parameter $b_{H,Cl}$ at different temperatures from the results of that study:

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

Other parameters for the activity coefficient equations were estimated here from appropriate literature data. To summarize, the procedures and tests of the resulting parameters are as follows:

1. Harned cell data of Harned[25] for aqueous mixtures of HCl + NaCl were used to estimate the values of the parameter $b_{Na,Cl} + \theta_{H,Na}$ at different temperatures.
2. Harned cell data of Harned and Ehlers[20,21] for aqueous mixtures of HA + NaA + NaCl were used to estimate the values of the thermodynamic dissociation constants K_a and the values of the parameter $b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$ at different temperatures. The parameter B_A was found to be independent of temperature, and it was also estimated from these data.
3. Harned cell data of Harned and Robinson,[26] Harned and Murphy,[27] and Harned and Hickey[28] for 25 °C for aqueous mixtures of HA + NaCl were used to determine the parameter $\lambda_{HA,A}$, which was found to be independent of temperature.
4. The resulting parameter values for eqs 1−4 were tested with data used for the parameter estimations and additionally with the Harned cell of Harned and Murphy[27] and Harned and Hickey[28] at temperatures other than 25 °C in aqueous mixtures of HA + NaCl, the pH data of Cohn et al.[29] for aqueous mixtures of HA + NaA, and the pK_m data of Mesmer et al.,[30] Larsson and Adell,[31] and Kiss and Urmánczy[32] from liquid junction cells containing NaCl solutions dilute with respect to HA + NaA.
5. Parameter values were also tested with equations proposed by DeRobertis et al.,[33] Barriada et al.,[34] and Partanen[18] for K_m of acetic acid in NaCl solutions dilute with respect to HA + NaA derived from glass or quinhydrone electrode data.
6. To predict pH values and for the pH test calculations, the additional assumption that $\theta_{H,Na} = 0.070$ at all temperatures is necessary.

Results and Discussion

Determination of the Values of the Parameter $b_{Na,Cl} + \theta_{H,Na}$. Some of the interaction parameters of eqs 1−4 can be reliably determined for various temperatures from existing data measured with Harned cells where the electrolyte solution comprises aqueous mixtures of HCl and NaCl dilute with respect to HCl. The most important data of this kind are probably those measured by Harned;[25] see also ref 35. In those, the data are for (0 to 60) °C, and the cell is represented by

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|\ HCl(aq,}\ m_{HCl} = 0.01\ \mathrm{mol\ kg^{-1}),\ NaCl(aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \tag{6}$$

where f is fugacity. Data for salt molalities of (0 to 2) mol

kg^{-1} were used in parameter estimations. The cell potential difference (cpd $= E$) for cells of type 6 is given by

$$E = E° - (RT/F)\ln\left[\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}m_{\mathrm{H}}m_{\mathrm{Cl}}}{(m°)^2}\right] \tag{7}$$

where $E°$ is the standard cell potential difference. The following equation can be derived from eqs 1, 2, and 7:

$$\begin{aligned} &E + (RT/F)\ln(m_{\mathrm{HCl}}/m°) + (RT/F)\ln[(m_{\mathrm{HCl}} + m_{\mathrm{s}})/m°] - \\ &\frac{2(RT/F)\alpha\sqrt{I_{\mathrm{m}}}}{1 + B_{\mathrm{H}}\sqrt{I_{\mathrm{m}}}} + (RT/F)b_{\mathrm{H,Cl}}[(2m_{\mathrm{HCl}} + m_{\mathrm{s}})/m°] = \\ &y_1 = E° - (RT/F)(b_{\mathrm{Na,Cl}} + \theta_{\mathrm{H,Na}})(m_{\mathrm{s}}/m°) = \\ &E° - (RT/F)u_{\mathrm{Na}}(m_{\mathrm{s}}/m°) \end{aligned} \tag{8}$$

where $I_{\mathrm{m}} = m_{\mathrm{HCl}} + m_{\mathrm{s}}$. Equation 8 represents an equation of a straight line, quantity y_1 can be directly calculated from the experimental data, and the parameter u_{Na} ($=b_{\mathrm{Na,Cl}} + \theta_{\mathrm{H,Na}}$) can be determined from the slope of the straight line. The results of these parameter estimations are shown in Table 1, including for each regression line the value of the standard deviation about the regression (s) defined by the equation

$$s = \sqrt{\frac{\sum_{i=1}^{N}[y_i(\mathrm{obsd}) - y_i(\mathrm{pred})]^2}{N - 2}} \tag{9}$$

where in this case $y = y_1$ and where N is the number of points in the set.

The experimental u_{Na} values shown in Table 1 can be correlated to the temperature using eq 10:

$$u_{\mathrm{Na}} = 0.12175 + 0.001075(t/°\mathrm{C}) - 0.0000104(t/°\mathrm{C})^2 \tag{10}$$

Predicted values from eq 10 are also shown in Table 1 and agree well with the experimental values. Predicted values of u_{Na} were used to reproduce the data of Harned,[25] and they apply well to these data. Error plots for selected temperatures between (0 to 60) °C are presented in Figure 1, where the deviation e_{E}, defined by

$$e_{\mathrm{E}} = E(\mathrm{obsd}) - E(\mathrm{pred}) \tag{11}$$

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

The value $u_{\mathrm{Na}} = 0.1421$ for 25 °C agrees well with previous results in the literature for this temperature, as shown, first, by the fact that the Hückel equation for the mean activity coefficient of NaCl in pure electrolyte solutions at 25 °C

$$\ln\gamma_{\pm} = -\frac{\alpha\sqrt{I_{\mathrm{m}}}}{1 + B_{\mathrm{NaCl}}\sqrt{I_{\mathrm{m}}}} + b_{\mathrm{NaCl}}(I_{\mathrm{m}}/m°) \tag{12}$$

gave parameter values of $B_{\mathrm{NaCl}} = 1.41\ (\mathrm{mol\ kg}^{-1})^{-1/2}$ and $b_{\mathrm{NaCl}} = 0.0724$.[36] These values were determined from data of both cell potential difference and isopiestic measurements. Second, eq 13 can be derived from Pitzer theory[37,38] for activity coefficients of H^+ ion in aqueous mixtures of HCl and NaCl:

$$\ln\gamma_{\mathrm{H}} = f^{\gamma} + 2B_{\mathrm{H,Cl}}(m_{\mathrm{Cl}}/m°) + 2\theta_{\mathrm{H,Na}}(\mathrm{P})(m_{\mathrm{Na}}/m°) + f'(B) \tag{13}$$

where f^{γ}, B, and $f'(B)$ are functions of the ionic strength of the solution (see eq 39 below and ref 38) and where $\theta(\mathrm{P})$ is a Pitzer parameter related to interactions between like-charged ions (between hydrogen and sodium ions in this case). Pitzer and Kim[39] have suggested that $\theta_{\mathrm{H,Na}}(\mathrm{P}) = 0.036$. Accordingly, the value of the quantity $b_{\mathrm{NaCl}} + 2\theta_{\mathrm{H,Na}}(\mathrm{P}) = 0.072 + 2 \times 0.036 = 0.144$ can be compared with the present value of u_{Na} ($=0.142$). Complete agreement cannot be expected in this comparison because the present B value for hydrogen and chloride ions $[1.40\ (\mathrm{mol\ kg}^{-1})^{-1/2}]$ is not exactly the same as that determined previously for NaCl solutions $[B_{\mathrm{NaCl}} = 1.41\ (\mathrm{mol\ kg}^{-1})^{-1/2}]$. These results, however, support well the suggested value of u_{Na} at 25 °C.

