Determination of Stoichiometric Dissociation Constants of Formic Acid in Aqueous Sodium or Potassium Chloride Solutions at 298.15 K

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Equations were determined for the calculation of the stoichiometric (molality scale) dissociation constant K_m of formic acid in dilute aqueous NaCl and KCl solutions at 298.15 K from the thermodynamic dissociation constant K_a of this acid and from the ionic strength I_m of the solution. The salt alone determines mostly the ionic strength of the solutions considered in this study, and the equations for K_m were based on the single-ion activity coefficient equations of the Hückel type. The data measured by potentiometric titrations in a glass electrode cell were used in the estimation of the parameters for the Hückel equations of formate ions. The Hückel parameters obtained in these estimations agree well with those published previously for acetate ions, and therefore, the acetate parameters are also recommended for formate ions. By means of the calculation method based on the Hückel equations, K_m can be obtained almost within experimental error at least up to I_m of about 2 mol kg^{-1} for formic acid in NaCl and KCl solutions.

Introduction

Formic acid (HCOOH = ForOH) is the simplest carboxylic acid, and it is an industrially important chemical substance. It is used in textile and leather industries and in silage and grain preservations, where this acid appears to inhibit or prevent mold growth. This acid is also biologically important: it occurs in fruits, vegetables, and leaves and roots of plants and also in the secretions of numerous insects. Formic acid is in water solutions the strongest of the unsubstituted series of carboxylic acids. It is approximately 10 times stronger than the second member in this series, acetic acid.

The exact determination of the thermodynamic dissociation constant K_a of this acid at 298.15 K proved to be a much more difficult problem than that for, for example, acetic acid. For the latter acid, the high-precision conductivity measurements of MacInnes and Shedlovsky (1932) and the Harned-cell measurements of Harned and Ehlers (1932) gave exactly the same value for K_a. For formic acid, the conductivity measurements of Saxton and Darken (1940) gave a value of 1.84×10^{-4} for K_a and the Harned-cell measurements of Harned and Embree (1934) gave a value of 1.78×10^{-4} [see also Partanen (1996)]. Prue and Read (1966) also pointed out this problem and redetermined this K_a from results of their own Harned-cell measurements. They obtained in this redetermination a value of 1.82×10^{-4}, which is closer to the previous conductivity value. In addition, the conductivity measurements of Bell and Miller (1963) support Prue and Read's value. In the present study, this value is used and the potentiometric results presented below support this K_a.

In practical studies in electrolyte solutions, the stoichiometric dissociation constants (e.g., the dissociation constants on the molality scale, K_m) of weak acids are in common use. The weak acid solutions considered, for example, in analytical applications contain usually a large amount, compared to the amount of the weak acid, of a proper salt to keep the ionic strength I_m of the solution constant despite the dissociation of the acid. It has been observed in such solutions that the K_m of the weak acid is dependent only on the molality of the salt (or on I_m). It has been, in addition, observed that the dependence K_m versus I_m is strong for most charge types of dissociation reactions. If it were possible to determine K_m for these solutions, it would also be possible to calculate directly the molalities (or other composition variables) for the species existing in the weak acid solution.

Stoichiometric dissociation constants have been nowadays often determined with glass electrodes. For amino acids, these works have been reviewed by IUPAC [see, e.g., Kiss et al. (1991) and Sóvágó et al. (1993)]. These reviews revealed the absence of systematic studies on the influence of I_m on K_m. For other weak acids, the systematic studies are also rare, and the existing studies in this field are usually concentrated on the acids used as pH buffer substances (see, however, a recent study of De Robertis et al. (1999), and this research group has also previously done important studies of this topic). Results of the systematic glass electrode works have been reviewed by Daniele et al. (1997) and Sastre de Vicente (1997).

In the present study, a simple method (called below the Hückel method) is given for the calculation of K_m at different ionic strengths from K_a for formic acid in aqueous NaCl or KCl solutions at 298.15 K. The Hückel method is based on semiempirical equations for ionic activity coefficients. These equations originate partially from the Debye−Hückel theory. In previous studies, the Hückel method has been used for the determination of K_m of, for example, acetic and formic acids (Partanen, 1998) in salt solutions. In that study, all experimental data were taken from the literature and measured on Harned cells.

