

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

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Single-ion activity coefficient equations were determined for the calculation of the molality scale dissociation constants, K_m , for propionic acid in dilute aqueous NaCl or KCl solutions at 298.15 K. The salt alone determines the ionic strength, I_m , of the solutions considered in this study. The activity coefficient equations are of the Hückel type, and K_m can be calculated by those for a certain ionic strength from the thermodynamic dissociation constant. The data used for the estimation of the parameters for these equations were measured by potentiometric titrations in a glass electrode cell. Three different methods to calculate the experimental K_m values from the titration data were considered. The activity parameters for the Hückel equation were determined from the K_m values calculated by all of these methods. The parameters obtained by the different methods are very consistent with each other and also with the Hückel parameters obtained previously for light fatty acids from the literature data measured by Harned cells. The final activity parameters recommended in this study seem to be reliable. Despite the theoretical difficulties associated with the single-ion activity coefficients and the simplicity of the calculation method based on Hückel equations, K_m can be obtained by this method almost within experimental error for propionic acid in NaCl and KCl solutions up to I_m of about 1 mol kg⁻¹.

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 in, e.g., analytical applications usually contain a large amount, compared to the amount of 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 K_m for the weak acid is dependent only on the molality of the salt (or on I_m). 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. Recently, considerable success has been achieved in the evaluations of the dependence of K_m of weak acids on the ionic strength in the salt solutions, and this topic has been reviewed by Sastre de Vicente.¹

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 the thermodynamic dissoci-

ation constant, K_a , for propionic acid in aqueous sodium or potassium chloride solutions at 298.15 K. The Hückel method is based on empirical 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 for acetic acid at 298.15 K in NaCl,^{2,3} KCl³ and LiCl³ solutions, for formic acid in NaCl^{3,4} and KCl³ solutions, for propionic and *n*-butyric acids^{3,4} in NaCl solutions, for lactic acid³ in NaCl and LiCl solutions, and for glycolic acid³ in KCl and LiCl solutions. In addition, the method has been previously applied to the determination of stoichiometric values for the first and second dissociation constants ($K_{m,1}$ and $K_{m,2}$) of glutamic acid⁵ in aqueous NaCl and KCl solutions, and of glycine⁶ in NaCl solutions at 298.15 K. In the previous propionic acid study,⁴ the experimental data were taken from the literature and ionic strengths up to only 0.1 mol kg⁻¹ were considered.

Potentiometric titrations in a glass electrode cell were used in this study to determine experimental K_m values for propionic acid in aqueous NaCl and KCl solutions. It is not easy to solve such values from titration data.

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Calibrations, asymmetry potentials and liquid junction potentials are difficult problems associated with the determination of K_m by this experimental technique. In this study, three calculation methods are presented to overcome these problems. K_m for propionic acid at different experimental molalities of NaCl and KCl was calculated by all these three methods. The activity coefficient parameters for the Hückel equation were also estimated from the results of all methods. These parameters agree well with each other and also with the parameters obtained previously²⁻⁴ for light fatty acids from the literature data measured by Harned cells. On the basis of these parameters, it is possible to recommend equations for the calculations of K_m for propionic acid at 298.15 K in NaCl and KCl solutions up to I_m of about 1 mol kg⁻¹. The recommended values of K_m at rounded ionic strengths are also tabulated below.

In the thermodynamic treatment of electrolyte solutions, Pitzer formalism (see, e.g., Pitzer⁷) 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. In their tables, Pitzer and Mayorga⁸ have suggested binary Pitzer parameters for sodium propionate (NaPropO) but not for potassium propionate (KPropO). Estes *et al.*⁹ suggest for NaPropO different binary Pitzer parameters from those of Pitzer and Mayorga,⁸ and additionally they suggest mixing parameters for aqueous mixtures of NaPropO and NaCl. The Pitzer method is not considered in the present study because too many new parameters ought to be estimated from the titration data to obtain a satisfactory Pitzer model. The Pitzer model is not necessary in this case owing to the fact that the titration data can be correlated within experimental error by means of the simpler Hückel model.

Experimental

Potentiometric acetic and propionic acid (AcOH and PropOH, respectively) titrations were carried out in aqueous NaCl and KCl solutions at 298.15 K. The AcOH titrations were needed for the calibration of the glass electrode cell (see below). The potentiometric titration data obtained from NaCl solutions are shown in Tables 1 and 2. Table 1 shows the data for the AcOH titrations and Table 2 those for the PropOH titrations. The potentiometric titration data for KCl solutions are presented in Tables 3 and 4, and Table 3 shows the data for AcOH titrations and Table 4 for PropOH titrations.

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, 0.700 and 1.350 M (however, the NaCl series was slightly different: the solution where $c=0.400$ mol dm⁻³ was missing, and the concentration $c=0.320$ mol dm⁻³ was measured twice, see Tables 1 and 2). Also two AcOH (pro analysi, Riedel-de Haën), two PropOH (puriss., p.a. Fluka), two NaOH (Fixanal, Riedel-de Haën) solutions and a KOH (Titrisol, Merck) solution were prepared; the concentrations of these solutions are shown in Tables 1-4. The concentrations of the base solutions were determined by potentiometric titrations against potassium hydrogen phthalate (pro analysi, Merck). The exact equivalence points were calculated from the titration results of three replicates by the method of Kolthoff.¹⁰

The solutions titrated were prepared by mixing a volume of 10.00 cm³ of a weak acid solution, 100.0 cm³ of a salt solution and 25.00 cm³ of water; for details see Refs. 11-13. The KCl solutions were titrated by using the KOH solution as the titrant and the NaCl solutions by using either of the two NaOH titrants (Tables 1 and 2). 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 accuracy of the reading was 0.1 mV. The titrant was added in increments of 0.050 cm³ by a Dosimat (Metrohm).

