Determination of the Thermodynamic Values of the First and Second Dissociation Constants of Bis(2,2-dimethyl-3-oxopropanol) Amine in Aqueous Solutions at 298.15 K

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The thermodynamic values of the first and second dissociation constants of bis(2,2-dimethyl-3-oxopropanol) amine were determined at 298.15 K by a method developed recently. In this method a simple equation was used for activity coefficients of the ionic species. This equation originates from the Debye–Hückel theory. The dissociation constants of the amino acid and the parameters of the activity coefficient equation were determined from results of potentiometric titrations performed in a glass electrode cell. The ionic strength of the solutions titrated were adjusted by either NaCl or KCl, and ionic strengths up to 0.4 mol kg^{-1} were used. These new data can be explained within experimental error by the resulting equations for ionic activity coefficients. The following thermodynamic values were obtained: $K_{a,1} = 2.0 \times 10^{-3}$ and $K_{a,2} = 1.02 \times 10^{-4}$.

Electromotive force (EMF) measurements on cells without a liquid junction have been considered as one of the most accurate methods to determine the thermodynamic values of dissociation constants (K_a) of weak acids. This method was developed in the 1930s to a high precision by Harned and Ehlers.[1] Much experimental work has since been done by this method, and for many acids the most reliable values for K_a have been obtained by this method (see, e.g., Robinson and Stokes).[2] In a recent study,[3] a new method was introduced for a reliable determination of K_a-values, based on measurements in a glass electrode cell. For this determination, a series of potentiometric titrations was carried out at different ionic strengths. Liquid-junction problems, which are serious difficulties associated with cells of this kind, were solved in that study by a new method of treating the titration data.

In the present investigation, the first and second dissociation constants of bis-(2,2-dimethyl-3-oxopropanol) amine (abbreviated henceforth as the amino acid) were determined. This compound is a new one and was synthetized and patented by the Finnish company Neste Ltd.[4] The formula of the amino acid is HN[CH$_2$C(CH$_3$)$_2$COOH]$_2$. The experimental data for the present study were obtained by potentiometric titrations in a glass electrode cell. Two series of solutions of

this acid were titrated: in one of these series the inert electrolyte was NaCl and in the other KCl. The experimental data are treated here in the same way as the corresponding data obtained previously from glutamic acid solutions[3] and aspartic acid solutions.[5]

Experimental

Bis(2,2-dimethyl-3-oxopropanol) amine was delivered to us by Neste as the hydrochloride in a purified form. It was purified by crystallization with an acetic acid–ethyl acetate mixture (1:2, v:v) and by washing the crystals with a methylethylketone–toluene mixture (1:1, v:v) and lastly with diethyl ether.

The titrations of this amino acid hydrochloride were essentially carried out in the same way as described by Seymour[6] and in a previous paper.[7] Thus only a brief description of the procedure is given. The following solutions were prepared: 2.00 M NaCl, 2.00 M KCl, 0.010 M amino acid hydrochloride, 0.100 M NaOH and two primary buffer solutions of NIST (potassium hydrogen phthalate and 0.025 molal disodium hydrogen phosphate plus potassium dihydrogen phosphate). From the NaCl and KCl solutions, the following solutions were diluted for the titrations: 0.08, 0.16, 0.24, 0.32, 0.40 and 0.50 M. All solutions were prepared in RO-filtered water (Millipore) with a conductivity less than 1.0 μS cm^{-1}.

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The titration vessels were thermostatted during operations to 298.15 ± 0.15 K by using a thermobath. A CG803 pH meter and a N62 combination electrode by Schottgeräte were used in the pH measurements. The calibration was made carefully by means of the two buffer solutions. The solutions titrated were prepared by mixing 100 cm³ of a diluted NaCl or KCl solution, 25.0 cm³ of Millipore water and 10.0 cm³ of the amino acid solution. Titrations were carried out by reading the pH after increments of 0.050 cm³ of the base solution. The base solution was added by a Metrohm 655 Dosimat. The readings between 0 and 0.3 cm³ were not recorded in the titrations in the KCl solutions. At the end of the titration, the pH was checked using one of the buffers. The read-

ings of the meter were stable within ± 0.002 pH units during the work.

