

Calculation of Stoichiometric Dissociation Constants of Formic, Acetic, Glycolic and Lactic Acids in Dilute Aqueous Potassium, Sodium or Lithium Chloride Solutions at 298.15 K

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Single-ion activity coefficient equations are presented for the calculation of stoichiometric (molality and concentration scale) dissociation constants (K_m and K_c , respectively) for formic, acetic, glycolic and lactic acids in dilute aqueous salt solutions at 298.15 K. These equations are of the Hückel type, and they apply when the ionic strength of the acid solution is adjusted by KCl, NaCl or LiCl. For acetic acid for the solutions of these salts, the equations of the Pitzer type are also given. The K_m value for a certain ionic strength can be calculated from the thermodynamic dissociation constant (K_a) by means of the equations for ionic activity coefficients. Formulas are also given for the conversion of K_m into K_c . The experimental data used in the estimation of the parameters for the activity coefficient equations were taken from the literature. Results of measurements on galvanic cells without a liquid junction (i.e. on cells of the Harned type) were included in these data. Despite the theoretical difficulties associated with the single-ion activity coefficients and the simplicity of the new calculation method based on Hückel equations, this method is very useful. It is shown that K_m can be calculated by this method almost within experimental error at least up to an ionic strength of about 0.1 mol kg^{-1} for the acids considered. The results obtained previously by this method for weak acids in NaCl solutions are summarized in the present study.

In practical studies in electrolyte solutions, e.g. in biochemistry and analytical chemistry, the stoichiometric dissociation constants of weak acids (i.e. the dissociation constants on the concentration scale, K_c) are in common use. They are for example needed when the amount of a weak acid is determined by a potentiometric glass electrode titration and the results of the titration are analyzed by an appropriate linear representation (see for example Ingman and Still¹). Often the ionic strength (I_c) of the weak acid solution titrated is adjusted to be constant by an inert electrolyte, e.g. by KCl. It has been observed that K_c for the weak acid also remains constant during such a titration. It is, in addition, well known that even in very dilute salt solutions (even at a concentration of 0.01 mol dm^{-3}), K_c differs considerably from the thermodynamic dissociation constant (K_a), see for instance tables below. Usually the latter value, therefore, cannot be used in quantitative analysis based on potentiometric titration data. In practice for most cases, K_c must first be experimentally determined from data of a separate titration for these analyses.

In the present study, a simple method (called below the Hückel method) is given for the calculation of K_c at different ionic strengths from K_a for formic, acetic, glycolic and lactic acids in aqueous KCl, NaCl or LiCl solutions at 298.15 K. The Hückel method is based on empirical equations for ionic activity coefficients. These equations originate partially from Debye–Hückel theory. It is shown below that almost the same parameter values apply in these equations to many different ions, and thus the final equations are exceptionally simple.

Here the activity coefficient equations are first determined for the calculation of the molality scale dissociation constants (K_m) from the literature results of appropriate galvanic cells. The cells chosen contain a hydrogen electrode and a silver–silver chloride electrode in the solutions of the weak acid studied. Cells of this kind are called Harned cells. The Harned cell data are used in the parameter estimations instead of data measured on glass electrode cells to avoid the problems associated with the latter (for example with liquid junc-

tion potentials and calibrations). It is shown below that the use of the Harned cell data in these estimations leads to an improvement in the accuracy of K_m values. Equations are then given to convert the K_m values onto the concentration scale. In previous studies, the Hückel method has been used for the determination of K_m for acetic acid² and for formic, propionic and *n*-butyric acids³ in NaCl solutions at 298.15 K. The results of these studies are also considered below.

The empirical equations determined in the present study and in Refs. 2 and 3 are also theoretically important. It is shown below that K_m can be calculated by these equations, despite their simplicity and despite the theoretical problems associated with single-ion activity coefficients, almost within experimental error at least up to ionic strengths of about 0.1 mol kg⁻¹ in the salt solutions considered. Therefore, the K_m values predicted by these equations for the different acids can be reliably used as reference values in the theoretical calculations where the interest is focused on the ionic-strength dependence of K_m , in such as those of, e.g., Vilarino and Sastre de Vicente.⁴

In the thermodynamic treatment of electrolyte solutions, Pitzer formalism (see, e.g. Pitzer⁵) has proved to be useful on many occasions, and therefore this formalism is nowadays widely accepted. This formalism also permits, after ignoring the non-determinable part of a single-ion activity coefficient equation which cancels when the equations are combined to give mean activity coefficients, the calculation of ionic activity coefficients in weak acid solutions. The Pitzer parameters are available for potassium, sodium and lithium acetate (KAcO, NaAcO and LiAcO) but not, as far as the author knows, for the other salts considered in the present study. Mixing parameters for aqueous mixtures of NaAcO–NaCl have been determined by Estes *et al.*⁶ and by Manohar and Ananthaswamy⁷ by using sodium-ion selective glass electrodes. The mixing parameters for the aqueous mixtures of KAcO–KCl and LiAcO–LiCl are missing in the literature as well as the mixing parameters describing the interactions between acetic acid (AcOH) molecules and the other species. Reasonable estimates for the missing mixing parameters are determined here, and the K_m values obtained for acetic acid by the Pitzer method are compared to those of the Hückel method. Both methods are tested below with the Harned cell data taken from the literature.

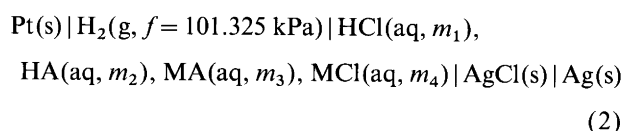
Results

Hückel equation for ionic activity coefficients. Aqueous mixtures of acetic, formic, glycolic or lactic acid (AcOH, ForOH, GlycOH or LacOH, respectively) and KCl, NaCl or LiCl (generally MCl) at 298.15 K are investigated in this study. In these solutions, the following equation is generally used for the activity coefficient (γ) of ion i on the molality scale:

$$\ln \gamma_i = -\alpha z_i^2 (I_m)^{1/2} / [1 + B_i (I_m)^{1/2}] + b_{i,\text{MCl}} I_m / m^\circ \quad (1)$$

where $m^\circ = 1 \text{ mol kg}^{-1}$, z_i is the charge number of ion i , 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.⁸ B_i and $b_{i,\text{MCl}}$ are the parameters that are dependent on ion i , and $b_{i,\text{MCl}}$ is additionally dependent on the salt MCl present in the system. Equation (1) is not very far from the parameter-free equation suggested by Davies⁹ generally for electrolyte solutions. The Davies equation can be obtained from eqn. (1) by setting $B_i = 1.0 \text{ (mol kg}^{-1}\text{)}^{-1/2}$ and $b_{i,\text{MCl}} = 0.2$, and this equation is often used, e.g. in complexometric studies.

