

# Determination of the Molality Scale Dissociation Constants of Acetic Acid in Aqueous Sodium Chloride Solutions at 298.15 K

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Equations are presented for the calculation of the molality scale dissociation constants (i.e. the  $K_m$  values) of acetic acid in aqueous solutions at 298.15 K. These equations apply when the ionic strength of the acetic 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 Debye–Hückel theory. The experimental data used in the parameter estimation and in the tests of the resulting equations were mainly taken from the literature. In these data were included results of measurements on galvanic cells without a liquid junction and on conductivity cells. New experimental data used in the tests were obtained by potentiometric titrations. For these titrations, a recently developed method was used to estimate the correction for the imperfections existing in glass electrode cells including the unknown liquid junction potentials. It is shown that almost all data used in the tests can be interpreted within experimental error by means of the model used. These data include salt molalities up to 3.0 mol kg<sup>-1</sup> and acetic acid molalities up to 5.4 mol kg<sup>-1</sup>.

Acetic acid has played a central role in the history of the thermodynamics of weak acid solutions. In this field there exist two classical works, and in both of these the solutions of this acid were investigated. In one paper Harned and Ehlers<sup>1</sup> determined from the results of measurements on galvanic cells without a liquid junction the thermodynamic value of the dissociation constant ( $K_a$ ) of acetic acid at temperatures from 273.15 to 303.15 K. In the other paper<sup>2</sup> MacInnes and Shedlovsky determined  $K_a$  from the results of conductivity measurements at 298.15 K. In both papers the experimental techniques and the calculation methods were developed to their best level to obtain the  $K_a$  values as accurately as possible. At 298.15 K, the former method gave a value of  $1.754 \times 10^{-5}$  for this  $K_a$  and the latter method a value of  $1.753 \times 10^{-5}$ , and these values therefore agree very well with each other.

In a recent study<sup>3</sup> a two-parameter equation was used for the estimation of the activity coefficients of ions in aspartic acid solutions at 298.15 K. It was shown in that study that the experimental data support well the new calculation method. In the present study, the new equation for ionic activity coefficients is tested with experimental data obtained from acetic acid solutions. Besides

the two high-precision sets mentioned above, for these tests many of the sets reported by Harned and Robinson<sup>4</sup> and by Harned and Murphy<sup>5</sup> are also available. These sets have been measured by galvanic cells without a liquid junction and the solutions of those contained acetic acid and NaCl. In these two papers, ionic strengths up to a molality of 3.0 mol kg<sup>-1</sup> were investigated.

For the tests of the ionic activity coefficient equations, new experimental data were also measured by potentiometric titrations of acetic acid solutions in a glass electrode cell. The ionic strength of the solutions titrated was adjusted by NaCl. In these titrations, the proper response of the glass electrode to protons was ascertained by using ionic strengths less than 0.35 mol kg<sup>-1</sup>. The liquid junction potential problems and the other difficulties associated with the cells containing a liquid junction were here overcome by the method described in the previous study.<sup>3</sup>

## Experimental

The titrations of acetic acid were carried out essentially in the same way as described by Seymour *et al.*<sup>6</sup> and in previous papers.<sup>3,7</sup> Thus only a brief description of the

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procedure is given. The following solutions were prepared: 2.00 M NaCl, 0.010 M acetic acid, 0.100 M NaOH and two primary buffer solutions of NIST, i.e. 0.05 mol kg<sup>-1</sup> potassium hydrogen phthalate (pH 4.008) and 0.025 mol kg<sup>-1</sup> disodium hydrogen phosphate + 0.025 mol kg<sup>-1</sup> potassium dihydrogen phosphate (pH 6.865). From the NaCl solution, the following solutions were diluted for the titrations: 0.08, 0.16, 0.32 and 0.40 M. All solutions were prepared in reverse-osmosis filtered water (Millipore) with a conductivity less than 1.0 μS cm<sup>-1</sup>. The titration vessels were thermostatted during operations to 298.15 ± 0.15 K using a thermobath. A pH meter, type CG803, and a combined electrode, type N62, both from the Schottgeräte company, were used in the pH measurements. The titrated solutions were prepared by mixing 100 cm<sup>3</sup> of a diluted NaCl solution, 5.0 or 25.0 cm<sup>3</sup> of water and 10.0 cm<sup>3</sup> of the acetic acid solutions. Titrations were carried out by reading the pH after increments of 0.050 cm<sup>3</sup> of the base solution. The base solution was added by a dosimat, type 655, from the Metrohm company. At the end of the titration, pH was checked by one of the buffers. The readings of the meter were stable within 0.002 pH units during the work.

