Determination of the Thermodynamic Values of the First and Second Dissociation Constants of Aspartic Acid in Aqueous Solutions at 298.15 K by Means of Formulas for Ionic Activity Coefficients

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A simple equation originating from the Debye–Hückel theory was used for activity coefficients of ionic species in thermodynamical studies of acidic solutions of aspartic acid at 298.15 K. The thermodynamic dissociation constants of this acid and the two ionic parameters for this equation were determined from experimental results of galvanic cells with and without a liquid junction. Of the cells of the latter type, those containing a hydrogen and a silver–silver chloride electrode in solutions of this acid were used. The experimental data for these cells were taken from the literature. Of the cells with a liquid junction, those containing a glass electrode were used, and for these cells the experimental data were measured by potentiometric titrations of aspartic acid solutions at several constant ionic strengths. The estimated dissociation constants and parameter values were tested with all electrochemical data found in the literature for this purpose. It is shown that almost all data used in the tests can be interpreted within experimental error by means of the new dissociation constants and ionic activity coefficient formulas. These data include ionic strengths up to a molality of 0.4 mol kg^{-1}. The thermodynamic values for the dissociation constants determined here (i.e. the values of $K_{a,1} = 0.0102$ and $K_{a,2} = 0.000\,130$) also agree quite well with the values suggested previously in the literature. For the potentiometric titrations, a new method was used to estimate the correction of the imperfections in the glass electrode cells including the unknown liquid junction potentials.

The most accurate values for the thermodynamic dissociation constants (K_a) of weak acids in aqueous solutions have been probably determined either by electromotive force (EMF) measurements on cells without a liquid junction or by conductivity measurements. The former method was developed to a high precision by Harned and Ehlers[1] and the latter by MacInnes and Shedlovsky.[2] In these pioneering studies, the solutions of acetic acid were investigated, and both methods gave at 298.15 K the same value of K_a for this acid. Later a large amount of experimental work has been especially done by the EMF method, and this work has resulted in the K_a values suggested for different weak acids in the critical tables (see, e.g., Ref. 3).

When the K_a values are solved from results of galvanic or conductivity cells, the ionic activity coefficients cause serious difficulties in these determinations because they

are not accessible by purely thermodynamical methods. However, these problems can be partially avoided by using an appropriate extrapolation procedure. In a typical procedure of this kind, the values of a quantity K are calculated by an expression similar to that of K_a, and the values of some derived quantity (y) of K are presented as a function of the ionic strength (I) for the solutions studied. The quantities K and y are so selected that they are directly obtainable from the experimental data and that K_a can be easily determined from the intercept of the extrapolation line with the y-axis. The extrapolation gives in this case the value of K_a, owing to the solute convention for activity coefficients according to which these coefficients are unity at the y-axis where $I = 0$. Also a procedure of this kind is affected by the unknown ionic activity coefficients: to obtain a straight extrapolation line a model is needed for these coefficients.

According to the Debye–Hückel theory for the dilute electrolyte solutions, the only composition variable re-

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quired in the calculation of ionic activity coefficients is the total ionic strength I. In the literature is also available a great amount of experimental evidence that the factor containing the activity coefficients in the expression of K_a remains constant when I is fixed. In analytical chemistry especially, the concept of a 'concentration constant' K (often the symbol is K_c or K_m depending on whether the concentration or the molality scale is used) is in common use. According to the definition, this quantity includes only the composition variable factor in the expression of K_a, and it is often observed (as the Debye–Hückel theory suggests) that K, indeed, remains constant at a fixed ionic strength. In more concentrated solutions, it is also well known that the characteristics of the electrolyte used to adjust the ionic strength have an influence on K.

As mentioned above, the activity coefficients for a certain ion cannot be obtained from the experimental thermodynamic data without some extra assumption. In the literature there are not many studies in which activity coefficients for ions are proposed; see, however, for example Bates and Guggenheim[4] and Lito *et al.*[5] In the present study ionic activity coefficients are also used. In a recent study[6] a two-parameter equation for the activity coefficients of ions in aqueous solutions at 298.15 K was introduced, and the parameters for this equation were determined for acidic solutions of formic acid, glycine and glutamic acid. This equation was used here in the treatment of aspartic acid solutions. The thermodynamical value of the first dissociation constant $(K_{a,1})$ of this acid was determined from the EMF measurements of Smith and Smith[7] on galvanic cells without a liquid junction, and the determination of $K_{a,2}$ was based on new experimental data obtained by potentiometric titrations. The new K_a-values and the activity parameters resulting from the determination of these values were tested with pertinent data found in the literature. Almost all data used in these tests can probably be predicted within experimental error up to a molality of 0.4 mol kg^{-1} by means of the K_a-values and the activity coefficient formulas determined here or in the recent study.[6]

Like glutamic acid, aspartic acid is also one of those 20 amino acids which are the constituents of proteins in living organisms. Therefore, the results of the present study also have biochemical significance.

