

Determination of the Molality Scale Dissociation Constants of Formic, Propionic and *n*-Butyric Acids in Aqueous Sodium Chloride Solutions at 298.15 K

Jaakko Ilmari Partanen

Department of Chemical Technology, Lappeenranta University of Technology, PO Box 20, FIN-53851 Lappeenranta, Finland

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Equations were presented for the calculation of the molality scale dissociation constants (i.e. the K_m values) of formic, propionic and *n*-butyric acids in aqueous solutions at 298.15 K. These equations apply when the ionic strength of the acid solutions has been adjusted by NaCl. The K_m value for a certain ionic strength can be calculated from the thermodynamic dissociation constant by means of formulas for ionic activity coefficients. The ionic activity coefficient formulas used in this study originate from the Debye–Hückel theory. The data used in the parameter estimation and in the tests were taken from the literature. In these data were included results of measurements on conductivity cells and on galvanic cells of the Harned type. Despite the simplicity of the calculation method used, it seems probable that the K_m values obtained by this method are known up to 0.1 molal solutions almost as accurately as the thermodynamical K_a values. For formic acid solutions it is shown that the calculation method applies up to salt molalities of about 2.0 mol kg⁻¹. The results of the present method were also compared to those obtained by the other methods suggested for the thermodynamical treatment of solutions of these weak acids.

Accurate extrapolation methods for the determination of the thermodynamic dissociation constant (K_a) of a weak acid from electromotive force (EMF) measurements (see, e.g., Harned and Ehlers¹) and conductivity measurements (see, e.g., Shedlovsky and MacInnes²) were developed more than 60 years ago. For analytical purposes the K_a values of weak acids apply only seldom because the activity coefficients for the ions resulting from the acids are usually not known, and they are inevitably needed in the calculation of concentrations from the K_a values. The stoichiometric dissociation constants (the K_m or K_c values where *m* or *c* refers to the molality or concentration, respectively) are expressed by means of the composition variables, and hence the activity coefficients are included in these constants. In the usual analytical practice, K_m or K_c values are experimentally determined for the solutions considered.

In a previous paper³ it was shown that the molality scale dissociation constants (i.e. the K_m values) for acetic acid in NaCl solutions at 298.15 K can be calculated within experimental error at least up to ionic strengths of about 0.5 mol kg⁻¹ by using a simple equation for ionic activity coefficients. In that paper, K_a for this acid was determined from conductivity results² and the activ-

ity parameters for the ionic activity coefficient equation from EMF data¹ (see also Refs. 4 and 5).

It is interesting to see how well the method presented for acetic acid in NaCl solutions³ applies to other light fatty acids in these solutions. In the present study, the calculation method is tested with the results obtained from solutions of formic, propionic and *n*-butyric acids at 298.15 K. For these tests, there is available in the literature a sufficient number of sets containing precise experimental data. In these tests, only the data measured by galvanic cells without a liquid junction were used. There are available in the literature also a few studies where the dissociation constants of these acids have been determined by measurements on cells with a liquid junction (see, e.g., De Robertis *et al.*⁶). These studies have been usually measured by glass electrodes. Because of the calibration problems and the difficulties associated with the liquid junction potentials in measurements of this kind, it was preferred here experimental data obtained on the cells that are free from such problems. Therefore, only the results of measurements on cells without a liquid junction were used in the present tests. In these tests, it was observed that the activity coefficient equations used in the acetic acid study³ apply to formic,

propionic and *n*-butyric acid solutions with only slight modifications.

In the thermodynamical treatment of electrolyte solutions, Pitzer's formalism (see, e.g., Ref. 7) has nowadays been widely used. Pitzer's method has been applied, for example, to the thermodynamics of solutions of the following weak or moderately weak acids: phosphoric acid ($K_{a,1}$, Pitzer and Silvester;⁸ and $K_{a,2}$, Covington and Ferra⁹), sulfuric acid (Pitzer *et al.*,¹⁰ Clegg *et al.*¹¹ and Clegg and Brimblecombe¹²), carbonic acid (Peiper and Pitzer¹³), glycine (Fiol *et al.*¹⁴) and *o*-phthalic acid ($K_{a,2}$, Chan *et al.*¹⁵). In addition, Pitzer parameters for sodium formate and sodium propionate have been presented by Pitzer and Mayorga,¹⁶ and for sodium propionate by Jackson and Seymour.¹⁷

Pitzer's formalism also permits one, after some additional assumptions, to calculate the activity coefficients for the species existing in weak acid solutions and, therefore, also the K_m values for the weak acid under consideration. In the present study, the results of the new activity coefficient equations were compared to those obtained by the methods based on the Pitzer equations. Under certain circumstances the ionic activity coefficients can also be determined in aqueous mixtures of electrolytes by a method of Guggenheim (see, e.g., Guggenheim and Turgeon¹⁸). The methods derived from the Guggenheim equation are also included in the comparisons of this communication.

