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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

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Equations were determined for the calculation of stoichiometric (molality scale) dissociation constants K_m of propionic and *n*-butyric acids in buffer solutions from their thermodynamic dissociation constants K_a and molalities of components in solution at temperatures from (0 to 60) °C. These equations are based on single-ion activity coefficients from Hückel-type equations. The required thermodynamic dissociation constants and propionate and *n*-butyrate parameters were determined from Harned cell data of Harned and Ehlers (1933) and Harned and Sutherland (1934). The parameters agreed closely with parameters for acetate species determined recently. The required interaction parameters between hydrogen ions and chloride ions were taken from recent HCl data reassessment, and between hydrogen ions and sodium ions and between sodium ions and chloride ions were taken from the recent acetate work. The new equations were used to calculate pH values of propionate buffers with equal molalities of propionic acid and sodium propionate of (0.01 or 0.1) mol kg^{-1} at temperatures from (0 to 60) °C. Values of p(m_H), giving molality of protons directly, calculated from these equations are tabulated, and p(m_H) values for buffer solutions with NaCl as major component and propionate species as minor components are also given. The Hückel equations were also applied to a re-evaluation of K_a for formic acid and activity parameters for formate species at 25 °C from Harned cell data of Prue and Read (1966) and the parameter values for species from acetic, formic, propionic (propanoic), *n*-butyric (*n*-butanoic), 2-methylpropanoic, *n*-pentanoic, 2,2-dimethylpropanoic, *n*-hexanoic, 4-methylpentanoic, and *n*-heptanoic acids at 18 °C from quinhydrone electrode data of Larsson and Adell (1931).

Introduction

Solutions of acetic acid and sodium or potassium acetate have been used for many years as standards 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 studied intensively. Harned and co-workers also studied, using Harned cells, dilute solutions of formic acid, potassium formate and KCl,[8] of propionic acid, sodium propionate and NaCl,[9] and of *n*-butyric acid, sodium butyrate, and NaCl[10] at temperatures from (0 to 60) °C. The last two studies were considered here. Prue and Read[11] investigated at 25 °C formic acid, sodium formate, and NaCl solutions using Harned cells, and Harned and Owen[12] measured formic acid and NaCl solutions. Larsson and Adell[13,14] used quinhydrone (qh) electrode cells to study several aliphatic carboxylic acids in NaCl or KCl solutions at 18 °C, but only the NaCl data were considered here.

The purpose of the Harned cell studies mentioned above was principally to estimate the thermodynamic dissociation constants (K_a) of the weak acids at various temperatures. Stoichiometric dissociation constants (K_m where m refers to the molality scale) were usually not calculated by the original authors. It has been shown earlier (see, e.g., ref 15) that K_m values can be often determined more reliably from appropriate Harned cell data than from (apparently more direct) potentiometric titration data measured using glass and reference electrodes with a liquid junction. It seems important therefore to reanalyze, using a recently developed calculation method for acetic acid,[15] high-precision Harned cell data available in the literature for some other carboxylic acids. Here, the calculation method is applied to formic, propionic, and *n*-butyric acids as well as to a few other, more complex, aliphatic carboxylic acids in aqueous solutions containing NaCl.

For formic acid,[16] propionic acid,[17] and *n*-butyric acid,[18] equations have been already given for calculation of K_m values in aqueous NaCl and KCl solutions at 25 °C from the ionic strength of the solutions but the values from these equations apply in less dilute solutions only when the salt effectively determines the ionic strength of the solution. The parameters for these equations were partially determined from the potentiometric titration data, and the equations for NaCl solutions are considered below.

The new calculation method, given in the present study for the calculation of K_m values for propionic and butyric acid solutions from the composition variables of solutions, is applicable to temperatures from (0 to 60) °C and to ionic strengths probably up to about 2.0 mol kg^{-1}. This method

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Table 1. Experimental K_m ($\times 10^5$) Values Obtained for Propionic Acid from the Data Measured by Harned and Ehlers[9] on Cell 7 Where $m_a = m_b = m_s$ in the Temperature Range 0−30 °C, and the Debye−Hückel Parameter (α) and Standard Potential of Silver−Silver Chloride Electrode ($E°$) as a Function of the Temperature

	t/°C						
$m_a/m°$ [a]	0	5	10	15	20	25	30
0.004899					1.628	1.629	1.618
0.005918					1.670	1.670	1.660
0.006442	1.593	1.632	1.653	1.664	1.660		
0.006722	1.592	1.630	1.652	1.666	1.667		
0.007055	1.612	1.651	1.674	1.627[b]	1.691		
0.008117					1.492[b]	1.494[b]	1.485[b]
0.008716					1.716	1.719	1.708
0.009225	1.654	1.688	1.714	1.725	1.727		
0.009630					1.737	1.740	1.731
0.010812	1.676	1.716	1.740	1.756	1.757		
0.011181	1.699	1.742	1.764	1.775	1.773		
0.012812					1.787	1.792	1.784
0.013393	1.738	1.781	1.805	1.821	1.820		
0.016054					1.847	1.852	1.844
0.016431					1.841	1.844	1.836
0.016600	1.761	1.800	1.827	1.844	1.847		
0.017153					1.854	1.855	1.854
0.018106					1.864	1.867	1.861
0.018669					1.879	1.882	1.874
0.018882	1.804	1.848		1.896			
0.021153	1.816	1.858	1.880	1.898	1.900		
0.021977					1.914	1.916	1.909
0.022736	1.853	1.894	1.917	1.940	1.943		
0.025546					1.953	1.950	1.943
0.026480					1.964	1.965	1.959
0.026833	1.883	1.927	1.954	1.972	1.979		
0.030666	1.917	1.960	1.988	2.009	2.004		
0.031078	1.926	1.966	1.994	2.014	2.026		
0.031126					2.019	2.015	2.009
0.031793					2.017	2.012	2.003
0.035686					2.046	2.044	2.036
($E°$/mV)[c]	236.64	234.15	231.49	228.63	225.64	222.53	219.22
[$\alpha/(m°)^{-1/2}$][a]	1.1293	1.1376	1.1462	1.1552	1.1646	1.1744	1.1848

[a] $m° = 1$ mol kg^{-1}. [b] Omitted as a probable outlier. [c] Determined previously[22] from the HCl data of Harned and Ehlers.[19,24]

is not limited to the case where NaCl alone determines the ionic strength of the solution and is based on single-ion activity-coefficient equations of the Hückel type. The necessary parameters at different temperatures for propionate and butyrate species were estimated from Harned cell data. The resulting parameters agree with the acetate parameters determined recently[15] from cell potential data of Harned and Ehlers;[19,20] therefore, these acetate parameters are also recommended for propionate and butyrate ions. The resulting activity-coefficient equations were tested with reliable cell potential data obtained from the literature for these and for the other monoprotic aliphatic carboxylic acids.

With K_m values from this new model, speciation in propionic, or butyric, acid solutions can be solved and the hydrogen ion molalities can be calculated. The $m(H^+)$ values obtained were used, with one reasonable, extra assumption,[15] to calculate the pH values for the propionate buffers from (0 to 60) °C where the molality of the acid and its sodium salt is either 0.01 or 0.1 mol kg^{-1}. These p[$m(H^+)$] values, i.e., the values of $-\log[(m(H^+)/(\text{mol kg}^{-1})]$, were also calculated from K_m for buffer solutions containing NaCl as the major component and propionate species as minor components. These values can be used for the calibration of glass electrode cells in acidity determination, and such cells thus calibrated measure directly hydrogen ion molality.

Theory

The following equations were used for activity coefficients (γ) on the molality scale of species in solutions of a monobasic weak acid (HA), its sodium salt (NaA), and sodium chloride

$$\ln \gamma_H = -\frac{\alpha (I_m)^{1/2}}{1 + B_H (I_m)^{1/2}} + b_{H,Cl}(m_{Cl}/m°) + \theta_{H,Na}(m_{Na}/m°) \quad (1)$$

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

$$\ln \gamma_A = -\frac{\alpha (I_m)^{1/2}}{1 + B_A (I_m)^{1/2}} + b_{Na,A}(m_{Na}/m°) \quad (3)$$

$$\ln \gamma_{HA} = \lambda_{HA,Na}(m_{Na}/m°) \quad (4)$$

where $m° = 1$ mol kg^{-1} and the following symbols are used: H = H$^+$, Cl = Cl$^-$, Na = Na$^+$, HA = RCOOH, and A = 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 Tables 1 and 2,[21] 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 recent HCl results,[22] the value of $B_H = B_{Cl} = 1.4$ (mol kg^{-1})$^{-1/2}$ was taken for eqs 1 and 2 for all temperatures under consideration. The following equation

Table 2. Experimental K_m ($\times 10^5$) Values Obtained for Propionic Acid from the Data Measured by Harned and Ehlers[9] on Cell 7 Where $m_a = m_b = m_s$ in the Temperature Range 35−60 °C, and the Debye−Hückel Parameter (α) and Standard Potential of Silver−Silver Chloride Electrode ($E°$) as a Function of the Temperature

	t/°C					
$m_a/m°$ [a]	35	40	45	50	55	60
0.004899	1.598	1.741[b]				
0.005354		1.650[b]	1.558	1.529	1.488	1.446
0.005571		1.588	1.559	1.531	1.493	1.457
0.005918	1.641	1.616			1.552[b]	1.510[b]
0.006111		1.599	1.577	1.546		
0.008117	1.468[b]	1.449[b]				
0.008716	1.688					
0.009630	1.712	1.687				
0.010525		1.704	1.673	1.643	1.598	1.553
0.010592		1.694	1.668	1.638	1.599	1.558
0.012812	1.765	1.744				
0.013388		1.748	1.719	1.688	1.646	1.602
0.013933		1.756	1.727	1.695	1.656	1.608
0.015012		1.774	1.743	1.712	1.671	1.626
0.015819		1.782	1.751	1.718	1.675	1.630
0.016054	1.824	1.797				
0.016431	1.817	1.789				
0.017153	1.833	1.809				
0.018070		1.813	1.783	1.749	1.706	1.660
0.018106	1.844	1.808				
0.018669	1.859	1.833				
0.021258		1.901[b]	1.866[b]	1.834[b]	1.792[b]	1.748[b]
0.021977	1.889	1.864				
0.023284		1.882	1.853	1.820	1.779	1.732
0.025546	1.919	1.895				
0.026480	1.941	1.918				
0.027217		1.910	1.882	1.853	1.816	1.770
0.028469		1.932	1.902	1.865	1.822	1.777
0.031126	1.990	2.043[b]				
0.031553		1.961	1.931	1.898	1.861	1.820
0.031793	1.969	1.962				
0.035686	2.016	1.995				
0.045243		2.073	2.038	2.005	1.961	1.914
($E°$/mV)[c]	215.75	212.12	208.36	204.50	200.46	196.29
[$\alpha/(m°)^{-1/2}$][a]	1.1956	1.2068	1.2186	1.2308	1.2436	1.2568