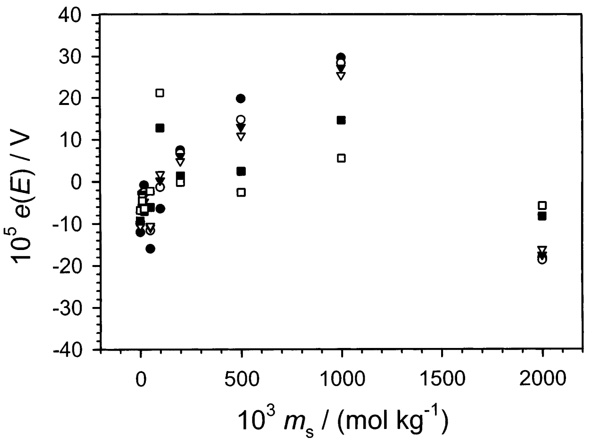

Figure 1. Deviation between the observed and predicted cell potential difference (cpd), e_{E} in eq 11, as a function of the salt molality m_{s} in the HCl + NaCl data sets measured by Harned[25] on cell 6 at various temperatures. The predicted cpd was calculated by eqs 1, 2, and 7 with the $E°$ values in Table 1. ●, 0 °C; ○, 20 °C; ▼, 25 °C; ▽, 30 °C; ■, 50 °C; □, 60 °C.

Determination of the Parameters B_A and $b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$. Harned and Ehlers[20,21] have measured very precisely the following Harned cell at temperatures from (0 to 60) °C:

$$\begin{aligned} &\mathrm{Pt(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|HA(aq,}\ m_{\mathrm{a}}), \\ &\mathrm{NaA(aq,}\ m_{\mathrm{b}}),\ \mathrm{NaCl(aq,}\ m_{\mathrm{s}})\mathrm{|AgCl(s)|Ag(s)} \end{aligned} \tag{14}$$

The molalities m_{a}, m_{b}, and m_{s} used are given in Tables 2 and 3. Experimental K_{m} values were obtained from these data as follows: The thermodynamic dissociation constant (K_{a}) for acetic acid is given by

$$K_{\mathrm{a}} = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{A}}m_{\mathrm{H}}m_{\mathrm{A}}}{\gamma_{\mathrm{HA}}m_{\mathrm{HA}}m°} = (\gamma_{\mathrm{H}}\gamma_{\mathrm{A}}/\gamma_{\mathrm{HA}})K_{\mathrm{m}} \tag{15}$$

The stoichiometric dissociation constant K_{m} in this equation is defined by $K_{\mathrm{m}} = m_{\mathrm{H}}m_{\mathrm{A}}/(m_{\mathrm{HA}}m°)$. The observed K_{m} value was calculated from each experimental point from the equations

$$\ln(m_{\mathrm{H}}/m°) = \frac{(E° - E)F}{RT} - \ln(\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}m_{\mathrm{Cl}}/m°) \tag{16}$$

$$K_{\mathrm{m}} = \frac{m_{\mathrm{H}}(m_{\mathrm{b}} + m_{\mathrm{H}})}{(m_{\mathrm{a}} - m_{\mathrm{H}})m°} \tag{17}$$

Table 2. Experimental 10^5K_m Values for Acetic Acid from Data of Harned and Ehlers[20] on Cell 14

	10^5K_m						
t/°C	(point 1)[a]	(point 2)[b]	(point 3)[c]	(point 4)[d]	(point 5)[e]	(point 6)[f]	(E°/mV)[g]
0	2.015	2.188	2.323	2.585	2.757	2.798	236.64
5	2.066	2.245	2.391	2.665	2.830	2.878	234.15
10	2.101	2.287	2.437	2.719	2.904	2.944	231.49
15	2.122	2.314	2.473	2.762	2.955	3.002	228.63
20	2.129	2.328	2.485	2.789	2.983	3.036	225.64
25	2.141	2.341	2.503	2.812	3.011	3.064	222.53
30	2.138	2.338	2.501	2.812	3.022	3.073	219.22
35	2.115	2.318	2.479	2.805	3.019	3.069	215.75

[a] $m_a = 0.004\,779$, $m_b = 0.004\,599$, and $m_s = 0.004\,896$ mol kg^{-1}. [b] $m_a = 0.012\,035$, $m_b = 0.011\,582$, and $m_s = 0.012\,328$ mol kg^{-1}. The value given by Harned and Ehlers for m_s (i.e. the value of 0.012 426 mol kg^{-1}) is probably not correct. [c] $m_a = 0.021\,006$, $m_b = 0.020\,216$, and $m_s = 0.021\,516$ mol kg^{-1}. [d] $m_a = 0.049\,22$, $m_b = 0.047\,37$, and $m_s = 0.050\,42$ mol kg^{-1}. [e] $m_a = 0.081\,01$, $m_b = 0.077\,96$, and $m_s = 0.082\,97$ mol kg^{-1}. [f] $m_a = 0.090\,56$, $m_b = 0.087\,16$, and $m_s = 0.092\,76$ mol kg^{-1}. [g] Determined from the HCl data of Harned and Ehlers[20,40] in ref 24.

Table 3. Experimental 10^5K_m Values for Acetic Acid from Data of Harned and Ehlers[21] on Cell 14 Where $m_a = m_b = m_s$

	10^5K_m at the following values of t/°C					
(m_a/m°)[a]	35	40	45	50	55	60
0.006 313	2.171	2.143	2.101	2.066	2.008	1.958
0.008 419	2.225	2.201	2.167	2.125	2.077	2.020
0.010 131	2.269	2.244		2.162	2.115	2.058
0.011 845	2.314	2.286	2.250	2.210	2.160	2.104
0.012 869	2.325	2.306	2.266			2.113
0.014 868	2.373	2.350	2.312	2.274	2.224	2.167
0.021 015	2.473	2.446	2.410	2.379	2.322	2.258
0.047 973	2.785	2.765	2.726	2.698	2.640	2.580
0.076 13	2.984	2.971	2.928	2.895	2.843	2.782
0.100 31	3.090	3.068	3.049	3.008	2.959	2.899
(E°/mV)[b]	215.75	212.12	208.36	204.50	200.46	196.29

[a] $m° = 1$ mol kg^{-1}. [b] Determined from the HCl data of Harned and Ehlers[20,40] in ref 24.