Potentiometric titrations were carried out here in a glass electrode cell containing aqueous mixtures of ForOH and NaCl or KCl at 298.15 K, and the results of these titrations

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were used to determine experimental K_m values. It is not easy to solve K_m from titration data.

Calibrations, asymmetry potentials and liquid junction potentials are difficult problems associated with the determination of K_m by this experimental technique, and these problems are not at the moment entirely solved. In this study, a new calculation method is presented to overcome these problems. K_m for ForOH at different experimental salt molalities was calculated by this method. Activity parameters for the Hückel equation were then estimated from the K_m values obtained by this method. The estimated parameters agree well with the parameters obtained previously (Partanen, 1998) for acetic acid solutions from the literature data measured on Harned cells. On the basis of these parameters, it is possible to recommend equations for K_m of ForOH in NaCl and KCl solutions up to I_m of about 3 mol kg^{-1}. The recommended K_m values are tabulated below at rounded ionic strengths. Formic acid solutions (like acetic acid solutions) have been used as buffer solutions for acidity determinations (Bates and Gary, 1961). Therefore, the equations for the calculation of K_m of this acid are especially important.

Experimental Section

Potentiometric ForOH titrations were carried out in aqueous NaCl and KCl solutions at 298.15 K. For the measurements, two series of salt solutions were prepared in RO-filtered water (Millipore). One of those series consisted of NaCl (pro analysi, Riedel-de Haën) solutions and the other of KCl (pro analysi, Merck) solutions, and the concentrations in these series were as follows: 0.080, 0.160, 0.240, 0.320, 0.400, 0.500, and 0.700 M. Also a 0.01013 M ForOH (pro analysi, May & Baker) solution, a 0.0996 M NaOH (Fixanal, Riedel-de Haën) solution, and a 0.0998 M KOH (Titrisol, Merck) solution were prepared.

The solutions titrated were prepared by mixing a volume of 10.00 cm^3 of the ForOH solution, 100.0 cm^3 of a salt solution, and 25.00 cm^3 of water; see Partanen et al. (1995a). The NaCl solutions were titrated by using the NaOH titrant, and the KCl solutions, by using the KOH titrant. During the titrations, the electromotive force (emf) was measured by means of an N62 combination electrode and a CG841 pH-meter, both manufactured by Schottgeräte. The resolution of the meter was 0.1 mV. The titrant was added in increments of 0.050 cm^3 with a Dosimat (Metrohm). Standard buffer solutions of pH = 4.005 and pH = 6.865 (Covington et al., 1985) were used to check the stability of the measuring system between titrations. The pH-meter reproduced usually the same reading within 0.2 mV in these buffer solution tests.

Theory

In the Hückel method, the following equation is generally used for the activity coefficient (γ) of ion i on the molality scale:

$$\ln \gamma_i = -\alpha(I_m)^{1/2}/[1 + B_i(I_m)^{1/2}] + b_{i,\mathrm{MCl}} I_m/m° \qquad (1)$$

where $m° = 1$ mol kg^{-1}, I_m is the ionic strength on the molality scale, and α is the Debye–Hückel parameter equal to 1.17444 (mol kg^{-1})$^{-1/2}$; see Archer and Wang (1990). B_i and $b_{i,\mathrm{MCl}}$ are the parameters that are dependent on ion i, and $b_{i,\mathrm{MCl}}$ is, in addition, dependent on the salt MCl present in the system. In Table 1 are given the parameter values which have been determined previously for this equation and are considered here.

Table 1. Ion Parameters for the Hückel Equation (Eq 1) in NaCl and KCl Solutions at 298.15 K and Results of the Regression Analysis Obtained by Using Eq 15

ion	H^+	Cl^-	$HCOO^-$	CH_3COO^-
$(10^5\ K_a)$[a]			18.2[b]	1.758[c]
(pK_a)[d]			3.740	4.755
$[10^5 K_{a,obsd}(NaCl)]$[e]			18.2	
$p[K_{a,obsd}(NaCl)]$[e]			3.740 ± 0.007	
$[10^5 K_{a,obsd}(KCl)]$[e]			18.1	
$p[K_{a,obsd}(KCl)]$[e]			3.743 ± 0.004	
B/(mol kg^{-1})$^{-1/2}$	1.25[f]	1.25[f]	1.4[g]	1.6[h]
b_{NaCl}	0.238[f]	0.238[f]	0.189[i]	0.189[h]
b_{KCl}	0.178[g]	0.178[g]	0.308[i]	0.308[g]
b_{NaCl}(obsd)[j]			0.24 ± 0.05	
b_{KCl}(obsd)[j]			0.33 ± 0.04	