Results

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

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

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. In this term $\alpha = 1.17444$ (kg mol^{-1})$^{1/2}$,

Table 1. Results of the titrations of bis(2,2-dimethyl-3-oxopropanol) amine hydrochloride in NaCl solutions with a base (NaOH) solution.

| I_m/mol kg^{-1}:	0.0595	0.1191	0.1789	0.2388	0.2988	0.3741
V^a/cm³	pH^b	pH^b	pH^b	pH^b	pH^b	pH^b
0	3.227	3.215	3.211	3.206	3.201	3.193
0.05	3.244	3.232	3.230	3.223	3.218	3.211
0.10	3.264	3.252	3.247	3.242	3.237	3.228
0.15	3.283	3.271	3.264	3.261	3.256	3.247
0.20	3.303	3.290	3.284	3.279	3.274	3.266
0.25	3.323	3.310	3.305	3.300	3.293	3.286
0.30	3.346	3.329	3.323	3.318	3.315	3.306
0.35	3.366	3.352	3.346	3.339	3.335	3.327
0.40	3.390	3.373	3.368	3.361	3.356	3.347
0.45	3.413	3.397	3.391	3.383	3.380	3.371
0.50	3.439	3.420	3.413	3.405	3.402	3.393
0.55	3.464	3.446	3.437	3.430	3.425	3.417
0.60	3.488	3.470	3.463	3.454	3.451	3.442
0.65	3.515	3.495	3.488	3.481	3.476	3.468
0.70	3.544	3.522	3.517	3.509	3.502	3.493
0.75	3.575	3.551	3.543	3.534	3.531	3.522
0.80	3.605	3.578	3.571	3.563	3.558	3.549
0.85	3.636	3.609	3.602	3.594	3.588	3.578
0.90	3.670	3.641	3.633	3.624	3.621	3.609
0.95	3.704	3.675	3.665	3.655	3.651	3.641
1.00	3.740	3.709	3.699	3.689	3.685	3.675
1.05	3.777	3.745	3.734	3.724	3.721	3.711
1.10	3.816	3.784	3.772	3.760	3.758	3.746
1.15	3.857	3.823	3.809	3.797	3.796	3.784
1.20	3.899	3.865	3.852		3.836	3.825
1.25	3.945	3.908	3.894		3.877	3.867
1.30	3.996	3.952	3.940	3.926	3.925	3.911
1.35	4.047	4.003	3.989	3.976	3.972	3.959
1.40	4.105	4.054	4.040	4.027	4.025	4.011
1.45	4.164	4.112	4.098	4.081	4.079	4.066
1.50	4.231	4.174	4.159	4.142	4.140	4.125
1.55	4.304	4.242	4.225	4.205	4.205	4.191
1.60	4.387	4.319	4.300	4.278	4.281	4.266
$10^4 K_{m,2}$(obsd)^c	1.49	1.60	1.66	1.71	1.71	1.75
$10^4 K_{m,2}$(pred)^d	1.483	1.602	1.667	1.705	1.726	1.737
$10^4 n_t$/mol^e	0.947	0.961	0.963	0.967	0.963	0.966
10^3pH$_{lj}$^{f}	−44.4	−68.5	−81.2	−91.1	−100.9	−110.4
$10^3 s_0$^{g}	0.95	0.96	0.80	0.91	0.76	0.63

^{a} V is the volume of the titrant added. ^{b}pH means the measured pH value. ^{c}Obtained by minimization of the square sum defined by eqn. (A6) in Ref. 5. ^{d}Calculated by eqn. (5) with the new value of $K_{a,2}$ and by eqn. (1) with the new values for the ion parameters. ^{e}Amount of the acid in the titration vessel. ^{f}Liquid-junction potential correction, see Appendix of Ref. 5. ^{g}Standard deviation of residuals, defined by means of S in eqn. (A6) of Ref. 5 according to $s_0 = [S/(N-2)]^{1/2}$, where N is the number of points in the set in question.

see Archer and Wang,[8] and B_i is dependent on ion i in the same way as b_i in the second term, which is an empirical correction term. The composition variable in this equation is the molal ionic strength I_m. In our previous paper[3] the following parameter values for this equation were obtained: $B(H^+) = B(Cl^-) = 1.25$ (kg mol^{-1})$^{1/2}$ and $b(H^+) = b(Cl^-) = 0.238$.

The titration data of the amino-acid hydrochloride (H_3ACl) solutions are presented in Tables 1 and 2. Table 1 contains the results of the titrations where the ionic strengths were adjusted by NaCl and Table 2 those where KCl was used in this adjustment.

The titration data were corrected for the differences 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 of a previous paper.[5] The titration data were treated thermodynamically as follows.