Table 4. Standard Deviation about Regression (s in Eq 9 Where $y = y_2$) as a Function of the Parameter B_A (A Refers to Acetate Ions) in the Regression Analysis Obtained by Eq 18 from the Experimental K_m Values of Harned and Ehlers[20] at 25 °C (see Table 2)

B_A/(mol kg^{-1})$^{-1/2}$	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
10^3s	2.03	1.69	1.38	1.12	0.93	0.87	0.96	1.15

Table 5. Results from Least-Squares Fitting of Equation 18 from the Acetic Acid Data of Harned and Ehlers (Tables 2 and 3)

t/°C	$-$lg K_a	s(lg K_a)	[q_{Na}(1)][a]	(q_{Na})[b]	s(q_{Na})	(10^3s)[c]	q_{Na}(pred)[d]
0	4.7785	0.0007	0.147	0.153	0.015	2.4	0.152
5	4.7676	0.0005	0.156	0.161	0.010	1.7	0.140
10	4.7610	0.0003	0.133	0.139	0.006	1.0	0.127
15	4.7571	0.0002	0.106	0.112	0.005	0.8	0.115
20	4.7562	0.0003	0.086	0.091	0.006	1.0	0.103
25	4.7546	0.0003	0.084	0.090	0.005	0.9	0.090
30	4.7563	0.0002	0.076	0.082	0.005	0.8	0.078
35[e]	4.7618	0.0003	0.041	0.047	0.007	1.1	0.066
35[f]	4.7625	0.0004	0.074	0.074	0.012	2.3	0.066
40	4.7685	0.0005	0.065	0.065	0.014	2.7	0.053
45	4.7773	0.0003	0.042	0.042	0.008	1.5	0.041
50	4.7861	0.0006	0.031	0.031	0.014	2.7	0.029
55	4.7980	0.0005	0.014	0.014	0.013	2.5	0.016
60	4.8114	0.0006	$-$0.001	$-$0.001	0.015	2.9	0.004

[a] $q_{Na} = b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$; obtained when the term $\lambda_{HA,A}(m_a - m_b)/m°$ was omitted from eq 18. [b] $q_{Na} = b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$. [c] Standard deviation about the regression; see eq 9. [d] Predicted by eq 19. [e] Results of Harned and Ehlers;[20] see Table 2. [f] Results of Harned and Ehlers;[21] see Table 3.

In this revaluation, E° values determined previously[24] from the HCl data of Harned and Ehlers[20,40] were used (Tables 2 and 3). Equations 1 and 2 were used for the activity coefficients of H^+ and Cl^- ions, with the values of relevant parameters given above. Iterative calculations were needed because the dissociation of acetic acid influences the ionic strength. Tables 2 and 3 show the experimental K_m values obtained.

The thermodynamic dissociation constant K_a and the parameters B_A and $b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$ were determined at each temperature from the K_m values in Tables 2 and 3 from

$$\ln K_m - \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{1}{1 + B_A\sqrt{I_m}}\right) + b_{H,Cl}(m_{Cl}/m°) + \lambda_{HA,A}[(m_{HA} - m_A)/m°] = y_2 = \ln K_a - (b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na})(m_{Na}/m°) = \ln K_a - q_{Na}(m_{Na}/m°) \quad (18)$$

where $q_{Na} = b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$. It is assumed that $m_{HA} - m_A \approx m_a - m_b$. The term containing the difference of $m_{HA} - m_A$ is first omitted from eq 18 in the determination of the values of the parameters K_a and q_{Na}. This is necessary because the values of the parameter $\lambda_{HA,A}$ are not known. The errors resulted from this omission are not very significant because the values of m_a and m_b are always close to each other (see below and Tables 2 and 3). With this assumption for a fixed value of B_A, the quantity y_2 can be calculated from each experimental point, and therefore, eq 18 represents an equation of the straight line y_2 versus (m_{Na}/m°). B_A was determined by searching for the value of this parameter that gives at all temperatures the best least-squares fit by this equation. $B_A = 1.8$ (mol kg^{-1})$^{-1/2}$ was obtained. The standard deviation about regression (s) at each temperature, see eq 9 where now $y = y_2$, is sensitive to this parameter, as the results in Table 4 for 25 °C, for example, confirm.

Once the value of the parameter B_A was determined, the data shown in Tables 2 and 3 were used for the regression analysis using eq 18, with the results shown in Table 5. These show that the data obtained in 1932[20] (the low-temperature data, Table 2) are more precise than the data reported a year later[21] (the high-temperature data, Table 3).

The experimental q_{Na} values given in Table 5 can be linearly correlated with temperature, giving

$$q_{Na} = 0.15214 - 0.00247(t/°C) \quad (19)$$

Predicted values from eq 19, shown in Table 5, agree well with the experimental values.

Determination of Parameter $\lambda_{HA,A}$. The parameter $\lambda_{HA,A}$ was then determined from the existing data measured

Table 6. Values of $\lambda_{HA,A}$ from Data from Cell 20 Containing Acetic Acid and Sodium Chloride Solutions at 25 °C

symbol	ref	$(m_a/m°)^a$	N^b	$-\lambda_{HA,A}$	$s(\lambda_{HA,A})$	$(s_0)^c$
HaRb(0.1)	26	0.1	11	0.24	0.07	0.010
HaRb(0.2)	26	0.2	7	0.42	0.04	0.012
HaRb(0.5)	26	0.519	9	0.30	0.02	0.014
HaRb(1.0)	26	1.002	8	0.247	0.007	0.025
HaMu25(0.2)	27	0.2	7	0.38	0.04	0.009
HaHi25(0.1)	28	0.1	4	0.33	0.07	0.005
HaHi25(0.2)	28	0.2	7	0.31	0.04	0.009
HaHi25(0.5)	28	0.52	7	0.285	0.014	0.008

[a] $m° = 1$ mol kg^{-1}. [b] Number of points (all salt molalities included were smaller than about 2.0 mol kg^{-1}). [c] Standard deviation of the pK_m errors for the Hückel model (see eqs 23 and 24 and Figure 3).

on Harned cells in unbuffered solutions of acetic acid and NaCl. Harned and Robinson,[26] Harned and Murphy,[27] and Harned and Hickey[28] have measured cells of the following type at 25 °C:

$$\mathrm{Pt(s)|H_2(g,}\ f = 101\ \mathrm{kPa)|HA(aq,}\ m_a\mathrm{),}\quad \mathrm{NaCl(aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \tag{20}$$

Some details of these data are shown in Table 6.

The data measured at 25 °C can be used in the determination of $\lambda_{HA,A}$ because at this temperature the thermodynamic dissociation constant of acetic acid is accurately known. From the high-precision conductance measurements of MacInnes and Shedlovsky,[41] a value of 1.758 × 10^{-5} was previously[42] obtained for this temperature.

In the present determination, a $\lambda_{HA,A}$ value was calculated from each experimental point in the data sets considered in Table 6, and the mean value of these values and its standard deviation are shown in Table 6 for all of these sets. According to these results, a value of $\lambda_{HA,A} = -0.3$ is here suggested, and this value is used in the subsequent calculations for all temperatures.