Experimental

The titrations of aspartic acid solutions were carried out essentially in the same way as described by Seymour and Fernando[8] and in a previous paper.[9] Thus only a brief description of the procedure used is sufficient. The following solutions were prepared: titrant solutions (NaOH and HCl; the concentration of both solutions was 0.100 mol dm^{-3}), two primary buffer solutions (i.e. 0.05 molal potassium hydrogen phthalate and 0.025 molal disodium hydrogen phosphate + 0.025 molal potassium dihydrogen phosphate), an aspartic acid solution

(0.010 mol dm^{-3}) and a KCl solution (2.00 mol dm^{-3}). Into six 100 cm^3 volumetric flasks was prepared a series of KCl solutions the ionic strengths of which were 0.080, 0.160, 0.240, 0.320, 0.400 and 0.500 mol dm^{-3}. These flasks were emptied into the titration vessels, all empty flasks were rinsed with a 25.00 cm^3 aliquot of pure water, and the rinsing waters were added into the titration vessels. Lastly into each vessel was added an aliquot of 10.00 cm^3 of the aspartic acid solution. The pH of the titrated solution was measured by a CG803 pH meter and an N62 combination electrode, both manufactured by Schottgeräte. The pH meter was calibrated by the buffers, using in the calibration a procedure called by Covington *et al.*[10] the bracketting procedure. The titration vessels and the buffers were thermostatted during the operations to a temperature of 298.15 ± 0.15 K. Two series of aspartic acid solutions were titrated: one by using the NaOH solution and the other by using the HCl solution. The titrant was added in increments of 0.05 cm^3 by a 655 Dosimat (Metrohm).

Results

Equation for ionic activity coefficients. In the present study, the following equation was used for the molal activity coefficient (γ) of ion i:

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

where $m° = 1$ mol kg^{-1} and z_i is the charge number of ion i. The first term in this equation results from the Debye–Hückel theory and the second term is an empirical correction term. In the Debye–Hückel term $\alpha = 1.17444$ (kg mol^{-1})$^{1/2}$ and $B_i = \beta a_i^*$ where $\beta = 3.2849$ (kg mol^{-1})$^{1/2}$ nm^{-1} and a_i^* is the ion size parameter; for the numerical values above, see Archer and Wang.[11] Like B_i, also b_i in the empirical correction term is a parameter that is dependent on ion i. As the composition variable in this equation is the molal ionic strength (I_m), defined by

$$I_m = (1/2) \sum_i (z_i^2 m_i) \qquad (2)$$

where i includes all ions in the solution. In the previous study,[6] the following parameter values in eqn. (1) were obtained: $B(H^+) = B(Cl^-) = 1.25$ (kg mol^{-1})$^{1/2}$ and $b(H^+) = b(Cl^-) = 0.238$.

Determination of the second dissociation constant. The titration data of the aspartic acid solutions are presented in Tables 1 and 2. Table 1 contains the results of the base titrations and Table 2 those of the acid titrations. From the results of the potentiometric titrations, $K_{a,2}$ of aspartic acid was first determined. $K_{a,1}$ of this acid is so large that the titration data do not provide sufficient information from the first dissociation such that this value could also be determined accurately from these data. In the estimation of $K_{a,2}$, the titration data were corrected for the dif-

Table 1. Results of the titrations of aspartic acid solutions with a base (NaOH) solution.

I_m/mol kg^{-1}: V^a	0.0596 pH^b	0.1193 pH^b	0.1792 pH^b	0.2393 pH^b	0.2997 pH^b	0.3755 pH^b
0	3.603		3.599	3.603	3.602	3.597
0.05	3.638	3.636	3.633	3.636	3.636	3.630
0.10	3.674	3.671	3.668	3.671	3.671	3.663
0.15	3.712	3.709	3.704	3.707	3.707	3.699
0.20	3.752	3.748	3.743	3.745	3.745	3.737
0.25	3.794	3.790	3.783	3.786	3.786	3.778
0.30	3.838	3.834	3.826	3.829	3.828	3.820
0.35	3.884	3.880	3.871	3.874	3.873	3.865
0.40	3.934	3.929	3.919	3.923	3.921	3.913
0.45	3.987	3.981	3.971	3.974	3.973	3.964
0.50	4.044	4.037	4.027	4.029	4.029	4.019
0.55	4.105	4.098	4.087	4.089	4.090	4.078
0.60	4.171	4.165	4.153	4.155	4.157	4.143
0.65	4.245	4.239	4.227	4.228	4.232	4.216
0.70	4.328	4.324	4.311	4.311	4.317	4.299
0.75	4.425	4.423	4.408	4.406	4.416	4.395
0.80	4.541	4.541	4.524	4.523		4.511
$10^4 K_{m,2}$ (obsd)^c	1.90	2.07	2.16	2.20	2.30	2.30
$10^4 K_{m,2}$ (pred)^d	1.897	2.065	2.164	2.228	2.271	2.305
$10^4 n_t$/mol^e	0.988	0.981	0.985	0.986	0.976	0.986
10^3 pH$_{lj}^f$	−38.7	−48.9	−55.2	−52.6	−58.6	−61.5
$10^3 s_0^g$	0.57	0.58	0.58	0.75	0.82	0.57

^{a} V is the volume of the titrant added. ^{b} pH means the pH (measured) value in the text. ^{c} Obtained by minimization of the square sum defined in eqn. (A6). ^{d} Calculated by eqns. (1) and (6) with the new value of $K_{a,2}$. ^{e} The amount of aspartic acid in the titration vessel. ^{f} The liquid junction potential correction, see text. ^{g} The standard deviation of residuals, defined by means of S in eqn. (A6) according to $s_0 = [S/(N-2)]^{1/2}$, where N is the number of points in the set in question.

ference between the liquid junction potentials in the solutions titrated and those used in the calibration of the pH meter. The correction method is presented in the Appendix.