## Results

*Theoretical considerations.* In the present study, the following equation was used for the molal activity coefficient ( $\gamma$ ) of ion  $i$ :

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

where  $m^\circ = 1 \text{ mol kg}^{-1}$ ,  $z_i$  is the charge number of ion  $i$ , and  $\alpha = 1.17444 (\text{kg mol}^{-1})^{1/2}$ , see Archer and Wang.<sup>8</sup>  $B_i$  and  $b_i$  are parameters that are dependent in the cases studied here only on ion  $i$ . The composition variable in this equation is the molal ionic strength ( $I_m$ ). As in the previous study,<sup>3</sup> the following parameter values in eqn. (1) were used:  $B_{\text{H}} = B_{\text{Cl}} = 1.25 (\text{kg mol}^{-1})^{1/2}$  and  $b_{\text{H}} = b_{\text{Cl}} = 0.238$ , where  $\text{H} = \text{H}^+$  and  $\text{Cl} = \text{Cl}^-$ .

The dissociation equilibrium constant for the dissociation equilibrium of acetic acid is given by:

$$K_a = \gamma_{\text{H}} \gamma_{\text{A}} m_{\text{H}} m_{\text{A}} / (m^\circ m_{\text{HA}}) = \gamma_{\text{H}} \gamma_{\text{A}} K_m \quad (2)$$

where  $\text{A} = \text{A}^- = \text{CH}_3\text{COO}^-$ ,  $m_{\text{A}}$  is its molality, and it is assumed as usual that the activity coefficients of the neutral species HA ( $= \text{CH}_3\text{COOH}$ ) are unity.  $K_m$  in eqn. (2) is defined by

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

*Determination of  $K_a$ .* The classical conductivity measurements of MacInnes *et al.*<sup>2</sup> were made in pure and mainly very dilute acetic acid solutions. Therefore the results of these measurements seem to be the most reliable source to determine  $K_a$  for this acid. From each point measured

by these researchers, they calculated a value of  $K_c$ , defined by

$$K_c = c_{\text{H}} c_{\text{A}} / (c^\circ c_{\text{HA}}) \quad (4)$$

where  $c^\circ = 1 \text{ mol dm}^{-3}$ . From these  $K_c$  values, a  $K_m$  value was calculated for each point. In this calculation, the molalities for the species  $i$  were obtained from the concentrations given by MacInnes *et al.*<sup>2</sup> by the following equation:

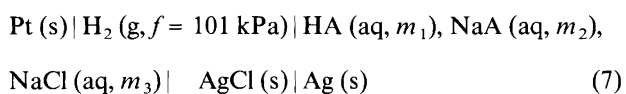
$$m_i = c_i / (\rho - M_{\text{HA}} c_i) \quad (5)$$

where  $\rho$  is the density of the solution,  $M_{\text{HA}}$  is the molar mass of acetic acid and  $c_i$  its total concentration. As in the original calculations,<sup>2</sup> it was observed that only the ten most dilute points of this conductivity set (i.e. only the points for which  $c_i < 0.1 \text{ mol dm}^{-3}$ ) could be included in the determination of  $K_a$ . For these points it is sufficient to assume in eqn. (5) that  $\rho = 0.997 \text{ g cm}^{-3}$ . By means of the resulting  $K_m$  values,  $K_a$  can be determined by the following extrapolation formula:

$$\ln K_m - 2\alpha m_i^{1/2} / [1 + B m_i^{1/2}] = y = \ln K_a + b m_i / m^\circ \quad (6)$$

where  $m_i$  is the molality of acetic acid as the ion form in the solutions studied [ $m_i = m_{\text{H}} = m_{\text{A}}$ ; the  $m_i$  values were calculated by eqn. (5) from the  $c_i$  values given by MacInnes *et al.*<sup>2</sup>]. Equation (6) represents straight-line equation, and  $K_a$  can be determined by linear regression analysis with this equation from the ten most dilute points of this set. In this determination, it was observed that the value of  $B$  in eqn. (6) is irrelevant when it is between 1.0 and 2.0 ( $\text{kg mol}^{-1})^{1/2}$ . By this regression analysis, a value of  $(1.758 \pm 0.001) \times 10^{-5}$  was obtained for  $K_a$  and 4.755 for  $\text{p}K_a$ .