Three methods to obtain stoichiometric dissociation constants were tested in this study. In the first of those (method I), the pH values of the solutions titrated were used. pH was calculated from the measured electromotive forces, E , by the bracketing method suggested by IUPAC.¹⁴ In this calculation, the following relationship was used:

$$E/(\text{mV}) = 382.86 - 58.392 \text{ pH} \quad (1)$$

For data sets PNC4b and PNC6-8 in Table 2, however, the relationship was slightly different (i.e. $E/\text{mV} = 383.86 - 58.566 \text{ pH}$). The constants were determined for this equation by measuring the EMF values for the two standard buffer solutions recommended by IUPAC, i.e. for 0.05 mol kg⁻¹ potassium hydrogen phthalate (Art. 4878, Merck) and for 0.025 mol kg⁻¹ potassium dihydrogen phosphate (Art. 4881, Merck) plus 0.025 mol kg⁻¹ disodium hydrogen phosphate (Art. 6589, Merck). The recommended pH of the former solution is 4.005 at 298.15 K and of the latter is 6.865.

In the second method, the measured EMF was directly used. In this method (method II) a titration of AcOH was carried out before the PropOH titration at the same molality of NaCl or KCl as that used in the latter titration. The former was regarded as a calibration titration owing to the fact that K_m for AcOH and, therefore, also the molalities of all species resulting from AcOH are accurately known in the salt solutions considered (Ref. 3). The results of the calibration titration were used to fix the slope parameter for the glass electrode cell, see below.

In the third method, the electromotive forces were also

Table 1. Results of titrations of acetic acid in NaCl solutions at different ionic strengths (I_m) with a base (NaOH) solution^a at 298.15 K. Series ANC.

$I_m/(m^\circ)^b$	0.0595	0.1191	0.1789	0.2388	0.2388	0.3741	0.5251	1.0222
V/cm^3^c	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d
0.05		148.8	149.4	150.5	149.9	151.3	152.7	155.4
0.10	143.9	144.8	145.6	146.5	146.2	147.4	148.8	151.4
0.15	139.6	140.6	141.6	142.3	142.2	143.4	144.9	147.4
0.20	135.8	136.5	137.4	138.5	138.2	139.5	140.9	143.3
0.25	131.4	132.4	133.3	134.3	134.0	135.4	136.9	139.3
0.30	127.2	128.4	129.3	130.5	130.1	131.5	133.0	135.3
0.35	123.0	124.3	125.1	126.4	126.0	127.4	128.9	131.2
0.40	118.8	120.1	121.1	122.4	122.0	123.4	124.9	127.0
0.45	114.6	115.9	117.0	118.2	117.9	119.2	120.7	122.7
0.50	110.2	111.6	112.8	113.9	113.7	114.9	116.5	118.4
0.55	105.8	107.0	108.5	109.6	109.3	110.5	112.2	114.0
0.60	101.2	102.6	103.8	105.0	104.5	105.9	107.5	109.2
0.65	96.5	97.8	98.9	100.2	99.8	100.9	102.6	104.2
0.70	91.1	92.6	93.7	95.0	94.7	95.9	97.4	98.8
0.75	85.3	86.6	87.9	89.3	89.1	90.1	91.6	92.6
0.80	78.9	80.1	81.4	82.9	82.8	83.4	85.0	85.7
0.85	71.2	72.7	73.7	75.1	74.9	75.5	77.4	77.0
Symbol	ANC1	ANC2	ANC3	ANC4a	ANC4b	ANC6	ANC7	ANC8
$10^4 n_{t,0}/\text{mol}^e$	1.034	1.034	1.034	1.034	1.041	1.041	1.041	1.041
$10^5 K_m^f$	2.62	2.88	3.03	3.13	3.13	3.24	3.26	3.02
$10^4 n_i/\text{mol}^g$	1.015	1.018	1.014	1.017	1.024	1.016	1.018	0.991
k^h	0.9749	0.9833	0.9779	0.9798	0.9797	0.9804	0.9797	0.9584
$\sigma(k)^i$	0.0011	0.0011	0.0009	0.0010	0.0011	0.0007	0.0008	0.0008
E_0/mV^j	376.59	377.96	376.71	377.61	377.16	378.24	379.37	378.42
σ/mV^k	0.099	0.108	0.087	0.096	0.103	0.070	0.079	0.075

^aSets ANC1–ANC4a were titrated with a base solution where $c=0.0993 \text{ mol dm}^{-3}$ and sets ANC4b–ANC8 with a base solution where $c=0.0998 \text{ mol dm}^{-3}$. ^b $m^\circ=1 \text{ mol kg}^{-1}$. ^cThe volume of titrant added. ^dThe measured EMF. ^eThe analytical amount of acetic acid. ^fThe stoichiometric dissociation constant of acetic acid calculated by eqn. (9) with the parameter values given in Table 5. ^gThe optimized amount of acetic acid. It was determined by optimizing the least-squares fit of eqn. (8). ^hThe slope parameter obtained by the least-squares fit using eqn. (8). ⁱThe standard deviation for the k parameter. ^jThe intercept parameter obtained by the least-squares fit using eqn. (8). ^kThe standard deviation of residuals for the least-squares fit obtained by using eqn. (8).

directly used. This method (method III) is more approximate than either of the former, and a perfect Nernstian response for a glass electrode is assumed. Also the analytical amounts of PropOH were used in the calculations of this method. On the contrary, in the former methods this amount was adjusted for each titration, probably because of the salting-out effect (occurring in salt solutions). This effect slightly decreased the amount of weak acid in the titration vessel during each titration, and the largest influence was observed in the titrations of concentrated salt solutions. We believe, additionally, that this effect had its largest influence during each titration at the beginning when the EMF slowly stabilized.

Results and discussion

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

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

where $m^\circ=1 \text{ mol kg}^{-1}$, I_m is the ionic strength on the molality scale and α is the Debye–Hückel parameter equal to $1.17444 (\text{mol kg}^{-1})^{-1/2}$.¹⁵ 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. Previously, the following parameters have been determined for eqn. (2): $B_{\text{H}}=1.25 (\text{mol kg}^{-1})^{-1/2}$, $b_{\text{H},\text{NaCl}}=0.238$,¹⁶ $b_{\text{H},\text{KCl}}=0.178$,³ $B_{\text{AcO}}=1.6 (\text{mol kg}^{-1})^{-1/2}$, $b_{\text{AcO},\text{NaCl}}=0.189$ ² and $b_{\text{AcO},\text{KCl}}=0.308$,³ where the following symbols are used: $\text{H}=\text{H}^+$ and $\text{AcO}=\text{CH}_3\text{COO}^-$. These values are also used in the present study.