Determination of the Thermodynamic Dissociation Constant (K_a). With the value of $\lambda_{HA,A}$ determined, eq 18 in its complete form can be used in the determination of the thermodynamic dissociation constant of acetic acid and the parameter q_{Na} at the different temperatures. The results of the regression analysis by the full eq 18 are shown in Table 5, which shows that the new $\lambda_{HA,A}$ value does not significantly change the values of q_{Na} determined without the term containing it. Also, the values of K_a are independent of the value of $\lambda_{HA,A}$, and therefore, only one set of K_a values is given in Table 5. The value of K_a (=1.760 × 10^{-5}) for 25 °C in this table agrees well with the value recommended previously (=1.758 × 10^{-5}), derived from conductance measurements; see above.

Values of ln K_a in Table 5 were fitted to a quadratic equation in temperature,

$$\ln K_a = -10.9973 + 0.004244(t/°\mathrm{C}) - 0.000094(t/°\mathrm{C})^2 \tag{21}$$

The results of the comparison between the fitted and experimental K_a values are shown in Table 7, and the fitted values are recommended here. The table also shows the K_a values calculated from

$$\lg K_a = 18.67257 - 0.0076792(T/\mathrm{K}) - \frac{1500.65\mathrm{K}}{T} - 6.50923\ \lg(T/\mathrm{K}) \tag{22}$$

Table 7. Thermodynamic Dissociation Constant K_a of Acetic Acid as a Function of Temperature (t)

t/°C	10^5K_a(obsd)^a	10^5K_a(recd)^b	10^5K_a(H&E)^c
0	1.665	1.675	1.667
5	1.707	1.707	1.702
10	1.734	1.731	1.728
15	1.750	1.747	1.745
20	1.753	1.756	1.752
25	1.760	1.756	1.751
30	1.753	1.748	1.741
35^d	1.731	1.732	1.724
35^e	1.728	1.732	1.724
40	1.704	1.707	1.700
45	1.670	1.676	1.669
50	1.637	1.637	1.633
55	1.592	1.592	1.592
60	1.544	1.540	1.547

[a] Experimental value; see Table 5. [b] Calculated from eq 21 and recommended here. [c] Calculated from eq 22 given by Harned and Ehlers.[21] [d] From results of Harned and Ehlers;[20] see Table 2. [e] From results of Harned and Ehlers;[21] see Table 3.

This equation was used by Harned and Ehlers[21] 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 K_a values calculated by this equation agree satisfactorily with those recommended in Table 7 but are in general slightly smaller. It is noted that more adjustable parameters need to be determined for eq 22 than for eq 21.

Results with New Parameter Values from the Data of Harned and Ehlers. The experimental K_m values given in Tables 2 and 3 were reproduced by means of the resulting Hückel model. For these calculations, the recommended K_a values are given in Table 7, the $E°$ values are given in Tables 2 and 3, the $b_{H,Cl}$ values are obtained from eq 5, the q_{Na} values are obtained from eq 19, and the value of $\lambda_{HA,A}$ is -0.30. The results are shown as error plots where the pK_m error is defined by

$$e(\mathrm{p}K_m) = \mathrm{p}K_m(\mathrm{obsd}) - \mathrm{p}K_m(\mathrm{pred}) \tag{23}$$

and these errors are presented as a function of the ionic strength of the solution in Figure 2.

The results for the data in Table 2 are shown in graph A (0 °C ≤ t ≤ 35 °C),[20] and those for the data in Table 3 (35 °C ≤ t ≤ 60 °C),[21] in graph B. The error plots support well the suggested model.

Results with New Parameter Values from the Harned Cell Data for Mixtures of HA + NaCl. Experimental K_m values obtained from the data sets shown in Table 6 were also used to test the present model. The results are also shown in Table 6 and as pK_m error plots (see eq 23) in Figure 3. In Table 6 are included for each data set (of N points) the values of the standard deviation of errors (s_0), defined by

$$s_0 = [\Sigma e(\mathrm{p}K_m)^2/N]^{1/2} \tag{24}$$

The errors in Figure 3 are larger than those in Figure 2, but also they support, almost within their precision, the Hückel model suggested.

The data sets measured by Harned and Murphy[27] and by Harned and Hickey[28] on cells of type 20 at temperatures other than 25 °C are introduced in Table 8, and also these data were used in the tests of the Hückel model. The s_0 values calculated from eq 24 for these sets are shown in Table 8. It may be noted that the values are of the same order as those in Table 6 and, therefore, also support the Hückel model.

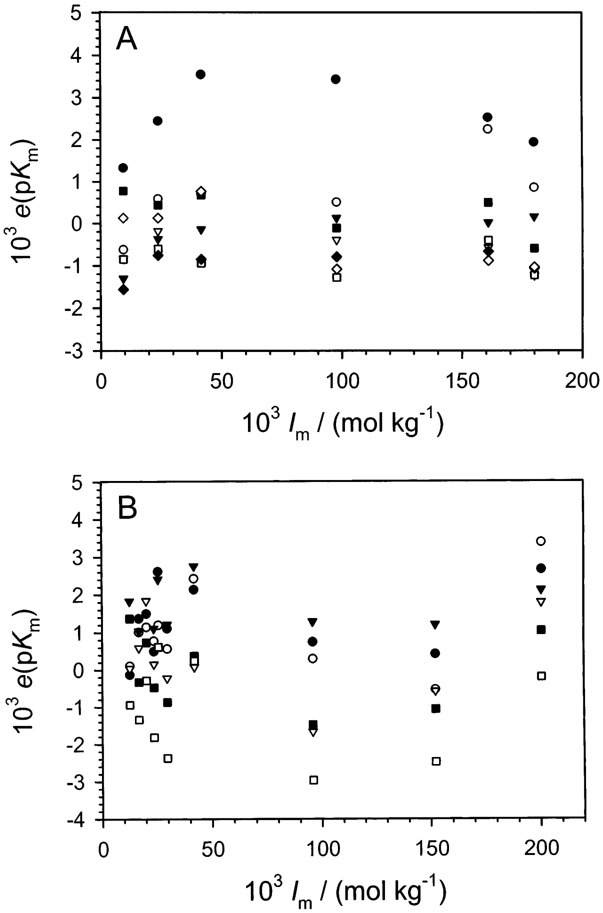

Figure 2. Differences, $e(\mathrm{p}K_\mathrm{m})$ in eq 23, between the experimental $\mathrm{p}K_\mathrm{m}$ values obtained from the cell potential data of Harned and Ehlers (graph A, Table 2[20] and graph B, Table 3[21]) and those predicted by the Hückel method as a function of the ionic strength I_m. The K_m values were predicted from eqs 1, 3, 4, and 15 with the recommended K_a values shown in Table 7 and with the determined parameter values. ●, 0 °C (graph A), 35 °C (graph 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); ◇, 35 °C (A).