Results

Theoretical considerations. The dissociation equilibrium for formic, propionic or *n*-butyric acid (HA) can be presented by the following reaction:



where A^- represents formate, propionate or *n*-butyrate ions, respectively. The thermodynamic dissociation constant (K_a) for this equilibrium is given by

$$K_a = \gamma_H \gamma_A m_H m_A / (m^0 m_{HA}) = \gamma_H \gamma_A K_m \quad (2)$$

where γ refers to the molality scale activity coefficients, and where $H = H^+$, $A = A^-$ and $m^0 = 1 \text{ mol kg}^{-1}$. It is assumed in eqn. (2), as usual, that the activity coefficients of the neutral species are unity, and the molality scale dissociation constant K_m is defined by

$$K_m = m_H m_A / (m_{HA} m^0) \quad (3)$$

Methods for the calculation of activity coefficients.

A. The Hückel method. In the previous study³ the following equation was used for the molal activity coefficient of a univalent ion i , and this equation is also used here and will be called the Hückel equation:

$$\ln \gamma_i = -\alpha(I_m)^{1/2} / [1 + B_i(I_m)^{1/2}] + b_i I_m / m^0 \quad (4)$$

where $\alpha = 1.17444(m^0)^{-1/2}$, see Archer and Wang.¹⁹ B_i and b_i are parameters that are dependent in the cases considered here only on ion i . As the composition variable in this equation is the molal ionic strength (I_m). Previously,⁴ the following parameter values for eqn. (4) were suggested: $B_H = B_{Cl} = 1.25(m^0)^{-1/2}$ and $b_H = b_{Cl} = 0.238$ where $Cl = Cl^-$, and these values are also used now as in the acetic acid study.³ In the latter study, in addition, the following parameter values were determined for acetate ions: $B = 1.6(m^0)^{-1/2}$ and $b = 0.189$.

In this study, the results obtained by eqn. (4) were compared to those obtained by the other equations presented for ionic activity coefficients.

B. The Guggenheim method. Guggenheim and Turgeon¹⁸ have presented an equation for the mean activity coefficients of electrolytes in aqueous mixtures of electrolytes. It has been suggested²⁰ that their equation is in some cases equivalent to equations for ionic activity coefficients. When for example the strong electrolyte NaCl fixes alone the ionic strength, according to this interpretation, the ionic activity coefficients of the Guggenheim method can be calculated by the following equations:

$$\ln \gamma_H = -\alpha(I_m)^{1/2} / [1 + B_G(I_m)^{1/2}] + 2b_G(HCl)I_m / m^0 \quad (5)$$

$$\ln \gamma_X = -\alpha(I_m)^{1/2} / [1 + B_G(I_m)^{1/2}] + 2b_G(NaX)I_m / m^0 \quad (6)$$

where for all ions $B_G = 1.0(m^0)^{-1/2}$ and in eqn. (6) X is either Cl^- or A^- (i.e. the anion resulting from the weak acid). For the tests of the present study, the following b_G values can be obtained from the table of Guggenheim and Turgeon:¹⁸ $b_G(HCl) = 0.27$, $b_G(NaCl) = 0.15$ and $b_G(NaOOCH) = 0.1$ (the last value was estimated from the b_G values of sodium acetate at 273.15 K and at 298.15 K and from the b_G value of sodium formate at 273.15 K).

C. The Ciavatta method. Ciavatta²¹ also used equations of types 5 and 6 in the analysis of weak acid results but he proposed that in those a value of $B_G = 1.5(m^0)^{-1/2}$ should be used. For the present use, the following b_G values are given in Ciavatta's tables:²¹ $b_G(HCl) = 0.138$, $b_G(NaCl) = 0.0345$ and $b_G(NaOOCH) = 0.0345$.