[a] $m° = 1$ mol kg^{-1}. [b] Omitted as a probable outlier. [c] Determined previously[22] from the HCl data of Harned and Ehlers.[19,24]

can also be used in these equations for parameter $b_{H,Cl}$ at different temperatures from the results of that study

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

In the acetic acid study,[15] the following equation was determined from the Harned cell data of Harned[23] for aqueous mixtures of HCl + NaCl

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

This equation was also used here. Other parameters for the activity-coefficient equations were estimated here from appropriate literature data, and similarities are observed in many cases with the acetate parameter values.[15]

Results and Discussion

Determination of Parameter $b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$ for Propionate and n-Butyrate Species. Harned and Ehlers[9] and Harned and Sutherland[10] have measured precisely the following Harned cell at temperatures from (0 to 60) °C

$$\mathrm{Pt(s)|H_2(g,}\ f = 101.325\ \mathrm{kPa)|HA(aq,}m_a\mathrm{),\ NaA(aq,}m_b\mathrm{),NaCl(aq,}m_s\mathrm{)|AgCl(s)|Ag(s)} \tag{7}$$

where *f* is the fugacity. In the former of these studies, A refers to propionate ion and in the latter to butyrate ion. The molalities m_a, m_b, and m_s are given in Tables 1 and 2 for the propionic acid data and in Tables 3, 4, and 5 for the butyric acid data. The cell potential difference (CPD = *E*) for cells of type 7 is given by

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

where $E°$ is the standard CPD.

Experimental K_m values were obtained from these data as follows: The thermodynamic dissociation constant (K_a) for a weak monoprotic acid is given by

$$K_a = \frac{\gamma_H \gamma_A m_H m_A}{\gamma_{HA} m_{HA} m°} = (\gamma_H \gamma_A/\gamma_{HA})K_m \tag{9}$$

The stoichiometric dissociation constant K_m in this equation is defined by $K_m = m_H m_A/(m_{HA} m°)$. The observed K_m value was calculated from each experimental point of cell 7 from equations

$$\ln(m_H/m°) = \frac{(E° - E)F}{RT} - \ln(\gamma_H \gamma_{Cl} m_{Cl}/m°) \tag{10}$$

$$K_m = \frac{m_H(m_b + m_H)}{(m_a - m_H)m°} \tag{11}$$

In this evaluation, $E°$ values determined previously[22] from the HCl data of Harned and Ehlers[19,24] were used (see

Table 3. Experimental K_m ($\times 10^5$) Values Obtained for *n*-Butyric Acid from the Data Measured by Harned and Sutherland[10] on Cell 7 in the Temperature Range 0−15 °C

			t/°C			
$m_a/m°$ [a]	$m_b/m°$ [a]	$m_s/m°$ [a]	0	5	10	15
0.00564	0.00641	0.00606	1.941	1.949	1.950	1.941
0.00935	0.01063	0.01005	2.038	2.042	2.046	2.037
0.01374	0.01563	0.01477	2.124	2.126	2.129	2.121
0.01808	0.02056	0.01943	2.190	2.193	2.195	2.186
0.02381	0.02707	0.02559	2.244	2.250	2.257	2.236
0.02866	0.03258	0.03080	2.293	2.297	2.306	2.294
0.03575	0.04064	0.03842	2.346	2.357	2.362	2.346
0.04040	0.04594	0.04343	2.371	2.386	2.394	2.382

[a] $m° = 1$ mol kg^{-1}.

Table 4. Experimental K_m ($\times 10^5$) Values Obtained for *n*-Butyric Acid from the Data Measured by Harned and Sutherland[10] on Cell 7 in the Temperature Range 20−40 °C

			t/°C				
$m_a/m°$ [a]	$m_b/m°$ [a]	$m_s/m°$ [a]	20	25	30	35	40[b]
0.00717	0.00687	0.00706	1.935	1.906	1.865	1.819	1.757
0.01273	0.01220	0.01254	2.050	2.015	1.972	1.921	1.858
0.01515	0.01453	0.01493	2.061	2.036	2.003	1.954	1.898
0.01756	0.01683	0.01730	2.108	2.086	2.038	1.989	1.935
0.02232	0.02139	0.02198	2.165	2.132	2.102	2.047	1.990
0.04100	0.03931	0.04039		2.306	2.263	2.208	2.155
0.05106	0.04895	0.05029		2.388	2.339	2.282	2.221

[a] $m° = 1$ mol kg^{-1}. [b] The symbol of this set is 40a, see also Table 5.

Tables 1 and 2). Equations 1 and 2 were used for the activity coefficient of H^+ and Cl^- ions, using the values of relevant parameters given above. Iterative calculations were needed because the dissociation of the weak acid influences the ionic strength. Tables 1−5 show the K_m values obtained.

The thermodynamic dissociation constant K_a and parameter q_{Na} ($= b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$) were determined at each temperature from the K_m values in Tables 1−5 from

$$\ln K_m - \alpha(I_m)^{1/2}\left(\frac{1}{1 + B_H(I_m)^{1/2}} + \frac{1}{1 + B_A(I_m)^{1/2}}\right) + b_{H,Cl}(m_{Cl}/m°) = y_1 = \ln K_a - (b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na})(m_{Na}/m°) = \ln K_a - q_{Na}(m_{Na}/m°) \quad (12)$$

The preliminary calculations revealed that the value of $B_A = 1.8$ (mol kg^{-1})$^{-1/2}$ can be used for both acids at all temperatures. The same value was found in the previous acetic acid study[15] for acetate ions. For a fixed value of $B_A = 1.8$ (mol kg^{-1})$^{-1/2}$, the quantity y_1 can be calculated from each experimental point, and eq 12 represents an equation of the straight line of y_1 vs $m_{Na}/m°$. When the data in Tables 1 and 2 are used for the regression analysis using eq 12, the results shown in Table 6 were obtained for propionic acid. From the K_m values in Tables 3−5, the results shown in Table 7 were obtained for butyric acid.

The parameter values of q_{Na} for propionic acid in temperature range (25 to 60) °C shown in Table 6 agree well with the acetate values[15] shown also in the table. The q_{Na} values for propionic acid at temperatures from (0 to 15) °C have larger standard deviations than the values at the other temperatures, and there is no clear trend in the values with respect to the temperature. Therefore, it seems that the experimental data at these low temperatures may be affected by some systematic experimental errors. At 20 °C, the same solutions (in addition to several other solutions) were measured as at the lower temperatures (see Table 1), and these errors probably also appear in the results of this temperature. The most reliable parameter values also for the temperatures of (0 to 20) °C are probably

Table 5. Experimental K_m ($\times 10^5$) Values Obtained for *n*-Butyric Acid from the Data Measured by Harned and Sutherland[10] on Cell 7 in the Temperature Range 40−60 °C

			t/°C				
$m_a/m°$ [a]	$m_b/m°$ [a]	$m_s/m°$ [a]	40[b]	45	50	55	60
0.00597	0.00679	0.00642	1.756	1.702	1.647	1.588	1.525
0.00854	0.00971	0.00917	1.816	1.763	1.705	1.641	1.577
0.01327	0.01509	0.01426	1.913	1.856	1.800	1.737	1.671
0.01650	0.01876	0.01773	1.966	1.909	1.851	1.785	1.719
0.02381	0.02707	0.02558	2.060	1.998	1.937	1.867	1.799
0.02784	0.03166	0.02992	2.111	2.046	1.982	1.912	1.841
0.03656	0.04158	0.03929	2.192	2.131	2.061	1.992	1.918
0.03921	0.04459	0.04214	2.215	2.152	2.082	2.012	1.940

[a] $m° = 1$ mol kg^{-1}. [b] The symbol of this set is 40b, see also Table 4.

Table 6. Results from Least-Squares Fitting of Equation 12 from the Propionic Acid Data of Harned and Ehlers (Tables 1 and 2)

t/°C	$-\lg K_a$	$s(\lg K_a)$	K_a (10^5)	q_{Na}[a]	$s(q_{Na})$	s[b] (10^3)	q_{Na} (recd)[c]	K_a[d] ($\times 10^5$) (exp)
0	4.8914	0.0012	1.284	−0.19	0.08	4.7	0.152	1.299
5	4.8814	0.0013	1.314	−0.12	0.08	5.2	0.140	1.325
10	4.8762	0.0013	1.330	−0.08	0.08	5.0	0.127	1.339
15	4.8741	0.0015	1.336	−0.14	0.09	5.4	0.115	1.348
20	4.8742	0.0008	1.336	−0.05	0.04	4.3	0.103	1.343
25	4.8733	0.0007	1.339	0.09	0.04	2.8	0.090	1.339
30	4.8766	0.0007	1.329	0.08	0.04	3.0	0.078	1.328
35	4.8821	0.0010	1.312	0.12	0.06	4.1	0.066	1.309
40	4.8915	0.0007	1.284	0.02	0.04	3.5	0.053	1.285
45	4.9011	0.0004	1.256	−0.01	0.02	1.8	0.041	1.258
50	4.9103	0.0004	1.229	0	0.02	1.7	0.029	1.230
55	4.9229	0.0005	1.194	−0.03	0.03	2.2	0.016	1.196
60	4.9364	0.0007	1.158	−0.05	0.04	3.1	0.004	1.160

[a] $q_{Na} = b_{Na,A} + \Theta_{H,Na} - \lambda_{HA,Na}$. [b] Standard deviation about the regression. [c] Calculated by the equation $q_{Na} = 0.15214 - 0.00247$ (*t*/°C) that was previously[15] determined for acetate species (and is now also recommended for propionate species). [d] The experimental value of K_a was determined by using the recommended q_{Na} value.