The thermodynamic dissociation constant (K_a) for acetic or propionic acid, generally HA, is given by

$$K_a = \gamma_{\text{H}}\gamma_{\text{A}}m_{\text{H}}m_{\text{A}}/(\gamma_{\text{HA}}m_{\text{HA}}m^\circ) = (\gamma_{\text{H}}\gamma_{\text{A}}/\gamma_{\text{HA}})K_m \quad (3)$$

where HA and A refer to AcOH or PropOH molecules and acetate (AcO^-) or propionate (PropO^-) ions, respectively. For neutral species HA, it is assumed in the Hückel method that $\gamma_{\text{HA}}=1$. Assuming that the data are treated by the Hückel method with this assumption for

Table 2. Results of titrations of propionic acid in NaCl solutions at different ionic strengths (I_m) with a base (NaOH) solution^a at 298.15 K. Series PNC.

$I_m/(m^\circ)^b$	0.0595	0.1191	0.1789	0.2388	0.2388	0.3741	0.5251	1.0222
V/cm^3^c	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d	E/mV^d
0.05	144.4	145.7	145.9	145.8	147.1	148.2	149.8	152.5
0.10	139.5	141.3	141.6	141.6	142.8	143.9	145.5	148.3
0.15	135.2	136.7	137.1	137.2	138.6	139.6	141.2	144.0
0.20	130.5	132.4	132.7	132.9	134.3	135.4	136.9	139.7
0.25	126.0	128.0	128.4	128.7	129.9	131.2	132.8	135.3
0.30	121.8	123.7	124.2	124.4	125.7	127.0	128.5	131.1
0.35	117.3	119.4	120.0	120.2	121.5	122.8	124.3	126.7
0.40	113.1	115.0	115.8	116.0	117.4	118.6	120.1	122.6
0.45	108.7	110.6	111.4	111.7	113.1	114.4	115.8	118.3
0.50	104.2	106.5	107.1	107.4	108.7	110.1	111.4	114.0
0.55	100.0	102.0	102.6	103.1	104.4	105.8	107.1	109.7
0.60	95.4	97.6	98.2	98.4	100.0	101.1	102.6	105.1
0.65	90.7	92.8	93.3	93.7	95.3	96.4	97.9	100.3
0.70	85.6	87.8	88.1	88.6	90.4	91.3	92.8	95.2
0.75	80.1	82.2	82.6	82.9	84.8	85.8	87.0	89.5
0.80	73.9	76.1	76.1	76.4	78.7	79.6	80.9	83.1
0.85	66.8	68.8	69.0	69.0	72.0	72.5	73.4	75.7
Symbol	PNC1	PNC2	PNC3	PNC4a	PNC4b	PNC6	PNC7	PNC8
$10^4 n_{t,0}/\text{mol}^e$	1.059	1.059	1.059	1.059	1.064	1.064	1.064	1.064
$10^5 K_m(\text{I})^f$	2.04	2.21	2.38	2.53	2.43	2.58	2.59	
$10^5 K_m(\text{II})^f$	1.97	2.19	2.31	2.47	2.36	2.50	2.50	2.29
$10^5 K_m(\text{III})^f$	2.04	2.18	2.27	2.37	2.44	2.48	2.44	2.39
$10^5 K_m^g$	2.00	2.19	2.31	2.38	2.38	2.45	2.46	2.28
$10^4 n_{t,i}/\text{mol}^h$	1.044	1.041	1.034	1.033	1.055	1.047	1.042	
pH_{ij}^i	-0.0199	-0.0446	-0.0508	-0.0522	-0.0614	-0.0846	-0.1131	
$10^4 n_{t,j}/\text{mol}^j$	1.038	1.038	1.028	1.020	1.051	1.038	1.032	1.023
k^k	0.9793	0.9832	0.9778	0.9676	0.9847	0.9768	0.9751	0.9579
E_0/mV^l	376.96	378.08	376.49	373.74	378.64	377.58	378.75	378.64
σ/mV^m	0.098	0.079	0.093	0.052	0.082	0.072	0.073	0.064
$E_0(\text{III})/\text{mV}^n$	381.70	381.74	381.20	380.81	382.19	382.72	384.12	388.26

^aSets PNC1–PNC4a were titrated with a base solution where $c=0.0993 \text{ mol dm}^{-3}$ and sets PNC4b–PNC8 with a base solution where $c=0.0998 \text{ mol dm}^{-3}$. ^b $m^\circ=1 \text{ mol kg}^{-1}$. ^cThe volume of titrant added. ^dThe measured EMF. ^eThe analytical amount of propionic acid. ^fThe stoichiometric dissociation constant determined by the method shown. ^gThe stoichiometric dissociation constant calculated by eqn. (9) with the recommended parameter values given in Table 5. ^hThe optimized amount of propionic acid used in the calculation of the pH errors for the tests of method I (see text). ⁱLiquid-junction potential correction, see Appendix of Ref. 11, used in the calculation of the pH errors for the tests of method I (see text). ^jThe optimized amount of propionic acid. It was determined by optimizing the least-squares fit of eqn. (8). ^kThe slope parameter obtained by the least-squares fit using eqn. (8). ^lThe intercept parameter obtained by the least-squares fit using eqn. (8). ^mThe standard deviation of residuals for the least-squares fit obtained by using eqn. (8). ⁿThe value of parameter E_0 used in the calculation of the EMF errors for Fig. 2 (method III). It was determined by requiring that the sum of all errors in each data set is zero.

γ_{HA} and assuming additionally that $\ln \gamma_{\text{HA}}$ is in reality linearly dependent on the ionic strength of the solution (the Setchenow equation for the salting out effect). Then the slope of the straight line $\ln \gamma_{\text{HA}}$ vs. $I_m/(m^\circ)$ 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. The stoichiometric dissociation constant K_m in eqn. (3) is defined by

$$K_m = m_{\text{H}} m_{\text{A}} / (m_{\text{HA}} m^\circ) \quad (4)$$

The experimental K_m values obtained by the different calculation methods are included in Tables 2 and 4. The calculations of these methods were made as follows.