D. The Pitzer method. According to Pitzer's formalism (see, e.g., Pitzer and Silvester⁸), the following equations can be presented for the calculation of the ionic activity coefficients in dilute aqueous mixtures of HA, NaA and NaCl at 298.15 K:

$$\ln \gamma_H = f^r + 2m_{Cl} B_{HCl} + 2m_{Na} \Theta_{H,Na} + f(B') \quad (7)$$

$$\ln \gamma_{Cl} = f^r + 2m_H B_{HCl} + 2m_{Na} B_{NaCl} + 2m_A \Theta_{Cl,A} + f(B') \quad (8)$$

$$\ln \gamma_A = f^r + 2m_{Na} B_{NaA} + 2m_{Cl} \Theta_{Cl,A} + f(B') \quad (9)$$

where

$$f(B') = m_{Na} m_A B'_{NaA} + m_H m_{Cl} B'_{HCl} + m_{Na} m_{Cl} B'_{NaCl} \quad (10)$$

The λ terms, resulting from the ion-neutral or the neutral-neutral interactions, were omitted from eqns. (7)–(9) because their values are not available in the literature. The following symbols have been used in eqns. (7)–(10):

$$f^{\gamma} = -\alpha_{\text{P}} \{I_{\text{m}}^{1/2}/[1 + 1.2(I_{\text{m}}/m^0)^{1/2}] + [2(m^0)^{1/2}/1.2] \ln[1 + 1.2(I_{\text{m}}/m^0)^{1/2}]\} \quad (11)$$

$$B_{\text{MX}} = \beta_{\text{MX}}^0/(m^0) + \beta_{\text{MX}}^1 f_2 \quad (12)$$

$$B'_{\text{MX}} = \beta_{\text{MX}}^1 f_3 \quad (13)$$

$$f_2 = [1/(2I_{\text{m}})] \{1 - [1 + 2(I_{\text{m}}/m^0)^{1/2}] e^{-2(I_{\text{m}}/m^0)^{1/2}}\} \quad (14)$$

$$f_3 = [1/(2I_{\text{m}}^2)] \{-1 + [1 + 2(I_{\text{m}}/m^0)^{1/2}] + 2(I_{\text{m}}/m^0)\} e^{-2(I_{\text{m}}/m^0)^{1/2}} \quad (15)$$

In eqns. (11)–(13) the following parameter values given by Pitzer and Mayorga¹⁶ were used: $\alpha_{\text{P}} = 0.392(m^0)^{-1/2}$. NaCl: $\beta^0 = 0.0765$, $\beta^1 = 0.2664$; HCl: 0.1775, 0.2945; NaOOCCH₂CH₃: 0.0820, 0.2872; and NaOOCCH₂CH₃: 0.1875, 0.2789. In addition the following Θ values were used in the tests: $\Theta_{\text{H,Na}} = 0.036$ (see Pitzer and Kim²²) and $\Theta_{\text{Cl,A}} = -0.087$ (this value was estimated from the results measured by Harned and Murphy²³ on the Harned cells containing acetic acid and sodium chloride; see also Ref. 3).

E. The Jackson method. Jackson and Seymour¹⁷ suggested recently also Pitzer's formalism for the weak acid treatment, but they observed that the Θ values can be usually omitted from the Pitzer equations in this treatment. Additionally, they suggested the following β values for NaOOCCH₂CH₃: $\beta^0 = 0.1165$ and $\beta^1 = 0.312$. In the present study, the Pitzer calculations were also made with these new β values and without the Θ values, and this calculation method is called the Jackson method.

F. The Fiol method. On the basis of Pitzer's formalism, the following equation was presented by Fiol *et al.*²⁴ for the calculation of the $\text{p}K_{\text{m}}$ values [$\text{p}K_{\text{m}} = -\log(K_{\text{m}})$, see eqn. (3)] for formic and propionic acids in aqueous solutions where the ionic strength is adjusted by tetraethylammonium iodide, (C₂H₅)₄NI [= EI where E = (C₂H₅)₄N⁺ and I = I⁻]:

$$\ln K_{\text{m}} = \ln K_{\text{a,F}} - 2f^{\gamma} - 2\beta_{\text{EI}}^1 f_{\text{m}}^2 f_3 - 2\beta_{\text{HI}}^0 I_{\text{m}} - 2\beta_{\text{HI}}^1 I_{\text{m}} f_2 - 2A_{\text{F}} I_{\text{m}} - 2B_{\text{F}} I_{\text{m}} f_2 \quad (16)$$

where the functions f^{γ} , f_2 and f_3 are defined by eqns. (11), (14) and (15), respectively. In the tables of Pitzer and Mayorga,¹⁶ the following β values are given for eqn. (16): $\beta_{\text{HI}}^0 = 0.2362$, $\beta_{\text{HI}}^1 = 0.392$ and $\beta_{\text{EI}}^1 = -0.599$. From the potentiometric titration results of De Robertis and his co-workers,⁶ Fiol *et al.*²⁴ determined the following parameter values for eqn. (16). HCOOH: $K_{\text{a,F}} = 1.841 \times 10^{-4}$, $A_{\text{F}} = -0.11$ and $B_{\text{F}} = 0.762$;

CH₃CH₂COOH: 1.355×10^{-5} , 0.059 and 0.76. When eqn. (16) was used in the present tests, the K_{m} values were calculated by this equation from the ionic strengths of the solutions studied. The necessary activity coefficients for these tests were calculated by the Pitzer equations presented above.