[a] The thermodynamic dissociation constant for the corresponding acid. [b] Determined by Prue and Read (1966) from the emf data. [c] Determined from the conductivity data measured by MacInnes and Shedlovsky (1932); see Partanen et al. (1995c). [d] $pK_a = -\log K_a$. [e] An estimate of K_a of formic acid; see also footnote d. It was determined from the titration data, and the standard deviation is also given. [f] Determined by Partanen et al. (1995b) from Harned-cell data. [g] Determined by Partanen (1998) from Harned-cell data. [h] Determined by Partanen et al. (1995c) from Harned-cell data. [i] Recommended in this study. [j] b for formate ions determined from the titration data, and the standard deviation is also given.

The thermodynamic dissociation constant (K_a) for formic acid is given by

$$K_a = \gamma_H \gamma_A m_H m_A/(\gamma_{HA} m_{HA} m°) = (\gamma_H \gamma_A/\gamma_{HA}) K_m \qquad (2)$$

where HA refers to formic acid molecules and A to formate ions. For neutral species HA, it is assumed in the Hückel method that $\gamma_{HA} = 1$ [the validity of this assumption has been discussed previously (Partanen, 1998)]. The stoichiometric dissociation constant K_m in eq 2 is defined by

$$K_m = m_H m_A/(m_{HA} m°) \qquad (3)$$

The following equation can be presented for K_m of ForOH in aqueous NaCl or KCl solutions:

$$\ln K_{m,\mathrm{MCl}} = \ln K_a + \alpha(I_m)^{1/2}\{1/[1 + B_H(I_m)^{1/2}] + 1/[1 + B_A(I_m)^{1/2}]\} - (b_{H,\mathrm{MCl}} + b_{A,\mathrm{MCl}}) I_m/(m°) \qquad (4)$$

where MCl refers to either NaCl or KCl. Here, the values of $B_H = 1.25$ (mol kg^{-1})$^{-1/2}$, $B_A = 1.4$ (mol kg^{-1})$^{-1/2}$, $b_{H,NaCl} = 0.238$, and $b_{H,KCl} = 0.178$ were used in this equation (see Table 1) and the parameters K_a, $b_{ForO,NaCl}$, and $b_{ForO,KCl}$ were determined from potentiometric titration data.

Results

The missing activity parameters of formate ions for eq 1 were determined from the potentiometric titration data measured for this study. The experimental K_m values obtained from these data for NaCl and KCl solutions are shown in Tables 2 and 3, respectively. In these determinations, a glass electrode parameter (E_0, the exact definition is given below), the dissociation constant (K_m), and the amount of the acid (n_t) were simultaneously estimated from each titration data set. In general, the following equation is valid for electromotive forces measured on a glass electrode cell:

$$E = E^0 + (kRT/F) \ln a_H \qquad (5)$$

where a_H is the activity of the protons and $E°$ is a term that includes the contributions of the reference electrode,

Table 2. Results Obtained from the Potentiometric Titrations of Formic Acid in NaCl Solutions at 298.15 K Series FNC

$I_m/(m°)$[a]	0.0595	0.1789	0.2388	0.2988	0.3741	0.5251
symbol	FNC1	FNC3	FNC4	FNC5	FNC6	FNC7
$[10^4K_m(\text{obsd})]$[b]	2.79	3.11	3.22	3.33	3.32	3.43
$[10^4K_m]$[c]	2.74	3.19	3.30	3.37	3.43	3.47
$(10^4n_t/\text{mol})$[d]	0.987	0.985	0.984	0.983	0.975	0.977
$[E_0/\text{mV}]$[e]	382.52	382.51	382.62	382.48	383.01	384.39

[a] $m° = 1$ mol kg^{-1}. [b] The stoichiometric dissociation constant determined from the titration data by the method described in the text. [c] The stoichiometric dissociation constant calculated by eq 4 with the recommended activity parameters. [d] The optimized amount of formic acid. [e] The value of parameter E_0 used in the calculation of the emf errors for Figure 1. It was determined by requiring that the sum of all errors in the data set is zero (eqs 17−19).