In the determination of experimental K_m values for

PropOH by method I, the measured pH values were treated as described in Appendix of Ref. 11. The following equation can be derived for the titration data presented in Tables 1–4 from eqn. (4) and from the equations for the material balance and for the electroneutrality:

$$m_{\text{H}}^2 + (K_m m^\circ + m_{\text{b}}) m_{\text{H}} + K_m m^\circ (m_{\text{b}} - m_{\text{t}}) = 0 \quad (5)$$

In eqn. (5) m_{b} is the molality of base, NaOH or KOH, in the solution titrated and $m_{\text{b}} = c_{\text{b}} V/w_1$, 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; see also text under eqn. (9) in Ref. 11. m_{t} in eqn. (5) of the present study is the total molality of the weak acid in the solution titrated and $m_{\text{t}} = n_{\text{t}}/w_1$, where n_{t} is the amount of this substance. In the present

Table 3. Results of titrations of acetic acid in KCl solutions at different ionic strengths (I_m) with a base (KOH) solution ($c = 0.0997 \text{ mol dm}^{-3}$) at 298.15 K. Series AKC.

$I_m/(m^\circ)^a$	0.0595	0.1193	0.1792	0.2393	0.2997	0.3755	0.5280	1.0331
V/cm^3^b	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c
0.05	147.9	148.7	148.9	149.0	148.6	148.9	149.7	150.9
0.10	143.7	144.8	144.8	145.2	144.8	145.1	145.9	146.7
0.15	139.5	140.7	141.0	141.1	140.8	141.2	142.0	142.7
0.20	135.3	136.4	136.9	137.1	136.8	137.1	137.9	138.8
0.25	131.1	132.5	132.8	132.9	132.9	133.1	133.9	134.5
0.30	126.7	128.3	128.8	128.9	129.0	129.0	129.9	130.3
0.35	122.6	124.1	124.8	124.8	124.8	124.9	125.8	126.1
0.40	118.4	119.9	120.6	120.7	120.8	120.8	121.6	122.0
0.45	114.1	115.7	116.4	116.5	116.6	116.5	117.5	117.8
0.50	109.9	111.4	112.0	112.3	112.3	112.5	113.2	113.4
0.55	105.3	107.0	107.8	108.1	107.9	108.0	108.9	109.1
0.60	100.8	102.6	103.1	103.6	103.6	103.5	104.2	104.4
0.65	96.1	97.6	98.3	98.7	98.6	98.8	99.6	99.6
0.70	90.9	92.6	93.2	93.7	93.5	93.5	94.5	94.4
0.75	85.2	86.7	87.5	87.9	87.7	87.9	88.9	88.6
0.80	78.8	80.5	81.2	81.8	81.4	81.3	82.4	82.2
0.85	71.2	72.9	73.7	74.2	73.9	73.8	75.0	74.7
Symbol	AKC1	AKC2	AKC3	AKC4	AKC5	AKC6	AKC7	AKC8
$10^4 n_{t,0}/\text{mol}^d$	1.034	1.034	1.034	1.034	1.034	1.034	1.034	1.034
$10^5 K_m^e$	2.61	2.86	3.00	3.09	3.14	3.17	3.16	2.84
$10^4 n_t/\text{mol}^f$	1.028	1.029	1.028	1.033	1.023	1.026	1.031	1.023
k^g	0.9840	0.9883	0.9855	0.9901	0.9781	0.9880	0.9902	0.9799
$\sigma(k)^h$	0.0006	0.0009	0.0010	0.0009	0.0010	0.0008	0.0007	0.0010
E_0/mV^i	378.34	379.04	377.91	378.56	375.39	377.80	379.03	379.14
σ/mV^j	0.060	0.081	0.089	0.084	0.095	0.071	0.068	0.096

^a $m^\circ = 1 \text{ mol kg}^{-1}$. ^b The volume of titrant added. ^c The measured EMF. ^d The analytical amount of acetic acid. ^e The stoichiometric dissociation constant of acetic acid calculated by eqn. (9). ^f The optimized amount of acetic acid. It was determined by optimizing the least-squares fit of eqn. (8). ^g The slope parameter obtained by the least-squares fit using eqn. (8). ^h The standard deviation for the k parameter. ⁱ The intercept parameter obtained by the least-squares fit using eqn. (8). ^j The standard deviation of residuals for the least-squares fit obtained by using eqn. (8).

calculations, m_H needs to be determined for each titration point using a given value of K_m . The experimental K_m value for each titration data set was obtained by searching the minimum of the pH square sum defined by eqn. (A6) in Appendix of Ref. 11 when both K_m and n_t were varied. The predicted pH for each titration point was calculated by

$$\text{pH}(\text{predicted}) = -\log(\gamma_H m_H/m^\circ) \quad (6)$$

For this equation, γ_H was calculated by eqn. (2) and m_H by eqn. (5). The experimental K_m values obtained in this way for PropOH [denoted as $K_m(I)$] at the different NaCl and KCl solutions are shown in Tables 2 and 4, respectively.

In the determination of experimental K_m values for PropOH by method II, the slope parameter for the glass electrode cell was determined at each ionic strength by an AcOH titration that preceded the PropOH titration, see above. In general, the following equation is valid for the EMF of a glass electrode cell:

$$E = E^\circ + k(RT/F) \ln a_H \quad (7)$$

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

junction, standard glass electrode and asymmetry potentials (see, e.g. May *et al.*¹⁷). It is assumed in all present weak acid titrations that this term remained constant during the titration. The slope parameter k was determined by linear regression analysis from the results of the AcOH titrations by using the following equation:

$$\begin{aligned} E &= E^\circ + k(RT/F) \ln \gamma_H + k(RT/F) \ln(m_H/m^\circ) \\ &= E_0 + k(RT/F) \ln(m_H/m^\circ) \end{aligned} \quad (8)$$

where $E_0 = E^\circ + k(RT/F) \ln \gamma_H$ is also constant during each titration at a constant ionic strength [see eqn. (2)]. m_H was calculated for each titration point by eqn. (5), and K_m for AcOH at each ionic strength is given by

$$\begin{aligned} \ln K_{m,\text{MCl}} &= \ln K_a + \alpha(I_m)^{1/2} \\ &\times \{1/[1 + B_H(I_m)^{1/2}] + 1/[1 + B_A(I_m)^{1/2}]\} \\ &- (b_{H,\text{MCl}} + b_{A,\text{MCl}})I_m/(m^\circ) \end{aligned} \quad (9)$$

This equation was presented in Ref. 3, and the parameter values for this equation are given in Table 5 of the present study. These values have been determined in Refs. 2–4 and 16 from the literature data measured on Harned cells. The K_m values predicted by eqn. (9) for the AcOH solutions considered now are also shown in

Table 4. Results of titrations of propionic acid in KCl solutions at different ionic strengths (I_m) with a base (KOH) solution ($c=0.0997 \text{ mol dm}^{-3}$) at 298.15 K. Series PKC.