*Determination of the activity parameters for acetate ions.* The most reliable value of  $B$  for acetate ions in eqn. (1) can probably be determined from the set of Harned and Ehlers<sup>1</sup> measured by cells of following type



where  $f$  is the fugacity of hydrogen. The electromotive force ( $E$ ) of cells of type (7) can be calculated by

$$E = E^\circ - (RT/F) \ln(\gamma_{\text{H}} \gamma_{\text{Cl}}) - (RT/F) \ln[m_{\text{H}} m_{\text{Cl}} / (m^\circ)^2] \quad (8)$$

where  $E^\circ$  is the value of the standard electromotive force and in this case  $m_{\text{Cl}} = m_3$ . For  $E^\circ$ , a value of 0.22250 V was used. This value was obtained in a previous paper<sup>9</sup> from the results measured by Harned and Ehlers<sup>1</sup> on hydrogen-silver chloride cells. From each EMF value measured by Harned and Ehlers on cells of type (7), an experimental value of  $K_m$  was obtained by requiring that the predicted EMF value is exactly the same one as that mea-

sured. The predicted value was calculated by eqn. (8).  $m_H$  for this equation was obtained by

$$m_H^2 + (K_m m^\circ + m_b) m_H + K_m (m_b - m_l) m^\circ = 0 \quad (9)$$

where in this case  $m_b = m_2$  and  $m_l = m_1 + m_2$ , and  $\gamma_H$  and  $\gamma_{Cl}$  were obtained by eqn. (1). In this way the following experimental  $K_m$  values were obtained: ( $I_m = 0.009517 m^\circ$ ,  $10^5 K_m = 2.140$ ), (0.024032, 2.323), (0.041758, 2.504), (0.097819, 2.806), (0.16096, 2.989) and (0.17995, 3.036). These values can then be predicted by means of eqns. (1) and (2) and the value of  $K_a = 1.758 \times 10^{-5}$ .  $B$  and  $b$  for acetate ions were searched by minimizing in this set the following sum of squared prediction errors:

$$S(K_m) = \sum_i e_i (K_m)^2 \quad (10)$$

where

$$e(K_m) = K_m (\text{observed}) - K_m (\text{predicted}) \quad (11)$$

In this way the following values were obtained for acetate ions:  $B = B_A = 1.6 (\text{kg mol}^{-1})^{1/2}$  and  $b = b_A = 0.189$ , and these values were used in the subsequent considerations.

*Tests for the activity parameters.* Above, the  $B$  and  $b$  parameters for acetate ions were determined from the EMF data of Harned and Ehlers.<sup>3</sup> By means of the new activity coefficient equation for acetate ions and the new  $K_a$  value for acetic acid, the experimental data of these researchers were predicted, and the results are shown as an error plot in Fig. 1. In this plot the errors, defined by

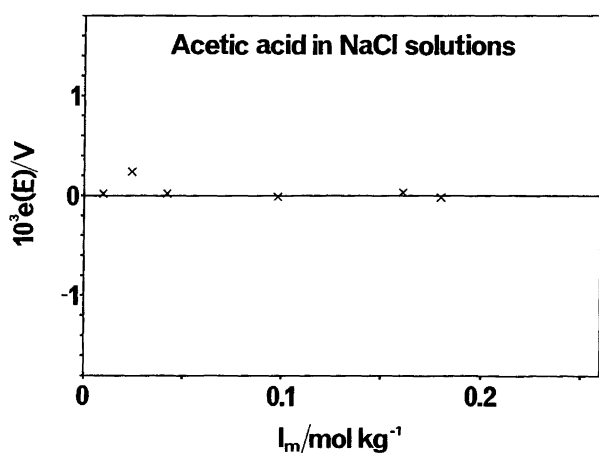
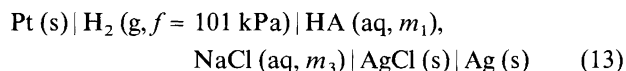