Table 3. Results Obtained from the Potentiometric Titrations of Formic Acid in KCl Solutions at 298.15 K Series FKC

$I_m/(m°)$[a]	0.0595	0.1193	0.1792	0.2393	0.2997	0.3755
symbol	FKC1	FKC2	FKC3	FKC4	FKC5	FKC6
$[10^4K_m(\text{obsd})]$[b]	2.70	3.01	3.07	3.21	3.27	3.32
$[10^4K_m]$[c]	2.73	3.00	3.16	3.25	3.32	3.36
$(10^4n_t/\text{mol})$[d]	0.994	0.994	0.991	0.985	0.988	0.990
$[E_0/\text{mV}]$[e]	381.90	381.32	380.86	380.77	380.33	380.52

[a−e] See footnotes to Table 2.

the liquid junction, the standard glass electrode, and the asymmetry potentials [see, e.g., May et al. (1982)]. It is assumed in all present titrations that this term remained constant during the titration. The slope parameter k in this equation has a value of 1 for electrodes obeying completely the Nernst equation. In preliminary calculations, it was confirmed that the Nernstian response for the glass electrode can be used in all formic acid solutions considered. The three parameters were estimated by means of the following equation:

$$E = E° + (RT/F)\ln\gamma_H + (RT/F)\ln(m_H/m°) = E_0 + (RT/F)\ln(m_H/m°) \quad (6)$$

where $E_0 = E° + (RT/F)\ln\gamma_H$ is the glass electrode parameter that must be estimated and it is also constant during each titration at a constant ionic strength (see eq 1). m_H is calculated for each titration point by

$$m_H^2 + (K_m m° + m_b)m_H + K_m m°(m_b - m_t) = 0 \quad (7)$$

where m_b is the molality of the base, NaOH or KOH, in the solution titrated and $m_b = c_bV/w_1$, where c_b is the concentration, V is the volume of the base solution added in the titration, and w_1 is the mass of water in the solution titrated. m_t in eq 7 is the total molality of ForOH in the solution titrated, and $m_t = n_t/w_1$, where n_t is the amount of this substance.

K_m and the glass electrode parameter E_0 were calculated for each data set studied, containing N points, by the following equations

$$\sum_{i=1}^{N}(E_i - E_{\text{pred},i}) = 0 \quad (8)$$

$$\ln(x_i/m°) = (E_i - E_0)F/(RT) \quad (9)$$

$$K_{m,i} = x_i(x_i + m_{b,i})/\{[(n_t/w_{1,i}) - m_{b,i} - x_i]m°\} \quad (10)$$

$$K_m = \sum_{i=1}^{N} K_{m,i}/N \quad (11)$$

$$m_{H,i} = \{[(K_m m° + m_{b,i})^2 + 4[(n_t/w_{1,i}) - m_{b,i}]K_m m°]^{1/2} - (K_m m° + m_{b,i})\}/2 \quad (12)$$

$$E_{\text{pred},i} = E_0 + (RT/F)\ln(m_{H,i}/m°) \quad (13)$$

where x_i is the experimental molality of H$^+$ ions at point i. Additionally, the amount of ForOH (n_t) was optimized by requiring that the following square sum $S(E)$ attains the minimum:

$$S(E) = \sum_{i=1}^{N}(E_i - E_{\text{pred},i})^2 \quad (14)$$

This amount had to be adjusted for each titration, probably because of the salting-out effect [this effect has been discussed in a recent paper (Partanen et al., 1999)]. Tables 2 and 3 show the K_m values obtained in these calculations for ForOH, denoted as K_m(obsd).

The activity parameters $b_{A,NaCl}$ and $b_{A,KCl}$ were determined by equation

$$\ln K_{m,MCl} - \alpha(I_m)^{1/2}\{1/[1 + B_H(I_m)^{1/2}] + 1/[1 + B_A(I_m)^{1/2}]\} = y = \ln K_a - (b_{H,MCl} + b_{A,MCl})I_m/(m°) \quad (15)$$

This equation represents an equation of a straight line y versus $I_m/(m°)$. The thermodynamic dissociation constant K_a can be obtained from the intercept of the line with the y axis, and the slope of the straight line is $(b_{H,MCl} + b_{A,MCl})$. The results obtained by linear regression analysis with this equation from the K_m(obsd) data presented in Tables 2 and 3 are shown in Table 1. In this table are also included the activity parameters for salt solutions of acetic acid (AcOH) determined previously from data measured by the Harned cells of the following general type