$I_m/(m^\circ)^a$	0.0595	0.1193	0.1792	0.2393	0.2997	0.3755	0.5280	1.0331
V/cm^3^b	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c	E/mV^c
0.05	144.3	144.4	145.2	145.1	145.7	145.6	145.9	147.0
0.10	139.5	139.9	141.0	140.8	141.5	141.4	141.6	142.6
0.15	134.8	135.4	136.6	136.4	137.2	137.1	137.4	138.2
0.20	130.3	130.9	132.2	132.1	132.8	132.7	133.1	133.6
0.25	125.8	126.6	127.9	127.9	128.4	128.3	128.6	129.2
0.30	121.4	122.3	123.6	123.7	124.1	124.2	124.2	125.0
0.35	117.0	118.0	119.4	119.3	120.0	119.9	120.1	120.6
0.40	112.8	113.8	115.1	115.2	115.9	115.8	115.8	116.2
0.45	108.4	109.5	110.9	110.7	111.6	111.4	111.6	112.1
0.50	104.1	105.2	106.7	106.6	107.2	107.3	107.4	107.7
0.55	99.6	100.7	102.2	102.2	102.9	102.8	103.0	103.3
0.60	95.1	96.2	97.7	97.7	98.5	98.1	98.4	98.5
0.65	90.4	91.5	92.8	93.0	93.5	93.3	93.6	93.8
0.70	85.3	86.6	87.9	87.9	88.7	88.2	88.5	88.5
0.75	79.7	80.9	82.6	82.6	83.2	82.9	82.9	83.1
0.80	73.7	74.7	76.6	76.6	77.2	76.5	76.6	76.6
0.85	66.8	67.8	69.8	69.4	70.4	69.3	69.3	69.7
Symbol	PKC1	PKC2	PKC3	PKC4	PKC5	PKC6	PKC7	PKC8
$10^4 n_{t,0}/\text{mol}^d$	1.059	1.059	1.059	1.059	1.059	1.059	1.059	1.059
$10^5 K_m(\text{I})^e$	1.99	2.23	2.29	2.38	2.35	2.46	2.45	
$10^5 K_m(\text{II})^e$	1.96	2.22	2.28	2.39	2.30	2.47	2.47	2.22
$10^5 K_m(\text{III})^e$	2.04	2.25	2.37	2.42	2.43	2.40	2.39	2.23
$10^5 K_m^f$	2.00	2.18	2.28	2.34	2.38	2.40	2.39	2.14
$10^4 n_{t,i}/\text{mol}^g$	1.049	1.048	1.052	1.049	1.050	1.041	1.040	
pH_{ij}^h	-0.0163	-0.0243	-0.0422	-0.0432	-0.0541	-0.0598	-0.0705	
$10^4 n_{t,i}/\text{mol}^i$	1.050	1.043	1.053	1.047	1.053	1.037	1.034	1.032
k^j	0.9883	0.9803	0.9883	0.9838	0.9914	0.9814	0.9786	0.9716
E_0/mV^k	378.86	376.06	378.17	376.61	378.75	376.39	376.07	376.95
σ/mV^l	0.085	0.080	0.090	0.082	0.093	0.095	0.074	0.137
$E_0(\text{III})/\text{mV}^m$	381.65	380.69	381.03	380.43	380.78	380.46	380.76	383.50

^a $m^\circ = 1 \text{ mol kg}^{-1}$. ^bThe volume of titrant added. ^cThe measured EMF. ^dThe analytical amount of propionic acid. ^eThe stoichiometric dissociation constant determined by method shown (see text). ^fThe stoichiometric dissociation constant calculated by eqn. (9) with the recommended parameter values given in Table 5. ^gThe optimized amount of propionic acid used in the calculation of the pH errors for the tests of method I (see text). ^hLiquid-junction potential correction, see Appendix of Ref. 11, used in the calculation of the pH errors for the tests of method I (see text). ⁱThe optimized amount of propionic acid. It was determined by optimizing the least-squares fit of eqn. (8). ^jThe slope parameter obtained by the least-squares fit using eqn. (8). ^kThe intercept parameter obtained by the least-squares fit using eqn. (8). ^lThe standard deviation of residuals for the least-squares fit obtained by using eqn. (8). ^mThe value of parameter E_0 used in the calculation of the EMF errors for the tests of method III (see text). It was determined by requiring that the sum of all errors in each data set is zero.

Tables 1 and 3. The results obtained by the regression analysis with eqn. (8) are also presented in these tables. For each data set are given the optimized value of n_t and the values for parameters k and E_0 . To show the quality of the fits, the standard deviation of residuals, σ , and the standard deviation for k parameter, $\sigma(k)$, are also shown for each data set.

The k parameter obtained from the AcOH titration (Tables 1 and 3) was then used for the determination of K_m for PropOH from the results of each titration. This K_m and the glass electrode parameter E_0 were calculated by equations:

$$\sum_{i=1}^N (E_i - E_{\text{pred},i}) = 0 \quad (10)$$

$$\ln(x_i/m^\circ) = (E_i - E_0)F/(kRT) \quad (11)$$

$$K_{m,i} = x_i(x_i + m_{b,i})/\{(n_t/w_{1,i}) - m_{b,i} - x_i\}m^\circ \quad (12)$$

$$K_m = \sum_{i=1}^N K_{m,i}/N \quad (13)$$

$$m_{\text{H},i} = \{[(K_m m^\circ + m_{b,i})^2 + 4\{(n_t/w_{1,i}) - m_{b,i}\}K_m m^\circ]^{1/2} - (K_m m^\circ + m_{b,i})\}/2 \quad (14)$$

$$E_{\text{pred},i} = E_0 + (kRT/F) \ln(m_{\text{H},i}/m^\circ) \quad (15)$$

where N is the number of points in the data set considered. Additionally, the amount of propionic acid n_t was optimized by requiring that the following square sum S attains the minimum:

$$S = \sum_{i=1}^N (E_i - E_{\text{pred},i})^2 \quad (16)$$

Tables 2 and 4 show the K_m values obtained in this way

Table 5. Results of the regression analysis obtained by using Equation 17 and the ion parameters for the Hückel equation [eqn. (2)] in NaCl and KCl solutions at 298.15 K.