The dissociation equilibria existing in acidic solutions of aspartic acid are as follows:

$$H_3A^+ \rightleftharpoons H^+ + H_2A \tag{3}$$

$$H_2A \rightleftharpoons H^+ + HA^- \tag{4}$$

where H_2A indicates a neutral aspartic acid molecule (or a zwitterion) and so on. The equilibrium constants for these reactions are given by the following equations:

$$K_{a,1} = a(H^+)a(H_2A)/a(H_3A^+)$$
$$= [\gamma(H^+)/\gamma(H_3A^+)]m(H^+)m(H_2A)/$$
$$[m^\circ m(H_3A^+)] = [\gamma(H^+)/\gamma(H_3A^+)]K_{m,1} \tag{5}$$

$$K_{a,2} = a(H^+)a(HA^-)/a(H_2A)$$
$$= \gamma(H^+)\gamma(HA^-)m(H^+)m(HA^-)/[m(H_2A)m^\circ]$$
$$= \gamma(H^+)\gamma(HA^-)K_{m,2} \tag{6}$$

where it is assumed (as usually) that the activity coefficients of the neutral species H_2A are unity at all ionic strengths under consideration and where

$$K_{m,1} = m(H^+)m(H_2A)/[m(H_3A^+)m^\circ] \tag{7}$$

$$K_{m,2} = m(H^+)m(HA^-)/[m(H_2A)m^\circ] \tag{8}$$

The following equation can be derived on the basis of the equation for the material balance for aspartic acid and of the equation electroneutrality:

$$m(H^+)^3 + (m_t + K_{m,1}m^\circ + m)m(H^+)^2$$
$$+ K_{m,1}m^\circ(K_{m,2}m^\circ + m)m(H^+)$$
$$+ K_{m,1}K_{m,2}(m^\circ)^2(m - m_t) = 0 \tag{9}$$

In eqn. (9) in the case of the base titrations, $m (= m_b)$ is the molality of the base, NaOH, in the solution titrated and $m_b = c_b V/w_1$, where c_b is the 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 the case of the acid titrations, $-m (= m_a)$ is the molality of the acid, HCl, in the solution titrated and $m_a = c_a V/w_1$, where c_a is the concentration of the HCl solution used as the titrant. The initial mass of water [$= w_1$(initial)] in the solution titrated was calculated by means of the density of this solution and by assuming that it contains KCl as the only solute. During the titration, w_1 was calculated by $w_1 = w_1$(initial) $+ \rho_1 V$, where it is sufficient to assume that

$\rho_1 = 1.00$ g cm^{-3}. In eqn. (9), in addition, m_t is the total molality of aspartic acid in the solution titrated and $m_t = n_t/w_1$, where n_t is the amount of aspartic acid in this solution. The ionic strength for each titration was obtained by $I_m = n_s/w_1$(initial), where n_s is the amount of KCl in the solution titrated.

Equation (9) is a polynomial of the third degree in $m(H^+)$, and in the subsequent calculations $m(H^+)$ had to be determined by this polynomial from each titration point using the given values of $K_{m,1}$ and $K_{m,2}$. It was determined numerically by the Newton–Raphson method.

To obtain the value of $K_{a,2}$ for aspartic acid, a value of $K_{m,2}$ was first determined from the results of each base titration set by the following method. In these determinations it was assumed that $K_{m,1}$ is 0.01 in all ionic strengths under consideration. This assumption was verified below by the galvanic cell results of Smith et al.[7] The value of $K_{m,2}$ for a certain ionic strength was obtained by searching the minimum of the square sum defined in eqn. (A6) (see Appendix), where thus the liquid junction correction pH_{lj} has been taken into account. The value of pH(predicted) for each point of the titration at this I_m was calculated by

$$pH(predicted) = -\log[\gamma(H^+)m(H^+)/(m^\circ)] \qquad (10)$$

Table 2. Results of the titrations of aspartic acid solutions with an acid (HCl) solution.

I_m/mol kg^{-1}:	0.0596	0.2393	0.3755
V^a/cm^3	pH^b	pH^b	pH^b
0	3.613	3.604	3.599
0.05	3.579	3.572	3.567
0.10	3.547	3.543	3.538
0.15	3.516	3.513	3.508
0.20	3.487	3.486	3.482
0.25	3.459	3.459	3.454
0.30	3.433	3.432	3.430
0.35	3.406	3.408	3.404
0.40	3.382	3.382	3.379
0.50	3.335	3.337	3.335
0.55	3.311	3.316	3.315
0.60	3.291	3.296	3.292
0.65	3.269	3.276	3.272
0.70	3.250	3.255	3.253
0.75	3.231	3.238	3.233
0.80	3.211	3.220	3.216
0.85	3.194	3.203	3.199
0.90	3.175	3.184	3.182
0.95	3.160	3.167	3.165
1.00	3.143	3.152	3.150
1.05	3.128	3.136	3.135
1.10	3.111	3.121	3.120
1.15	3.096	3.106	3.106
1.20	3.082	3.091	3.091
$10^4 K_{m,2}$ (pred)^c	1.897	2.228	2.305
$10^4 n_t$/mol^d	0.98	0.975	0.975
$10^3 pH_{lj}{}^e$	-32.0	-54.0	-60.7

$^{a-e}$ See notes in Table 1.

and for this equation $\gamma(H^+)$ by eqn. (1) and $m(H^+)$ by eqn. (9). The amount of aspartic acid (n_t) was also used as an adjustable parameter in the evaluation of $K_{m,2}$. The accurate determination of the amount of the acid is especially required by the most basic titration points in each titration. The experimental values of $K_{m,2}$ determined by this method [i.e. the $K_{m,2}$(obsd) values] are shown in Table 1.