Fig. 1. The difference between the observed and predicted EMF values as a function of ionic strength in the set measured by Harned and Ehlers<sup>1</sup> on cells of type (7). The predicted values were calculated by means of eqns. (1), (2), (8) and (9) by using the following values for the parameters:  $E^\circ = 0.22250 \text{ V}$ ,  $K_a = 1.758 \times 10^{-5}$ ,  $B(\text{H}^+) = B(\text{Cl}^-) = 1.25 (\text{kg mol}^{-1})^{1/2}$ ,  $B(\text{CH}_3\text{COO}^-) = 1.6 (\text{kg mol}^{-1})^{1/2}$ ,  $b(\text{H}^+) = b(\text{Cl}^-) = 0.238$  and  $b(\text{CH}_3\text{COO}^-) = 0.189$ .

$$e(E) = E_m (\text{observed}) - E (\text{predicted}) \quad (12)$$

are presented as a function of  $I_m$ .

Harned *et al.*<sup>4,5</sup> have measured electromotive forces on cells of the following type:



These data can also be used in the tests of the activity parameters for acetic acid solutions. The latter of these papers contains a set of EMF measurements in NaCl solutions, and in this set  $m_1$  was  $0.2 m^\circ$ , and the former contains six sets where  $m_1$  varied from 0.1 to  $10.2 m^\circ$ . The experimental data of these seven sets are predicted by the calculation method tested. The results are shown as error plots in Fig. 2.

In this study, in addition, the activity parameters for acetic acid solutions were tested with new experimental data. As explained above, these data were obtained by potentiometric titrations of acetic acid solutions at the constant ionic strengths adjusted by NaCl. The titration data are presented in Table 1. As in the previous study,<sup>3</sup> these data were corrected for the errors associated with the liquid junction potentials. The correction method (i.e. the  $\text{pH}_{ij}$  correlation) is presented in the Appendix of the previous paper.<sup>3</sup>

In the titrations of Table 1, eqn. (9) is valid in all points. In this case,  $m_b$  is the molality of the base, NaOH, in the solution titrated and  $m_b = c_b V/w_1$ , where  $c_b$  is the

Table 1. Results of the titrations of acetic acid solutions with a base (NaOH) solution at the different ionic strength adjusted by sodium chloride

$I_m/\text{mol kg}^{-1}$	0.0699	0.1401	0.2388	0.2809	0.3511
$V^0/\text{cm}^3$					
	pH <sup>b</sup>	pH <sup>b</sup>	pH <sup>b</sup>	pH <sup>b</sup>	pH <sup>b</sup>
0.30		4.360	4.351	4.327	4.317
0.35	4.456	4.438	4.425	4.402	4.392
0.40	4.532	4.512	4.500	4.479	4.467
0.45	4.609	4.588	4.575	4.556	4.544
0.50	4.688	4.668	4.652	4.636	4.622
0.55	4.769	4.748	4.734	4.715	
0.60	4.855	4.833	4.817	4.800	4.788
0.65	4.945	4.925	4.907	4.891	4.877
0.70	5.042	5.023	5.006	4.989	4.976
0.75	5.152	5.133	5.118	5.102	5.086
0.80	5.278	5.262	5.246	5.230	5.217
$V_0/\text{cm}^3$ <sup>c</sup>	115	115	135	115	115
$10^5 K_m (\text{pred})$ <sup>d</sup>	2.680	2.941	3.129	3.175	3.226
$10^4 n_t/\text{mol}^\circ$ <sup>e</sup>	0.988	0.984	0.979	0.981	0.982
$10^3 \text{pH}_{ij}$ <sup>f</sup>	-35.7	-44.9	-63.6	-69.5	-78.5

<sup>a</sup>  $V$  is the volume of the titrant added. <sup>b</sup> pH means the measured pH value. <sup>c</sup>  $V_0$  is the initial volume of the solution titrated. <sup>d</sup> Calculated by eqns. (1) and (2) with  $K_a = 1.758 \times 10^{-5}$  and with the new values for the ionic parameters. <sup>e</sup> The amount of acetic acid in the titration vessel. <sup>f</sup> The liquid junction potential correction, see Appendix in Ref. 3.