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

where f is the fugacity, where M refers to either Na$^+$ or K$^+$, and where in this case HA = AcOH and A$^-$ = AcO$^-$. (The literature data measured by cells of this type in formic acid solutions were also used in this study to test Hückel parameters; see below.) Table 1 shows that the present calculation method gives for formate ions b parameters that agree well with those of acetate ions. Therefore, the following Hückel parameters can be recommended in this study for eq 1: $B_{ForO} = 1.4$ (mol kg^{-1})$^{-1/2}$, $b_{ForO,NaCl} = 0.189$, and $b_{ForO,KCl} = 0.308$.

The regression analysis by eq 15 also gives two estimates for K_a of ForOH, shown in Table 1. Both estimates agree well with the thermodynamic value suggested above for this acid (i.e., with $K_a = 1.82 \times 10^{-4}$). The recommended K_m values, calculated by eq 4 by means of this K_a and the activity parameters recommended in the previous paragraph, are shown in Tables 2 and 3 for all formic acid solutions considered.

Discussion

The Hückel parameters determined above are tested with the titration data obtained in this study. The recommended K_m values given in Tables 2 and 3 were used in these tests. The parameter E_0 for eq 6 was calculated for

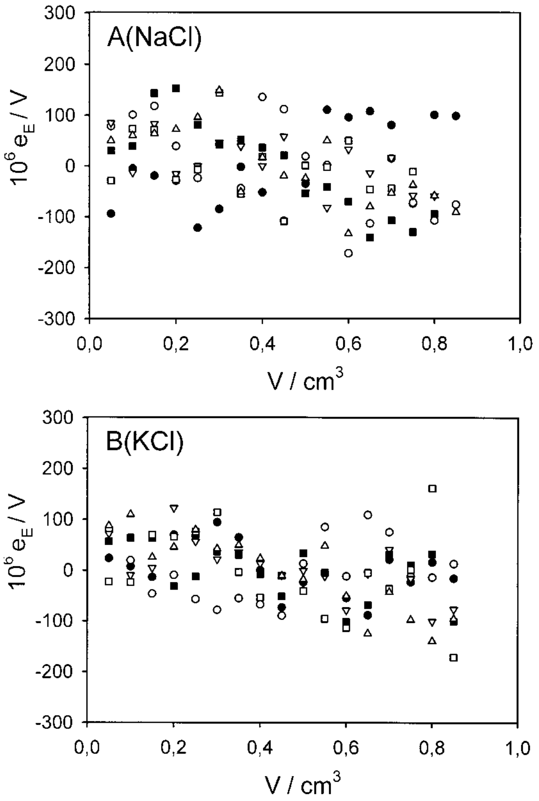

Figure 1. Difference between the observed and predicted electromotive forces, e_E in eq 20, as a function of the titrant volume in the titrations of formic acid by the base (NaOH or KOH) solution in NaCl solutions (series FNC, graph A) and in KCl solutions (FKC, B). The predicted emf was calculated by eqs 4, 6, and 7 using the thermodynamic dissociation constant 1.82×10^{-4}, the recommended activity parameters, and the glass electrode parameter E_0 shown in Tables 2 and 3. Symbols for the different sets are the following. Graph A: (●) FNC1; (○) FNC3; (△) FNC4; (▽) FNC5; (■) FNC6; (□) FNC7. Graph B: (●) FKC1; (○) FKC2; (△) FKC3; (▽) FKC4; (■) FNC5; (□) FNC6.

each data set by using the equations:

$$m_{H,i} = \{[(K_m m^\circ + m_{b,i})^2 + 4[(n_t/w_{1,i}) - m_{b,i}]K_m m^\circ]^{1/2} - (K_m m^\circ + m_{b,i})\}/2 \qquad (17)$$

$$E_{0,i} = E_i - (RT/F)\ln(m_{H,i}/m^\circ) \qquad (18)$$

$$E_0 = (\sum_{i=1}^{N} E_{0,i})/N \qquad (19)$$

The resulting values for E_0 are included in Tables 2 and 3. The results of the tests are shown as error plots in graphs A (NaCl) and B (KCl) of Figure 1, where the emf error defined by

$$e_E = E(\text{obsd}) - E(\text{pred}) \qquad (20)$$

is presented for each data set as a function of the added base volume. Most of the error plots in these graphs are random, and all errors are comparable to the resolution of the pH meter (0.1 mV). Therefore the data dealt with in Tables 2 and 3 support well the calculation method.