Table 7. Results from Least-Squares Fitting of Equation 12 from the *n*-Butyric Acid Data of Harned and Sutherland (Tables 3−5)

t/°C	$-\lg K_a$	$s(\lg K_a)$	K_a (10^5)	q_{Na}[a]	$s(q_{Na})$	s[b] (10^3)	q_{Na} (recd)[c]	K_a[d] ($\times 10^5$) (exp)
0	4.8000	0.0009	1.585	0.44	0.04	2.8	0.152	1.563
5	4.8002	0.0005	1.584	0.43	0.02	1.6	0.140	1.563
10	4.8006	0.0004	1.583	0.420	0.015	1.1	0.127	1.560
15	4.8031	0.0008	1.574	0.47	0.04	2.6	0.115	1.547
20	4.809	0.003	1.55	0.6	0.3	5.8	0.103	1.529
25	4.8211	0.0016	1.510	0.25	0.07	5.1	0.090	1.499
30	4.8304	0.0010	1.478	0.27	0.04	3.1	0.078	1.464
35	4.8424	0.0009	1.437	0.29	0.04	3.0	0.066	1.422
40a[e]	4.8578	0.0003	1.387	0.234	0.014	1.1	0.053	1.376
40b[f]	4.8566	0.0004	1.391	0.09	0.02	1.1	0.053	1.389
45	4.8709	0.0004	1.346	0.10	0.02	1.3	0.041	1.342
50	4.8857	0.0004	1.301	0.15	0.02	1.4	0.029	1.294
55	4.9031	0.0007	1.250	0.14	0.03	2.2	0.016	1.242
60	4.9216	0.0007	1.198	0.14	0.03	2.2	0.004	1.190

[a] $q_{Na} = b_{Na,A} + \Theta_{H,Na} - \lambda_{HA,Na}$. [b] Standard deviation about the regression. [c] Calculated by the equation $q_{Na} = 0.15214 - 0.00247$ (*t*/°C) that was previously[15] determined for acetate species (and is now also recommended for *n*-butyrate species). [d] The experimental value of K_a was determined by using the recommended q_{Na} value. [e] The data of the set shown in Table 4 were used. [f] The data of the set shown in Table 5 were used.

Table 8. Thermodynamic Dissociation Constant K_a ($\times$ 10^5) of Propionic Acid as a Function of the Temperature (t)

t/°C	K_a (obsd)[a]	K_a (recd)[b]	K_a[c]	K_a[d]
0	1.299	1.305	1.276	1.274
5	1.325	1.323	1.303	1.302
10	1.339	1.335	1.323	1.323
15	1.348	1.342	1.335	1.335
20	1.343	1.343	1.340	1.340
25	1.339	1.338	1.337	1.337
30	1.328	1.327	1.327	1.328
35	1.309	1.311	1.311	1.311
40	1.285	1.289	1.289	1.289
45	1.258	1.263	1.261	1.262
50	1.230	1.231	1.230	1.229
55	1.196	1.195	1.194	1.193
60	1.160	1.156	1.554	1.553

[a] The experimental value; see Table 6. [b] Calculated by eq 13 and recommended in this study. [c] Calculated by the equation (eq 14) suggested by Harned and Ehlers.[9] [d] Calculated by the equation (eq 15) suggested by Robinson and Stokes.[25]

the acetate values in this table. Table 6 also shows the experimental K_a values obtained from these data by using the acetate parameter values.

The experimental values of q_{Na} in Table 7 for butyric acid seem to fall in three categories in the same way as the molalities of the components in Tables 3−5. From the experimental data in Table 3 (0 °C $\leq$ t $\leq$ 15 °C), an approximate value of q_{Na} = 0.45 is obtained, and from the data in Tables 4 (25 °C $\leq$ t $\leq$ 40 °C) and 5 (40 °C $\leq$ t $\leq$ 60 °C), the corresponding values are 0.26 and 0.13, respectively. The data at 20 °C in Table 4 are only for dilute solutions, and q_{Na} cannot be accurately determined from these data. It seems that these apparent q_{Na} values at different temperatures result from the experimental errors in the molalities of components and, therefore, as for propionate species the acetate parameters,[15] shown also in Table 7, are recommended for butyrate species. This table also gives the experimental K_a values obtained from these data using the acetate parameter values.

Determination of the Thermodynamic Dissociation Constant (K_a) for Propionic and n-Butyric Acids. The experimental values of ln K_a in Table 6, obtained with the recommended q_{Na} values, for propionic acid were fitted to a quadratic equation in temperature

$$\ln K_a = -11.2463 + 0.003128(t/°\mathrm{C}) - 0.000086(t/°\mathrm{C})^2 \tag{13}$$

The results of the comparison between the fitted and experimental K_a values are shown in Table 8, and the fitted values are recommended here. The table also shows the K_a values obtained by the equations

$$\log K_a = 6.48708 - 0.012843(T/\mathrm{K}) - \frac{1274.95\ \mathrm{K}}{T} - 1.31574\log(T/\mathrm{K}) \tag{14}$$

$$\log K_a = 3.3860 - 0.014055(T/\mathrm{K}) - \frac{1213.26\ \mathrm{K}}{T} \tag{15}$$

The former equation was used by Harned and Ehlers[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 was suggested by Robinson and Stokes.[25] The K_a values calculated by these equations agree well with those recommended in Table 8 at temperatures from (20 to 60) °C. Below 20 °C, the K_a values from these equations are significantly smaller than the new values but the new values are more reliable because they were based above on more reliable activity parameters. It is noted that more adjustable parameters needed to be determined for eq 14 than for eqs 13 or 15.

Table 9. Thermodynamic Dissociation Constant K_a ($\times$ 10^5) of *n*-Butyric Acid as a Function of the Temperature (t)

t/°C	K_a (obsd)[a]	K_a (recd)[b]	K_a[c]	K_a[d]
0	1.563	1.568	1.563	1.571
5	1.563	1.565	1.573	1.576
10	1.561	1.556	1.574	1.572
15	1.547	1.541	1.566	1.560
20	1.528	1.521	1.549	1.540
25	1.499	1.494	1.523	1.513
30	1.464	1.463	1.490	1.481
35	1.422	1.427	1.448	1.442
40a[e]	1.376	1.386	1.400	1.400
40b[e]	1.389	1.386	1.400	1.400
45	1.342	1.341	1.345	1.353
50	1.294	1.293	1.286	1.302
55	1.242	1.242	1.221	1.250
60	1.190	1.188	1.154	1.195

[a] The experimental value; see Table 7. [b] Calculated by eq 16 and recommended in this study. [c] Calculated by the equation (eq 17) suggested by Harned and Sutherland.[10] [d] Calculated by the equation (eq 18) suggested by Robinson and Stokes.[25] [e] See Table 7.

Experimental values of ln K_a in Table 7 for butyric acid, obtained with the recommended q_{Na} values, were also fitted to a quadratic equation in temperature

$$\ln K_a = -11.0629 - 0.00001(t/°\mathrm{C}) - 0.000077(t/°\mathrm{C})^2 \tag{16}$$

The results of comparison between the fitted and experimental K_a values are shown in Table 9, and the fitted values are recommended here. Table 9 also shows the K_a values calculated by the equations

$$\log (K_a/K_{a,\max}) = -0.00005\left(\frac{T-\theta}{°\mathrm{C}}\right)^2 \tag{17}$$

$$\log K_a = 2.6215 - 0.013334(T/\mathrm{K}) - \frac{1033.39\ \mathrm{K}}{T} \tag{18}$$

Equation 17 was used by Harned and Sutherland,[10] and they suggested that the value of 0.00005 in it is independent of the weak acid in the neighborhood of the maximum of K_a. This maximum is $K_{a,\max}$, and it is attained at $t = \theta$. For butyric acid, the values of these parameters are: $K_{a,\max}$ = 1.575 × 10^{-5} and θ = 8 °C. Equation 18 was given by Robinson and Stokes.[25] The K_a values calculated by these equations agree well with those recommended in Table 9 at 0 °C. At the other temperatures, recommended K_a values are significantly smaller than those obtained by eq 18 (which seems to be more accurate from these two equations). The recommended K_m values are probably more reliable because they were based above on more reliable activity parameters. It should be mentioned, additionally, that the simple equation of Harned and Sutherland (eq 17) applies satisfactorily in this case to all temperatures.

Determination of the Parameter $b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$ for Formate Species and the Thermodynamic Dissociation Constant K_a for Formic Acid at 25 °C. Prue and Read[11] measured precisely the Harned cell of type 7 in formic acid solutions at 25 °C. Molalities m_a, m_b, and m_s used in that study are given in Table 10, and the experimental K_m values, also shown in Table 10, were

Table 10. Experimental K_m ($\times$ 10^4) Values Obtained for Formic Acid from the Data Measured by Prue and Read[11] on Cell 7 at 25 °C

$m_a/m°$ [a]	m_a/m_b	m_a/m_s	K_m
0.008964	1.0039	1.5769	2.320
0.009650	0.70608	1.2201	2.413
0.013731	1.0039	1.5769	2.422
0.017186	0.70608	1.2201	2.587
0.020401	1.0039	1.5769	2.544
0.025503	1.0039	1.5769	2.614
0.026626	0.70608	1.2201	2.740
0.036609	1.0039	1.5769	2.751
0.043270	0.70608	1.2201	2.946

[a] $m° = 1$ mol kg^{-1}.

obtained from these data as above the K_m values for propionic and butyric acids (see Tables 1−5). The thermodynamic dissociation constant K_a and parameter q_{Na} ($= b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$) were estimated from the K_m values for formic acid using linear regression analysis with eq 12. The value of $B_A = 1.8$ (mol kg^{-1})$^{-1/2}$ was again used. The resulting straight line is

$$y_1 = -8.6053 \pm 0.0009 - (0.03 \pm 0.02)(m_{Na}/m°) \quad (19)$$

and the following values were determined from this equation: $K_a = 1.831 \times 10^{-4}$ and $q_{Na} = 0.03$. The K_a value agrees well with the value of 1.84×10^{-4} determined in a previous study[26] (see also Figure 1A in that study) from the conductance data of Saxton and Darken[27] and with the value of 1.82×10^{-4} determined by Prue and Read[11,16] from their own data. The new K_a and q_{Na} values are recommended in the present study, and thus the q_{Na} value for formate at 25 °C is different from that of acetate, propionate, and butyrate species ($q_{Na} = 0.090$, see above).