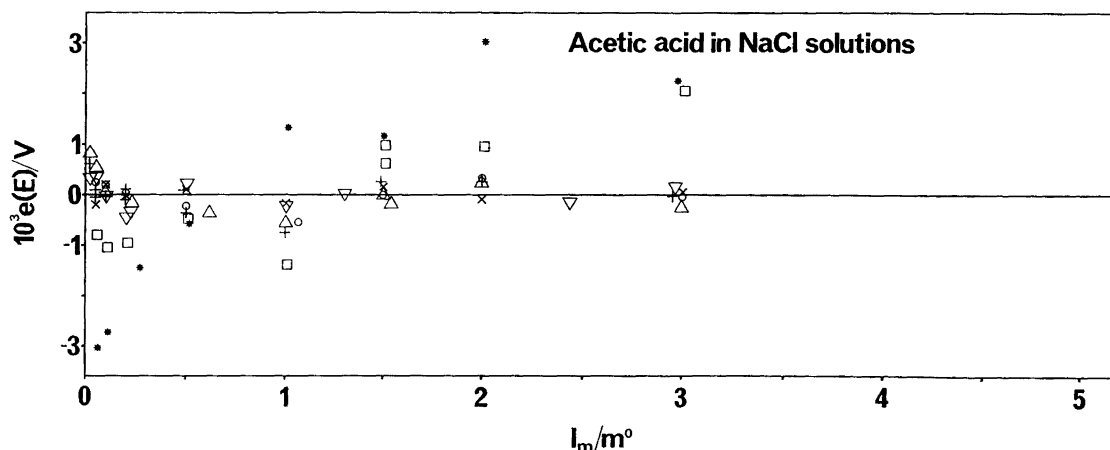


Fig. 2. The difference between the observed and predicted EMF values as a function of ionic strength in the sets measured by Harned and Robinson<sup>4</sup> and Harned and Murphy<sup>5</sup> on cells of type (13). The predicted values were calculated by eqns. (1), (2), (8) and (9). In the calculation, the parameter values given in Fig. 1 were used except that the values of  $E^\circ$  were adjusted. The following symbols and  $E^\circ$  values are used: Harned and Murphy: ( $m_1 = 0.2 m^\circ$ ,  $E^\circ = 0.22150$  V,  $\times$ ); Harned and Robinson: (0.1, 0.22211, +), (0.2, 0.22137,  $\circ$ ), (0.52, 0.22047,  $\Delta$ ), (1.00, 0.21929,  $\nabla$ ), (5.40, 0.20868,  $\square$ ), (10.2, 0.19853, \*).

concentration of the NaOH solution used as the titrant,  $V$  is the volume of this solution added in the titration and  $w_1$  is the mass of water in the solution titrated. In eqn. (9), in addition,  $m_t$  is the total molality of acetic acid in the solution titrated.

In the present tests, the  $K_m$  values for each ionic strength were first calculated by eqns. (1) and (2) with the value of  $K_a = 1.758 \times 10^{-5}$ . These predicted  $K_m$  values are shown in Table 1. Then the value of pH(predicted) for each point in the titration at this  $I_m$  was calculated by

$$\text{pH (predicted)} = -\log(\gamma_H m_H / m^\circ) \quad (14)$$

and for this equation  $\gamma_H$  by eqn. (1) and  $m_H$  by eqn. (9). The correction of  $\text{pH}_{ij}$  was also made for the predicted set, and the resulting value is shown in the table. In each titration, the exact amount of acetic acid ( $n_t$ ) was estimated by means of eqn. (A6) in the appendix in Ref. 3. The results of the tests with these titration data are shown as error plots in Fig. 3. In these plots the errors, defined by

$$e(\text{pH}) = \text{pH (corrected)} - \text{pH (predicted)} \quad (15)$$

are presented at each ionic strength as a function of the volume of the titrant added.