Estimation of the Hückel parameters for protons and chloride ions. In a previous study¹⁰ the following parameter values were determined for eqn. (1): $B_{\text{H}} = B_{\text{Cl}} = 1.25 \text{ (mol kg}^{-1}\text{)}^{-1/2}$ and $b_{\text{H,NaCl}} = b_{\text{Cl,NaCl}} = 0.238$ where $\text{H} = \text{H}^+$ and $\text{Cl} = \text{Cl}^-$. In the present study, this B was also used. $b_{\text{H,KCl}}$ (assumed to be equal to $b_{\text{Cl,KCl}}$) and $b_{\text{H,LiCl}} (= b_{\text{Cl,LiCl}})$ were here estimated from the electromotive force (EMF) data measured by Harned and Åkerlöf,¹¹ Harned and Swindells,¹² Harned and Murphy,¹³ Harned and Copson,¹⁴ and Harned and Hamer¹⁵ on cells of the following general type:



where f and m refer to the fugacity and molality, respectively. In the sets of Harned and co-workers,^{11–15} m_2 and m_3 were zero, and some details of these sets are shown in Table 1. In the literature are also available other studies measured on Harned cells in aqueous mixtures of HCl and KCl^{16–19} or of HCl and LiCl^{19–21} at 298.15 K. The results of these data sets were not included in the determination of b for H^+ and Cl^- ions because in these sets only few points were measured in sufficiently dilute solutions with respect to HCl for the present purpose. In this determination, the following results were obtained: $b_{\text{H,KCl}} = b_{\text{Cl,KCl}} = 0.178$ and $b_{\text{H,LiCl}} = b_{\text{Cl,LiCl}} = 0.298$.

The EMF data used in the estimation of b_{H} and b_{Cl} for eqn. (1) were then predicted by using this equation with the estimated parameters, and the results are shown as error plots in Fig. 1. In these plots the EMF errors, defined by

$$e_E = E_{\text{observed}} - E_{\text{predicted}} \quad (3)$$

are presented for the data sets of Harned and Åkerlöf¹¹ as a function of the molality of hydrochloric (m_1), graph A, and for the other data sets as the function of the ionic strength (I_m) of the solutions, graph B. The predicted EMF was calculated by

$$E = E^\circ - (RT/F) \ln [\gamma_{\text{H}} \gamma_{\text{Cl}} m_{\text{H}} m_{\text{Cl}} / (m^\circ)^2] \quad (4)$$

where E° is the standard EMF. E° was adjusted for each set used in this estimation (see discussions below), and the adjusted values are given in Table 1.

Table 1. List of the sets measured on the cell Pt(s) | H₂(g, $f = 101.325$ kPa) | HCl(aq, m_1), HA(aq, m_2), MA(aq, m_3), MCl(aq, m_4) | AgCl(s) | Ag(s) [cell (2)] and used in the tests of activity coefficient equations.

Symbol ^a	N^b	$(m_1/m^\circ)^c$	$(m_2/m^\circ)^c$	m_3/m_1	$(m_4/m^\circ)^c$	$(E^\circ/V)^d$
[HCl/KCl(1) ¹¹] ^e	6	0.001 ... 0.05	0	0	0.1-(m_1/m°)	0.26873
[HCl/KCl(2) ¹¹] ^e	9	0.001 ... 0.1	0	0	1-(m_1/m°)	0.26860
[HCl/LiCl(1) ¹¹] ^e	6	0.001 ... 0.05	0	0	0.1-(m_1/m°)	0.26880
[HCl/LiCl(2) ¹¹] ^e	4	0.001 ... 0.1	0	0	1-(m_1/m°)	0.26803 ^f
[HCl/LiCl(3) ¹¹] ^e	4	0.001 ... 0.1	0	0	3-(m_1/m°)	0.26803 ^f
HCl/LiCl(1) ¹²	11	0.01	0	0	0.008 ... 2.2	0.22280
HCl/LiCl(2) ¹²	6	0.1	0	0	0.07 ... 1	0.22209
HCl/KCl ¹³	7	0.01	0	0	0.05 ... 2	0.22248
HCl/LiCl ¹⁴	23	0.01	0	0	0.01 ... 4	0.22215
HCl/KCl ¹⁵	10	0.01	0	0	0.01 ... 2	0.22230
AcOH/KCl ¹³	7	0	0.2	0	0.05 ... 2	0.22183
AcOH/NaCl ¹³	8	0	0.2	0	0.05 ... 3	0.22250 ^g
AcOH/KCl(1) ²²	6	0	0.1005	0	0.05 ... 2	0.22244
AcOH/KCl(2) ²²	7	0	0.2001	0	0.05 ... 2	0.22177
AcOH/NaCl(1) ²²	12	0	0.1	0	0.02 ... 2.95	0.22250 ^g
AcOH/NaCl(2) ²²	8	0	0.2	0	0.02 ... 3	0.22250 ^g
AcOH/NaCl(3) ²²	10	0	0.519	0	0.02 ... 2.993	0.22250 ^g
AcOH/LiCl ²²	7	0	0.21	0	0.045 ... 2.07	0.22152
AcOH/NaCl(1) ²³	4	0	0.1	0	0.1 ... 0.5	0.22250 ^g
AcOH/NaCl(2) ²³	8	0	0.2	0	0.05 ... 3	0.22250 ^g
AcOH/NaCl(3) ²³	8	0	0.52	0	0.05 ... 3	0.22250 ^g
AcOH/KCl(1) ²⁴	6	0	0.21	0	0.1 ... 2.01	0.22161
AcOH/KCl(2) ²⁴	4	0	0.485	0	0.1 ... 2	0.22075
AcOH/LiCl(1) ²⁴	6	0	0.2	0	0.1 ... 2	0.22154
AcOH/LiCl(2) ²⁴	3	0	0.5	0	0.1 ... 1	0.22080
ForOH/KCl ²⁵	8	0	0.10031	0	0.05 ... 3	0.22221
[LacOH/NaCl(1) ²⁶] ^h	6	0	0.2	0	0.1 ... 2	0.21919
LacOH/NaCl(2) ²⁶	6	0	0.5	0	0.1 ... 2	0.21776
GlycOH/KCl ²⁷	9	0.002 ... 0.034	0	1.92	0	0.22250 ^g
GlycOH/LiCl ²⁷	9	0.002 ... 0.038	0	2.1	0	0.22250 ^g
LacOH/LiCl ²⁸	9	0.002 ... 0.048	0	2	0	0.22250 ^g
AcOH/NaCl ²⁹	6	0	0.005 ... 0.09	0.962 ⁱ	1.024(m_2/m°) ^j	0.22250 ^g
ForOH/KCl ³⁰	6	0	0.007 ... 0.1	1.25 ⁱ	1.079(m_2/m°)	0.22250 ^g

^aThe symbol of the weak acid (or HCl) is followed by the salt used and finally the reference number. ^bNumber of determinations. ^c $m^\circ = 1$ mol kg⁻¹. ^dAdjusted value of the standard EMF for the Hückel method. It was determined by requiring that the sum of all errors in the set considered is zero. ^eA mercury-mercurous chloride electrode was used in cell (2) instead of the silver-silver chloride electrode. ^f E° for the unified sets. ^gNot adjusted, see Harned and Ehlers.²⁹ ^hThe results under the temperature of 12.5 °C were used. It seems to be possible that the columns are not correctly denoted in Table 1 of the original paper.²⁶ ⁱ m_3/m_2 is given instead of m_3/m_1 . ^jFor the second point a value of $m_1 = 0.012328$ mol kg⁻¹ was used instead of the probably erroneous value 0.012426 mol kg⁻¹ given in the original paper.²⁹