Results with New Parameter Values from the pH Data from Cells Containing a Liquid Junction. Cohn et al.[29] measured at 18 °C pH in chloride-free acetate buffer solutions by cells of the following type:

$$\mathrm{Hg(l)|Hg_2Cl_2(s)|KCl(aq,}\ c = 0.1\ \mathrm{mol\ dm^{-3})|}$$
$$\mathrm{|HA(aq,}\ m_\mathrm{a}\mathrm{),\ NaA(aq,}\ m_\mathrm{b}\mathrm{)|H_2(g,}\ f = 101\ \mathrm{kPa)|Pt(s)} \quad (25)$$

The data consist of series of pH measurements at different total molalities of the acetate from (0.02 to 4) mol kg^{-1}. In each series, the mol fraction of sodium acetate to total acetate can vary from (0.1 to 0.9). These data can be predicted by using the present Hückel model and eqs 26–28.

$$\mathrm{pH} = -\lg(\gamma_\mathrm{H} m_\mathrm{H}/m^\circ) + \mathrm{pH_{corr}} \quad (26)$$

$$\ln \gamma_\mathrm{H} = -\frac{\alpha\sqrt{I_\mathrm{m}}}{1 + B_\mathrm{H}\sqrt{I_\mathrm{m}}} + \theta_\mathrm{H,Na}(m_\mathrm{Na}/m^\circ) \quad (27)$$

$$m_\mathrm{H} = \frac{\sqrt{(m_\mathrm{b} + K_\mathrm{m}m^\circ)^2 + 4m_\mathrm{a}K_\mathrm{m}m^\circ} - (m_\mathrm{b} + K_\mathrm{m}m^\circ)}{2} \quad (28)$$

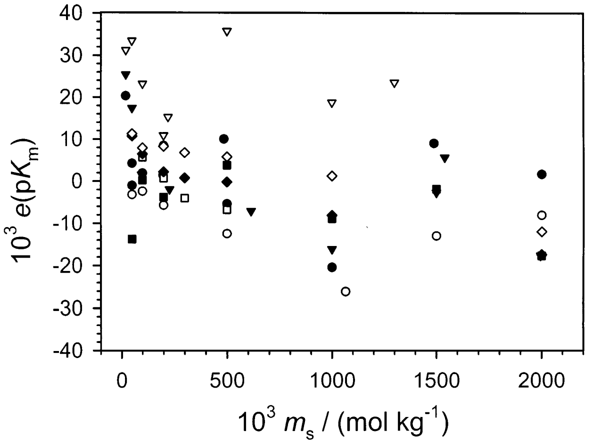

Figure 3. Differences, $e(\mathrm{p}K_\mathrm{m})$ in eq 23, between the experimental $\mathrm{p}K_\mathrm{m}$ values obtained from the cell potential data of Harned and Robinson,[26] Harned and Murphy,[27] and Harned and Hickey[28] from the unbuffered cells of type 20 at 25 °C (see Table 6), and those predicted by the Hückel method as a function of salt molality m_s. K_m values were predicted from eqs 1, 3, 4, and 15 with the $K_\mathrm{a} = 1.76 \times 10^{-5}$ (see Table 7) and with the determined parameter values. ●, HaRb(0.1); ○, HaRb(0.2); ▼, HaRb(0.5); ▽, HaRb(1.0); ■, HaMu25(0.2); □, HaHi25(0.1); ◆, HaHi25(0.2); ◇, HaHi25(0.5).

Table 8. Standard Deviation (s_0 in Eq 24) for pK_m Errors of the Hückel Model from Data Sets from Cell 20 at Temperatures Other Than 25 °C

symbol	t/°C	ref	$(m_\mathrm{a}/m^\circ)^a$	N^b	s_0
HaMu20(0.2)	20	27	0.2	7	0.013
HaMu30(0.2)	30	27	0.2	7	0.007
HaHi0(0.1)	0	28	0.1	4	0.010
HaHi0(0.2)	0	28	0.2	7	0.017
HaHi5(0.2)	5	28	0.2	7	0.016
HaHi10(0.2)	10	28	0.2	7	0.014
HaHi15(0.2)	15	28	0.2	7	0.013
HaHi20(0.2)	20	28	0.2	7	0.011
HaHi30(0.2)	30	28	0.2	7	0.007
HaHi35(0.2)	35	28	0.2	7	0.006
HaHi40(0.2)	40	28	0.2	7	0.006
HaHi0(0.5)	0	28	0.52	4	0.017
HaHi5(0.5)	5	28	0.52	7	0.015
HaHi10(0.5)	10	28	0.52	7	0.014
HaHi15(0.5)	15	28	0.52	7	0.012
HaHi20(0.5)	20	28	0.52	7	0.011
HaHi30(0.5)	30	28	0.52	7	0.007
HaHi35(0.5)	35	28	0.52	7	0.008
HaHi40(0.5)	40	28	0.52	7	0.009

[a] $m^\circ = 1$ mol kg^{-1}. [b] Number of points (all salt molalities included were ≤ 2.0 mol kg^{-1}).

where the correction term $\mathrm{pH_{corr}}$ arises from errors in the reference electrode potential and in the liquid junction potential of cell 25. It was observed, see below, that this term is dependent in less dilute acetic acid solutions on the total molality of acetate species in the solution. For the parameter $\theta_\mathrm{H,Na}$, the value of $u_\mathrm{Na} - b_\mathrm{Na,Cl} = 0.142 - 0.072 = 0.07$, determined for 25 °C as shown above, must now be used. It seems that the use of this value at 18 °C (which is different from the temperature where it was determined) is not an important limitation because the pH data are not comparable in precision with the cell data considered above. Additionally, pH calculations below for buffer solutions at other temperatures reveal that this value is not strongly dependent on the temperature. The K_m values for eq 28 were calculated from

$$\ln K_\mathrm{m} = \ln K_\mathrm{a} + \frac{\alpha\sqrt{I_\mathrm{m}}}{1 + B_\mathrm{H}\sqrt{I_\mathrm{m}}} + \frac{\alpha\sqrt{I_\mathrm{m}}}{1 + B_\mathrm{A}\sqrt{I_\mathrm{m}}} - q_\mathrm{Na}(m_\mathrm{b}/m^\circ) - \lambda_\mathrm{HA,A}(m_\mathrm{a} - m_\mathrm{b}) \quad (29)$$