The experimental values of $K_{m,2}$ were used in the determination of $K_{a,2}$ for aspartic acid. For this purpose, the following equation can be derived from eqn. (6):

$$\ln K_{m,2} - \alpha(I_m)^{1/2}/[1 + B(H^+)(I_m)^{1/2}] - \alpha(I_m)^{1/2}/$$
$$[1 + B(HA^-)(I_m)^{1/2}] = y$$
$$= \ln K_{a,2} - [b(H^+) + b(HA^-)]I_m/m^\circ \qquad (11)$$

If the left-hand side of this equation (y) is presented as a function of the quantity (I_m/m°), a straight line is obtained. The slope of the straight line is $-[b(H^+) + b(HA^-)]$ and from the intercept of this line with the y-axis $K_{a,2}$ can be solved. This straight line was most reliably determined by the method of least squares. The unknown quantity $B(HA^-)$ in y was determined by minimizing the square sum of the residuals of this regression line when $B(HA^-)$ was varied. By means of the $K_{m,2}$(obsd) values in Table 1, the best value of 2.5 (kg mol^{-1})$^{1/2}$ was obtained for B of hydrogen aspartate ions in eqn. (1), and the corresponding straight line of eqn. (11) is

$$y = -8.949 - 0.315 I_m/m^\circ \qquad (12)$$

From this equation, the results of $K_{a,2} = 1.30 \times 10^{-4}$ and of $b(HA^-) = 0.077$ can be deduced.

Determination of the first dissociation constant. In the evaluation of $K_{a,2}$ for aspartic acid, it was assumed above that $K_{m,1}$ for this acid is 0.01 in all solutions studied. This assumption can be tested with the experimental data measured by Smith et al.[7] on cells of the type

$$Pt(s) \mid H_2(g, f = 101 \text{ kPa}) \mid HCl(aq, m_1),$$
$$H_2A(aq, m_2) \mid AgCl(s) \mid Ag(s) \qquad (13)$$
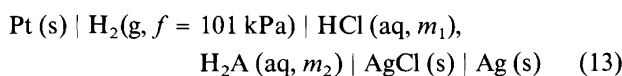
where f is the fugacity of hydrogen and where H_2A denotes (as earlier) aspartic acid. The analytical molality of this acid varied in these measurements in the range of ca. 0.03–0.08 mol kg^{-1}, and in all points the acid was is approximately half-neutralized by HCl. The electromotive force (E) of cells of type (13) can be calculated by

$$E = E^\circ - (RT/F)\ln[\gamma(H^+)\gamma(Cl^-)]$$
$$- (RT/F)\ln\{[m(H^+)m(Cl^-)/(m^\circ)^2]\} \qquad (14)$$

where in this case $m(Cl^-) = m_1$. For the value of the standard electromotive force (E°), a value of 0.222 50 V was used. This value was obtained in a previous paper[12] from the results measured by Harned and Ehlers[1] on hydro-

gen–silver chloride cells where the same type of silver–silver chloride electrodes was used as those used by Smith et al.[7] To obtain $K_{a,1}$, the Smiths' data were treated as follows.

For cells of type (13), E(predicted) was calculated by eqn. (14). For this equation for the fixed values of $K_{m,1}$ and $K_{m,2}$, $m(H^+)$ was obtained from eqn. (9), where in this case $-m = m_a = m_1$ and $m_t = m_2$. For a certain experimental point, the following equations hold:

$$m(H_3A^+) = m(H^+)^2 m_2 / [m(H^+)^2 + K_{m,1} m^\circ m(H^+)$$
$$+ K_{m,1} K_{m,2} (m^\circ)^2] \tag{15}$$

$$m(HA^-) = K_{m,1} K_{m,2} m_2 (m^\circ)^2 / [m(H^+)^2$$
$$+ K_{m,1} m^\circ m(H^+) + K_{m,1} K_{m,2} (m^\circ)^2] \tag{16}$$

$$I_m = [m(H^+) + m(H_3A^+) + m(HA^-) + m_1 + m_3$$
$$+ 2m_4]/2 \tag{17}$$

where now $m_3 = m_4 = 0$ [these quantities are required later in connection with cell (18)]. In the calculation of the values for E(predicted) by eqn. (14), $\gamma(H^+)$ and $\gamma(Cl^-)$ were estimated from eqn. (1) with the parameter values given above and with I_m obtained from eqn. (17).