Ion	H ⁺	CH ₃ COO ⁻	CH ₃ CH ₂ COO ⁻
(10 ⁵ K _a) ^a		1.758 ^b	1.347 ^c
(pK _a) ^d		4.755	4.871
p[K _{a,I} (NaCl)] ^e			(4.865 ± 0.005) ^f
p[K _{a,II} (NaCl)] ^e			4.870 ± 0.004
p[K _{a,III} (NaCl)] ^e			4.873 ± 0.004
p[K _{a,I} (KCl)] ^e			(4.870 ± 0.005) ^f
p[K _{a,II} (KCl)] ^e			4.873 ± 0.006
p[K _{a,III} (KCl)] ^e			4.861 ± 0.004
B/(mol kg ⁻¹) ^{-1/2}	1.25 ^g	1.6 ^h	1.7 ⁱ
b _{NaCl}	0.238 ^g	0.189 ^h	0.189 ⁱ
b _{KCl}	0.178 ⁱ	0.308 ^j	0.308 ^k
b _{NaCl(I)'}			(0.10 ± 0.04) ^f
b _{NaCl(II)'}			0.18 ± 0.02
b _{NaCl(III)'}			0.15 ± 0.02
b _{KCl(I)'}			(0.27 ± 0.04) ^f
b _{KCl(II)'}			0.26 ± 0.03
b _{KCl(III)'}			0.30 ± 0.02

^aThe thermodynamic dissociation constant for the corresponding acid. ^bDetermined in Ref. 2 from the conductivity data measured by MacInnes and Shedlovsky.¹⁸ ^cDetermined in Ref. 4 from the conductivity data measured by Belcher.²⁰ ^dpK_a = -log K_a. ^eAn estimate of K_a for propionic acid, see also footnote d. It was determined from the K_m values of the method shown. The standard deviation for the estimate is also given. ^fThe K_m value for the strongest solution has been omitted from the regression analysis. ^gDetermined in Ref. 16 from Harned cell data. ^hDetermined in Ref. 2 from Harned cell data. ⁱDetermined in Ref. 4 from Harned cell data. ^jDetermined in Ref. 3 from Harned cell data. ^kA probable value on the basis of the activity-parameter analogy observed in Ref. 3. ^lb for propionate ions determined from the K_m values of the method shown. The standard deviation is also given.

for PropOH [denoted as K_m(II)] in NaCl and KCl solutions, respectively.

In the determination of the experimental K_m values for PropOH by method III, it was assumed that k=1 and the analytical amount of PropOH, n_{t,0} (shown in Tables 2 and 4), was used. To obtain good fits by this more approximate method, only the first 14 points in each data set (Tables 2 and 4) were included in the calculations. For this method, K_m was calculated by eqns. (10)–(15), where k=1 and n_t=n_{t,0}. The values obtained in this way [denoted as K_m(III)] are also shown in Tables 2 and 4.

The activity parameters were then determined from the experimental K_m values obtained by all three methods. For these determinations, the following equation can be derived from eqns. (2) and (3):

$$\ln K_m - \alpha(I_m)^{1/2} \times \{1/[1 + B_H(I_m)^{1/2}] + 1/[1 + B_{PropO}(I_m)^{1/2}]\} = y = \ln K_a - (b_H + b_{PropO})I_m/(m^\circ) \quad (17)$$

This equation represents an equation of a straight line y vs. I_m/(m^o). Parameter B_{PropO} can be optimized to obtain the best fit. In the case of all three methods, however,

the fit is not very sensitive to this parameter. It was assumed, therefore, that the value of this parameter is the same as that determined previously⁴ from the Harned cell data of Harned and Ehlers,¹⁹ i.e. B_{PropO}=1.7 (mol kg⁻¹)^{-1/2}. The results of the linear regression analysis with eqn. (17) from the K_m data obtained by methods I, II and III are shown in Table 5. In this table are also included the activity parameters determined previously^{2-4,16} from Harned cell data for AcOH and PropOH. The b parameter for PropO⁻ ions in KCl solutions was not previously determined, but the value shown in Table 5 (b_{PropO,KCl}=0.308) seems to be probable owing to the analogy observed previously for AcOH and PropOH in NaCl solutions⁴ and for acetic acid and other weak acids (especially for formic acid) in salt solutions^{3,4} (see Table 2 in Ref. 3).

Table 5 in this study shows that for PropOH methods I, II and III give the activity parameters that agree well with each other and that also agree within experimental error with those suggested on the basis of measurements on Harned cells. It seems to us that the most reliable values for B and b of PropO⁻ ions up to I_m of about 1 mol kg⁻¹ are those determined from the Harned cell data^{3,4} even though no measurements were performed in PropOH–KCl mixtures and the measurements in PropOH–NaCl mixtures (i.e. those of Harned and Ehlers)^{4,19} extended only up to I_m of 0.1 mol kg⁻¹. Therefore, the following Hückel parameters are here recommended for eqn. (2): B_{PropO}=1.7 (mol kg⁻¹)^{-1/2}, b_{PropO,NaCl}=0.189 and b_{PropO,KCl}=0.308.

The calculation methods used above give also estimates for the thermodynamic dissociation constant of PropOH. These estimates are shown in Table 5. All these estimates agree well with the thermodynamic value suggested in Ref. 4 for this acid (i.e. with K_a=1.347 × 10⁻⁵) on the basis of the conductivity measurements of Belcher.²⁰ According to this study, this value is also supported by potentiometric titration results.