Estimation of the Hückel parameters for acetate, formate, glycolate and lactate ions. The thermodynamic dissociation constant (K_a) for a monobasic acid HA is given by

$$K_a = \gamma_H \gamma_A m_H m_A / (\gamma_{HA} m_{HA} m^\circ) = (\gamma_H \gamma_A / \gamma_{HA}) K_m \quad (5)$$

where HA and A refer to AcOH, ForOH, GlycOH or LacOH molecules and acetate (AcO^-), formate (ForO^-), glycolate (GlycO^-) or lactate (LacO^-) ions, respectively. In the Hückel method it is assumed that $\gamma_{HA} = 1$. Assuming that the results are treated by the Hückel method with this assumption, and assuming additionally that $\ln \gamma_{HA}$ is in reality linearly dependent on I_m (the Setchenow equation for the salting-out effect), then the slope of this straight line would appear in the b parameter of A^- . This is not serious because of the empirical nature of the treatment and because of the fact that these two quantities are not separately needed in the calculation of K_m values. Possible dependence of γ_{HA} on the molality of the neutral acid species is considered

below. The stoichiometric dissociation constant K_m in eqn. (5) is defined by

$$K_m = m_H m_A / (m_{HA} m^\circ) \quad (6)$$

Harned and Murphy,¹³ Harned and Robinson²² and Harned and Hickey^{23,24} studied the thermodynamics of aqueous mixtures of AcOH and KCl, NaCl or LiCl on cells of the type (2) where $m_1 = m_3 = 0$. Details of their data sets, as of all other data sets considered in this study, are given in Table 1. Harned and Owen²⁵ used cells of this type in aqueous mixtures of ForOH and KCl or NaCl, and Hickey²⁶ in aqueous mixtures of LacOH and NaCl. Nims²⁷ measured in the GlycOH and KCl or LiCl solutions on cells of type (2), where $m_2 = m_4 = 0$, and Nims and Smith²⁸ on cells of the same type in the LacOH and LiCl solutions. Finally, Harned and Ehlers²⁹ used for the determination of the thermodynamic dissociation constant of AcOH cells of type (2), where $M = \text{Na}^+$ and $m_1 = 0$, and Harned and Embree³⁰ used for the

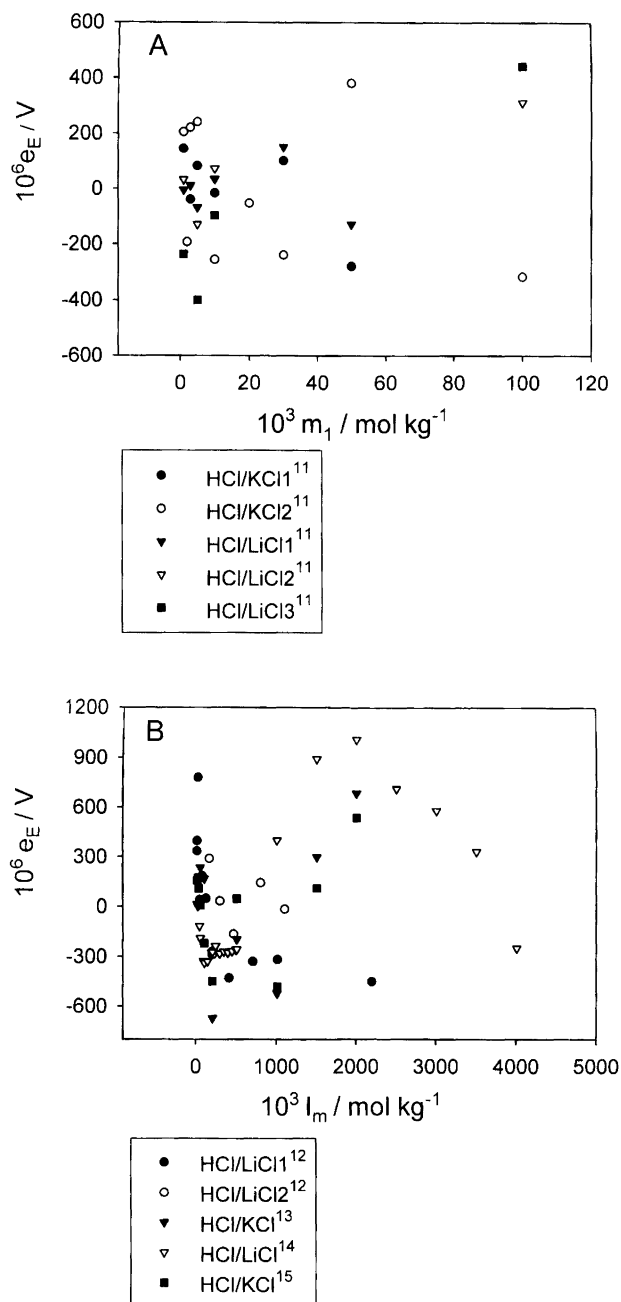


Fig. 1. (A) Difference, e_E in eqn. (3), between the observed EMF values and those predicted by the Hückel method as a function of the molality of HCl (m_1) for the data sets measured by Harned and Åkerlöf¹¹ (see Table 1) on cells of type (2) where $m_2 = m_3 = 0$ [see also footnote (e) in Table 1]. (B) Difference, e_E in eqn. (3), between the observed EMF values and those predicted by the Hückel method as a function of the ionic strength (I_m) for the data sets measured by Harned and Swindells,¹² Harned and Murphy,¹³ Harned and Copson¹⁴ and Harned and Hamer¹⁵ (see Table 1) on cells of type (2) where $m_2 = m_3 = 0$. The symbols of the sets are shown in the legends of the graphs; see also Table 1. The predicted EMF values were calculated by eqn. (4) with the E° values given in Table 1 and with eqn. (1) where the parameter values given in Table 2 were used.

determination of K_a of ForOH cells of the same type, but M in this case was K^+ .

The following parameters were estimated for eqn. (1) from the appropriate data sets shown in Table 1: $b_{\text{AcO},\text{KCl}} = 0.308$, $b_{\text{AcO},\text{LiCl}} = -0.068$, $B_{\text{GlycO}} = 1.4 (\text{mol kg}^{-1})^{-1/2}$ and $B_{\text{LacO}} = 1.3 (\text{mol kg}^{-1})^{-1/2}$. The following parameters were taken from the literature: $B_{\text{ForO}} = 1.4 (\text{mol kg}^{-1})^{-1/2}$ (Ref. 10) and $B_{\text{AcO}} = 1.6 (\text{mol kg}^{-1})^{-1/2}$ (Ref. 2). During the estimation process, it was observed that the same B for a certain ion can be used in KCl, NaCl and LiCl solutions. In addition it was observed, as in the previous NaCl studies,^{2,3} that parameter b for anions AcO^- , ForO^- , GlycO^- and LacO^- does not depend much on the anion but only on MCl. All suggested ion parameters for eqn. (1) are collected in Table 2. The standard deviations (σ) for the estimated parameters are given at the footnotes to the table. They were determined from the data set that was mainly used in the estimation of the parameter in question. The K_a values at 298.15 K are also included in this table for the acids considered. These values were taken from the literature. The parameters determined in Refs. 2 and 3 for NaCl solutions are also included in Table 2.