The dissociation equilibria existing in acidic solutions of the amino acid are the following:

$$H_3A^+ \rightleftharpoons H^+ + H_2A \qquad (2)$$
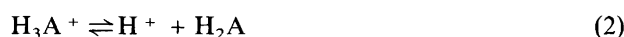
$$H_2A \rightleftharpoons H^+ + HA^- \qquad (3)$$

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

$$K_{a,1} = a(H^+)a(H_2A)/a(H_3A^+)$$
$$= [\gamma(H^+)/\gamma(H_3A^+)]m(H^+)m(H_2A)/[m°m(H_3A^+)]$$
$$= [\gamma(H^+)/\gamma(H_3A^+)]\, K_{m,1} \qquad (4)$$

$$K_{a,2} = a(H^+)a(HA^-)/a(H_2A)$$
$$= \gamma(H^+)\gamma(HA^-)m(H^+)m(HA^-)/[m(H_2A)m°]$$
$$= \gamma(H^+)\gamma(HA^-)\, K_{m,2} \qquad (5)$$

where a refers to the activities of the species, where it is assumed that the activity coefficients of the neutral species H_2A are unity at all ionic strengths under consideration, and where

$$K_{m,1} = m(H^+)m(H_2A)/[m(H_3A^+)m°] \qquad (6)$$

Table 2. Results of the titrations of bis(2,2-dimethyl-3-oxopropanol) amine hydrochloride in KCl solutions with a base (NaOH) solution.

I_m/mol kg^{-1}:	0.0596	0.1193	0.1792	0.2393	0.2997	0.3754
V^a/cm^3	pH^b	pH^b	pH^b	pH^b	pH^b	pH^b
0	3.235	3.254	3.260	3.262	3.256	3.255
0.30	3.350	3.368	3.372	3.374	3.368	3.368
0.35	3.372	3.389	3.392	3.394	3.389	3.388
0.40	3.393	3.411	3.414	3.416	3.411	3.411
0.45	3.416	3.435	3.437	3.438	3.434	3.433
0.50	3.440	3.458	3.461	3.461	3.456	3.456
0.55	3.463	3.482	3.485	3.485	3.480	3.480
0.60	3.489	3.507	3.511	3.510	3.504	3.504
0.65	3.516	3.533	3.537	3.535	3.531	3.530
0.70	3.543	3.559	3.564	3.561	3.557	3.556
0.75	3.572	3.587	3.588	3.587	3.584	3.585
0.80	3.601	3.616	3.619	3.618	3.612	3.612
0.85	3.632	3.646	3.648	3.647	3.641	3.641
0.90	3.663	3.677	3.679	3.677	3.671	3.672
0.95	3.696	3.710	3.711	3.708	3.704	3.704
1.00	3.731	3.745	3.745		3.737	3.738
1.05	3.767	3.780	3.780	3.777	3.772	3.773
1.10	3.804	3.817	3.817	3.813	3.808	3.809
1.15	3.845	3.856	3.855	3.852	3.846	3.847
1.20	3.886	3.897	3.895	3.892	3.886	3.887
1.25	3.931	3.940	3.938	3.935	3.928	3.929
1.30	3.978	3.985	3.982	3.979	3.974	3.975
1.35	4.027	4.034	4.030	4.027	4.021	4.022
1.40	4.078	4.085	4.080	4.075	4.073	4.074
1.45	4.135	4.141		4.130	4.128	4.128
1.50	4.195	4.201	4.195	4.189	4.187	4.188
1.55	4.261	4.267	4.260	4.254	4.253	4.254
1.60	4.335	4.342	4.333	4.326	4.325	4.327
1.65	4.419	4.425	4.415	4.408	4.407	4.409
1.70	4.515	4.521	4.509	4.503	4.502	4.505
$10^4 K_{m,2}(pred)^d$	1.483	1.602	1.668	1.706	1.726	1.737
$10^4 n_t$/mol^e	0.969	0.968	0.970	0.971	0.968	0.967
$10^3 pH_{lj}{}^f$	−30.8	−26.5	−29.2	−33.4	−43.6	−46.1
$10^3 s_0{}^g$	0.85	0.63	1.08	0.86	0.62	0.62

$^{a,b,d-g}$See notes in Table 1.

$$K_{m,2} = m(\text{H}^+)m(\text{HA}^-)/[m(\text{H}_2\text{A})m^\circ] \qquad (7)$$

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

$$m(\text{H}^+)^3 + (K_{m,1}m^\circ + m_b)m(\text{H}^+)^2 +$$
$$K_{m,1}m^\circ(K_{m,2}m^\circ + m_b - m_t)m(\text{H}^+) +$$
$$K_{m,1}K_{m,2}(m^\circ)^2(m_b - 2m_t) = 0 \qquad (8)$$

In eqn. (8) 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. 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 NaCl or KCl as the only solute. During the titration, w_1 was calculated by $w_1 = w_1$(initial) $+ \rho_1 V$, where ρ_1 is the density of water. In eqn. (8), in addition, m_t is the total molality of the amino acid in the solution titrated and $m_t = n_t/w_1$, where n_t is the amount of the amino 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 NaCl or KCl in the solution titrated. Equation (8) is a polynomial of the third degree in $m(\text{H}^+)$. In the present calculations, $m(\text{H}^+)$ 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.