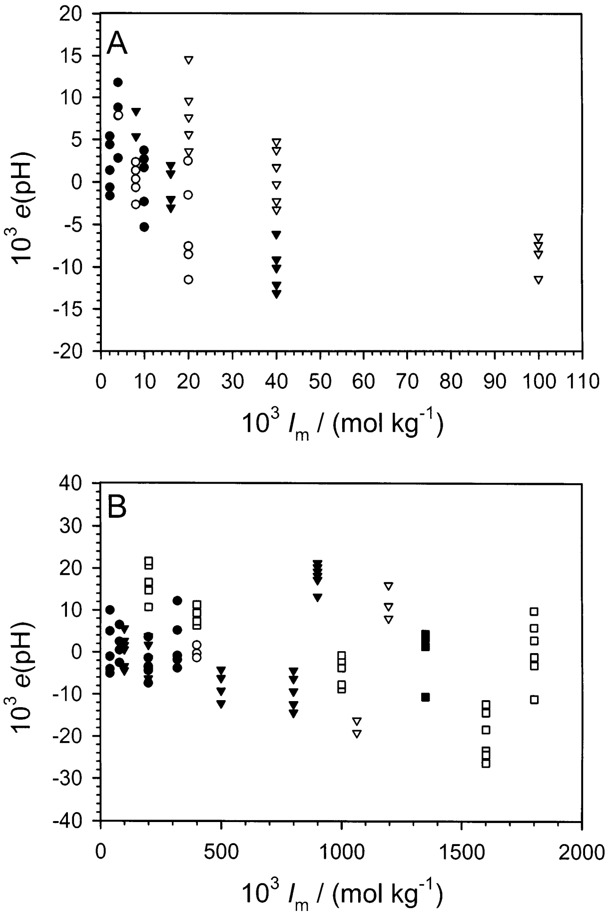

Figure 4. Differences between the observed and predicted pH values, *e*(pH) in eq 30, as a function of the ionic strength I_m in the data of Cohn et al.[29] with the chloride free cells of type 25 at 18 °C. Predicted pH values were calculated as described in the text, and the errors are given in graph A for data for the acetate molality ≤ 0.2 mol kg^{-1} and in graph B for the rest. The following pH$_{corr}$ values were used in the calculation. Graph A: pH$_{corr}$ = −0.0272; ●, $m_a + m_b$ = 0.02 mol kg^{-1}; ○, 0.04; ▼, 0.08; ▽, 0.20. Graph B: ●, $m_a + m_b$ = 0.4 mol kg^{-1}, pH$_{corr}$ = −0.0224; ○, 0.8, −0.0086; ▼, 1.0, 0.0064; ▽, 1.33, 0.0179; ■, 1.5, 0.0450; □, 2.0, 0.0579.

where the following values at 18 °C were used: $K_a = 1.753 \times 10^{-5}$, $\alpha = 1.1601$ (mol kg^{-1})$^{-1/2}$, and $q_{Na} = 0.108$, in addition to the values given above. Results are shown as error plots in Figure 4. The pH error is defined by

$$e(\mathrm{pH}) = \mathrm{pH(obsd)} - \mathrm{pH(pred)} \qquad (30)$$

and is shown in the error plots as a function of ionic strength.

The results for the total acetate molalities of (0.02 to 0.2) mol kg^{-1} (see Table 1 in the original paper of Cohn et al.[29]) are shown in graph A, and those for the total molalities of (0.40 to 2.00) mol kg^{-1} (see Table 4 in Cohn's paper), in graph B. For dilute solutions (graph A), the recommended value of $\lambda_{HA,A} = -0.3$ was used, and the results in this graph support well the choice of parameter values.

At total acetate molalities above 0.2 mol kg^{-1} (graph B), the value $\lambda_{HA,A} = -0.3$ is no longer valid, and it is not used in the calculations of graph B, where it is seen that the fit is more sensitive to this parameter than for the earlier data sets considered. The preliminary calculations revealed, however, that a value of $\lambda_{HA,A} = -0.2$ applies well to these higher total molalities, and this value was used in graph B. It is close to the recommended value if the uncertainty of the latter is taken into account (see Table 6). According to graph B, the pH data of Cohn obtained at higher acetate molalities support, almost within their precision, the Hückel method used in this way.

Table 9. Recommended Values of the Stoichiometric Dissociation Constant, 10^5K_m, of Acetic Acid from Eq 31 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous NaCl Solution When NaCl Molality Effectively Determines the Ionic Strength

	10^5K_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	1.675	2.38	2.57	2.76	2.83	2.83	2.54	2.16	1.80
5	1.707	2.43	2.64	2.83	2.91	2.92	2.65	2.27	1.91
10	1.731	2.47	2.69	2.90	2.98	3.01	2.75	2.38	2.02
15	1.747	2.51	2.73	2.95	3.04	3.08	2.84	2.49	2.13
18	1.753	2.52	2.74	2.97	3.07	3.12	2.89	2.54	2.19
20	1.756	2.53	2.76	2.99	3.09	3.14	2.93	2.58	2.23
25	1.756	2.54	2.77	3.01	3.13	3.19	3.01	2.68	2.33
30	1.748	2.54	2.78	3.03	3.15	3.23	3.07	2.76	2.42
35	1.732	2.53	2.77	3.02	3.15	3.25	3.12	2.83	2.51
40	1.707	2.50	2.75	3.01	3.15	3.25	3.16	2.89	2.59
45	1.676	2.47	2.72	2.98	3.13	3.25	3.18	2.94	2.65
50	1.637	2.42	2.67	2.94	3.09	3.22	3.19	2.98	2.71
55	1.592	2.37	2.62	2.89	3.04	3.19	3.19	3.01	2.76
60	1.540	2.30	2.55	2.83	2.98	3.14	3.17	3.02	2.80

[a] $m° = 1$ mol kg^{-1}.

Results with New Parameter Values from the K_m Data Measured on Cells Containing a Liquid Junction in NaCl Solutions That Are Very Dilute in Acetate Species. For aqueous mixtures of HA, NaA, and NaCl that are very dilute with respect to the acetate species, the following equation can be obtained on the basis of the Hückel model:

$$\ln K_m = \ln K_a + \alpha\sqrt{I_m}\left(\frac{1}{1 + B_H\sqrt{I_m}} + \frac{1}{1 + B_A\sqrt{I_m}}\right) - (b_{H,Cl} + q_{Na})(I_m/m°) \qquad (31)$$

The values predicted by this equation are given at rounded ionic strengths and at the different temperatures in Table 9. Values from eq 31 can be compared to K_m values of acetic acid given in the literature for the NaCl solutions of this kind.

Mesmer et al.[30] have measured cell potentials using hydrogen electrodes in acetic acid solutions. They measured concentration cells of the following type:

$$\mathrm{Pt(s)|H_2(g)|HA(aq),\ NaA(aq),\ NaCl(aq,\ } m_s)|| \ \mathrm{HCl(aq),\ NaCl(aq,\ } m_s)|\mathrm{H_2(g)|Pt(s)} \qquad (32)$$

where the symbol || means that the liquid junction potentials (E_{lj}) in the cells were evaluated. The observed potential is related to the cell composition by the relationship

$$E = -(RT/F)\ln(m_{H,t}/m_{H,r}) - E_{lj} \qquad (33)$$

where r and t refer to the reference and test solutions, respectively. According to the authors, the use of matching ionic media minimizes E_{lj} in eq 33, reduces the ratio of the activity coefficients for minor ions to unity, and permits use of molal concentrations rather than activities. The liquid junction potential E_{lj} was obtained by the Henderson equation and was always very small. Mesmer et al. (see Table 5 in that study) suggested the K_m values shown in Table 10 (of the present study) for acetic acid in NaCl solutions at 0, 25, and 50 °C (actually, they reported values for the logarithm of the molality dissociation quotient Q_a,

Table 10. pK_m Values Determined by Mesmer et al.[30] for Acetic Acid in NaCl Solutions from the Experimental Data Obtained by Cell 32

I_m/(mol kg^{-1})	pK_m(0 °C)	pK_m(25 °C)	pK_m(50 °C)
0	4.780	4.757	4.786
0.1	4.581	4.547	4.564
0.5	4.518	4.469	4.472
1.0	4.548	4.484	4.474
3.0	4.858	4.737	4.675