The Hückel parameters were further tested with the data measured by Harned and Embree (1934) and by Prue and Read (1966) on Harned cells of type 16 where HA = ForOH and A^- = $ForO^-$. In the solutions studied by Harned and Embree, M was K^+ and the molalities were related by $m_a = 0.8021 m_b = 0.9268 m_s$. In the study of Prue and Read, M was Na^+ and two series of solutions were investigated. In the first series (denoted below as series A) $m_a = 1.0039 m_b = 1.5769 m_s$, and in the second (series B) $m_a = 0.70608 m_b = 1.2201 m_s$. The electromotive force E of cell 16 is given by

$$E = E^\circ_{H-C} - (RT/F)\ln[\gamma_H \gamma_{Cl} m_H m_{Cl}/(m^\circ)^2] \qquad (21)$$

where Cl refers to chloride ions, E°_{H-C} is the standard emf (this value was adjusted in the present tests for all sets considered, and hence possible constant systematic errors in these sets appear in the E°_{H-C} values obtained), and the data of Harned and Embree (1934) were updated by using a conversion factor of 1 abs V = 1.000 34 int V. The data in these two sets were used to test the activity parameters in the following way:

The observed K_m values were first calculated from the data of Harned and Embree and of Prue and Read, and the resulting values were then compared to the predictions of eq 4 calculated by means of the recommended parameters. In these calculations it was assumed that the observed K_m depends only on the ionic strength of the solution, as suggested in eq 4. This K_m was obtained by equations

$$\ln(m_H/m^\circ) = (E^\circ_{H-C} - E)F/(RT) - \ln[\gamma_H \gamma_{Cl} m_{Cl}/(m^\circ)] \qquad (22)$$

$$K_m = m_H(m_b + m_H)/[(m_a - m_H)m^\circ] \qquad (23)$$

In these calculations, eq 1 was used for the activity coefficients of H^+ and Cl^- ions and the relevant parameters for this equation are given in Table 1. These parameter values apply to HCl in NaCl or KCl solutions and are also very probably valid for HCl in dilute aqueous mixtures of different weak-acid species and NaCl or KCl (see Partanen, 1998). For all three series of measurements, E°_{H-C} was adjusted using the emf errors defined by eq 20. The predicted emf was calculated by eq 21, and m_H for this equation was obtained by eqs 4 and 7. Iterative calculations were needed because the dissociation of ForOH has an influence on the ionic strength. For the data set of Harned and Embree, E°_{H-C} was determined by requiring that the error of the most dilute point is zero, and for the two sets of Prue and Read, it was determined by requiring that the sum of all errors is zero. The resulting value for the set of Harned and Embree is 0.223 05 V, and for both sets of Prue and Read it is 0.222 49 V. Harned and Ehlers (1932) have determined a value of 0.222 50 V for this quantity, and therefore a constant systematic error on the order of 0.5 mV appears in the electromotive forces reported by Harned and Embree (1934). In the calculation of the observed K_m values by eqs 22 and 23, these E°_{H-C} values were used. The results of the comparison between the observed and predicted K_m values are shown in graph A of Figure 2. In this figure, the pK_m error defined by

$$e(pK_m) = pK_m(\text{obsd}) - pK_m(\text{pred}) \qquad (24)$$

is presented for each experimental point as a function of the ionic strength. The predicted K_m values in this graph agree very well with the experimental counterparts. The largest absolute pK_m error in this graph is <0.004. This value can be compared to the maximum acceptable scatter of 0.06 in a pK_m value for a set of readings in any one estimation suggested by Albert and Serjeant in their well-known monograph (1984). Therefore, the recommended