The new parameters were tested by predicting the data shown in Table 1 by means of the resulting Hückel equations. The results are shown in Figs. 2 and 3. In the error plots of these figures, the EMF errors defined by eqn. (3) are presented as a function of the ionic strength for each data set in Table 1. $E_{\text{predicted}}$ for these figures was calculated by eqns. (4) and (5) with the adjusted E° values given in Table 1 and with the resulting Hückel equations. Successive approximations were needed in these calculations. The results of the AcOH, ForOH and LacOH/NaCl sets are shown in graphs A and B of Fig. 2, and those of the GlycOH sets and of sets LacOH/LiCl²⁸ and ForOH/KCl³⁰ are shown in Fig. 3.

Pitzer equations for ionic activity coefficients. According to the Pitzer formalism, the following simplified equations can be presented at 298.15 K for the activity coefficients of the species in dilute aqueous mixtures of AcOH (=HA), KAcO (=KA) and KCl [see, e.g. Refs. 37–39; the present Pitzer treatment is more comprehensive than that considered in Ref. 3]:

$$\ln \gamma_{\text{H}} = f^\gamma + 2B_{\text{HCl}}m_{\text{Cl}} + 2\Theta_{\text{H,K}}m_{\text{K}}/(m^\circ) + 2\lambda_{\text{H,HA}}m_{\text{HA}}/(m^\circ) + f'(B) \quad (7)$$

$$\ln \gamma_{\text{Cl}} = f^\gamma + 2B_{\text{HCl}}m_{\text{H}} + 2B_{\text{KCl}}m_{\text{K}} + 2\Theta_{\text{Cl,A}}m_{\text{A}}/(m^\circ) + 2\lambda_{\text{Cl,HA}}m_{\text{HA}}/(m^\circ) + f'(B) \quad (8)$$

$$\ln \gamma_{\text{A}} = f^\gamma + 2B_{\text{KA}}m_{\text{K}} + 2\Theta_{\text{Cl,A}}m_{\text{Cl}}/(m^\circ) + 2\lambda_{\text{HA,A}}m_{\text{HA}}/(m^\circ) + f'(B) \quad (9)$$

$$\ln \gamma_{\text{HA}} = 2\lambda_{\text{H,HA}}m_{\text{H}}/(m^\circ) + 2\lambda_{\text{K,HA}}m_{\text{K}}/(m^\circ) + 2\lambda_{\text{Cl,HA}}m_{\text{Cl}}/(m^\circ) + 2\lambda_{\text{HA,HA}}m_{\text{HA}}/(m^\circ) + 2\lambda_{\text{A,HA}}m_{\text{A}}/(m^\circ) \quad (10)$$

Table 2. Ion parameters for the Hückel equation [eqn. (1)] in salt solutions at 298.15 K.

Ion	$B/(\text{mol kg}^{-1})^{-1/2}$	b_{KCl}	b_{LiCl}	b_{NaCl}	$(10^5 K_a)^a$
H ⁺	1.25 ^b	0.178 ^c	0.298 ^d	0.238 ^e	
Cl ⁻	1.25 ^b	0.178 ^c	0.298 ^d	0.238 ^e	
CH ₃ COO ⁻	1.6 ^f	0.308 ^g	-0.068 ^h	0.189 ⁱ	1.76 ^j
HCOO ⁻	1.4 ^k	0.308		0.189	17.8 ^l
CH ₂ OHCOO ⁻	1.4 ^m	0.308	-0.068		14.8 ⁿ
CH ₃ CHOHCOO ⁻	1.3 ^o		-0.068	0.189	13.7 ^p
CH ₃ CH ₂ COO ⁻	1.7 ^r			0.189	1.35 ^s
CH ₃ CH ₂ CH ₂ COO ⁻	2.0 ^t			0.189 ^e	1.52 ^s

^aThe thermodynamic dissociation constant for the corresponding acid. ^bDetermined in Ref. 10. ^c $\sigma=0.003$ (determined from set HCl/KCl¹⁵). ^d $\sigma=0.002$ (determined from set HCl/LiCl¹⁴). ^eDetermined in Ref. 10; $\sigma=0.001$ (determined from set HCl/NaCl¹³). ^fDetermined in Ref. 2. ^g $\sigma=0.004$ [determined from set AcOH/KCl(2)²²]. ^h $\sigma=0.007$ [determined from set AcOH/LiCl(1)²⁴]. ⁱDetermined in Ref. 2; $\sigma=0.005$ (determined from set AcOH/NaCl¹³). ^jDetermined by MacInnes and Shedlovsky³¹ from conductivity data and by Harned and Ehlers²⁹ from EMF data. ^kDetermined in Ref. 10; $\sigma=0.04$ (mol kg⁻¹)^{-1/2} (determined from set ForOH/KCl²⁵). ^lDetermined by Harned and Embree³⁰ from EMF data; the conductivity data of Saxton and Darken,³² however, lead to a value of 18.4×10^{-5} , see Ref. 3. ^m $\sigma=0.02$ (mol kg⁻¹)^{-1/2} [determined from set GlycOH/KCl²⁷ ($I_m > 0.015$ mol kg⁻¹)]. ⁿDetermined by Nims²⁷ from EMF data. ^o $\sigma=0.04$ (mol kg⁻¹)^{-1/2} [determined from set LacOH/LiCl²⁸ ($I_m > 0.015$ mol kg⁻¹)]. ^pDetermined by Nims and Smith²⁸ from EMF data; Martin and Tartar³³ gave a value of 13.9×10^{-5} based on their conductivity data. ^r $\sigma=0.03$ (mol kg⁻¹)^{-1/2} [determined from EMF data of Harned and Ehlers³⁴ ($I_m > 0.015$ mol kg⁻¹)]. ^sDetermined in Ref. 3 from the conductivity data of Belcher.³⁵ ^t $\sigma=0.07$ (mol kg⁻¹)^{-1/2} [determined from the EMF data of Harned and Sutherland³⁶ ($I_m > 0.015$ mol kg⁻¹)].

where

$$f'(B) = m_{\text{H}}m_{\text{Cl}}B'_{\text{HCl}} + m_{\text{K}}m_{\text{Cl}}B'_{\text{KCl}} + m_{\text{K}}m_{\text{A}}B'_{\text{KA}} \quad (11)$$

The following symbols have been used in eqns. (7)–(11):

$$f^\gamma = -\alpha_{\text{P}} \left\{ (I_m)^{1/2} / [1 + 1.2(I_m/m^\circ)^{1/2}] + [2(m^\circ)^{1/2}/1.2] \ln[1 + 1.2(I_m/m^\circ)^{1/2}] \right\} \quad (12)$$

$$B_{\text{MX}} = \beta_{\text{MX}}^\circ / (m^\circ) + \beta_{\text{MX}}^1 f_2 \quad (13)$$

$$B'_{\text{MX}} = \beta_{\text{MX}}^1 f_3 \quad (14)$$

$$f_2 = [1/(2I_m)] \times \{ 1 - [1 + 2(I_m/m^\circ)^{1/2}] \exp[-2(I_m/m^\circ)^{1/2}] \} \quad (15)$$

$$f_3 = [1/(2I_m^2)] \{ -1 + [1 + 2(I_m/m^\circ)^{1/2} + 2(I_m/m^\circ)] \times \exp[-2(I_m/m^\circ)^{1/2}] \} \quad (16)$$

where $\alpha_{\text{P}} = \alpha/3 = 0.3915$ (mol kg⁻¹)^{-1/2} and M refers to a cation and X to an anion. These Pitzer equations also apply to the aqueous mixtures of AcOH, NaAcO or LiAcO and NaCl or LiCl. In these cases, K⁺ must be simply replaced by Na⁺ or Li⁺.