Results with New Parameter Values from the Harned Cell Data for Mixtures of RCOOH + RCOONa + NaCl. The experimental K_m values given in Tables 1 and 2 (propionic acid), in Tables 3−5 (butyric acid), and in Table 10 (formic acid) were reproduced by means of the new Hückel models. For propionic acid, the recommended K_a values are given in Table 8, the $E°$ values in Tables 1 and 2, the q_{Na} values in Table 6, and the $b_{H,Cl}$ values from eq 5. For butyric acid, the same parameter values were used except that the recommended K_a values are those given in Table 9. For formic acid at 25 °C, the values of $K_a = 1.831 \times 10^{-4}$ and of $q_{Na} = 0.03$ were used. The results are shown as error plots with the pK_m error defined by

$$e(\mathrm{p}K_m) = \mathrm{p}K_m(\mathrm{obsd}) - \mathrm{p}K_m(\mathrm{pred}) \quad (20)$$

which is presented as a function of the ionic strength of the solution. In graphs A (0 °C ≤ t ≤ 15 °C, and t = 25 °C), B (t = 20 and 40 °C), and C (t = (30 and 35) °C, and 45 °C ≤ t ≤ 60 °C) of Figure 1 are shown the propionic acid results (see Tables 1 and 2), and they support well the suggested model. In graphs A (0 °C ≤ t ≤ 30 °C) and B (35 °C ≤ t ≤ 60 °C) of Figure 2 are shown the butyric acid results (see Tables 3−5). For this acid, the data presented in graph B support well the suggested model, but the error plots in graph A are not random. As explained above, this probably results from errors in the concentrations reported in the original paper for these solutions. Also in graph A, however, the errors seem to be rather small. In Figure 3 the formic acid results are shown, and they support well the suggested model.

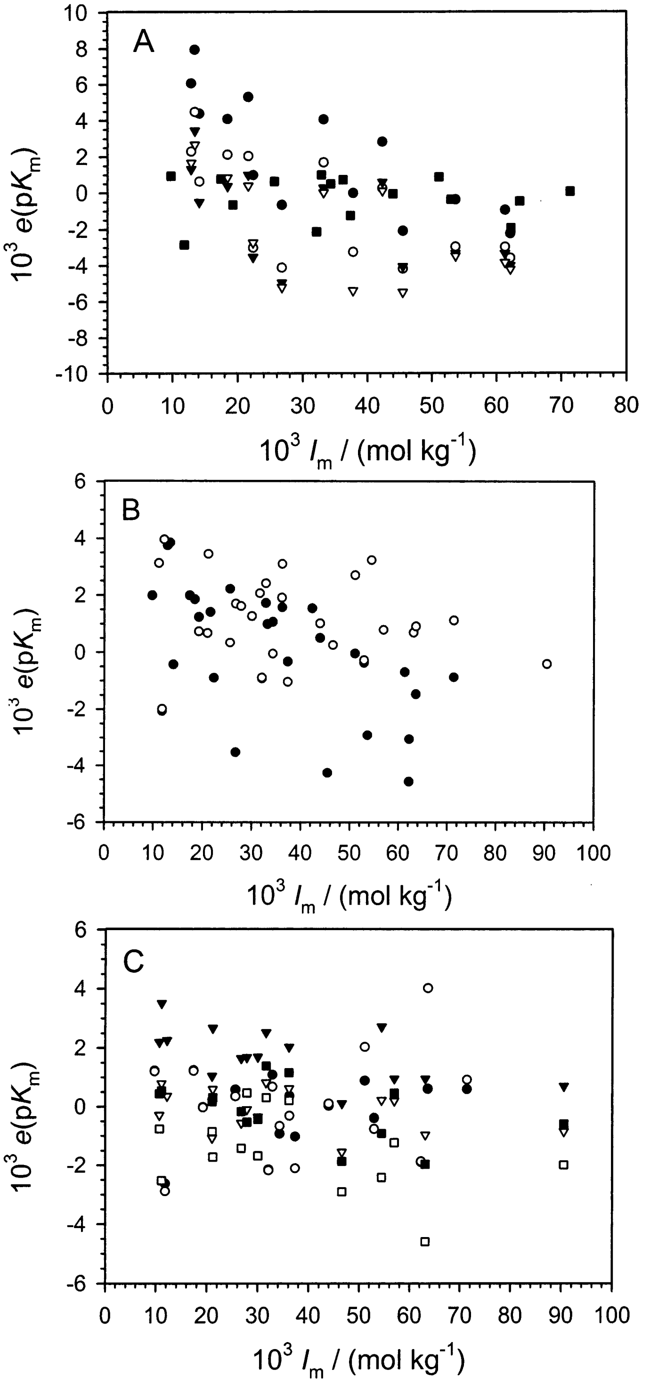

Figure 1. Differences, $e(\mathrm{p}K_m)$ in eq 20, between the experimental pK_m values obtained from the cell potential data of Harned and Ehlers[9] on cell 7 for propionic acid (see Tables 1 and 2) and those predicted by the Hückel method as a function of the ionic strength I_m. The K_m values were predicted by means eqs 1, 3, 4, and 9 with the recommended K_a values shown in Table 8 and with the parameter values recommended in this study. ●, 0 °C (graph A), 20 °C (graph B), 30 °C (graph C); ○, 5 °C (A), 40 °C (B), 35 °C (C); ▼, 10 °C (A), 45 °C (C); ▽, 15 °C (A), 50 °C (C); ■, 25 °C (A), 55 °C (C); □, 60 °C (C).

Results with New Parameter Values from the Harned Cell Data for Mixtures of HCOOH + NaCl. Harned and Owen[12] studied at 25 °C formic acid solutions on cells of the following type

$$\mathrm{Pt(s)|H_2(g,}\ f = 101\ \mathrm{kPa)|HCOOH(aq,}\ m_a\mathrm{)}\quad \mathrm{NaCl(aq,}\ m_s\mathrm{)|AgCl(s)|Ag(s)} \quad (21)$$

In these studies, the following three values of m_a were used: (0.10031, 1.0000, and 2.1253) mol kg^{-1}. Harned and

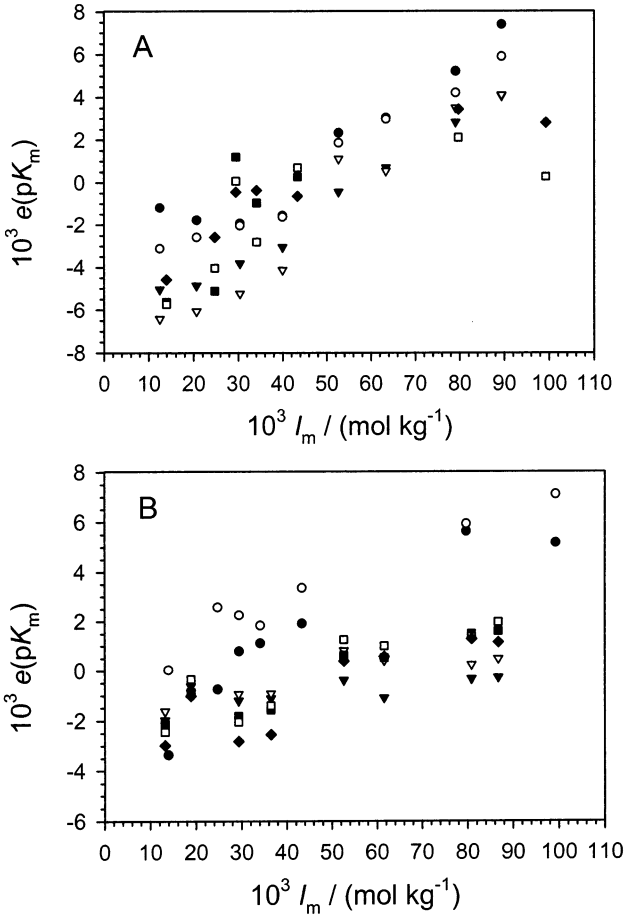

Figure 2. Differences, $e(pK_m)$ in eq 20, between the experimental pK_m values obtained from the cell potential data of Harned and Sutherland[10] on cell 7 for *n*-butyric acid (see Tables 3, 4, and 5) and those predicted by the Hückel method as a function of the ionic strength I_m. The K_m values were predicted by means of eqs 1, 3, 4, and 9 with the recommended K_a values shown in Table 9 and with the parameter values recommended in this study. ●, 0 °C (graph A), 35 °C (graph B); ○, 5 °C (A), 40 °C (B, set 40a in Table 4); ▼, 10 °C (A), 40 °C (B, set 40b in Table 5); ▽, 15 °C (A), 45 °C (B); ■, 20 °C (A), 50 °C (B); □, 25 °C (A), 55 °C (B); ◆, 30 °C (A), 60 °C (B).

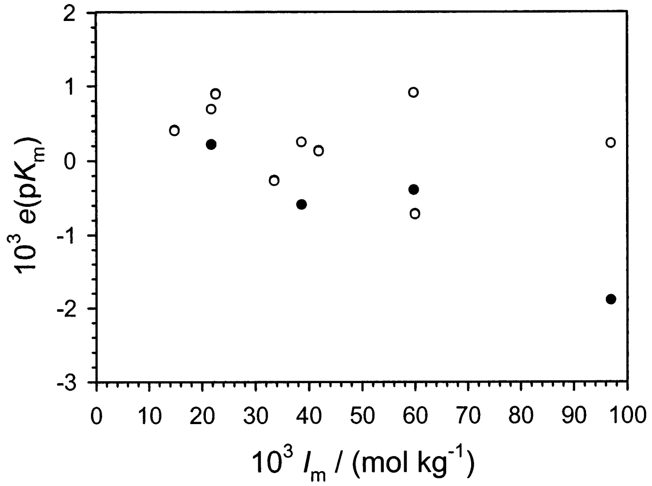

Figure 3. Differences, $e(pK_m)$ in eq 20, between the experimental pK_m values obtained from the cell potential data of Prue and Read[11] on cell 7 for formic acid (see Table 10) at 25 °C and those predicted by the Hückel method as a function of the ionic strength I_m. K_m values were predicted by eqs 1, 9, 22, and 23 with $K_a = 1.831 \times 10^{-4}$ and with the parameter values recommended in this study. ●, $\lambda_{HA,A} = -0.27$; ○, $\lambda_{HA,A} = 0$ (see text).