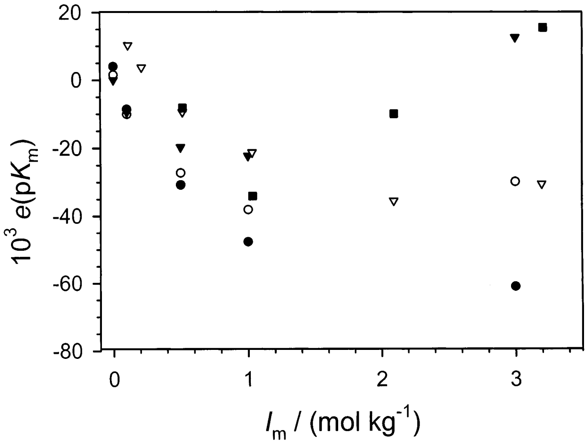

Figure 5. Differences, e(pK_m) in eq 23, between the pK_m values of Mesmer et al.[30] from concentration cells of type 32, those of Larsson and Adell[31] and Kiss and Urmánczy[32] from quinhydrone electrode cells of type 34, and those predicted by the Hückel method as a function of the salt molality m_s. K_m values are predicted from eq 31 with K_a values from Table 7 and with the derived parameter values. ●, Mesmer, t = 0 °C; ○, Mesmer, 25 °C; ▼, Mesmer, 50 °C; ▽, Larsson and Adell, 18 °C; ■, Kiss and Urmánczy, 25 °C.

which is same as K_m, at saturation vapor pressure, but these values can probably be used in this connection without any correction).

The results of the comparison of the pK_m value in Table 10 with those calculated by the Hückel method are shown in Figure 5, where the pK_m errors, defined by eq 23, are given. Agreement is satisfactory, but it should be pointed out that the accuracy of the K_m values given by Mesmer et al. is better at high temperatures than it is at those near room temperature.

Larsson and Adell[31] measured at 18 °C and Kiss and Urmánczy[32] at 25 °C cell potential differences on quinhydrone (qh) cells:

$$\mathrm{Pt(s)|qh(s)|HA(aq,}\ c_a\mathrm{),\ NaA(aq,}\ c_b\mathrm{),\ NaCl(aq,}\ c_s\mathrm{)||}\ \mathrm{KCl(aq,}\ c = 3.5\ \mathrm{mol\ dm^{-3})|Hg_2Cl_2(s)|Hg(l)} \quad (34)$$

In these data for both series, the concentrations of HA and NaA were the same and close to a value of 0.01 mol dm^{-3}. The concentration of salt (c_s) varied in these series from (0 to 3) mol dm^{-3} (ref 31) or from (0.5 to 5) mol dm^{-3}.[32] The K_c values (i.e., the stoichiometric dissociation constants on the concentration scale) reported in these two data sets were converted to K_m values by using the equation of Harned and Owen[43] for NaCl solutions at different temperatures:

$$\frac{cm°}{mc°} = \frac{\rho_0}{\mathrm{g\ cm^{-3}}} - A(m/m°) \quad (35)$$

where $c°$ = 1 mol dm^{-3}. The values of 0.0180 and 0.0183 were used for parameter A at 18 °C and at 25 °C, respectively. In eq 35, ρ_0 is the density of pure water, which is 0.9986 kg dm^{-3} at 18 °C and 0.9970 kg dm^{-3} at 25 °C; see ref 44. In this way, the K_m values shown in Table 11 were obtained from the data sets of Larsson and Adell[31] and Kiss and Urmáncy.[32] The experimental K_m values shown in this table were used to test the Hückel model. The results are shown in Figure 5. Both data sets support the model satisfactorily up to I_m of about 3.0 mol kg^{-1}.

Table 11. pK_m Values Calculated from the Reported K_c Values[a] Obtained by Larsson and Adell[31] and Kiss and Urmánczy[32] by Using a Quinhydrone Electrode Cell of Type 34 for Acetic Acid in NaCl Solutions

I_m/(mol kg^{-1})	pK_m(18 °C)[b]	pK_m(25 °C)[c]
0.1105	4.567	
0.2112	4.529	
0.5156	4.497	
1.0306	4.520	
2.0918	4.638	
3.1987	4.806	
0.5164		4.488
1.0326		4.491
2.0967		4.635
3.2078		4.812

[a] Stoichiometric dissociation constant on the concentration scale. [b] Calculated from data of Larsson and Adell.[31] [c] Calculated from data of Kiss and Urmánczy.[32]

The recommended K_m values in Table 9 can be compared to the values calculated by the equations suggested in the literature for K_m in this case. The following three of these equations are considered.

(i) Partanen[18] gave eq 36 for 25 °C on the basis of the data of Harned and Ehlers:[20]

$$\ln K_m = \ln K_a + \frac{\alpha\sqrt{I_m}}{1 + B_H\sqrt{I_m}} + \frac{\alpha\sqrt{I_m}}{1 + B_A\sqrt{I_m}} - (b_{H,NaCl} + b_{A,NaCl})(I_m/m°) \quad (36)$$

where K_a = 1.758 × 10^{-5}, B_H = 1.25 (mol kg^{-1})$^{-1/2}$, B_A = 1.6 (mol kg^{-1})$^{-1/2}$, $b_{H,NaCl}$ = 0.238, and $b_{A,NaCl}$ = 0.189. It has been shown previously[38,45] that this equation was also supported by potentiometric titration data measured using glass electrodes in dilute NaCl solution usually up to I_m = 0.5 mol kg^{-1}.

(ii) DeRobertis et al.[33] suggested from titrimetric data, obtained using glass electrodes, the following general equation for the dissociation constant of univalent carboxylic acids in aqueous NaCl solutions:

$$\lg K_m = \lg K_a + \frac{2\sqrt{I_m/m°}}{2 + 3\sqrt{I_m/m°}} - C(I_m/m°) - E(I_m/m°)^2 \quad (37)$$

In the present study, this equation was tested at the temperatures (20, 25, and 30) °C, and the values of parameter C 0.0955, 0.092, and 0.0885, respectively, were calculated for these temperatures by an equation given in the original paper. Parameter E does not depend on the temperature, and the value of 0.00634 was suggested.