In the Pitzer calculations, the parameter values given in Table 3 were used. The β parameters in this table were determined by Pitzer and Mayorga⁴⁰ and the Θ parameters by Pitzer and Kim.⁴¹ The $\Theta_{\text{Cl,A}}$ values suggested by Estes *et al.*⁶ ($\Theta_{\text{Cl,A}} \sim -0.009$) and by Manohar and Ananthaswamy⁷ (-0.005) are small, and therefore this parameter is assumed here to be zero. The following new Pitzer parameters were determined in this study from the EMF results of sets AcOH/NaCl,²⁹ AcOH/NaCl,¹³ AcOH/NaCl(1–3)²² and AcOH/NaCl(1–3)²³ in Table 1: $\lambda_{\text{H,HA}} = 0.08$, $\lambda_{\text{Na,HA}} = 0.087$, $\lambda_{\text{Cl,HA}} = 0$, $\lambda_{\text{A,HA}} = -0.09$ and $\lambda_{\text{HA,HA}} = -0.06$. Additionally, a value of $\lambda_{\text{K,HA}} = 0.044$ was determined from set AcOH/KCl(2)²² and a value of $\lambda_{\text{Li,HA}} = 0.129$ from set AcOH/LiCl(1).²⁴ These new parameter values are also presented in Table 3.

The Pitzer method was tested by predicting the acetic acid data shown in Table 1 by the means of the new activity coefficient equations. The results are shown in graphs A–D of Fig. 4. In the error plots of this figure, the EMF errors defined by eqn. (3) are presented as a function of the ionic strength of the solution. In graphs C and D, the error plots [obtained from sets AcOH/NaCl,²⁹ AcOH/NaCl¹³ and AcOH/KCl(2)²² (Table 1)] are shown for the following two cases, too: (1) Only the Debye–Hückel term in eqns. (7)–(10) is included in the calculations (i.e. all β , Θ and λ values are assumed to be zero). (2) Only the literature values for the parameters are used (i.e. all λ values are assumed to be zero). These error plots emphasize the significance of the specific interaction terms where neutral molecules have been taken into account. These terms are necessary to obtain good results by the Pitzer method.

Discussion

According to Fig. 1, the experimental data of Harned and co-workers support well the new b parameters for eqn. (1) for H⁺ and Cl⁻ ions. These values seem to apply satisfactorily up to ionic strengths of about 2 mol kg⁻¹. The adjusted E° values in Table 1 for the HCl sets agree at least satisfactorily with the value of $E^\circ = 0.22234$ V suggested by Bates and Bower⁴² for the standard potential of the silver–silver chloride electrode at 298.15 K (or with the value of 0.22250 V suggested by Harned and Ehlers²⁹ for this quantity) especially when the uncertainty associated with this quantity is taken into account; see Bates and Macaskill.⁴³ The data sets of Harned and Åkerlöf¹¹ were measured by using cells of type (2), where the Cl⁻|AgCl|Ag electrode had been replaced by a Cl⁻|Hg₂Cl₂|Hg electrode. The E° values for these sets agree satisfactorily with the value of

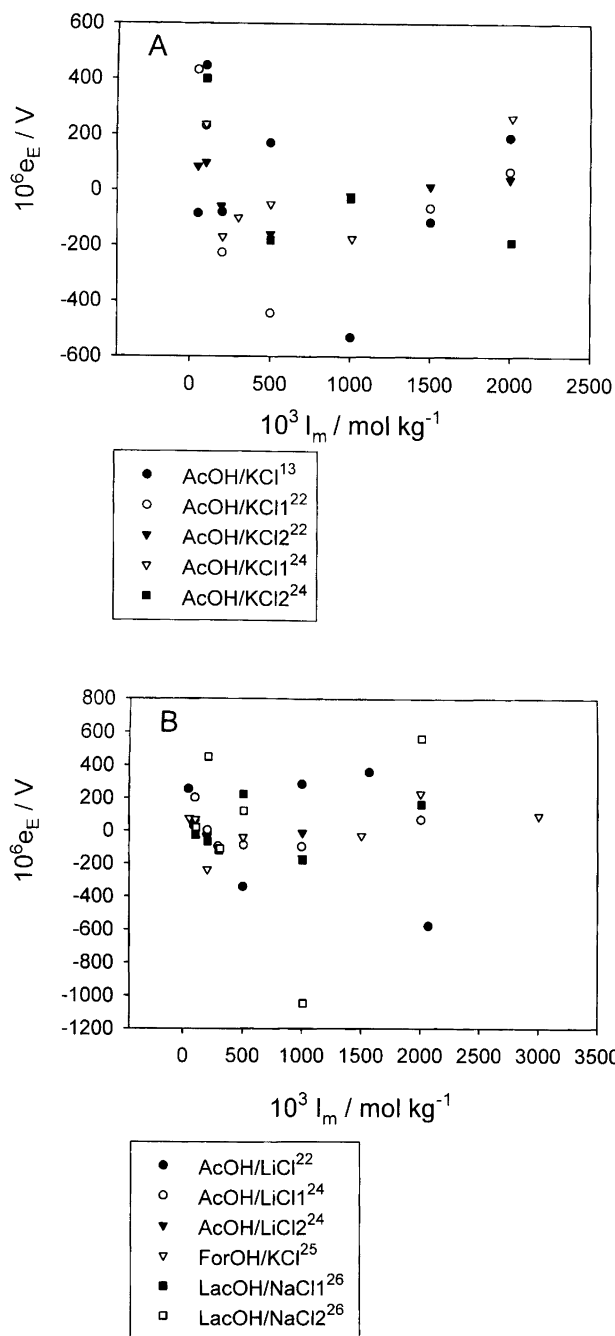


Fig. 2. Difference, e_E in eqn. (3), between the observed EMF values and those predicted by the Hückel method as a function of the ionic strength (I_m) for the acetic, formic and lactic acid data sets measured by Harned and Murphy¹³ (AcOH in KCl solutions), Harned and Robinson²² (AcOH in KCl or LiCl solutions), Harned and Hickey²⁴ (AcOH in KCl or LiCl solutions), Harned and Owen²⁵ (ForOH in KCl solutions) and Hickey²⁶ (LacOH in NaCl solutions) (see Table 1) on cells of type (2) where $m_1 = m_3 = 0$. Graph A shows the AcOH results for KCl solutions, and graph B shows the AcOH results for LiCl solutions and the ForOH and LacOH results. The symbols of the sets are shown in the legends of the graphs (see Table 1). The predicted EMF values were calculated by the Hückel method with the adjusted E° values given in Table 1.