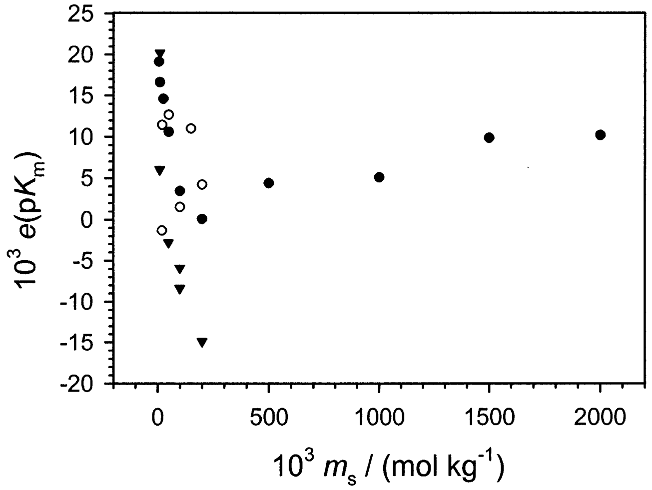

Figure 4. Differences, $e(pK_m)$ in eq 20, between the experimental pK_m values obtained from the cell potential data measured by Harned and Owen[12] on cell 21 at 25 °C for formic acid in NaCl solutions and those predicted by the Hückel method as a function of the salt molality m_s. K_m values were predicted by eqs 1, 9, 22, and 23 with the K_a value of 1.831×10^{-4} and with the parameter values recommended in this study. ●, $m_a = 0.10031$ mol kg^{-1}; ○, $m_a = 1.0000$ mol kg^{-1}; ▼, $m_a = 2.1253$ mol kg^{-1} (see text).

Owen measured three series of salt solutions where the molalities of NaCl (m_s) varied from (0.01 to 2) mol kg^{-1} in the case where $m_a = 0.10031$ mol kg^{-1} and from (0.04 to 0.23) mol kg^{-1} in the other two cases. These data were used to test the present model for formic acid.

The solutions measured by Harned and Owen on cell 21 contain a higher concentration of free formic acid, and so interactions between the formic acid molecules and ions are now more important than previously in this study. Therefore, equations for the activity coefficients of HCOO$^-$ (A) and HCOOH (HA) must now contain the $\lambda_{HA,A}$ terms and, thus, be presented as follows (compare with the acetic acid study[15])

$$\ln \gamma_A = -\frac{\alpha(I_m)^{1/2}}{1 + B_A(I_m)^{1/2}} + b_{Na,A}(m_{Na}/m^\circ) + \lambda_{HA,A}\,(m_{HA}/m^\circ) \quad (22)$$

$$\ln \gamma_{HA} = \lambda_{HA,Na}(m_{Na}/m^\circ) + \lambda_{HA,A}(m_A/m^\circ) \quad (23)$$

The data measured for m_a = (1.0000 and 2.1253) mol kg^{-1} can now be used to estimate the value of parameter $\lambda_{HA,A}$. A $\lambda_{HA,A}$ value was calculated relating to each experimental point in these sets, yielding a mean value of −0.27, which is therefore recommended for formic acid. It is close to the value of $\lambda_{HA,A} = -0.3$, obtained previously[15] by the same method for all temperatures for acetic acid. Experimental K_m values obtained, as described above from data of cell 7, for these three data sets were used to test the present model for formic acid, with the results shown as pK_m error plots (see eq 20) in Figure 4. The errors in Figure 4 are larger than those in Figures 1 to 3, but they support, almost within their precision, the Hückel model.

It is shown in Figure 3, additionally, that the inclusion of this new $\lambda_{HA,A}$ value in the calculations does not much affect the results obtained earlier from the data of Prue and Read[11] for formic acid.

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 Weak

Table 11. Recommended Values of the Stoichiometric Dissociation Constant, K_m (× 10^5), of Propionic Acid from Equation 24 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous NaCl Solution When NaCl Molality Effectively Determines the Ionic Strength

	$(I_m/m°)^a$								
t/°C	0	0.05	0.1	0.2	0.3	0.5	1.0	1.5	2.0
0	1.305	1.85	2.00	2.15	2.20	2.20	1.98	1.68	1.40
5	1.323	1.88	2.04	2.20	2.26	2.26	2.05	1.76	1.48
10	1.335	1.91	2.07	2.23	2.30	2.32	2.12	1.84	1.56
15	1.342	1.92	2.09	2.26	2.34	2.37	2.19	1.91	1.63
18	1.343	1.93	2.10	2.28	2.35	2.39	2.22	1.95	1.67
20	1.343	1.93	2.11	2.28	2.36	2.40	2.24	1.98	1.70
25	1.338	1.93	2.11	2.30	2.38	2.43	2.29	2.04	1.78
30	1.327	1.93	2.11	2.30	2.39	2.45	2.33	2.09	1.84
35	1.311	1.91	2.10	2.29	2.39	2.46	2.36	2.14	1.90
40	1.289	1.89	2.07	2.27	2.38	2.46	2.38	2.18	1.95
45	1.263	1.86	2.05	2.25	2.35	2.45	2.40	2.22	2.00
50	1.231	1.82	2.01	2.21	2.32	2.42	2.40	2.24	2.04
55	1.195	1.78	1.96	2.17	2.29	2.40	2.40	2.26	2.08
60	1.156	1.73	1.91	2.12	2.24	2.36	2.38	2.26	2.10

[a] $m° = 1$ mol kg^{-1}.

Table 12. Recommended Values of the Stoichiometric Dissociation Constant, K_m (× 10^5), of *n*-Butyric Acid from Equation 24 at Various Temperatures as a Function of the Ionic Strength (I_m) in Aqueous NaCl Solution When NaCl Molality Effectively Determines the Ionic Strength

	$(I_m/m°)^a$								
t/°C	0	0.05	0.1	0.2	0.3	0.5	1.0	1.5	2.0
0	1.568	2.22	2.41	2.58	2.65	2.65	2.38	2.02	1.68
5	1.565	2.23	2.42	2.60	2.67	2.68	2.43	2.08	1.75
10	1.556	2.22	2.42	2.60	2.68	2.70	2.47	2.14	1.82
15	1.541	2.21	2.41	2.60	2.68	2.72	2.51	2.19	1.88
18	1.529	2.20	2.39	2.59	2.68	2.72	2.53	2.22	1.91
20	1.520	2.19	2.39	2.59	2.68	2.72	2.54	2.24	1.93
25	1.494	2.16	2.36	2.56	2.66	2.71	2.56	2.28	1.98
30	1.463	2.12	2.32	2.53	2.63	2.70	2.57	2.31	2.03
35	1.427	2.08	2.28	2.49	2.60	2.67	2.57	2.33	2.07
40	1.386	2.03	2.23	2.44	2.55	2.64	2.56	2.35	2.10
45	1.341	1.97	2.17	2.39	2.50	2.60	2.55	2.35	2.12
50	1.293	1.91	2.11	2.32	2.44	2.55	2.52	2.35	2.14
55	1.242	1.85	2.04	2.26	2.37	2.49	2.49	2.34	2.16
60	1.188	1.78	1.97	2.18	2.30	2.42	2.45	2.33	2.16

[a] $m° = 1$ mol kg^{-1}.

Table 13. Recommended Values of the Stoichiometric Dissociation Constant, K_m (× 10^4), of Formic Acid at 25 °C from Equation 24 as a Function of the Ionic Strength (I_m) in Aqueous NaCl Solution When NaCl Molality Effectively Determines the Ionic Strength

I_m/mol kg^{-1}	0	0.05	0.1	0.2	0.3	0.5	1.0	1.5	2.0
K_m	1.831	2.66	2.91	3.18	3.32	3.43	3.33	3.05	2.74

Acid Species. For aqueous mixtures of HA, NaA, and NaCl that are very dilute with respect to the weak acid species, the following equation is obtained using the Hückel model

$$\ln K_m = \ln K_a + \alpha(I_m)^{1/2}\left(\frac{1}{1 + B_H(I_m)^{1/2}} + \frac{1}{1 + B_A(I_m)^{1/2}}\right) - (b_{H,Cl} + q_{Na})(I_m/m°) \quad (24)$$

The K_m values predicted from this equation for propionic and butyric acids are given at rounded ionic strengths and different temperatures in Tables 11 and 12. For formic acid at 25 °C, they are given in Table 13. Values from eq 24 can be compared to K_m values obtained from literature data for all monoprotic aliphatic carboxylic acids in the NaCl solutions of this kind.

Larsson and Adell[13,14] measured at 18 °C CPDs on quinhydrone (qh) cells of the following type

$$\text{Hg(l)}|\text{Hg}_2\text{Cl}_2\text{(s)}|\text{KCl(aq}, c = 3.5\ \text{mol dm}^{-3})|\text{HA(aq}, c_a) \ \text{NaA(aq}, c_b),\text{NaCl(aq}, c_s)|\text{qh(s)}|\text{Pt(s)} \quad (25)$$

In the data for each series, the concentrations of HA and NaA were exactly or approximately the same and close to (0.005 or 0.01) mol dm^{-3}. The concentration of NaCl varied in each series of measurements from (0 to 3) mol dm^{-3}, and each acid was also measured in KCl solutions. Larsson and Adell measured by these cells several aliphatic carboxylic acids. The experimental data have been reported on the molarity (concentration) scale. The data were converted into the molality scale using the equation of Harned and Owen[28] for NaCl solutions at different temperatures

$$\frac{cm°}{mc°} = \frac{\rho_0}{\text{g cm}^{-3}} - A(m/m°) \quad (26)$$

where $c° = 1$ mol dm^{-3}. A value of 0.0180 is used at 18 °C for parameter A, and a value of $\rho(H_2O) = 0.9986$ g cm^{-3} (Kell[29]) for the density of pure water at this temperature (ρ_0).

The CPD for cells of type 25 is given by

$$E = E^{\circ}_{QEC} + (RT/F)\ln(\gamma_H m_H/m°) + E_{corr} \quad (27)$$

where E°_{QEC} includes the standard qh potential and the potential of the calomel electrode on the left-hand side. The value of $E^{\circ}_{QEC} = 0.4520$ V, given by Larsson and Adell,[13] was used. The subsequent treatment is not critically dependent on this choice. The correction term E_{corr} is characteristic for a qh electrode cell. 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 for all experimental points the approximate corrections, but their values were not used as the correction can be evaluated more accurately as follows (see also ref 30).