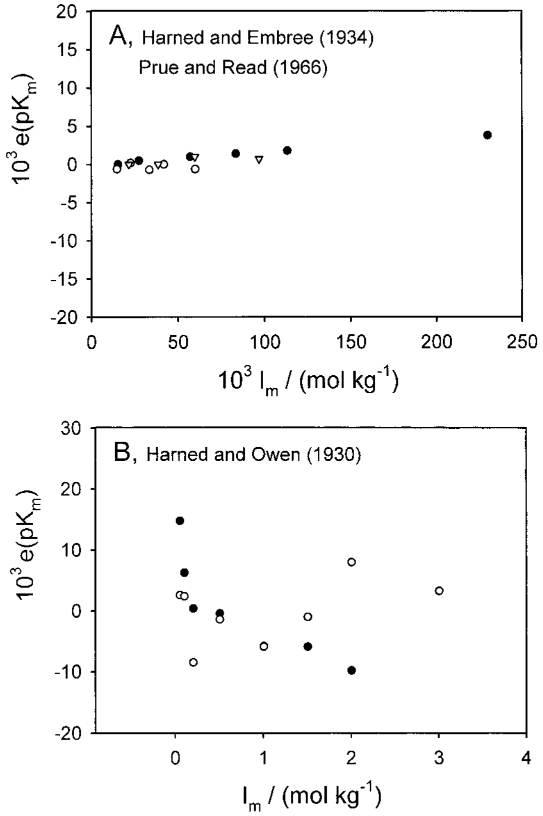

Figure 2. Difference between the observed and predicted pK_m values, e(pK_m) in eq 24, as a function of the ionic strength I_m in the sets measured by Harned and Embree (1934) and Prue and Read (1966) on cell 16, where HA = ForOH (graph A), and by Harned and Owen (1930) on cell 16, where HA = ForOH and m_b is zero (graph B). The observed pK_m values were calculated as described in the text with the values for $E^\circ_{\mathrm{H-C}}$ given. The predicted pK_m values were calculated by eq 4 using the thermodynamic dissociation constant 1.82 × 10^{-4} and the recommended activity parameters. The symbols of the data sets are the following (see text). Graph A: (●) Harned and Embree, $E^\circ_{\mathrm{H-C}}$ = 0.223 05 V; (○) Prue and Read, series A, $E^\circ_{\mathrm{H-C}}$ = 0.222 49 V; (▽) Prue and Read, series B, $E^\circ_{\mathrm{H-C}}$ = 0.222 49V. Graph B: (●) NaCl, $E^\circ_{\mathrm{H-C}}$ = 0.221 98 V; (○) KCl, $E^\circ_{\mathrm{H-C}}$ = 0.222 49 V.

Table 4. Stoichiometric Dissociation Constant (K_m) of Formic Acid as a Function of the Ionic Strength (I_m) in Aqueous NaCl and KCl Solutions at 298.15 K

I_m/(mol kg^{-1})^a	10^4K_m(NaCl)	10^4K_m(KCl)
0	1.82	1.82
0.01	2.23	2.23
0.02	2.39	2.38
0.03	2.50	2.50
0.04	2.59	2.59
0.05	2.67	2.66
0.07	2.80	2.79
0.10	2.94	2.93
0.20	3.23	3.19
0.30	3.38	3.32
0.40	3.44	3.36
0.50	3.47	3.37
0.70	3.43	3.29
1.00	3.26	3.08
1.50	2.88	2.63
2.00	2.47	2.19
2.50		1.80
3.00		1.46

^{a} I_m is the same as m_{NaCl} or m_{KCl}.

activity parameters are strongly supported by the data of Harned and Embree and of Prue and Read measured on cells without a liquid junction (despite the systematic error observed in the former emf data).

The activity parameters were also tested with the data measured by Harned and Owen (1930) on cells of type 16 where HA = ForOH and where m_b is zero. In that study, rather strong solutions with respect to ForOH were investigated. The smallest value of m_a in these solutions was 0.100 31 mol kg^{-1}, and two series of salt solutions (in one of those the salt was NaCl and in the other KCl) were measured at this molality of ForOH. Only these two series were considered here. In the NaCl series, in addition, the results of some very dilute and strong salt solutions were omitted from the consideration. The remaining data were used to test the recommended activity parameters in the same way as the data of Harned and Embree (1934) and Prue and Read (1966) above. The results of the K_m comparison are shown in graph B of Figure 2. For both data sets, $E^\circ_{\mathrm{H-C}}$ was estimated by requiring that the sum of all errors in the set is zero, and the resulting values are shown in the figure. The departure of $E^\circ_{\mathrm{H-C}}$ for the NaCl set (for this set $E^\circ_{\mathrm{H-C}}$ is 0.221 98 V) from the value suggested by Harned and Ehlers (i.e., from 0.222 50 V) can result from the medium effect due to the appreciable amount of undissociated formic acid present in the solutions of this data set; see Partanen et al. (1995c) and Partanen (1998). Otherwise, the emf data of Harned and Owen support well the calculation method up to large ionic strengths. For NaCl solutions the limit is about 2 mol kg^{-1}, and for KCl solutions it is 3 mol kg^{-1}. The largest pK_m error in this graph is <0.015. Also this error can be compared to the conventional pK_m error of 0.06 suggested by Albert and Serjeant (1984); see above.