In the determination of $K_{a,1}$ for aspartic acid, a value of $K_{m,1}$ was first determined by successive approximations from each experimental point of Smith et al.[7] From each point, the value of $K_{m,1}$ was sought that gave for E(predicted) exactly the same value as that measured. In this determination, $K_{m,2}$ was calculated for each point by eqn. (6) with the new value of $K_{a,2}$ and with eqn. (1), where the new ionic parameter values were used. The following seven $K_{m,1}$ values for this acid were obtained in this way:

I_m/m°	$10^2\ K_{m,1}$
0.01826	1.023
0.01880	1.039
0.02158	1.015
0.02298	1.013
0.02672	1.024
0.03308	1.029
0.04237	1.015

According to this short table, the variation of the $K_{m,1}$ values around their mean (0.01023) seems to be random, and it is difficult to determine from these values some functional relationship for the ionic strength dependence of $K_{m,1}$. Therefore we suggest at the moment that $K_{a,1}$ for aspartic acid is 0.0102, and in subsequent considerations we also use this value for $K_{m,1}$ up to the ionic strengths of about 0.4 mol kg^{-1}. It was checked, in addition, that the use of 0.0102 for $K_{m,1}$ instead of 0.01 in the determination of $K_{a,2}$ (see above) does not influence significantly the parameter values estimated.

Tests of the dissociation constants and activity parameters. To test the new K_a-values for aspartic acid and new values of the parameters for eqn. (1) for hydrogen aspartate ions, the results of the acid and base titrations presented in Tables 1 and 2 were first predicted by means of these values. The values of $K_{m,2}$ predicted by eqns. (1) and (6) [i.e. the $K_{m,2}$(pred) values] are also given in the tables, and these values were used in the calculations of the pH predictions. Also the corrections of pH_{lj} were made for the predicted sets as described in the Appendix, and the resulting values of pH_{lj} are shown in the tables. When the data for the base titrations were predicted, the n_t-values obtained in the parameter estimation were used, and in the case of the acid titrations these values were estimated by means of eqn. (A6). The results of these tests are shown as error plots in the two graphs of Fig. 1. In these plots the errors defined by eqn. (A7) are presented at each ionic strength as a function of the volume of the titrant added. Figure 1A shows the errors of the base titrations, and Fig. 1B shows those of the acid titrations.

Secondly the parameters estimated for aspartic acid were tested with the experimental data of Smith et al.[7] In addition to cells of type (13), these researchers have also made measurements on cells of the following type:

$$Pt\ (s)\ |\ H_2(g, f = 101\ kPa)\ |\ H_2A\ (aq, m_2),$$
$$NaOH\ (aq, m_3),\ NaCl\ (aq, m_4)\ |\ AgCl\ (s)\ |\ Ag\ (s) \tag{18}$$
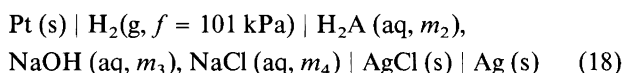
The EMF of cell (18) is also given by eqn. (14), where in this case $m(Cl^-) = m_4$. $m(H^+)$ for this equation can be calculated by eqn. (9) with $m = m_b = m_3$ and $m_t = m_2$. In the present tests the experimental data of cells (13) and (18) are predicted by means of the new activity coefficient equations and K_a-values. The results of these tests are shown as error plots in Fig. 2, where the EMF error, defined by

$$e(E) = E(\text{observed}) - E(\text{predicted}) \tag{19}$$

is presented as a function of the ionic strength. In the calculation of E(predicted) for each point of these cells, iterative calculations were needed. With an initial estimate of I_m the first estimate of $K_{m,2}$ was obtained by eqn. (6). With this value and with the value of $K_{m,1} = 0.0102$, $m(H^+)$ was calculated by eqn. (9) and $m(H_3A^+)$ and $m(HA^-)$ by eqns. (15) and (16), respectively. With these molalities, a new estimate of I_m was then obtained by eqn. (17) where in the case of cell (18) the molality m_1 is always zero. The iteration process was continued until the value of I_m no longer changed significantly. Usually this process could be stopped after a few steps. The E(predicted) values for the error plots were calculated by means of the final estimates of the iteration process.

Thirdly the parameters estimated for aspartic acid were tested with the EMF measurements of Simms[13] by cells of the following type:

$$Pt\ (s)\ |\ H_2\ (g, f = 101\ kPa)\ |\ H_2A\ (aq, m_2),$$
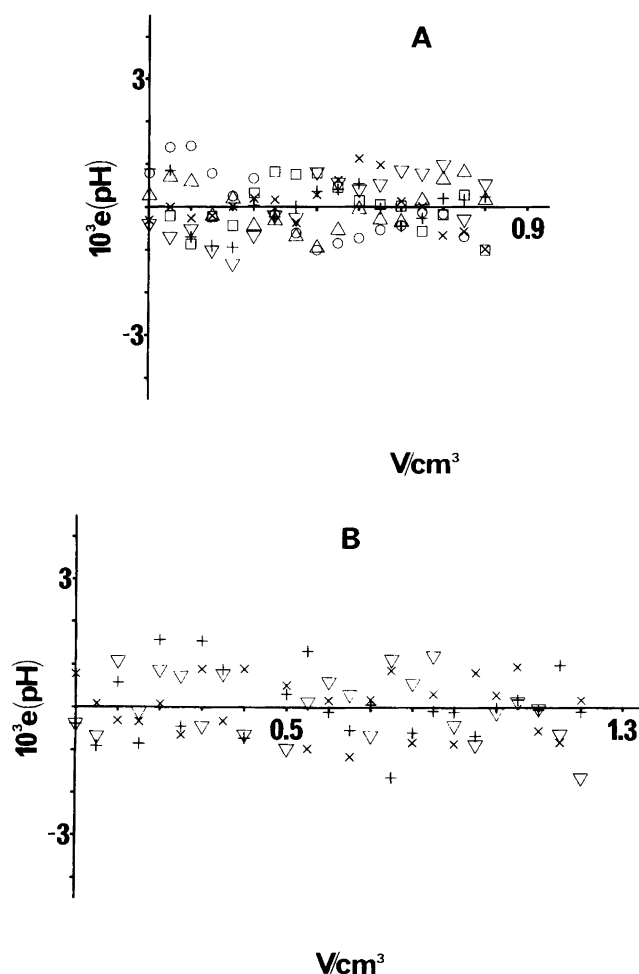$$HCl\ (aq, m_1)\ or$$
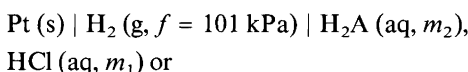
Fig. 1. The difference between the observed and predicted pH values as a function of the titrant volume in the titrations of aspartic acid solutions. Graph A contains the results of the base titrations, (Table 1), and graph B those of the acid titrations (Table 2). The observed pH values were corrected as described in Appendix and the predicted pH values were calculated by means of the new values of $K_{a,1}$ and $K_{a,2}$ for aspartic acid and the new values for the ionic parameters in eqn. (1), for details see text. Symbols for the ionic strengths $(I_m/\mathrm{mol\ kg^{-1}})$ of the titrations are as follows ×, 0.0596; □, 0.1193; △, 0.1792; ▽, 0.2393; ○, 0.2997; +, 0.3755.