(iii) Barriada et al.[34] suggested a Pitzer equation of the following type for the K_m values of weak acids in salt solutions:

$$\lg K_{m,MCl} = \lg K_a - \frac{2}{\ln(10)} f^{\gamma} - \frac{2\beta^1_{MCl}}{\ln(10)} I_m \exp(-2\sqrt{I_m/m°}) - A(I_m/m°) - B[1 - (1 + 2\sqrt{I_m/m°}) \exp(-2\sqrt{I_m/m°})] \quad (38)$$

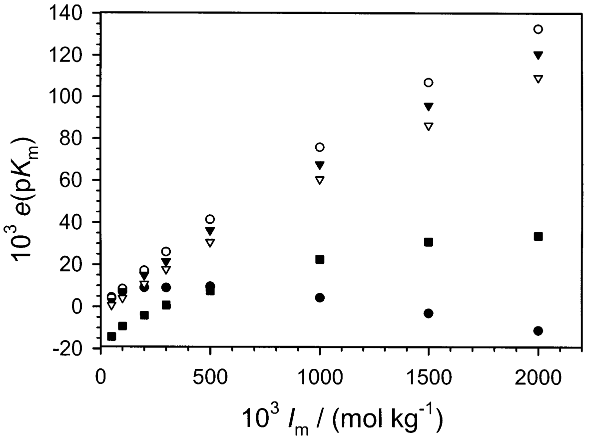

Figure 6. Differences between the recommended pK_m values (Table 9) and predicted pK_m values, $e(pK_m)$ = pK_m(recd) − pK_m(pred), as a function of the salt molality m_s. K_m values are predicted from eqs 36−38. For eq 37, K_a values of Table 7 were used. ●, eq 36, t = 25 °C; ○, eq 37, 20 °C; ▼, eq 37, 25 °C; ▽, eq 37, 30 °C; ■, eq 38, 18 °C.

where

$$f^{\gamma} = -(\alpha/3)\left\{\frac{\sqrt{I_m}}{1 + 1.2\sqrt{I_m/m^\circ}} + \frac{2\sqrt{m^\circ}}{1.2}\ln(1 + 1.2\sqrt{I_m/m^\circ})\right\} \tag{39}$$

and here MCl is NaCl. In eq 38, β^1 is a Pitzer parameter that is dependent on electrolyte MCl and the temperature. The adjustable parameters in this equation are K_a, A, and B. Barriada et al. estimated the parameters for this equation for different acids from the quinhydrone electrode data of Larsson and Adell (see above). For acetic acid in NaCl solutions, they obtained the following values: pK_a = 4.777, A = 0.228, and B = 0.126. For NaCl at 18 °C, the value of β_1 is 0.2615.[34]

In the present study, the three equations (eqs 36−38) were tested with the K_m values calculated by the recommended Hückel method and given in Table 9. In the calculations with eq 37, the K_a values recommended in this study (see eq 21) were used at the three different temperatures. The results are shown as error plots in Figure 6. These tests show that values obtained using eq 36 agree quite well with the recommended values in Table 9 up to I_m of 2.0 mol kg^{-1}, and also that eq 38 predicts satisfactorily the recommended values up to this ionic strength. On the other hand, the general equations suggested by DeRobertis et al. (eq 37) apply well, in this case, only to dilute salt solutions.

Suggestion of pH and p(m_H) Values for Acetate Buffers. IUPAC[5,9] suggested pH values for the following two acetate buffer solutions at temperatures from (0 to 60) °C: 0.01 mol kg^{-1} HA + 0.01 mol kg^{-1} NaA and 0.1 mol kg^{-1} HA + 0.1 mol kg^{-1} NaA. Use of the Hückel model permits the calculation of the pH values and the comparison of the resulting values with the IUPAC values, and also the calculation of the values of p(m_H) [= −lg(m_H/m°)] for these acetate buffer solutions. In the calculation of the pH values, an extra assumption concerning the value of the parameter $\theta_{H,Na}$ is needed, and it is assumed that its value is 0.070 at all temperatures; see above. This assumption is based on reasonable arguments and is supported by the pH data of Cohn at 18 °C. In the calculation of p(m_H) values, this assumption is not needed, and therefore, p(m_H) values can be predicted more reliably than pH values. The pH values recommended by IUPAC (see refs 5 and 7) and those suggested by Lito et al.[10] (based on the Bates−Guggenheim equation) and Nunes and Ferra[8] (based on the Pitzer equation) are compared to the pH values calculated by the Hückel method in Tables 12 and 13, where it can be seen that agreement is within 0.01.

Table 12. pH Values and p(m_H) Values for Acetate Buffer Solutions, CH_3COOH(aq, m_a) + CH_3COONa(aq, m_b), with $m_a = m_b$ = 0.01 mol kg^{-1}

t/°C	pH(IUPAC)[a]	pH(L)[b]	pH(N&F)[c]	pH[d]	p(m_H)[d]
0	4.737	4.740		4.737	4.694
5	4.730	4.728		4.728	4.685
10	4.725	4.721		4.722	4.678
15	4.722	4.716		4.717	4.673
20	4.720	4.714		4.715	4.670
25	4.720	4.713	4.720	4.714	4.670
30	4.722	4.714		4.716	4.671
35		4.719		4.719	4.674
40	4.730	4.725		4.725	4.679
45		4.733		4.733	4.686
50	4.745	4.742		4.742	4.696
55		4.754		4.754	4.707
60	4.768	4.766		4.768	4.720

[a] Covington et al.[5] and Camoes et al.[7] [b] Lito et al.[10] [c] Nunes and Ferra.[8] [d] Present study.

Table 13. pH Values and p(m_H) Values for Acetate Buffer Solutions, CH_3COOH(aq, m_a) + CH_3COONa(aq, m_b), with $m_a = m_b$ = 0.1 mol kg^{-1}

t/°C	pH(IUPAC)[a]	pH(N&F)[b]	pH[c]	p(m_H)[c]
0	4.683		4.681	4.576
5	4.673		4.671	4.566
10	4.665		4.664	4.558
15	4.656		4.659	4.552
20	4.656		4.655	4.547
25	4.654	4.653	4.654	4.545
30	4.654		4.654	4.545
35			4.657	4.546
40	4.660		4.662	4.550
45			4.668	4.555
50	4.675		4.677	4.562
55			4.687	4.572
60	4.684		4.700	4.583

[a] Covington et al.[5] and Camoes et al.[7] [b] Nunes and Ferra.[8] [c] Present study.

Table 14. p(m_H) Values at Various Temperatures for the Acetate Buffer Solutions, CH_3COOH(aq, m_a) + CH_3COONa(aq, m_b) + NaCl(aq, m_s), with $m_a = m_b$ = 0.01 mol kg^{-1} and m_s = 0.2 mol kg^{-1}, with $m_a = m_b$ = 0.01 mol kg^{-1} and m_s = 0.5 mol kg^{-1}, and with $m_a = m_b$ = 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	4.559	4.550	4.598
5	4.547	4.536	4.579
10	4.538	4.523	4.563
15	4.530	4.513	4.548
20	4.524	4.505	4.535
25	4.520	4.498	4.524
30	4.518	4.493	4.515
35	4.518	4.490	4.508
40	4.520	4.489	4.503
45	4.524	4.490	4.500
50	4.530	4.493	4.498
55	4.537	4.497	4.498
60	4.547	4.504	4.501

$p(m_H)$ values in salt solutions dilute with respect to the weak acid species can be used to calibrate glass electrode cells, particularly for titrimetry, in order that the cells should measure directly the molality of hydrogen ions; see refs 22, 46, and 47. For this purpose, $p(m_H)$ values are shown in Table 14 for three buffer solutions at temperatures from (0 to 60) °C: all buffer solutions contain 0.01 mol kg^{-1} acetic acid + 0.01 mol kg^{-1} sodium acetate and the NaCl molalities of (0.2, 0.5, or 1.0) mol kg^{-1}. The overriding advantage of the present approach is that it is free of the restrictions to ionic strengths not greater than 0.1 mol kg^{-1} of the Bates−Guggenheim convention (see refs 5 and 9).

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