Determination of the K_{a} values. In this study, the thermodynamic dissociation constant for each acid considered was determined from conductivity measurements. For each acid there are available in the literature reliable results of measurements of this kind, and these data are often measured in very dilute acid solutions. It seems to me that these data represent the most reliable source of experimental data for the determination of K_{a} of these acids, see below. In formic acid solutions, the measurements were made by Saxton and Darken,²⁵ in propionic acid solutions by Belcher,²⁶ and in *n*-butyric acid solutions by Saxton and Darken²⁵ and by Belcher.²⁶ To obtain K_{a} for each acid, these data were treated here as follows.

For each point of the conductivity measurements a value of K_{c} , defined by

$$K_{\text{c}} = c_{\text{H}} c_{\text{A}} / (c^0 c_{\text{HA}}) \quad (17)$$

where $c^0 = 1 \text{ mol dm}^{-3}$, was iteratively calculated from the reported concentrations and experimental molar conductivities (Λ_{m}). In this calculation the following relationship was used:

$$(\lambda_{\text{H}} + \lambda_{\text{A}}) / (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}) = \Lambda_{\text{m}}^{\infty} - x_1 (c_i/c^0)^{1/2} + x_2 (c_i/c^0) [1 - x_3 (c_i/c^0)^{1/2}] \quad (18)$$

where λ refers to the ionic conductivities and c_i to the ionic concentrations (i.e. $c_i = c_{\text{H}} = c_{\text{A}}$). The parameter values used in this equation (i.e. the values of $\Lambda_{\text{m}}^{\infty}$, x_1 , x_2 and x_3) for each acid are given in Table 1. From each resulting K_{c} value, a K_{m} value [see eqn. (3)] was calculated by

$$K_{\text{m}} = K_{\text{c}} c^0 / [(\rho - M_{\text{HA}} c_i) m^0] \quad (19)$$

where ρ is the density of the solution, M_{HA} is the molar mass of the acid considered and c_i its total concentration. Saxton and Darken²⁵ presented the following equation for the density of formic acid solutions at 298.15 K, and this equation was also used in the formic acid calculations:

$$\rho / (\text{kg dm}^{-3}) = 0.99704 + 0.012089(c_i/c^0) - 0.000690(c_i/c^0)^{3/2} \quad (20)$$

For the densities of the propionic and *n*-butyric acid solutions, it can be assumed that ρ is $\rho(\text{H}_2\text{O})$ [= 0.997 kg dm⁻³].

The K_{m} values that were obtained from the experi-

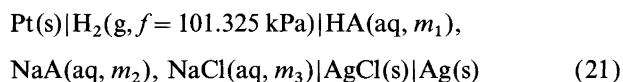
Table 1. Determination of K_a for formic, propionic and *n*-butyric acids from conductivity measurements at 298.15 K.

Acid	Source of data ^a	Parameters for eqn. (18)				I _m interval used ^b	10 ⁵ K _a ^c	10 ⁵ ε ^d
		Λ _m [∞]	x ₁	x ₂	x ₃			
Formic	25	404.31	151.88	161	0.228	0–31	18.41	0.01
Propionic	26	385.47	147.45	0	0	0.2–5	1.347	0.002
<i>n</i> -Butyric	26 ^e	381.69	146.57	180	0.228	0.2–5	1.517	0.0015

^aSee references, the reference number is given. ^bThe lower and upper limit for the ionic strength whose K_a estimates were used in the calculation of the thermodynamic value. Units 10⁻⁴ mol kg⁻¹. ^cThe final value of the thermodynamic dissociation constant. It was determined as the mean of the estimates. ^dProbable error, defined by equation $\varepsilon = 2\sigma(K_a)/N^{1/2}$, where $\sigma(K_a)$ is the standard deviation of the estimates used in the determination of K_a, and N is the number of these estimates (N is 14 for formic, 19 for propionic and 20 for *n*-butyric acid). ^eThe conductivity results were taken from Ref. 26 and the parameter values for eqn. (18) from Ref. 25.

mental conductivity data of each acid were then converted into the estimates of the K_a value for that acid by eqn. (2). For the activity coefficients, eqn. (4) was used. It was observed that the parameter values of the acetate ions (see above) can be used for the formate, propionate and butyrate ions in the dilute solutions which were finally used in the determination of K_a. The K_a estimates obtained by this method are shown in Fig. 1. Graph A in this figure contains the estimates of K_a for formic acid and graph B those for propionic and *n*-butyric acids. The details of the K_a determination for each of these three acids are explained in Table 1. According to this table, the thermodynamic dissociation constants of formic, propionic and *n*-butyric acids at 298.15 K are 1.841 × 10⁻⁴, 1.347 × 10⁻⁵ and 1.517 × 10⁻⁵, respectively.