Table 4 shows the recommended K_m values for formic acid in aqueous salt solutions at 298.15 K at rounded ionic strengths. These values apply to the case where NaCl or KCl alone determines the ionic strength of the solution. The K_m values were calculated by

$$\ln K_{\mathrm{m,MCl}} = \ln K_a + \alpha(I_m)^{1/2}\{1/[1 + B_{\mathrm{H}}(I_m)^{1/2}] + 1/[1 + B_{\mathrm{A}}(I_m)^{1/2}]\} - (b_{\mathrm{H,MCl}} + b_{\mathrm{A,MCl}})I_m/(m^\circ) \quad (25)$$

where $K_a = 1.82 \times 10^{-4}$, a = 1.174 44 (mol kg^{-1})$^{-1/2}$, B_{H} = 1.25 (mol kg^{-1})$^{-1/2}$, B_{A} = 1.4 (mol kg^{-1})$^{-1/2}$, $b_{\mathrm{H,NaCl}} = 0.238$, $b_{\mathrm{H,KCl}} = 0.178$, $b_{\mathrm{A,NaCl}} = 0.189$, and $b_{\mathrm{A,KCl}} = 0.308$, where A refers to formate ions. It was shown above that these parameter values are supported by potentiometric titration data and by emf data measured on cells without a liquid junction. Therefore, it seems to us that the K_m predictions obtained by eq 25 and presented in Table 4 are reliable.

Conclusions

Potentiometric titrations of formic acid were carried out in aqueous NaCl and KCl solutions at 298.15 K. In all solutions titrated, the molality of the salt was appreciably larger than that of the acid, and salt molalities up to 0.5 mol kg^{-1} were used. From the titration data at different ionic strengths, stoichiometric dissociation constants for formic acid were calculated. A new calculation method was used in this determination. In this method, the measured emfs were directly used without any calibrations and a perfect Nernstian response for the glass electrode was assumed.

The calculation method gives consistent K_m values with those calculated by the recommended activity coefficient equations (parameters for these equations were determined from Harned-cell data). The largest absolute difference between the experimental K_m values and those obtained by the activity coefficient equations in Tables 2 and 3 is <0.015 when it is expressed as a pK_m difference. This value can be compared to the conventional pK_m error of 0.06 suggested by Albert and Serjeant in their monograph (1984). This comparison shows that the new calculation method for potentiometric titration data is more accurate than those generally used. The comparison of this maximum error to the Harned-cell errors presented in Figure 2 reveals also that the accuracy of the new potentiometric method is comparable to those for the methods based on measurements by (accurate but experimentally more complicated) hydrogen electrode cells. In addition, the agreement between the activity parameters for formate and acetate ions observed in this study shows that the activity coefficients of the anions resulting from the different carboxylic acids seem to be close to each other in the dilute salt solutions (see also Partanen, 1998).

According to Table 4, K_m for formic acid in NaCl and KCl solutions is a sensitive function of the ionic strength [as also observed previously (Partanen, 1998) for other light fatty acids], especially in the I_m range 0−0.1 mol kg^{-1}. It is clear, therefore, that the use of the thermodynamic value (K_a, shown in the table) for this dissociation constant in calculations leads to a large error even in very dilute solutions. It seems to us that this fact is not sufficiently pointed out in the literature. On the other hand, it is encouraging to observe that the dependence of K_m on I_m follows in dilute solutions accurately the Debye−Hückel theory, and therefore, the final equations for this dependence also in more concentrated salt solutions are nevertheless quite simple (like eq 25 in the present study).

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