NaOH (aq, m_3), no inert salt or NaCl (aq, m_4) or

MgCl$_2$ (aq, m_5) || KCl (aq, saturated) | AgCl (s) | Ag (s)

$$\tag{20}$$
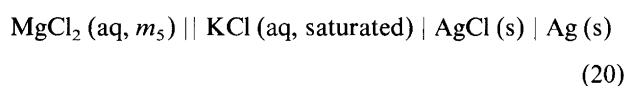
Cell (20) thus contains a liquid junction, and the concentrations used by Simms as the composition variable in this cell have been converted into the molalities simply by changing the unit. Such a simple conversion is possible owing to the dilute solutions used, and the fact that the precision of these measurements is not entirely comparable with the precision of the best EMF measurements made in aqueous solutions (see below). Simms performed
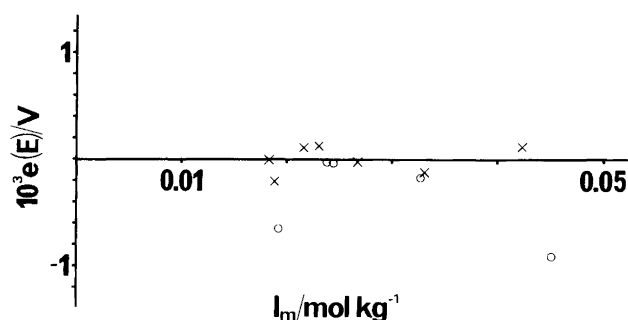

Fig. 2. The difference between the observed and predicted EMF values as a function of the ionic strength in the set measured by Smith et al.[7] on galvanic cells of type (13) (×) and of type (18) (○). The predicted values were calculated by means of eqn. (14) with eqns. (1), (6) and (9) by using the new $K_{a,1}$ and $K_{a,2}$ values for aspartic acid and new values for the ionic parameters in eqn. (1); for details see text.

potentiometric titrations in aspartic acid solutions by using in the titrations either an acid or a base titrant. The titrations were made in pure aspartic acid solutions (where $m_2 = 0.01$ mol kg^{-1}) and in solutions which contain in addition to aspartic acid also NaCl or MgCl$_2$. In cell (20), m_4 was 0.0375 or 0.075 mol kg^{-1} and m_5 was 0.0125 or 0.025 mol kg^{-1}. As the independent variable for the titrations, Simms has reported the fraction of aspartic acid neutralized by the titrant, with the dependent variable, being the pH of the solution titrated.

The pH values reported by Simms[13] were predicted in the present study by means of the activity coefficient equations for protons and hydrogen aspartate ions and the $K_{a,1}$ and $K_{a,2}$ values presented above. For each titration set of Simms, a liquid junction potential correction pH$_{lj}$ was made as described the Appendix. (This correction can be made as described in the Appendix, despite the facts that Simms used a hydrogen electrode instead of a glass electrode and that he calibrated his cells only by one buffer solution.[14]). The predicted pH values for these tests were calculated by eqn. (10) and the value of $m(\mathrm{H^+})$ for this equation by eqn. (9), where in this case $m_a = m_1$, $m_b = m_3$ and $m_t = m_2$, and $\gamma(\mathrm{H^+})$ by eqn. (1). In these titrations, the inert electrolyte does not alone determine the ionic strength, and so all ions of the solutions must be included in the calculation of I_m. In the present study, however, it is assumed that inside a titration the correction pH$_{lj}$ is constant because the I_m values of the points in the titration do not vary very much. The results of the tests with Simms' data are shown in two plots in Fig. 3. In these plots the pH error [see eqn. (A7)] is presented as function of the ionic strengths; graph A contains the results of the base titrations and graph B those of the acid titrations.