The Hückel parameters recommended above and the calculation methods I, II and III are then further tested with the experimental data presented in Tables 2 and 4. Method I was used in the previous studies,^{2,5,11,16,21} and it can be tested with the PropOH data in the same way as previously. The predicted K_m values were calculated from the K_a value of 1.347 × 10⁻⁵ by eqn. (9) with the recommended activity parameters, and the values obtained are given for all data sets in Tables 2 and 4. These K_m values were then used to calculate the pH predictions. In these calculations, the liquid junction correction was also made (see Appendix of Ref. 11), and the optimum amount of PropOH was searched for each data set, and the resulting values of pH_l and n_t (denoted as n_{t,l}) are shown in the tables. The results of these tests were presented as error plots which correspond exactly to the error plots of, e.g., Fig. 2 in Ref. 5. The pattern of errors in the pH error plots drawn in this way is almost random for all data sets used in the determination of experimental K_m values by this method (for the KCl

sets the randomness is very near to perfect), and the pH errors in these plots are usually less than ± 0.003 .

In method II, the K_m values were above determined by allowing both glass-electrode parameters k and E_0 to vary from one data set to another. Also the amount of the acid (n_t) was slightly adjusted. To simplify the estimation problem, k was determined for each PropOH set from the data of a separate calibration titration (i.e. of an acetic acid titration) at the same ionic strength, see above. Method II was tested by means of the recommended K_m values, shown in Tables 2 and 4, by using eqn. (8). Parameters k and E_0 and the optimized value of n_t were determined for each PropOH data set. The method used in the determination was exactly the same as that used above for the AcOH data (Tables 1 and 3), and the values for the estimated parameters are shown in Tables 2 and 4. k was also adjusted in these calculations because it is not probable that it has exactly the same value as that obtained from the corresponding AcOH titration. The results of these calculations are also shown as error plots in Fig. 1. In this figure, the EMF error defined by

$$e_E = E(\text{measured}) - E(\text{predicted}) \quad (18)$$

is presented for each data set as a function of the added base volume. Graph A shows the results for NaCl solutions and graph B for KCl solutions. All error plots in these graphs are random and all errors are very small, and therefore the experimental data presented in Tables 2 and 4 support the calculation method and the activity parameters used well.

In method III, the K_m values were determined above by allowing only the glass electrode parameter E_0 to vary from one data set to another. In this method, the analytical amount of propionic acid ($n_{t,0}$) was used and parameter k was assumed to be unity. The experimental data in Tables 2 and 4 and the recommended K_m values were used to test this method in the following way. For each data set, the parameter E_0 was determined by using the following equations:

$$m_{H,i} = \frac{\{[(K_m m^\circ + m_{b,i})^2 + 4[(n_{t,0}/w_{1,i}) - m_{b,i}]K_m m^\circ]^{1/2} - (K_m m^\circ + m_{b,i})\}}{2} \quad (19)$$

$$E_{0,i} = E_i - (RT/F) \ln(m_{H,i}/m^\circ) \quad (20)$$

$$E_0 = \left(\sum_{i=1}^N E_{0,i} \right) / N \quad (21)$$

The resulting values for E_0 are included in Tables 2 and 4 [denoted as $E_0(\text{III})$]. The results of these calculations were presented as error plots. In these plots, the EMF errors [defined by eqn. (18)] were shown for each data set as a function of the added base volume. The error plots obtained for the NaCl solutions are shown as examples in Fig. 2. The error plots for the KCl solutions are very similar. The calculation method is approximate, and therefore all error plots are not completely random. The method is simple, and the calculations can be directly made from the experimental EMF data. The fact that

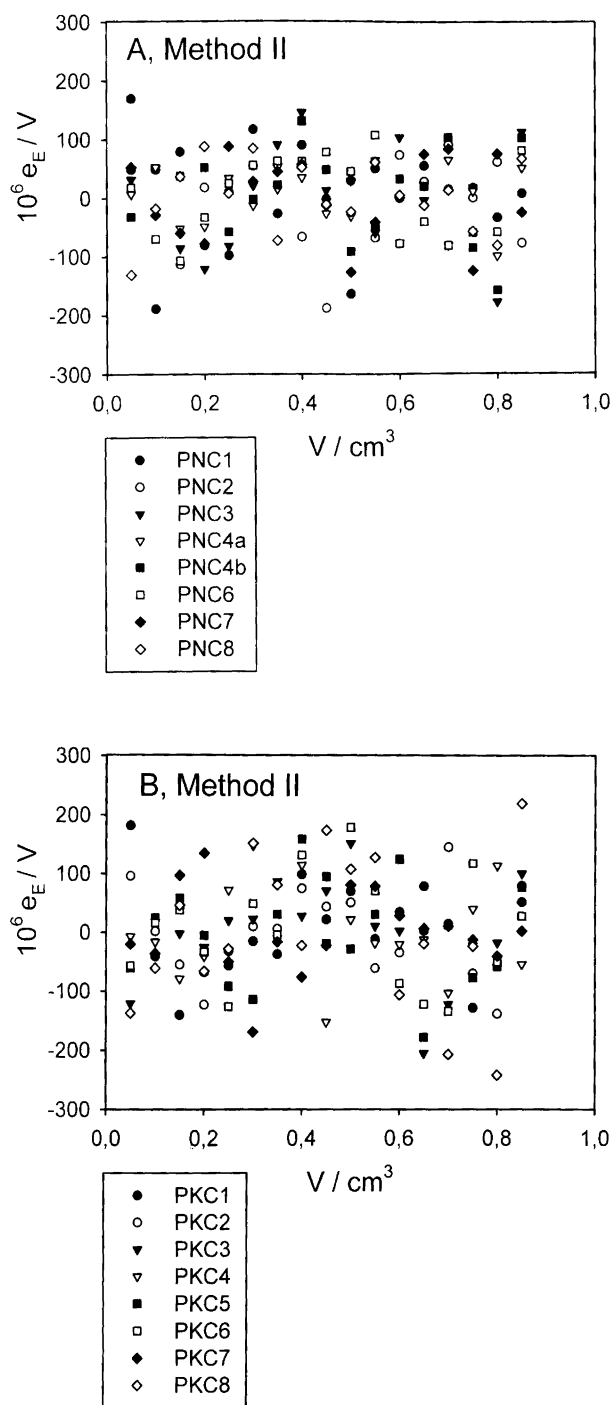


Fig. 1. The difference between the observed and predicted electromotive forces, e_E in eqn. (18), as a function of the titrant volume in the titrations of propionic acid by the base (NaOH or KOH) solution. Graph A shows the results of the titrations in NaCl solutions (series PNC) and graph B those in KCl solutions (PKC). The predicted EMF values were calculated by eqns. (5), (8) and (9) using the thermodynamic dissociation constant of 1.347×10^{-5} , the recommended activity parameters and the glass electrode parameters obtained by the regression analysis with eqn. (8); see method II in the text. Symbols of the different sets are shown in the legends of the graphs (Tables 2 and 4).