Larsson and Adell[13] also measured potential differences with the qh electrode cells of the type 25 where the weak acid species were replaced by hydrochloric acid. From the CPD data of these cells and known activity coefficients of HCl in NaCl solutions, empirical equations can be determined for the term E_{corr} in eq 27. The activity coefficients of H^+ and Cl^- ions can be represented at 18 °C by

$$\ln \gamma_H = \ln \gamma_{Cl} = -\frac{1.1601(I_m/m°)^{1/2}}{1 + 1.25(I_m/m°)^{1/2}} + 0.238\,(I_m/m°) \quad (28)$$

This estimation was based on the activity-coefficient data presented on pages 726 and 727 in the handbook of Harned and Owen.[28] The use of eq 28 (where the composition variable is the ionic strength) instead of eq 1 for activity coefficients of hydrogen ions makes the calculations simpler with practically the same results. From the use of eq 28 for these activity coefficients, the following equation resulted for E_{corr}, valid up to 3.0 mol kg^{-1}

$$\frac{E_{corr}}{\text{mV}} = -1.146 + 8.544(I_m/m°)^{1/2} \quad (29)$$

Equations 27 and 29 were used for the calculation of the K_m values for the following carboxylic acids from the data

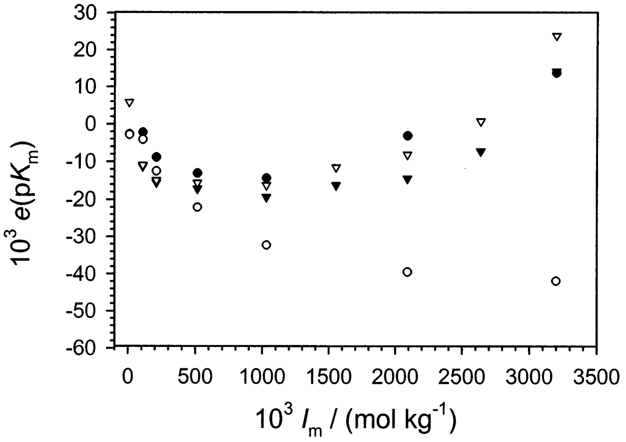

Figure 5. Differences, $e(\mathrm{p}K_m)$ in eq 20, between the pK_m values obtained from the cell potential data measured by Larsson and Adell on cell 25 at 18 °C for acetic acid[13] (Table 14) and for formic acid[14] (Table 15) and those predicted by the Hückel method as a function of the ionic strength I_m. K_m values were predicted by means of eq 24 with the K_a and q_{Na} values shown in Tables 14 and 15 and with other parameter values suggested in the text. ●, acetic acid, $q_{Na} = 0.068$; ○, acetic acid, $q_{Na} = 0.108$; ▼, formic acid, $q_{Na} = 0.037$; ▽, formic acid, $q_{Na} = 0.030$.

of Larsson and Adell:[13,14] acetic, formic, propionic (propanoic), *n*-butyric (*n*-butanoic), 2-methylpropanoic, *n*-pentanoic, 2,2-dimethylpropanoic, *n*-hexanoic, 4-methylpentanoic, and *n*-heptanoic acids. K_m values were calculated from each experimental point for these acids by equations

$$\ln(m_H/m^\circ) = \frac{(E - E^\circ_{QEC} - E_{corr})F}{RT} - \ln \gamma_H \qquad (30)$$

$$K_m = \frac{m_H(m_b + m_H)}{(m_a - m_H)m^\circ} \qquad (31)$$

In these calculations, it was assumed that the experimental K_m value depends only on the ionic strength of the solution. In each K_m determination, eq 28 was 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 the calculations are shown in Tables 14 (acetic acid), 15 (formic acid), 16 (propionic acid), 17 (*n*-butyric acid), 18 (2-methylpropanoic acid), 19 (*n*-pentanoic acid), 20 (2,2-dimethylpropanoic acid), 21 (*n*-hexanoic acid), 22 (4-methylpentanoic acid), and 23 (*n*-heptanoic acid).

The experimental K_m values shown in Tables 14–23 were used to test the present Hückel models. For all acids, the parameter value of B_A = 1.8 (mol kg^{-1})$^{-1/2}$ was used. For formic acid species, the value of $q_{Na} = 0.03$ (determined above for 25 °C) was used, and for species from all other acids, the acetate value 0.108 (at 18 °C) was used. The results of these calculations are shown as pK_m error plots in Figures 5 (acetic and formic acids), 6 (propionic and *n*-butyric acids), 7 (2-methylpropanoic and *n*-pentanoic acids), 8 (2,2-dimethylpropanoic and *n*-hexanoic acids), and 9 (4-methylpentanoic and *n*-heptanoic acids). The K_a values used in the calculations are shown in Tables 14–23.

Figures 5–9 show that the suggested Hückel models apply quite well to these qh electrode data. The formate value of $q_{Na} = 0.03$ applies well to formic acid data (see Figure 5), but the acetate value of $q_{Na} = 0.108$ does not apply as well to the other acids (see Figures 5–9). However, also for these other acids, the errors in the figures are small and close to the experimental uncertainty of the K_m values even at the highest molality used (about 3 mol kg^{-1}). It can be seen from these error plots that the value of q_{Na} = 0.108 does not explain the data within experimental error because all errors in these figures gradually decrease as the salt molality increases. This trend is, however, not very important. To show this for each acid, the value of parameter q_{Na} was determined that gives for this acid the best fit, and the resulting values are shown in Tables 14–23. Almost all of these best q_{Na} values are about 0.07 (including the acetate value which is 0.068, see Table 14), and this approximate value is not very far from the recommended acetate value of 0.108. Only the best value for 2,2-dimethylpropionate species (for which $q_{Na} = 0.015$, see Table 20) is an exception. It is a very important finding that almost all monoprotic aliphatic carboxylic acids (in-

Table 14. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where $c_a = c_b$ = 0.01008 mol dm^{-3}) for Acetic Acid[a] at 18 °C (K_a = 1.75 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0	0	0.01012	2.14
0.1	0.10034	0.11048	2.80
0.2	0.20105	0.21121	3.07
0.5	0.50540	0.51562	3.27
1.0	1.0204	1.0307	3.09
2.0	2.0813	2.0918	2.32
3.0	3.1880	3.1987	1.60

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.068 (see text and Figure 5). [b] Determined previously[15] from the data of Harned and Ehlers.[19,20]

Table 15. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where c_a = 0.00488 mol dm^{-3} and c_b = 0.00422 mol dm^{-3}) for Formic Acid[a] at 18 °C (K_a = 1.83 × 10^{-4})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^4)
0.00488	0.00489	0.09343	2.19
0.10488	0.10524	0.10977	3.00
0.20488	0.20595	0.21052	3.28
0.50488	0.51032	0.51494	3.51
1.0049	1.0253	1.0300	3.38
1.5049	1.5505	1.5551	3.03
2.0049	2.0863	2.0910	2.66
2.5049	2.6336	2.6383	2.27
3.0049	3.1931	3.1978	1.85

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(formate) = 0.030 and q_{Na}(best) = 0.037 (see text and Figure 5). [b] Determined in the present study for 25 °C from the data of Prue and Read.[11]

Table 16. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where $c_a = c_b$ = 0.01020 mol dm^{-3}) for Propionic Acid[a] at 18 °C (K_a = 1.34 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0	0	0.01023	1.63
0.1	0.10034	0.11060	2.22
0.2	0.20105	0.21132	2.38
0.5	0.50540	0.51573	2.51
1.0	1.0204	1.0308	2.36
1.5	1.5454	1.5560	2.10
2.0	2.0813	2.0919	1.82
3.0	3.1880	3.1989	1.26

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.072 (see text and Figure 6). [b] Determined in the present study from the data of Harned and Ehlers.[9]

Table 17. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where c_a = 0.01066 mol dm^{-3} and c_b = 0.01000 mol dm^{-3}) for *n*-Butyric Acid[a] at 18 °C (K_a = 1.53 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0	0	0.01004	1.87
0.1	0.10034	0.11040	2.53
0.2	0.20105	0.21113	2.75
0.5	0.50540	0.51553	2.91
1.0	1.0204	1.0306	2.72
1.5	1.5454	1.5558	2.43
2.0	2.0813	2.0917	2.07
2.5	2.6285	2.6391	1.78
3.0	3.1880	3.1987	1.46

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.072 (see text and Figure 6). [b] Determined in the present study from the data of Harned and Sutherland.[10]

Table 18. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where c_a = c_b = 0.01000 mol dm^{-3}) for 2-Methylpropanoic (Isobutyric) Acid[a] at 18 °C (K_a = 1.44 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0	0	0.01003	1.76
0.1	0.10034	0.11040	2.40
0.2	0.20105	0.21112	2.60
0.5	0.50540	0.51553	2.74
1.0	1.0204	1.0306	2.63
1.5	1.5454	1.5558	2.35
2.0	2.0813	2.0917	2.03
3.0	3.1880	3.1987	1.45

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.055 (see text and Figure 7). [b] Determined by Larsson and Adell.[14]

Table 19. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where c_a = c_b = 0.01121 mol dm^{-3}) for *n*-Pentanoic (*n*-Valeric) Acid[a] at 18 °C (K_a = 1.51 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0	0	0.01125	1.87
0.1	0.10034	0.11162	2.48
0.2	0.20105	0.21234	2.69
0.5	0.50541	0.51677	2.85
1.0	1.0204	1.0318	2.69
1.5	1.5455	1.5571	2.43
2.0	2.0813	2.0930	2.06
2.5	2.6286	2.6404	1.73
3.0	3.1881	3.2000	1.44

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.064 (see text and Figure 7). [b] Determined by Larsson and Adell.[14]

cluding acetic acid) have the same value of q_{Na} (= $b_{Na,A} + \theta_{H,Na} - \lambda_{HA,Na}$) for the Hückel model of K_m of these acids. Because of the approximations made in the present calculations and the experimental difficulties with the qh electrode method, it seems that the recommended acetate value of 0.108 for q_{Na} for these weak acids is preferable to the best values obtained from the individual data (see Tables 14−23).