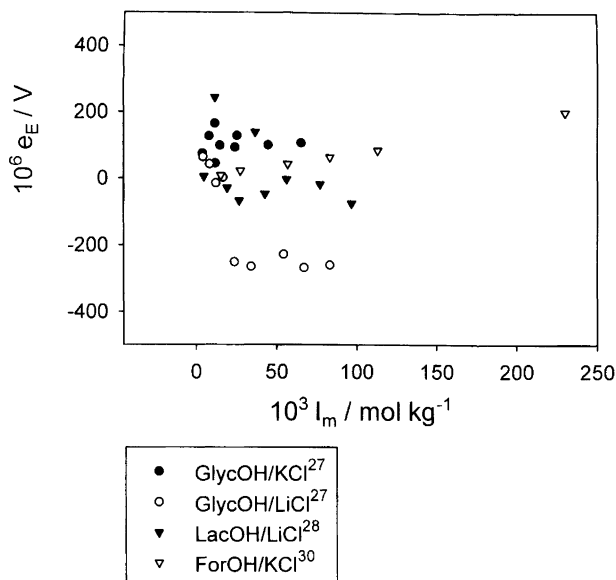


Fig. 3. Difference, e_E in eqn. (3), between the observed EMF values and those predicted by the Hückel method as a function of the ionic strength (I_m) for the formic, glycolic and lactic acid data sets measured by Harned and Embree,³⁰ Nims²⁷ and Nims and Smith²⁸ (see Table 1) on cells of type (2) where $m_2 = m_4 = 0$ [data set ForOH/KCl³⁰ was measured on cell (2), where only $m_1 = 0$]. The symbols of the sets are shown in the legend of the figure; see also Table 1. The predicted EMF values were calculated by the Hückel method with $E^\circ = 0.22250$ V.

Table 3. Interaction parameters for the Pitzer equations [eqns. (7)–(10)] at 298.15 K.

	β^0	β^1	Θ	λ
H ⁺ ,Cl ⁻	0.1775	0.2945		
K ⁺ ,Cl ⁻	0.04835	0.2122		
K ⁺ ,AcO ⁻	0.1587	0.3251		
Li ⁺ ,Cl ⁻	0.1494	0.3074		
Li ⁺ ,AcO ⁻	0.1124	0.2483		
Na ⁺ ,Cl ⁻	0.0765	0.2664		
Na ⁺ ,AcO ⁻	0.1426	0.3237		
H ⁺ ,K ⁺			0.005	
H ⁺ ,Li ⁺			0.015	
H ⁺ ,Na ⁺			0.036	
Cl ⁻ ,AcO ⁻			0	
H ⁺ ,AcOH				0.08
K ⁺ ,AcOH				0.044
Li ⁺ ,AcOH				0.129
Na ⁺ ,AcOH				0.087
Cl ⁻ ,AcOH				0
AcO ⁻ ,AcOH				-0.09
AcOH,AcOH				-0.06

0.26816 V suggested by Gupta *et al.*⁴⁴ for E° of cells of this kind.

According to Fig. 2, the EMF data of sets AcOH/KCl(1)²² and ForOH/KCl²⁵ (Table 1) can be predicted almost within experimental error by the Hückel method. For the data sets where m_2 (the analytical molality of weak acid) is about 0.2 mol kg⁻¹, a constant systematic error of the order of -0.8 mV is observed in

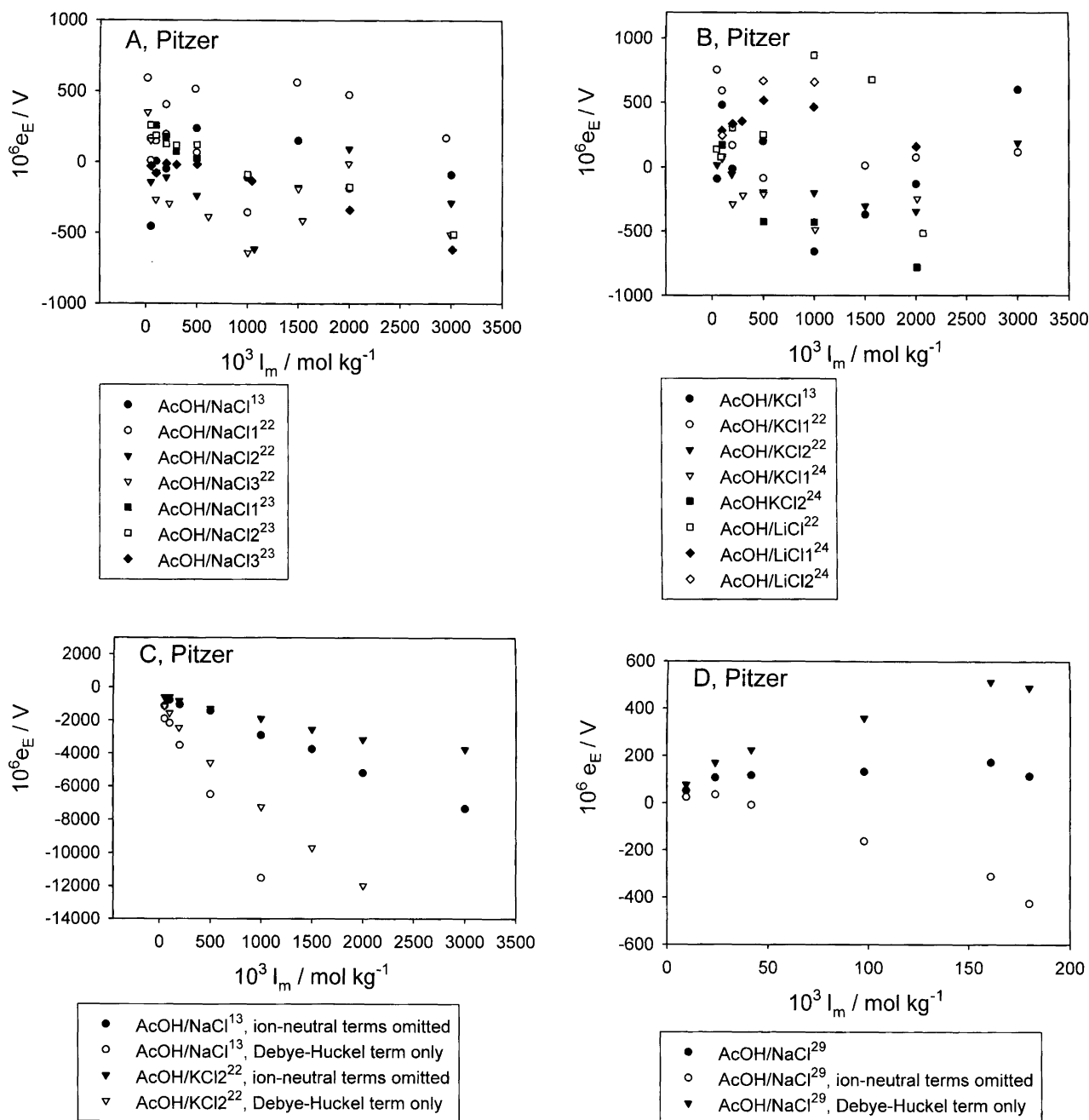


Fig. 4. Difference, e_E in eqn. (3), between the observed EMF values and those predicted by the Pitzer method as a function of the ionic strength (I_m) for the acetic acid data sets measured by Harned and Murphy,¹³ Harned and Robinson,²² Harned and Hickey^{23,24} and Harned and Ehlers²⁹ (see Table 1) on cells of type (2) where $m_1 = m_3 = 0$ [data set AcOH/NaCl²⁹ was measured on cell (2) where only $m_1 = 0$]. The predicted EMF values were calculated by the Pitzer method with $E^\circ = 0.22250$ V. Graph A shows the results obtained for the NaCl sets and graph B those obtained for the KCl and LiCl sets. Graph D shows the results for set AcOH/NaCl²⁹ and graphs C and D show the results obtained by means of the truncated Pitzer methods, see text and legends. The symbols of the sets are shown in the legends of the graphs; see also Table 1.