Discussion

The value of $K_{a,2}$ for aspartic acid and the parameters B and b for hydrogen aspartate ions were determined above
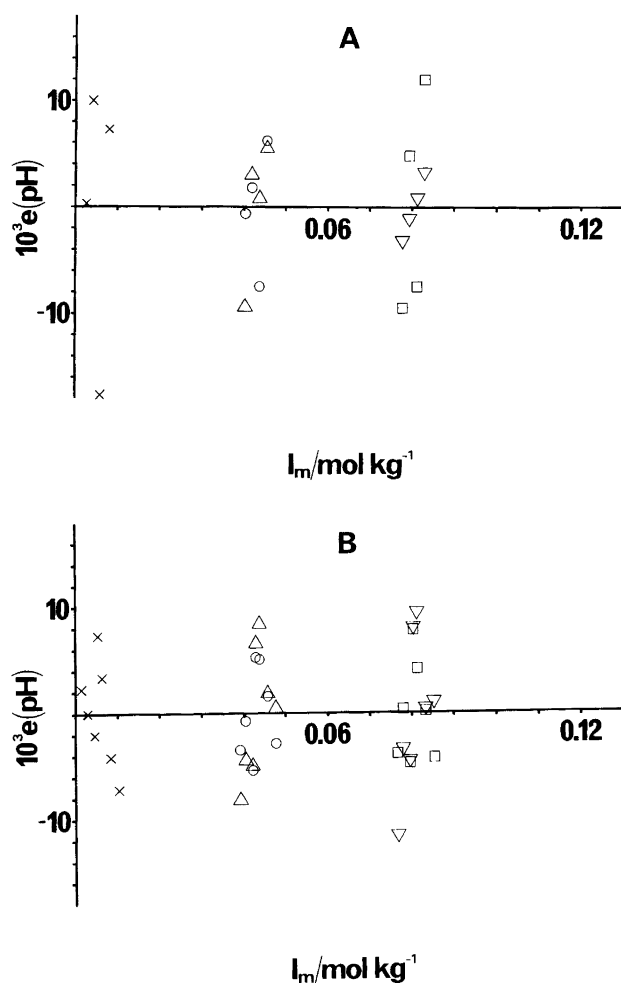
Fig. 3. The difference between the observed and predicted pH values as a function of the ionic strength in the sets measured by Simms[13] on aspartic acid cells of type (20). The results of the base titration are shown in graph A and those of the acid titrations in graph B. The predicted pH values have been calculated by means of the new values of $K_{a,1}$ and $K_{a,2}$ for aspartic acid and new values for the ionic parameters in eqn. (1), for the details see text. The observed pH values were corrected as described in Appendix. The following symbols and pH_{lj} values were used: no salt ($\times$), $pH_{lj} = -0.0075$ (A), $pH_{lj} = -0.0053$ (B); $m(NaCl) = 0.0375$ $m°$ (O), -0.0405 (A), -0.0419 (B); $m(MgCl_2) = 0.0125$ $m°$ ($\triangle$), -0.0468 (A), -0.0452 (B); $m(NaCl) = 0.075$ $m°$ ($\square$), -0.0513 (A), -0.0574 (B); and $m(MgCl_2) = 0.025$ $m°$ (∇), -0.0795 (A), -0.0627 (B).

from the results of the base titrations presented in Table 1. According to Fig. 1A these titration data can be accurately predicted by means of the resulting values. As shown in Fig. 1B also, the results of the acid titrations presented in Table 2 support strongly the new K_a-values and the new equations for the ionic activity coefficients. In the case of both base and acid titrations, the pH values predicted by the new model always agree with the experimental pH values (corrected for the liquid junction potential differences, see Appendix) within 0.002, and in

most cases the errors in these graphs form a random pattern. The agreement of Fig. 1 is very good in the light of the facts that the pH values were read in our measurements with an accuracy of 0.001 and that the calibration of the pH meter leads unavoidably to additional errors. According to Tables 1 and 2, in addition, the liquid junction potential correction, pH_{lj}, obtained for any ionic strength in the base titrations, is not far from that obtained for the same ionic strength in the acid titrations. In addition, it can be observed that pH_{lj} values determined in the previous study[6] for glutamic acid solutions at the different ionic strengths are close to those determined here for aspartic acid solutions.

The experimental data measured by Smith *et al.*[7] on cells of type (13) were used above in the determination of the value of $K_{a,1}$ for aspartic acid. These researchers have also made measurements on cells of type (18). The EMF values in these two sets have been reported with an accuracy of 0.0001 V. According to Fig. 2, almost all points of these sets can be predicted within 0.0002 V by the new model for aspartic acid solutions.

When Simms' measurements by cells with a liquid junction [see cell (20)] were used to test the K_a-values and the activity coefficient equation determined above, these data were corrected for the liquid junction potentials in the same way as the glass electrode data in Tables 1 and 2. According to Fig. 3, the pH measurements of Simms[13] are approximately a decade less precise than those presented in Tables 1 and 2. As shown in the two plots of this figure, nevertheless, the experimental results of Simms also support, within their precision, the calculation method used in this study. In this figure it is additionally interesting to remark that the correction pH_{lj} does not depend much on the electrolyte used to adjust the ionic strength (i.e. NaCl or $MgCl_2$) but on the value of the ionic strength. Also at the same ionic strength in the base and acid titration, the pH_{lj} values are usually close. However, the results of the base titration in the solution where $m_5 = 0.025$ mol kg^{-1} are exceptions to these rules.