The recommended K_m values in Tables 11−13 can be compared with those calculated from the equations suggested in the literature for K_m in these cases. The following three equations were considered: In ref 17 was given an equation of type 32 for propionic acid at 25 °C on the basis of potentiometric glass electrode data, and in refs 16 and 18 were given the corresponding equations for formic acid and butyric acid, respectively

Table 20. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where c_a = c_b = 0.01026 mol dm^{-3}) for 2,2-Dimethylpropanoic (Trimethylacetic) Acid[a] at 18 °C (K_a = 0.94 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0	0	0.01029	1.16
0.1	0.10034	0.11065	1.57
0.2	0.20105	0.21138	1.70
0.5	0.50540	0.51579	1.85
1.0	1.0204	1.0308	1.82
1.5	1.5454	1.5560	1.64
2.0	2.0813	2.0920	1.43
3.0	3.1880	3.1989	1.04

[a] For the Hückel model of the species from this acid, q_{Na}(best) = 0.015 and q_{Na}(acetate) = 0.108 (see text and Figure 8). [b] Determined by Larsson and Adell.[14]

$$\ln K_m = \ln K_a + \frac{\alpha(I_m)^{1/2}}{1 + B_H(I_m)^{1/2}} + \frac{\alpha(I_m)^{1/2}}{1 + B_A(I_m)^{1/2}} - (b_{H,NaCl} + b_{A,NaCl})(I_m/m°) \quad (32)$$

Parameter values for this equation have been collected in Table 24. These parameter values are also supported by Harned cell data in the literature, and they apply usually up to I_m of 0.5 mol kg^{-1}.

DeRobertis et al.[31] suggested, from titrimetric data obtained using glass electrodes, the following general equation for the dissociation constant of univalent carboxylic acids in NaCl aqueous solutions

$$\log K_m = \log K_a + \frac{2(I_m/m°)^{1/2}}{2 + 3(I_m/m°)^{1/2}} - C(I_m/m°) - E(I_m/m°)^2 \quad (33)$$

This equation was tested with propionic acid data (Table 11) at (20, 25, and 30) °C, and the values of parameter C of 0.0955, 0.092, and 0.0885, respectively, were obtained for these temperatures using an equation given in the original paper. Parameter E does not depend on the temperature, and the value of 0.00634 was suggested. Equation 33 was also tested with the data in Table 12 for butyric acid at 25 °C and with those in Table 13 for formic acid. In the calculations with this equation, the K_a values recommended in this study were used.

Barriada et al.[32] suggested a Pitzer equation of the following type for the K_m values of weak acids in salt solutions

$$\log K_{m,MCl} = \log K_a - \frac{2}{\ln(10)} f^{\gamma} - \frac{2\beta^1_{MCl}}{\ln(10)} I_m \exp(-2(I_m/m°)^{1/2}) - A(I_m/m°) - B[1 - (1 + 2(I_m/m°)^{1/2})\exp(-2(I_m/m°)^{1/2})] \quad (34)$$

$$f^{\gamma} = -(\alpha/3)\left\{\frac{(I_m)^{1/2}}{1 + 1.2(I_m/m°)^{1/2}} + \frac{2(m°)^{1/2}}{1.2}\ln(1 + 1.2(I_m/m°)^{1/2})\right\} \quad (35)$$

where MCl is NaCl. In eq 34, β^1 is a Pitzer parameter that is dependent on the 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

Table 21. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where $c_a = c_b$ = 0.00502 mol dm^{-3}) for *n*-Hexanoic (Caproic) Acid[a] at 18 °C ($K_a = 1.43 \times 10^{-5}$)[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0.00502	0.00503	0.01007	1.76
0.10502	0.10538	0.11044	2.33
0.20502	0.20609	0.21116	2.51
0.50502	0.51047	0.51557	2.64
1.00502	1.0255	1.0306	2.51
1.50502	1.5506	1.5558	2.25
2.00502	2.0865	2.0917	1.95
2.50502	2.6338	2.6391	1.64
3.00502	3.1934	3.1987	1.34

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.062 (see text and Figure 8). [b] Determined by Larsson and Adell.[14]

Table 22. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where $c_a = c_b$ = 0.00500 mol dm^{-3}) for 4-Methylpentanoic (Isocaproic) Acid[a] at 18 °C ($K_a = 1.46 \times 10^{-5}$)[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0.00500	0.00501	0.01003	1.80
0.10500	0.10536	0.11040	2.38
0.20500	0.20607	0.21112	2.58
0.50500	0.51045	0.51553	2.70
1.0050	1.0255	1.0306	2.53
1.5050	1.5506	1.5558	2.24
2.0050	2.0865	2.0917	1.95
2.5050	2.6338	2.6391	1.66
3.0050	3.1933	3.1987	1.36

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.081 (see text and Figure 9). [b] Determined by Larsson and Adell.[14]

Table 23. Results from Recalculations Obtained from the CPD Data of Larsson and Adell (Cell 25, Where $c_a = c_b$ = 0.00501 mol dm^{-3}) for *n*-Heptanoic Acid[a] at 18 °C (K_a = 1.42 × 10^{-5})[b]

c_s/(mol dm^{-3})	m_s/(mol kg^{-1})	I_m/(mol kg^{-1})	K_m (10^5)
0.00501	0.00502	0.01005	1.75
0.10501	0.10537	0.11042	2.34
0.20501	0.20608	0.21114	2.53
0.50501	0.51046	0.51555	2.68
1.0050	1.0255	1.0306	2.52
1.5050	1.5506	1.5558	2.27
2.0050	2.0865	2.0917	1.95
2.5050	2.6338	2.6391	1.61
3.0050[c]	3.1933	3.1987	1.35

[a] For the Hückel model of the species from this acid, q_{Na}(recd) = q_{Na}(acetate) = 0.108 and q_{Na}(best) = 0.062 (see text and Figure 9). [b] Determined by Larsson and Adell.[14] [c] c_a is 0.00364 mol dm^{-3} instead of 0.00501 mol dm^{-3}.

Table 24. Parameters for Equation 32 in NaCl Solutions at 25 °C

ion	K_a[d] (10^5)	B/(mol kg^{-1})$^{-1/2}$	b_{NaCl}
H^+		1.25	0.238
Cl^-		1.25	0.238
$(HCOO^-)$[a]	18.2	1.4	0.189
$(CH_3CH_2COO^-)$[b]	1.347	1.7	0.189
$(CH_3CH_2CH_2COO^-)$[c]	1.517	2.0	0.11

[a] See ref 16. [b] See ref 17. [c] See ref 18. [d] The thermodynamic dissociation constant for the corresponding acid.

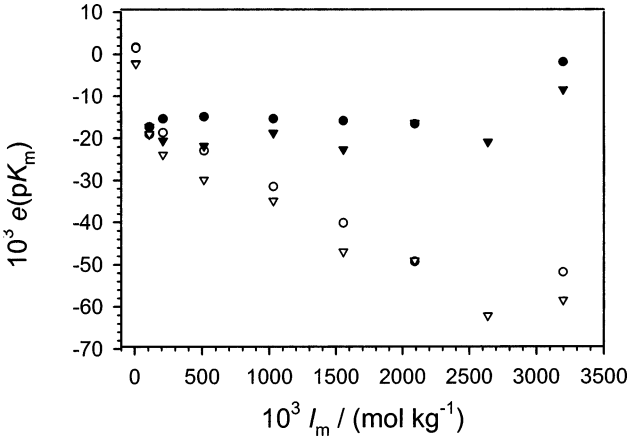

Figure 6. Differences, $e(pK_m)$ in eq 20, between the pK_m values obtained from the cell potential data measured by Larsson and Adell[14] on cell 25 at 18 °C for propionic acid (Table 16) and for *n*-butyric acid (Table 17) and those predicted by the Hückel method as a function of the ionic strength I_m. K_m values were predicted by means of eq 24 with the K_a and q_{Na} values shown in Tables 16 and 17 and with other parameter values suggested in the text. ●, propionic acid, q_{Na} = 0.072; ○, propionic acid, q_{Na} = 0.108; ▼, *n*-butyric acid, q_{Na} = 0.072; ▽, *n*-butyric acid, q_{Na} = 0.108.

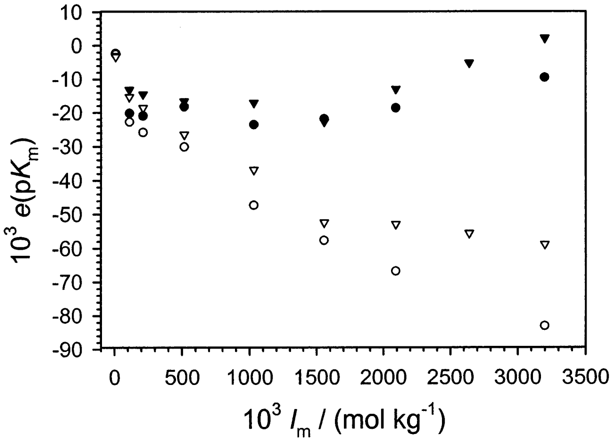

Figure 7. Differences, $e(pK_m)$ in eq 20, between the pK_m values obtained from the cell potential data measured by Larsson and Adell[14] on cell 25 at 18 °C for 2-methylpropanoic acid (Table 18) and for *n*-pentanoic acid (Table 19) and those predicted by the Hückel method as a function of the ionic strength I_m. K_m values were predicted by means of eq 24 with the K_a and q_{Na} values shown in Tables 18 and 19 and with other parameter values suggested in the text. ●, 2-methylpropanoic acid, q_{Na} = 0.055; ○, 2-methylpropanoic acid, q_{Na} = 0.108; ▼, *n*-pentanoic acid, q_{Na} = 0.064; ▽, *n*-pentanoic acid, q_{Na} = 0.108.

equation for different acids from the qh electrode data of Larsson and Adell (see above). For propionic acid in NaCl solutions, the following values were obtained: pK_a = 4.878, A = 0.218, and B = 0.166; and for *n*-butyric acid, the following values were obtained: pK_a = 4.816, A = 0.216, and B = 0.166. The data for these two acids (see Tables 11 and 12) were used in the present tests. For NaCl at 18 °C, the value of β_1 is 0.2615.[32]