Determination of the activity parameters. In the previous paper,³ the B and b values of acetate ions were determined for eqn. (4) (see above) from the experimental data measured by Harned and Ehlers¹ on cells of the following type:



where *f* is the fugacity of hydrogen. In the present study, the resulting value of *b* (i.e. *b* = 0.189) was also used for formate, propionate and butyrate ions.

The B values in eqn. (4) for HCOO⁻, CH₃CH₂COO⁻ and CH₃(CH₂)₂COO⁻ were determined from the results of appropriate Harned cells of type 21. In the previous paper,⁴ a value of 1.37(*m*⁰)^{-1/2} was determined for B of formate ions from the experimental data measured by Harned and Embree²⁷ on cells of type 21 containing HCOOK and KCl instead of HCOONa and NaCl. This value was used here.

The B value for propionate ions was determined here from the results measured by Harned and Ehlers²⁸ on cells of type 21. In this determination, the value of B_A

was searched that minimizes the following sum of squared prediction errors in the set of Harned and Ehlers:²⁸

$$S(E) = \sum_i e_i(E)^2 \quad (22)$$

where

$$e(E) = E(\text{observed}) - E(\text{predicted}) \quad (23)$$

For each point, E(predicted) was calculated by

$$E = E^0 - (RT/F) \ln(\gamma_H \gamma_{Cl}) - (RT/F) \ln[m_H m_{Cl}/(m^0)^2] \quad (24)$$

where E⁰ is the standard EMF. In this determination, E⁰ was adjusted because of the uncertainties associated with the standard potential of silver–silver chloride electrodes (see, e.g., Bates and Macaskill²⁹) and the calibration errors present sometimes in old EMF datasets (see, e.g., Fig. 7 in Ref. 5). The adjustment of E⁰ eliminates the constant systematic errors resulting from both of these types. The activity coefficients of H⁺ and Cl⁻ ions were calculated by eqn. (4) with the parameter values given above. m_H was calculated by the following equation:

$$m_H^2 + (K_m m^0 + m_2)m_H - K_m m_1 m^0 = 0 \quad (25)$$

K_m was calculated with the new K_a value (= 1.347 × 10⁻⁵) by eqn. (2) where eqn. (4) was again used for the activity coefficients. By this method a value of B = 1.7(*m*⁰)^{-1/2} was obtained for propionate ions.

Harned and Sutherland³⁰ have measured on cells of type 21 in *n*-butyric acid solutions. From these data, the result of B_A = 2.0(*m*⁰)^{-1/2} was obtained for butyrate ions by the method described in the previous paragraph.

Tests for the activity parameters. Above, the B parameters for propionate and *n*-butyrate ions were determined from the EMF data of Harned and co-workers (see Refs. 28 and 30). By means of the new activity coefficient equations for these ions and K_a values for propionic and *n*-butyric acids, the experimental data of these researchers