the error plots. These errors appear in the adjusted E° values shown in Table 1. This error increases with m_2 , as the results for the data sets where m_2 is about 0.5 mol kg^{-1} show. The same trend was previously observed in the results obtained from aqueous mixtures of acetic acid² or formic acid³ and NaCl. A possible explanation for this behaviour is the gradual departure

of the activity coefficients of HA from the assumed value $\gamma_{\text{HA}} = 1$ in these more concentrated acid solutions, i.e. γ_{HA} seems to be dependent on the molality of the neutral acid molecules. Also other medium effects can have an influence on this behaviour. If the constant systematic error is eliminated (as done in Fig. 2), according to this figure and according to Fig. 2 in Ref. 2 and Fig. 2B in

Ref. 3, the Hückel equations seem to apply to acetic acid solutions (where the salt is NaCl, KCl or LiCl), to formic acid solutions (NaCl or KCl) and to lactic acid solutions (NaCl) up to $I_m \approx 2.0 \text{ mol kg}^{-1}$. [However, a large constant systematic error appears to be in both sets LacOH/NaCl(1,2),²⁶ and in set LacOH/NaCl(1)²⁶ there is also another problem; see footnote (h) in Table 1.]

According to Fig. 3 in this study, the EMF data from the ForOH/ForO⁻, GlycOH/GlycO⁻ and LacOH/LacO⁻ data sets in Table 1 can be accurately predicted by the Hückel method. Unfortunately, these data extend in the best case only up to an ionic strength of about 0.2 mol kg^{-1} . In the set GlycOH/LiCl,²⁷ however, there seems to be a constant systematic error of about -0.27 mV in the five strongest points.

According to Fig. 4, the suggested Pitzer method is supported by the experimental data and, as mentioned above, the truncated versions of the Pitzer model do not accurately predict the data (see graphs C and D).

It is impossible to determine by thermodynamic means the activity coefficients for single ions. To obtain K_m values for weak acids by equations similar to that of eqn. (5), these activity coefficients are unavoidably needed. However, K_m is experimentally obtainable under certain circumstances, as under those considered most often in this study, as the following treatment reveals. The activity coefficients of HCl in KCl and LiCl solutions can be quite well predicted in dilute HCl solutions up to salt molalities of about 2 mol kg^{-1} by the equations suggested in this study for γ_H and γ_{Cl} . These equations are probably also valid in salt solutions that contain a small amount of some of the weak acids considered. For the solutions of cells of type (2), the following equation can be derived from eqns. (4) and (6):

$$E = E^\circ - (RT/F) \ln(\gamma_H \gamma_{Cl}) - (RT/F) \times \ln[(m_1 + m_4)/m^\circ] - (RT/F) \times \ln \{ [1/(2m^\circ)] \{ [K_m m^\circ + m_3 - m_1]^2 + 4K_m m^\circ (m_1 + m_2)^{1/2} - (K_m m^\circ + m_3 - m_1) \} \} \quad (17)$$

This equation shows that K_m is experimentally obtainable if the activity coefficients for H⁺ and Cl⁻ ions are known. Therefore, the K_m values predicted by the Hückel method are supported almost within the precision of the measurements by the experimental K_m values (Figs. 2 and 3). Another possibility to show this result is the following: from a certain E_{observed} value, $pK_{m,\text{observed}}$ [$pK_m = -\log(K_m)$] is calculated by eqn. (17), and then this value is compared in the error plot to the pK_m value predicted by the Hückel method. For a few data sets in Table 1 such an error plot is shown in Fig. 5. In these plots the pK_m error, defined by

$$e(pK_m) = pK_m(\text{observed}) - pK_m(\text{predicted}) \quad (18)$$

is presented as a function of the ionic strength. This figure illustrates the quality of the present Hückel models. The largest pK_m error in this figure is less than 0.008. This value can be compared to the conventional pK_m

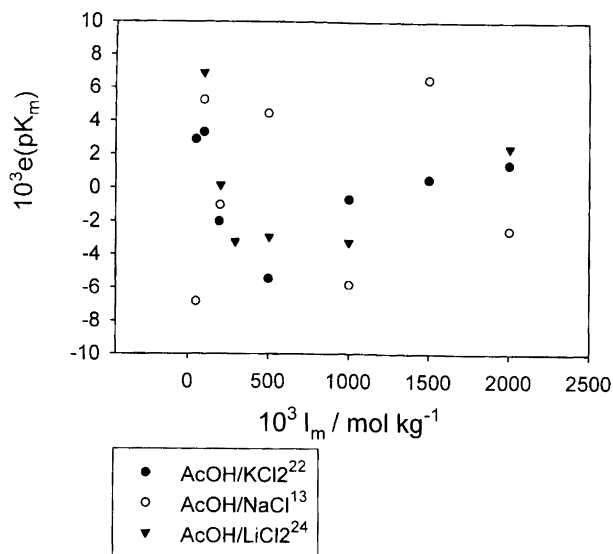


Fig. 5. Difference, $e(pK_m)$ in eqn. (18), between the observed pK_m values and those obtained by the Hückel method as a function of the ionic strength (I_m) for the acetic acid data sets measured by Harned and Murphy,¹³ Harned and Robinson²² and Harned and Hickey²⁴ (see Table 1) on cells of type (2) where $m_1 = m_3 = 0$. The symbols of the sets are shown in the legend of the figure; see Table 1. In the calculation of the observed pK_m values by eqn. (17), the E° values given in Table 1 were used (for set AcOH/NaCl¹³ a value of 0.22150 V was used).

error of 0.06 suggested by Albert and Serjeant in their well known monograph.⁴⁵ Additionally, on the basis of eqn. (17) it is possible to show that, for example, an absolute error of 0.3 mV in the EMF of a Harned cell of any type considered here leads only to an absolute error of less than 0.01 in the pK_m value. It is very difficult to obtain such a precision by means of potentiometric titrations performed in a glass electrode cell.

As mentioned above, the Hückel method seems to apply to acetic and formic acid solutions up to $I_m \approx 2 \text{ mol kg}^{-1}$. To glycolic, lactic, propionic and *n*-butyric acid solutions it seems to apply at least up to $I_m = 0.1 \text{ mol kg}^{-1}$ (see Fig. 3 in this study and Fig. 2A in Ref. 3). In the former case for KCl and LiCl solutions, the applicability limit is probably not, however, as high as 2.0 mol kg^{-1} , because the activity coefficients of HCl in the solutions of these salts cannot be predicted very accurately by the Hückel method between the ionic strengths 1 and 2 mol kg^{-1} (see Fig. 1 in this study).