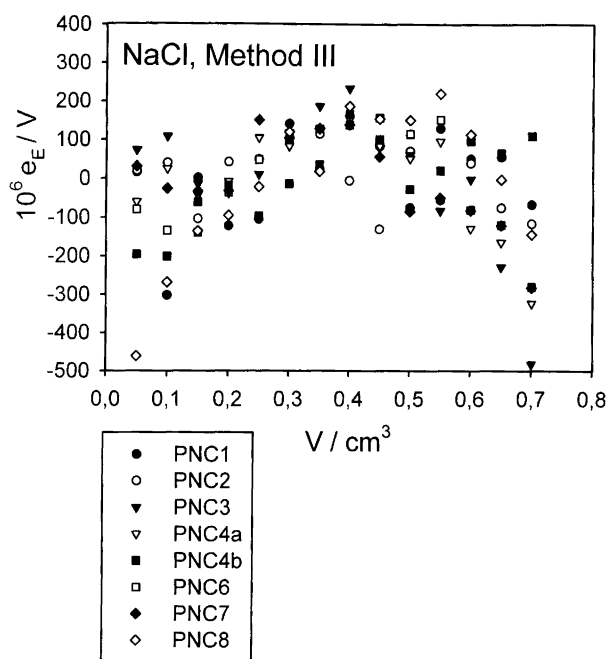


Fig. 2. The difference between the observed and predicted electromotive forces, e_E in eqn. (18), as a function of the titrant volume in the titrations of propionic acid in NaCl solutions by the base (NaOH) solution. The predicted EMF values were calculated by eqns. (5), (8) and (9) using the thermodynamic dissociation constant of 1.347×10^{-5} , the recommended activity parameters, the glass electrode parameter E_0 obtained by eqns. (19), (20) and (21) and the glass electrode parameter $k=1$; see method III in the text. Symbols of the different sets are shown in the legend of the figure (Table 2).

all errors are small (errors can be compared to the resolution of the meter which was 0.1 mV) supports that also this method applies satisfactorily to the determination of K_m for weak acids. However, the last titration points, where the amount of propionic acid has its largest influence on the EMF reading, had to be omitted from the calculations of the method.

In the present study, eqn. (9) is recommended for the calculation of stoichiometric dissociation constants of propionic acid in sodium and potassium chloride solutions at 298.15 K. For this equation, the following constants and parameter values were given above: $\alpha = 1.1744 \text{ (mol kg}^{-1}\text{)}^{-1/2}$, $K_a = 1.347 \times 10^{-5}$, $B_H = 1.25 \text{ (mol kg}^{-1}\text{)}^{-1/2}$, $B_A = 1.7 \text{ (mol kg}^{-1}\text{)}^{-1/2}$, $b_{H,NaCl} = 0.238$, $b_{H,KCl} = 0.178$, $b_{A,NaCl} = 0.189$ and $b_{A,KCl} = 0.308$, where H refers to the protons and A to the propionate ions. These equations apply up to an ionic strength of about 1 mol kg^{-1} . K_m at rounded ionic strengths for propionic acid in NaCl and KCl solutions is given in Table 6.

Conclusions

Potentiometric titrations of propionic acid were carried out in aqueous NaCl and KCl solutions at 298.15 K. In all solutions titrated, the molality of the salt was appre-

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

$I_m / (\text{mol kg}^{-1})^a$	$10^5 K_m (\text{NaCl})$	$10^5 K_m (\text{KCl})$
0	1.347	1.347
0.01	1.65	1.65
0.02	1.76	1.76
0.03	1.84	1.84
0.04	1.90	1.90
0.05	1.96	1.95
0.07	2.05	2.04
0.10	2.14	2.13
0.20	2.33	2.31
0.30	2.42	2.38
0.50	2.47	2.39
1.00	2.29	2.16

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

ciably larger than that of the acid, and salt molalities up to 1 mol kg^{-1} were used. From the titration data at different ionic strengths, stoichiometric dissociation constants for propionic acid were calculated. Three calculation methods were used and, as far as we know, only one of those has been previously presented. This method is based on the calibration of a pH meter by a procedure suggested by IUPAC,¹⁴ and K_m was determined from the experimental pH values by a method suggested in Ref. 11. In the other two calculation methods, the measured electromotive forces were directly used for the determination of K_m of propionic acid. In the first of those, the glass electrode parameters were partially determined from results of a calibration titration where acetic acid was titrated. K_m for acetic acid in NaCl and KCl solutions is accurately known on the basis of EMF results measured on appropriate galvanic cells without a liquid junction (i.e. on appropriate Harned cells).³ In the other new calculation method, a perfect Nernstian response for glass electrode was assumed. In this calculation method, however, the most basic titration points had to be omitted from the K_m determinations to obtain good fits.

All calculation methods used in this study give K_m values that are consistent with each other and also with those calculated from activity coefficient equations determined previously from Harned-cell results. The largest absolute difference between the experimental K_m values of all three methods and those obtained by the activity coefficient equations in Tables 2 and 4 is less than 0.027 when 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 well known monograph.²²

According to Table 6, the stoichiometric dissociation constant of propionic acid in NaCl and KCl solutions is a sensitive function of the ionic strength (as also observed previously³ for other light fatty acids), especially in the I_m range $0-0.1 \text{ mol kg}^{-1}$. 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 eqn. (9) in the present study]. The activity coefficients of the anions resulting from the different weak acids seem to be, in addition, rather close to each other in the salt solutions considered in this study and in previous studies.^{2–4}

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