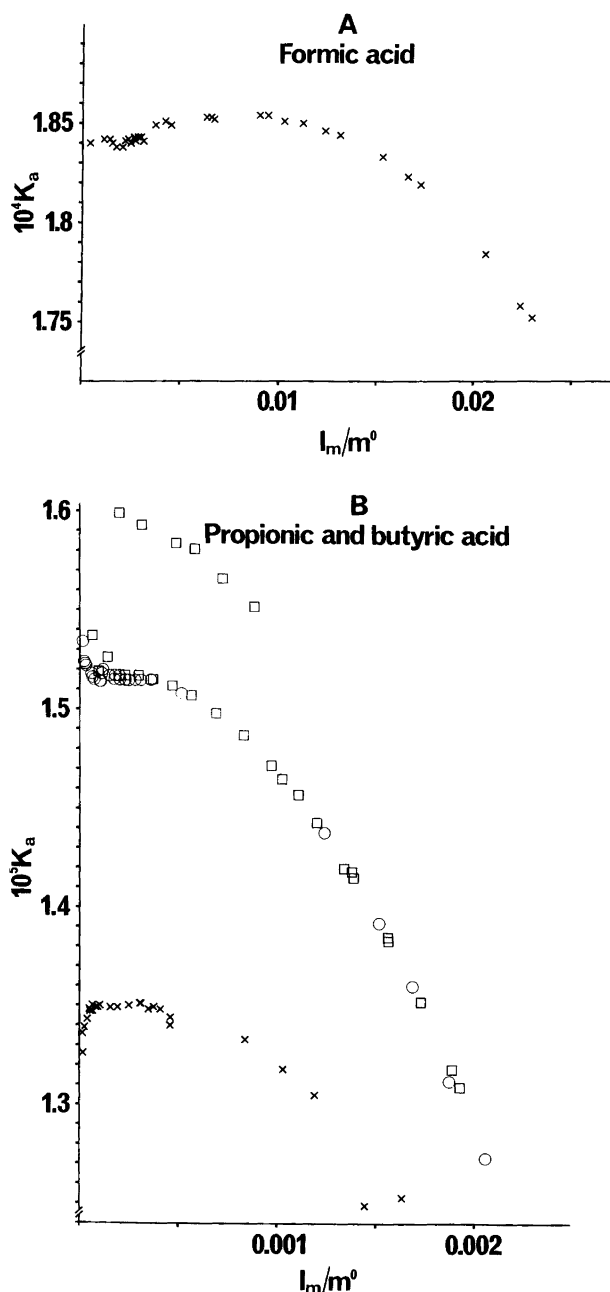


Fig. 1. Estimate of the thermodynamic dissociation constant, K_a , at 298.15 K as a function of the ionic strength I_m . The estimates were calculated from the conductivity measurements of Saxton and Darken²⁵ in formic acid solutions (graph A, symbol \times), of Belcher²⁶ in propionic acid solutions (B, \times), of Saxton and Darken²⁵ in *n*-butyric acid solutions (B, \square), of Belcher²⁶ in *n*-butyric acid solutions (B, \circ). The calculation method is presented in the text and Table 1. In the determination of the K_a value for each acid the estimates between the following I_m values were used: formic acid, 0–0.003 m^0 ; propionic acid and *n*-butyric acid, 0.000 02–0.0005 m^0 (see also Table 1).

were predicted. The results are shown as error plots in graph A of Fig. 2. In this plot the errors, defined by eqn. (23), are presented as a function of I_m .

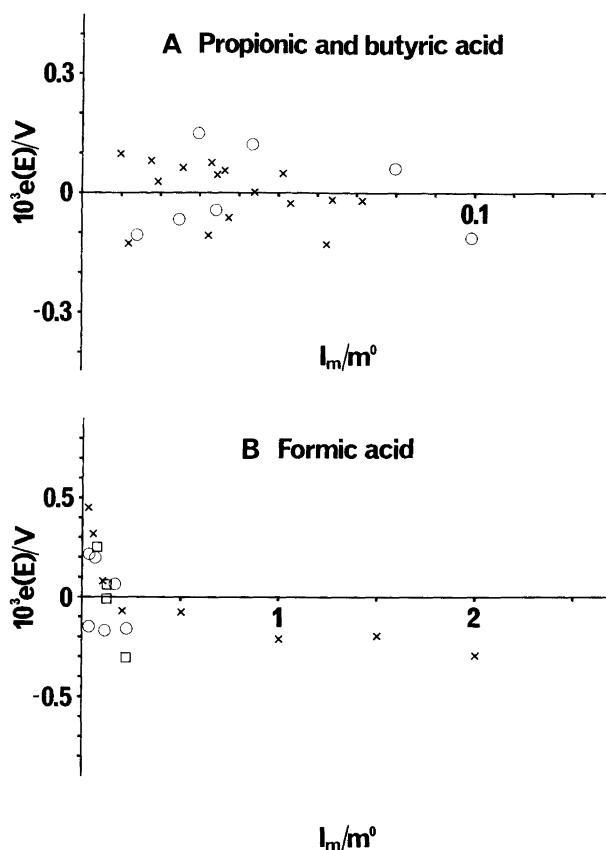
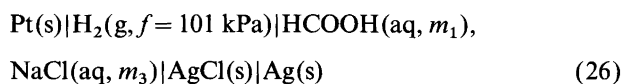


Fig. 2. The difference between the observed and predicted EMF values, $e(E)$, as a function of the ionic strength I_m . The predicted values were calculated by eqns. (2), (4), (24) and (25) with the parameter values given in Table 2 (method A in the text). Graph A contains the errors calculated from the set of Harned and Ehlers²⁸ (propionic acid, symbol \times and $E^0 = 0.222\ 64$ V) and of Harned and Sutherland³⁰ (*n*-butyric acid, \circ , 0.222 58 V) measured by cells of type 21, and graph B those calculated from the sets of Harned and Owen³¹ measured by cells of type 26. Symbols and E^0 values for the different formic acid sets in graph B: $m_1 = 0.100\ 31 m^0$, symbol \times , $E^0 = 0.222\ 24$ V; 1.0000, \circ , 0.219 47; and 2.1253, \square , 0.215 30.