K_m can be calculated at any ionic strength below about 1 mol kg^{-1} for acetic acid in KCl, NaCl or LiCl solutions, for formic acid in NaCl or KCl solutions and for lactic acid in NaCl solutions by eqn. (5) from the K_a value given in Table 2 by means of eqn. (1) with the parameter values also given in this table. The same is also true below an ionic strength of 0.1 mol kg^{-1} for glycolic acid in KCl and LiCl solutions, for lactic acid in LiCl solutions, and for propionic and *n*-butyric acids in NaCl solutions. K_m calculated in this way for AcOH in KCl solutions is shown at rounded ionic strengths in Table 4.

Table 4. Stoichiometric dissociation constant (K_m) of acetic acid at 298.15 K as a function of the ionic strength (I_m) in aqueous KCl solutions.

$I_m/(\text{mol kg}^{-1})^a$	$10^5 K_m(\text{Hückel})^b$	$10^5 K_m(\text{Pitzer})^c$	$10^5 K_c^d$
0	1.758	1.758	1.753
0.01	2.15	2.15	2.14
0.02	2.30	2.30	2.29
0.03	2.40	2.40	2.39
0.04	2.49	2.49	2.48
0.05	2.56	2.56	2.54
0.07	2.67	2.67	2.66
0.10	2.80	2.79	2.78
0.2	3.03	3.03	3.01
0.3	3.14	3.12	3.10
0.5	3.16	3.15	3.11
1	2.86	2.87	2.77

^a I_m is the same as m_{KCl} . ^bCalculated by the Hückel method. ^cCalculated by the Pitzer method. ^dDissociation constant on the concentration scale; calculated by means of eqns. (19) and (20).

For AcOH in NaCl and LiCl solutions, it is shown in Table 5. For ForOH in KCl and NaCl solutions and for LacOH in NaCl and LiCl solutions it is presented in Table 6. For glycolic acid in KCl and LiCl solutions and

for propionic and *n*-butyric acids in NaCl solutions, K_m is shown at rounded ionic strengths in Table 7.

The K_m values calculated by the Pitzer method for AcOH in KCl, NaCl or LiCl solutions are shown in Tables 4 and 5. These values agree well with those of the Hückel method up to $I_m=1.0 \text{ mol kg}^{-1}$ for KCl and NaCl solutions, but for LiCl solutions the agreement is limited only to $I_m \approx 0.1 \text{ mol kg}^{-1}$. It seems to the author that the K_m values obtained by the Hückel method for LiCl solutions above the limit of $I_m=0.1 \text{ mol kg}^{-1}$ are slightly more reliable than those of the Pitzer method.

The dissociation constants on the concentration scale (K_c) at 298.15 K can be calculated from the K_m values by the following way in the case where the inert electrolyte alone fixes the ionic strength of the solution considered. The concentration of the salt s is given as c_s . The molality of the salt (m_s) can be solved from

$$r = c_s m^\circ / (m_s c^\circ) = 0.9970 - A(m_s/m^\circ) + B(m_s/m^\circ)^2 \quad (19)$$

where $c^\circ=1 \text{ mol dm}^{-3}$ and where r is defined as a dimensionless ratio of the concentration to the molality. This equation was presented by Harned and Owen,⁴⁶ and they also gave the following parameter values for it: $A_{\text{KCl}}=0.0284$, $B_{\text{KCl}}=0.0003$, $A_{\text{LiCl}}=0.0182$, $B_{\text{LiCl}}=0$,

Table 5. Stoichiometric dissociation constant (K_m) of acetic acid at 298.15 K as a function of the ionic strength (I_m) in aqueous LiCl and NaCl solutions.

$I_m/(\text{mol kg}^{-1})^a$	$10^5 K_{m,\text{LiCl}}(\text{H})^b$	$10^5 K_{m,\text{LiCl}}(\text{P})^c$	$10^5 K_{m,\text{NaCl}}(\text{H})^b$	$10^5 K_{m,\text{NaCl}}(\text{P})^c$
0	1.76	1.76	1.76	1.76
0.01	2.15	2.16	2.15	2.15
0.02	2.31	2.31	2.30	2.30
0.03	2.42	2.43	2.41	2.41
0.04	2.51	2.52	2.49	2.49
0.05	2.59	2.61	2.56	2.57
0.07	2.72	2.74	2.68	2.68
0.10	2.87	2.90	2.81	2.81
0.2	3.19	3.25	3.07	3.07
0.3	3.39	3.47	3.19	3.20
0.5	3.60	3.73	3.26	3.27
1			3.04	3.09

^a I_m is the same as m_{LiCl} or m_{NaCl} . ^bCalculated by the Hückel method. ^cCalculated by the Pitzer method.

Table 6. Stoichiometric dissociation constant (K_m) at 298.15 K for formic acid (ForOH) and lactic acid (LacOH) as a function of the ionic strength (I_m) in aqueous KCl, LiCl and NaCl solutions.

$I_m/(\text{mol kg}^{-1})^a$	$10^4 K_{m,\text{KCl}}(\text{ForOH})$	$10^4 K_{m,\text{NaCl}}(\text{ForOH})$	$10^4 K_{m,\text{LiCl}}(\text{LacOH})$	$10^4 K_{m,\text{NaCl}}(\text{LacOH})$
0	1.78	1.78	1.37	1.37
0.01	2.18	2.18	1.68	1.68
0.02	2.33	2.33	1.81	1.80
0.03	2.44	2.45	1.90	1.89
0.04	2.53	2.54	1.97	1.96
0.05	2.61	2.61	2.04	2.02
0.07	2.73	2.74	2.15	2.12
0.10	2.86	2.88	2.27	2.23
0.2	3.12	3.16		2.46
0.3	3.24	3.30		2.57
0.5	3.29	3.39		2.65
1	3.01	3.19		2.51

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

Table 7. Stoichiometric dissociation constant (K_m) at 298.15 K for glycolic acid (GlycOH), propionic acid (PropOH) and *n*-butyric acid (ButOH) as a function of the ionic strength (I_m) in aqueous KCl, LiCl and NaCl solutions.

$I_m/(\text{mol kg}^{-1})^a$	$10^4 K_{m,\text{KCl}}(\text{GlycOH})$	$10^4 K_{m,\text{LiCl}}(\text{GlycOH})$	$10^5 K_{m,\text{NaCl}}(\text{PropOH})$	$10^5 K_{m,\text{NaCl}}(\text{ButOH})$
0	1.48	1.48	1.35	1.52
0.01	1.81	1.82	1.65	1.85
0.02	1.94	1.95	1.76	1.98
0.03	2.03	2.05	1.84	2.06
0.04	2.10	2.13	1.91	2.13
0.05	2.17	2.19	1.96	2.19
0.07	2.27	2.31	2.05	2.28
0.1	2.38	2.44	2.15	2.39

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

$A_{\text{NaCl}}=0.0183$ and $B_{\text{NaCl}}=0$. For the m_s value obtained, K_m is obtained as described above. K_c for the acid at this concentration c_s can then be calculated by

$$K_c = c_{\text{H}}c_{\text{A}}/(c^{\circ}c_{\text{HA}}) = K_m r \quad (20)$$

where r is given in eqn. (19). This equation, together with eqn. (19), shows that below an ionic strength of about 0.1 mol kg^{-1} , the difference between K_m and K_c is not very significant. K_c at rounded molal ionic strengths for AcOH in KCl solutions is shown in Table 4.

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