The three equations (eqs 32−34) were tested with K_m values calculated by the recommended Hückel method and given in Tables 11−13, and the results are shown as pK_m error plots in Figure 10. Graph A in this figure gives the propionic acid results and graph B those for formic and butyric acids. These tests show that K_m values obtained using eq 32 agree quite well with the recommended values in Tables 11−13 up to I_m of 2.0 mol kg^{-1}, but the best agreement is obtained up to a molality of about 0.5 mol kg^{-1}. Also eq 34 predicts quite well the recommended K_m values for propionic and butyric acids at all molalities considered. On the other hand, the general equation suggested by DeRobertis et al. (eq 33) for 25 °C applies

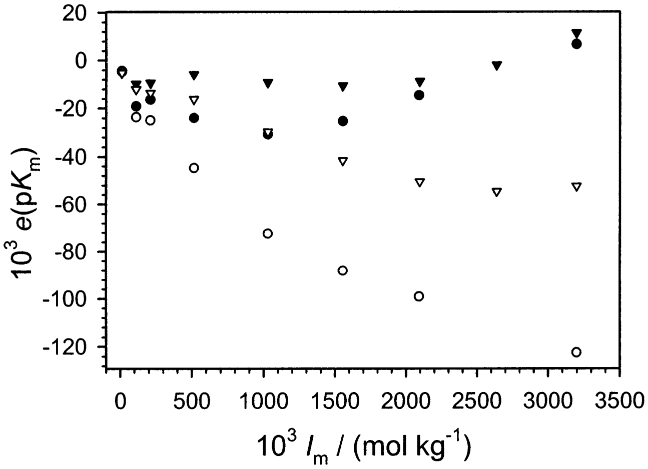

Figure 8. Differences, $e(\mathrm{p}K_\mathrm{m})$ in eq 20, between the $\mathrm{p}K_\mathrm{m}$ values obtained from the cell potential data measured by Larsson and Adell[14] on cell 25 at 18 °C for 2,2-dimethypropanic acid (Table 20) and for *n*-hexanoic acid (Table 21) and those predicted by the Hückel method as a function of the ionic strength I_m. K_m values were predicted by means of eq 24 with the K_a and q_Na values shown in Tables 20 and 21 and with other parameter values suggested in the text. ●, 2,2-dimethypropanic acid, $q_\mathrm{Na} = 0.015$; ○, 2,2-dimethypropanic acid, $q_\mathrm{Na} = 0.108$; ▼, *n*-hexanoic acid, $q_\mathrm{Na} = 0.062$; ▽, *n*-hexanoic acid, $q_\mathrm{Na} = 0.108$.

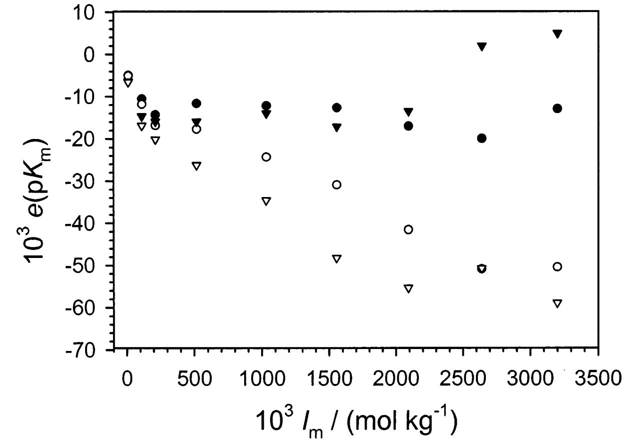

Figure 9. Differences, $e(\mathrm{p}K_\mathrm{m})$ in eq 20, between the $\mathrm{p}K_\mathrm{m}$ values obtained from the cell potential data measured by Larsson and Adell[14] on cell 25 at 18 °C for 4-methylpentanoic acid (Table 22) and for *n*-heptanoic acid (Table 23) and those predicted by the Hückel method as a function of the ionic strength I_m. K_m values were predicted by means of eq 24 with the K_a and q_Na values shown in Tables 22 and 23 and with other parameter values suggested in the text. ●, 4-methylpentanoic acid, $q_\mathrm{Na} = 0.081$; ○, 4-methylpentanoic acid, $q_\mathrm{Na} = 0.108$; ▼, *n*-heptanoic acid, $q_\mathrm{Na} = 0.064$; ▽, *n*-heptanoic acid, $q_\mathrm{Na} = 0.108$.

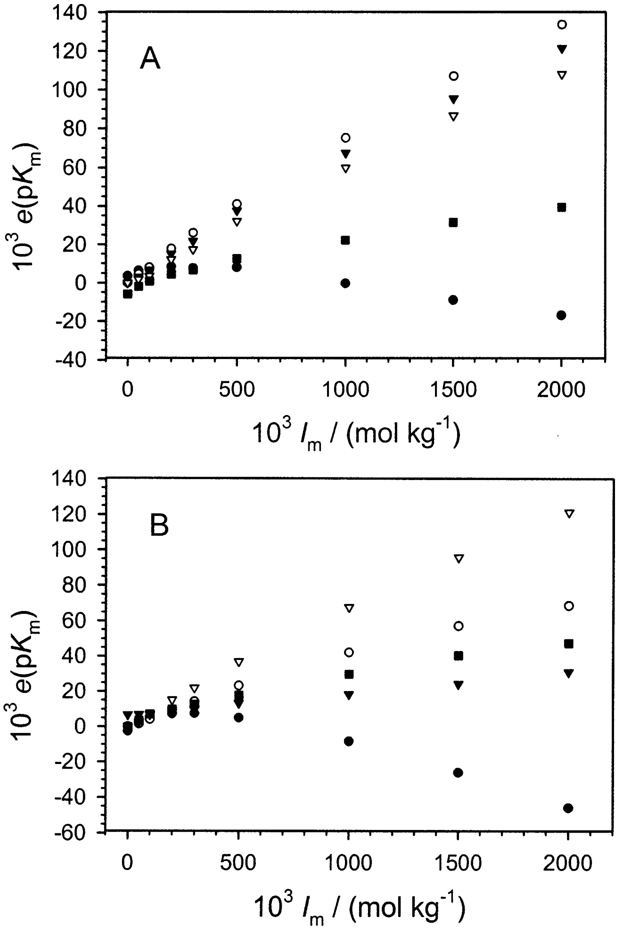

Figure 10. Differences between the recommended $\mathrm{p}K_\mathrm{m}$ values and the predicted $\mathrm{p}K_\mathrm{m}$ values, $e(\mathrm{p}K_\mathrm{m}) = \mathrm{p}K_\mathrm{m}(\mathrm{recd}) - \mathrm{p}K_\mathrm{m}(\mathrm{pred})$, as a function of the ionic strength I_m. Graph A shows the results obtained from the propionic acid values in Table 11, and graph B shows those from the *n*-butyric acid and formic acid values in Tables 12 and 13, respectively. K_m values were predicted by means eqs 32, 33, and 34. For eq 33, the K_a values recommended in the text were used. Graph A (propionic acid): ●, eq 32, t = 25 °C; ○, eq 33, t = 20 °C; ▼, eq 33, t = 25 °C; ▽, eq 33, t = 30 °C; ■, eq 34, t = 18 °C. Graph B: ●, formic acid, eq 32, t = 25 °C; ○, formic acid, eq 33, t = 25 °C; ▼, *n*-butyric acid, eq 32, t = 25 °C; ▽, *n*-butyric acid, eq 33, t = 25 °C; ■, *n*-butyric acid, eq 34, t = 18 °C.

Table 25. pH Values and p(m_H) Values for Propionate Buffer Solutions, CH_3CH_2COOH(aq, m_a) + CH_3CH_2COONa(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	4.845	4.802	4.789	4.685
5	4.838	4.795	4.782	4.677
10	4.834	4.791	4.777	4.671
15	4.831	4.788	4.773	4.666
20	4.831	4.787	4.772	4.664
25	4.832	4.787	4.772	4.663
30	4.835	4.790	4.774	4.664
35	4.840	4.794	4.778	4.667
40	4.847	4.801	4.784	4.672
45	4.855	4.809	4.791	4.678
50	4.866	4.819	4.800	4.686
55	4.878	4.831	4.812	4.696
60	4.892	4.844	4.824	4.708

satisfactorily to the formic acid data, but this equation and the equations for 20 and 30 °C do not apply well to propionic and butyric acid data in less dilute NaCl solutions.

Suggested pH and p(m_H) Values for Propionate Buffers. Use of the Hückel model permits the calculation of pH and p(m_H) [= −lg ($m_\mathrm{H}/m°$)] for, e.g., propionate buffer solutions. For the calculation of the pH values, however, an extra assumption concerning the value of parameter $\theta_\mathrm{H,Na}$ is needed, and the value of 0.070 is here assumed at all temperatures as in the previous acetic acid study.[15] In the calculation of p(m_H) values, this assumption is not needed, and therefore, the p(m_H) values can be predicted more reliably than pH values. Table 25 shows the pH and p(m_H) values for the following two propionate (A) 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.

p(m_H) values in salt solutions dilute with respect to the weak acid species can be used to calibrate a glass electrode

Table 26. p(m_H) Values at Various Temperatures for Propionate Buffer Solutions, $CH_3CH_2COOH(aq, m_a) + CH_3CH_2COONa(aq, m_b) + NaCl(aq, m_s)$, 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	4.667	4.658	4.706
5	4.657	4.646	4.689
10	4.650	4.636	4.675
15	4.644	4.627	4.662
20	4.640	4.620	4.651
25	4.638	4.615	4.642
30	4.637	4.612	4.634
35	4.639	4.610	4.629
40	4.642	4.610	4.624
45	4.646	4.612	4.622
50	4.653	4.616	4.621
55	4.661	4.621	4.622
60	4.671	4.628	4.625

cell, particularly for titrimetry, so the cell should measures directly the molality of hydrogen ions.[15] Hence p(m_H) values are shown in Table 26 for three propionate buffer solutions at temperatures from (0 to 60) °C; all buffer solutions contained 0.01 mol kg^{-1} propionic acid + 0.01 mol kg^{-1} sodium propionate and the NaCl molalities of (0.2, 0.5, or 1.0) mol kg^{-1}. These results are analogous to the results in Table 14 in the previous acetic acid study,[15] and they can be similarly used.

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