Harned and Owen³¹ have measured electromotive forces on cells of the following type:



These data can be used in the tests of the activity parameters for formic acid solutions. This paper contains three sets of EMF measurements made in NaCl solutions, and the sets differed from each other by the molality m_1 and the values of 0.100 31, 1.0000 and 2.1253 m^0 were used for this quantity. These data were predicted by the new calculation method, and the results are shown as error plots in graph B of Fig. 2.

Discussion

Above, the K_a values for formic, propionic and *n*-butyric acids were determined from the conductivity measurements of Saxton and Darken²⁵ and Belcher.²⁶ As explained in Table 1, only the dilute points of these sets were finally used in the determination of the K_a values. In the case of these points, the K_a estimates do not depend on I_m as shown in Fig. 1. In the case of the less dilute points, the K_a estimates can perhaps be used in the determination of this quantity by an appropriate extrapolation procedure, but here the method used in Table 1 was preferred. It should be pointed out that the dependence of K_a estimates (determined from the conductivity data) in Fig. 1 on I_m is not covered by activity coefficient equations because the ionic mobilities (the mobility is not a thermodynamical quantity) play the central role in the conductivity process. In very dilute solutions, however, the conductivity measurements give clear information of the amount of ions in solutions, and this part of the conductivity data (Table 1) was used here in the determination of the K_a value for each acid.

As shown in Fig. 1, the conductivity measurements in formic acid solutions were carried out in stronger solutions than those in propionic and *n*-butyric acid solutions. According to this figure, it is clear that the K_a values for propionic and *n*-butyric acid are somewhat more reliable than that of formic acid (a smooth extrapolation from the less dilute solutions leads in the formic acid case to a slightly different K_a value than that determined in Table 1). When the extremely dilute solutions of the former acids are omitted from the determination, as done in Table 1, the K_a value can be obtained from the experimental data almost with a precision of four significant digits. It is probable (see for example Ref. 4) that the precision of this kind cannot be obtained by EMF methods.

As shown in graph B of Fig. 1, the value of 1.517×10^{-5} for K_a of *n*-butyric acid (obtained above from Belcher's measurements²⁶) was also supported strongly by several points of Saxton and Darken²⁵ despite the fact that this set also contains at least six clear outliers. Belcher²⁶ suggested the following K_a values of propionic and *n*-butyric acids: 1.343×10^{-5} and 1.508×10^{-5} , respectively; these values therefore agree well with those determined here when they are converted into the molality scale.

For formic acid, a value of 1.841×10^{-4} was obtained above from the measurements of Saxton and Darken.²⁵ This value does not agree well with the value of 1.780×10^{-4} determined in the previous paper⁴ for this acid from the EMF results of Harned and Embree.²⁷ A possible explanation for this disagreement may arise from a constant systematic error existing in the EMF values measured by Harned and Embree. It was checked that good results with the K_a value of 1.841×10^{-4} were also obtained in this EMF set when a systematic error of +0.851 mV was eliminated from the results. The

disagreement between their K_a (1.825×10^{-4}) and the one of Harned and Embree²⁷ was also pointed out by Saxton and Darken.²⁵

The B parameters for propionate and *n*-butyrate ions in eqn. (4) were determined above from the EMF measurements of Harned and Ehlers,²⁸ and Harned and Sutherland,³⁰ respectively. According to graph A in Fig. 2, all points of these two sets can probably be explained within experimental error by the resulting model.

According to graph B in Fig. 2, the experimental data of Harned and Owen³¹ measured by cells of type 26 can be well predicted by the model suggested in this study for formic acid solutions. These data cover a wide area of formic acid and salt molalities. The results obtained in this graph can be compared to the corresponding results obtained in the acetic acid study³ (see discussion in connection of Fig. 2 in Ref. 3).

It is also interesting to compare the results of the present calculations to those obtained by the other methods proposed for the treatment of the weak acid results. The methods used in these tests have been introduced above. The equations presented for the formic acid solutions are tested with the data of Harned and Owen³¹ where $m_1 = 0.10031m^0$ [see cell (26)], and those for propionic acid solutions with the data of Harned and Ehlers²⁸ [see cell (21)]. The error plots obtained from the formic acid set for the methods of Guggenheim (see method B above), Ciavatta (C), Pitzer (D), Jackson (E) and Fiol (F) are shown in graph A of Fig. 3, and the error plots obtained from the propionic acid set by methods D, E and F are shown in graph B of this figure.