In the present study at 298.15 K, a value of 0.0102 was obtained for $K_{a,1}$ of aspartic acid and a value of 1.30×10^{-4} for $K_{a,2}$ of this acid. These values can be compared to the values presented previously. The values presented by Smith *et al.*[7] for these quantities are 0.0102 and 1.26×10^{-4}, respectively, and thus they are rather close to those obtained here. In addition, the following thermodynamic dissociation constants for aspartic acid at 298.15 K have been suggested: $K_{a,1} = 0.0115$ and $K_{a,2} = 1.26 \times 10^{-4}$, see Lumb and Martell;[15] and $K_{a,1} = 0.00977$ and $K_{a,2} = 1.27 \times 10^{-4}$, see Batchelder and Schmidt.[16]

For the ionic activity coefficient equation [eqn. (1)], the following parameter values were obtained here for hydrogen aspartate ions: $B = 2.5$ (kg mol^{-1})$^{1/2}$ and $b = 0.077$. It is interesting to note that these values are practically identical to those obtained for hydrogen glutamate ions.[6]

In the present study it is shown that eqn. (1) can be used successfully to predict the ionic activity coefficients required in thermodynamical studies of aspartic acid solutions at 298.15 K. This equation also has immediate analytical applications. By means of the new parameter values for eqn. (1), for example, the $K_{m,2}$-value for aspartic acid can be reliably calculated from the $K_{a,2}$-value for any ionic strength, at least up to a molality of 0.4 mol kg^{-1} when the ionic strength is adjusted by KCl or possibly also by NaCl.

Appendix: determination of the liquid junction correction for potentiometric glass electrode data

Let us consider potentiometric titrations, in which the pH of the solutions is measured by a pH meter equipped with a glass electrode and an appropriate reference electrode. The EMF between these two electrodes depends on the activity of protons according to

$$E = E' + E_{lj} - S \log[a(H^+)]$$
$$= E' + E_{lj} - S \log[\gamma(H^+)m(H^+)/m^\circ]$$
$$= E' + E_{lj} + S \, pH \quad (A1)$$

where E' and S are constants and E_{lj} represents the liquid junction potential between the solution titrated and that of the reference electrode. The liquid junction potentials, among other things, usually cause serious problems when the results of glass electrode cells are interpreted thermodynamically. An easy method is illustrated below by which these problems can be, according to our understanding, avoided under certain experimental conditions. In the calibration of the pH cell with two NIST buffers, the quantities $[E' + E_{lj}(\text{buffer})]$ and S [these quantities remain constant in eqn. (A1) during measurements] are determined with an assumption that E_{lj} is almost the same for both buffers. If the way to calibrate a pH meter is valid, the following equation is true during a whole potentiometric titration with the pH meter:

$$E = [E' + E_{lj}(\text{buffer})] + [E_{lj} - E_{lj}(\text{buffer})]$$
$$+ S \, pH \, (\text{real}) = [E' + E_{lj}(\text{buffer})]$$
$$+ S \, pH_{lj} + S \, pH \, (\text{real}) \quad (A2)$$

where pH(real) is the correct pH [the same as the pH in eqn. (A1)] and pH_{lj} is a pH correction resulting from liquid junction potential differences between the solution titrated and those used in the calibration. It is defined by

$$pH_{lj} = [E_{lj} - E_{lj}(\text{buffer})]/S \quad (A3)$$

and according to this definition it takes into account only the liquid junction errors. Nevertheless, the method of evaluating this quantity leads to a correction that also partly eliminates other imperfections in the measuring

system (i.e. possible systematic errors in the calibrations or in the activity coefficient equation for protons).

It is assumed, in addition, that all titrations are carried out at several ionic strengths adjusted by an inert electrolyte. In each titration I_m remains practically constant. It is reasonable to assume, therefore, that E_{lj} in eqn. (A1) and pH_{lj} in eqn. (A2) remain constant from point to point in each of these titrations. pH_{lj} can be determined for each titration set so that the pH values measured in this titration agree as well as possible with the pH values predicted by the tested model. Hence pH_{lj} was obtained for this set in the following way.

Let us consider a set of titration results [V_i, pH$_i$ (measured)] measured by a pH meter calibrated with two buffers as explained above. V_i is the volume of the titrant solution added and pH$_i$ (measured) is the reading of the pH meter. The total number of titration points in this set is N. The pH values of this set are predicted by a model containing K_a-values and equations for the activity coefficients of the species in the system. The predictions resulting from this model form another set of pH values: [V_i, pH$_i$ (predicted)]. By means of these two sets, the correction pH_{lj} is calculated by

$$pH_{lj} = \sum_{i=1}^{N} [pH_i(\text{measured}) - pH_i(\text{predicted})]/N \quad (A4)$$

and the corrected pH value is then obtained for point i by

$$pH_i(\text{corrected}) = pH_i(\text{measured}) - pH_{lj} \quad (A5)$$

and the value of pH(corrected) is the same as the pH-(real) value in eqn. (A2) if the model used in the prediction process is correct. When activity parameters or K_m-values for weak acids are estimated on the basis of the titration set, the following square sum of pH errors is minimized:

$$S = \sum_{i=1}^{N} e_i(pH)^2 \quad (A6)$$

where

$$e(pH) = pH(\text{corrected}) - pH(\text{predicted}) \quad (A7)$$

and the value of pH(corrected) for eqn. (A7) is calculated by eqn. (A5).

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