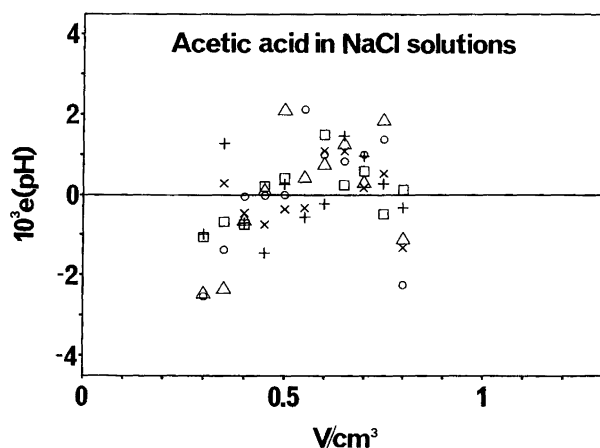


Fig. 3. The difference between the observed and predicted pH values as a function of the titrant volume in the titrations of acetic acid solutions. The observed pH values have been corrected as described in the Appendix of Ref. 3, and the predicted pH values were calculated by eqns. (1), (2), (9) and (14) with the parameter values given in Fig. 1. Symbols for the ionic strengths ( $I_m / \text{mol kg}^{-1}$ ) of the titrations are as follows:  $\times$ , 0.0699; +, 0.1401;  $\circ$ , 0.2388;  $\Delta$ , 0.2809;  $\square$ , 0.3511.

## Discussion

Above, the thermodynamic value of the dissociation constant of acetic acid was determined from the conductivity measurements of MacInnes *et al.*<sup>2</sup> The value of  $K_a$  presented by these researchers for this acid at the concentration scale ( $1.753 \times 10^{-5}$ ) agrees completely with the value obtained here when it is converted to the molality scale.

The  $B$  and  $b$  parameters for acetate ions in eqn. (1) were determined above from the EMF measurements of Harned and Ehlers.<sup>1</sup> According to Fig. 1, five points of this set can be explained within 0.05 mV by the resulting model. For the point where  $I_m = 0.024032 m^\circ$ , the error is 0.24 mV, and therefore this point also supports satisfactorily the calculation method used.

The EMF values are given in the sets of Harned and Murphy<sup>5</sup> with a precision of 0.01 mV, and in those of Harned and Robinson<sup>4</sup> the precision is 0.1 mV. Accord-

ing to Fig. 2 these experimental data, covering a wide range of acetic acid and salt molalities, support strongly the new activity coefficient formulas for ions in aqueous mixtures of CH<sub>3</sub>COOH and NaCl solutions. Only at an acetic acid molality of 10.2 *m*<sup>o</sup>, can some clear trends be recognized in the error plot, and even in this case all errors are less than about 3.0 mV. The new activity coefficient equations apply well to the extrapolation of the thermodynamic data: the strongest solution used in the parameter estimation of this study has an ionic strength that is less than 0.2 *m*<sup>o</sup> (see above), and according to this figure the resulting equations apply within experimental error up to three molal solutions. The agreement observed in this figure in the concentrated solutions, too, is very good in the light of the medium effect resulting from the presence of a large amount of undissociated acetic acid. The medium effect can be included in the model simply by adjusting the value of *E*<sup>o</sup> in eqn. (8). The *E*<sup>o</sup> values for the different sets are shown in the caption of Fig. 2. In addition, the relationship between *E*<sup>o</sup> and the total molality (*m*<sub>t</sub>) of acetic acid seems to be approximately linear.

The error plots obtained from the potentiometric results of Table 1 also support, according to Fig. 3, the new ionic activity coefficient equations. In the figure, the pH values predicted by the tested model always agree with the experimental pH values within 0.003, and in most cases the errors form a random pattern.

It is also interesting to compare the results of the present calculations with those obtained by the other methods presented in the literature for the treatment of the weak acid results. Probably the most well known of these methods are those of Pitzer<sup>10</sup> and of Guggenheim and Turgeon.<sup>11</sup> As far as we know, all necessary parameter values are, unfortunately, not available for the tests of the Pitzer method by acetic acid results. Therefore the new calculation method is compared only to that of Guggenheim and Turgeon. According to the specific interaction theory of these researchers, the following equation can be presented for the mean activity coefficient of a uni-univalent electrolyte RX (R is the cation and X is the anion) in aqueous mixtures of electrolytes:

$$\ln \gamma_{\pm}(\text{RX}) = -\alpha I_m^{1/2} / [1 + B_{\text{RX}}(I_m)^{1/2}] + \sum_{X'} [(\beta_{\text{RX}X'}) (m_{X'}) / m^o] + \sum_{R'} [(\beta_{R'X}) (m_{R'}) / m^o] \quad (16)$$

where it is additionally assumed for each electrolyte that  $B_{\text{RX}} = 1.0 \text{ (kg mol}^{-1}\text{)}^{1/2}$  and where  $\beta$  is a parameter that depends on the electrolyte. This equation can be tested with the experimental data measured by Harned and Ehlers<sup>1</sup> on cells of the type (7). When eqn. (16) is used for the activity coefficients, the following equation can be derived from eqn. (8) for these cells:

$$E = E^o - (RT/F) \ln [(m_1 - m_{\text{H}}) / (m_2 + m_{\text{H}})] - (RT/F) \ln (m_3 / m^o) - (RT/F) \ln K_a - (2RT/F)(\beta_{\text{NaCl}} - \beta_{\text{NaA}})(m_2 + m_3) / m^o \quad (17)$$

The predictions of this equation were compared to the experimental EMF values of Harned and Ehlers.<sup>1</sup> These predictions were calculated by using the following  $\beta$  values given by Guggenheim and Turgeon:<sup>11</sup>  $\beta_{\text{NaA}} = 0.23$  and  $\beta_{\text{NaCl}} = 0.15$ . In this calculation additionally the following values were used:  $E^o = 0.22250 \text{ V}$  and  $K_a = 1.758 \times 10^{-5}$ ; and  $m_{\text{H}}$  was calculated by  $m_{\text{H}} = K_a m_1 m^o / m_2$ , i.e. in the same way as suggested by these researchers. The errors for the different points of Harned and Ehlers are the following:  $[m_2 + m_3 = 0.009495 \text{ m}^o, e(E) = +0.08 \text{ mV}]$ ,  $(0.024008, +0.30)$ ,  $(0.041732, +0.08)$ ,  $(0.097779, -0.03)$ ,  $(0.16093, -0.13)$  and  $(0.17992, -0.24)$ . The model of Guggenheim and Turgeon explains the results of these dilute solutions satisfactorily but probably not within experimental error. As shown in Fig. 1, the new model applies better to these data. In addition, the specific interaction theory tested does not suggest any method for the evaluation of the  $K_m$  values for acetic acid at the different ionic strengths. It has been previously observed, in addition, that  $B_{\text{RX}}$  in eqn. (16) must be regarded in high-precision work as electrolyte dependent even in solutions of single electrolytes (see for example Refs. 9 and 12).

In analytical chemistry, the concentration constants of weak acids [i.e. the quantities similar to those as  $K_m$  or  $K_c$  defined by eqn. (3) or (4)] are in a common use. In the present study, the following parameter values in eqn. (1) were used in aqueous mixtures of CH<sub>3</sub>COOH and NaCl at 298.15 K:  $B(\text{H}^+) = B(\text{Cl}^-) = 1.25 \text{ (kg mol}^{-1}\text{)}^{1/2}$ ,  $b(\text{H}^+) = b(\text{Cl}^-) = 0.238$ ,  $B(\text{CH}_3\text{COO}^-) = 1.6 \text{ (kg mol}^{-1}\text{)}^{1/2}$  and  $b(\text{CH}_3\text{COO}^-) = 0.189$ . In addition, the value of  $1.758 \times 10^{-5}$  was obtained for  $K_a$  of this acid. With the simple set of equations containing these parameter values, the  $K_m$  values for acetic acid can reliably be calculated at least up to an ionic strength of 0.5 mol kg<sup>-1</sup> if this ionic strength is adjusted by NaCl. For practical calculations, these equations can be used in dilute solutions of other electrolytes, too. According to the experimental data of Harned and Robinson<sup>4</sup> measured by cells of type (13) in which NaCl was replaced by KCl, LiCl or BaCl<sub>2</sub>, these activity coefficient equations seem to apply satisfactorily up to ionic strengths of 0.2 mol kg<sup>-1</sup> in KCl or BaCl<sub>2</sub> solutions, but in LiCl solutions the limit of applicability of these equations is smaller than 0.05 mol kg<sup>-1</sup>.

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