According to graph A of Fig. 3, the models used in the tests do not predict these formic acid results as well as the model suggested in the present study (see also graph B in Fig. 2). As shown in graph B of this figure, the propionic acid set used in the tests consists of dilute solutions only. Both of the Pitzer methods (D and E) predict these data well. In these dilute solutions, the difference between these two methods is not apparent. In Fiol method (F), K_m values were determined by the equation [eqn. (16)] whose parameters were obtained from experimental data measured in tetraethylammonium iodide solutions (see above). This fact could explain

Table 2. Parameters of eqn. (4) for the calculation of K_m values for formic, acetic, propionic and *n*-butyric acids in aqueous NaCl solutions at 298.15 K ($m^0 = 1 \text{ mol kg}^{-1}$).

Ion	$B/(m^0)^{-1/2}$	b	$10^5 K_a^a$
H ⁺	1.25	0.238	
Cl ⁻	1.25	0.238	
HCOO ⁻	1.37	0.189	18.41
CH ₃ COO ⁻	1.6	0.189	1.758
CH ₃ CH ₂ COO ⁻	1.7	0.189	1.347
CH ₃ CH ₂ CH ₂ COO ⁻	2.0	0.189	1.517

^a Thermodynamic dissociation constant for the corresponding acid.

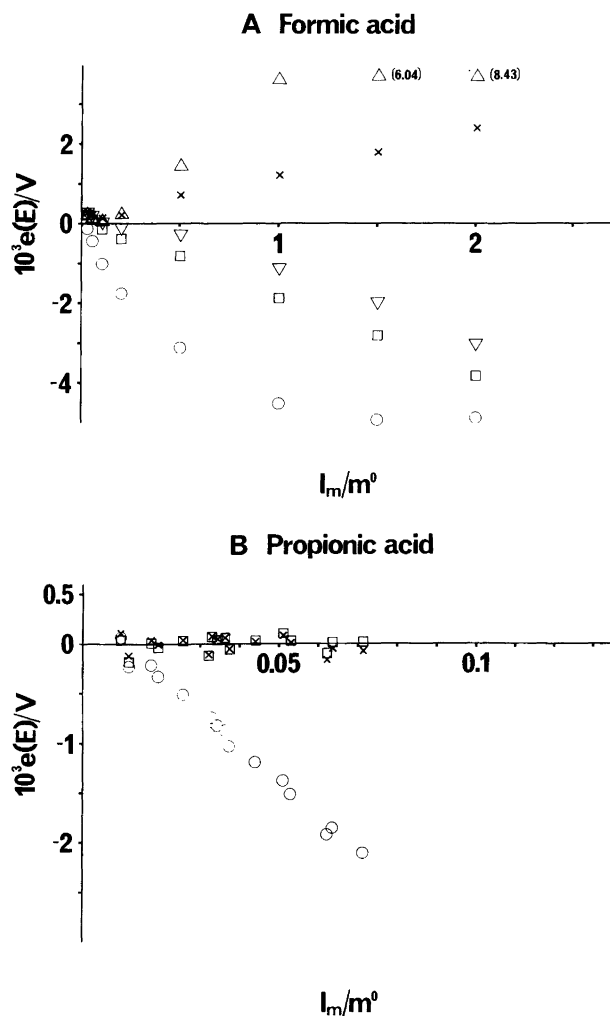


Fig. 3. The difference between the observed and predicted EMF values, $e(E)$, as a function of the ionic strength I_m . Graph A contains the errors obtained from the formic acid set where $m_1 = 0.10031m^0$ measured by Harned and Owen³¹ on cells of type 26, and graph B those obtained from the propionic acid set measured by Harned and Ehlers²⁸ on cells of type 21. The predicted EMF values were calculated by methods B–F as described in the text (the symbols and adjusted E^0 values for graph B are also shown): Guggenheim method (B), Δ ; Ciavatta method (C), ∇ ; Pitzer method (D), \times , $E^0 = 0.22266$ V; Jackson method (E), \square , $E^0 = 0.22290$ V; Fiol method (F), \circ , 0.22250 V (not adjusted). In graph A, the value of 0.22250 V was used in the calculations of all methods (see Refs. 3 and 5).

a part of the large disagreement between the experimental EMF values and the predictions calculated by this method.

In the present study, the parameter values presented in Table 2 were used in aqueous mixtures of HCOOH, CH₃CH₂COOH or CH₃CH₂CH₂COOH and NaCl at 298.15 K. With the simple set of equations containing these parameter values, K_m can be calculated for these acids within experimental error at any ionic strength at least up to $0.1m^0$ if this ionic strength is adjusted by NaCl.

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