At first both $K_{m,1}$ and $K_{m,2}$ were determined at the same time from the results of each titration in NaCl solutions (Table 1). The values of $K_{m,1}$ and $K_{m,2}$ were searched for each ionic strength that minimize the square sum defined in eqn. (A6) of our previous paper.[5] In this estimation, eqns. (A4), (A5) and (A7) in that paper were also needed (see Appendix to Ref. 5). The value of pH-(predicted) for each point of the titration in this I_m was calculated by

$$\text{pH(predicted)} = -\log[\gamma(\text{H}^+)m(\text{H}^+)/(m^\circ)] \qquad (9)$$

and for this equation $\gamma(\text{H}^+)$ by eqn. (1) and $m(\text{H}^+)$ by eqn. (8). The amount of the acid (n_t) was also used as an adjustable parameter in the evaluation of $K_{m,1}$ and $K_{m,2}$. By this method, the following results were obtained from the data presented in Table 1: ($I_m = 0.0595$ mol kg^{-1}, $K_{m,1} = 0.0019$, $K_{m,2} = 0.000\,148$, $n_t = 0.0946$ mmol), (0.1191, 0.0020, 0.000\,160, 0.0961), (0.1789, 0.0021, 0.000\,168, 0.0963), (0.2388, 0.0020, 0.001\,72, 0.0966), (0.2988, 0.0020, 0.000\,171, 0.0964) and (0.3741, 0.0018, 0.000\,174, 0.0963). In this list, $K_{m,1}$ seems to vary randomly around 0.0020, and the deviations from this value are probably not significant. Therefore in the final calculations, it was assumed that $K_{m,1}$ is always 0.0020 and that this value is also the thermodynamic one ($= K_{a,1}$).

The experimental $K_{m,2}$ values for the different ionic strengths of Table 1 were obtained by searching the mini-

mum of the square sum defined by eqn. (A6) in the appendix of the previous paper[5] when $K_{m,2}$ and n_t were varied. The results [i.e. the $K_{m,2}$(obsd) values] are shown in Table 1. By means of these values, $K_{a,2}$ can be determined by the following equation, which has been derived from eqns. (1) and (5):

$$\ln K_{m,2} - \alpha(I_m)^{1/2}/[1 + B(\text{H}^+)(I_m)^{1/2}] -$$
$$\alpha(I_m)^{1/2}/[1 + B(\text{HA}^-)(I_m)^{1/2}]$$
$$= y = \ln K_{a,2} - [b(\text{H}^+) + b(\text{HA}^-)]I_m/m^\circ \qquad (10)$$

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 $-[b(\text{H}^+) + b(\text{HA}^-)]$, and from the intercept of this line with the y-axis, $K_{a,2}$ can be solved. This straight line was determined by the method of least squares. In this regression analysis, it was observed that a value of 2.5 (kg mol^{-1})$^{1/2}$ can be used for the unknown quantity $B(\text{HA}^-)$. This value is the same as that obtained previously for B of hydrogen glutamate ions[3] and of hydrogen aspartate ions.[5] The straight line of eqn. (10) corresponding to this value is

$$y = -9.188 - 0.430 I_m/m^\circ \qquad (11)$$

From this equation, the results of $K_{a,2} = 1.02 \times 10^{-4}$ and of $b(\text{HA}^-) = 0.192$ can be deduced.

To test the new K_a-values and activity parameters, the results of the titrations presented in Tables 1 and 2 were predicted by means of these values. The values of $K_{m,2}$ predicted by eqns. (1) and (5) [i.e. the $K_{m,2}$(pred) values] are also given in the tables, and these values were used in the calculation of the pH predictions. Also the liquid junction corrections were made for the predicted sets (see Appendix of Ref. 5) and the resulting values of pH_{lj} are shown in the tables. For the NaCl results, the n_t-values obtained in the parameter estimation were usually used, and for the KCl results they were also estimated by means of eqn. (A6) of Ref. 5. The results of these tests are shown as error plots in Fig. 1. Graph A in this figure contains the results of the titrations where the ionic strength was adjusted by NaCl and graph B those where KCl was used. In these plots the errors defined by eqn. (A7) in the previous paper[5] are presented at each ionic strength as a function of the volume of the titrant added.

Discussion

The values of $K_{a,1}$ and $K_{a,2}$ for bis(2,2-dimethyl-3-oxo-propanol) amine and the activity parameters B and b in eqn. (1) for the monohydrogen anion of this amino acid (HA$^-$) were determined above from the titration results obtained from NaCl solutions (Table 1). These data and also the titration results obtained from the KCl solutions (Table 2) were used in the tests of the resulting K_a and parameter values. According to the two graphs of Fig. 1, all titration data can accurately be predicted by means of the model used. The pH values predicted by the new
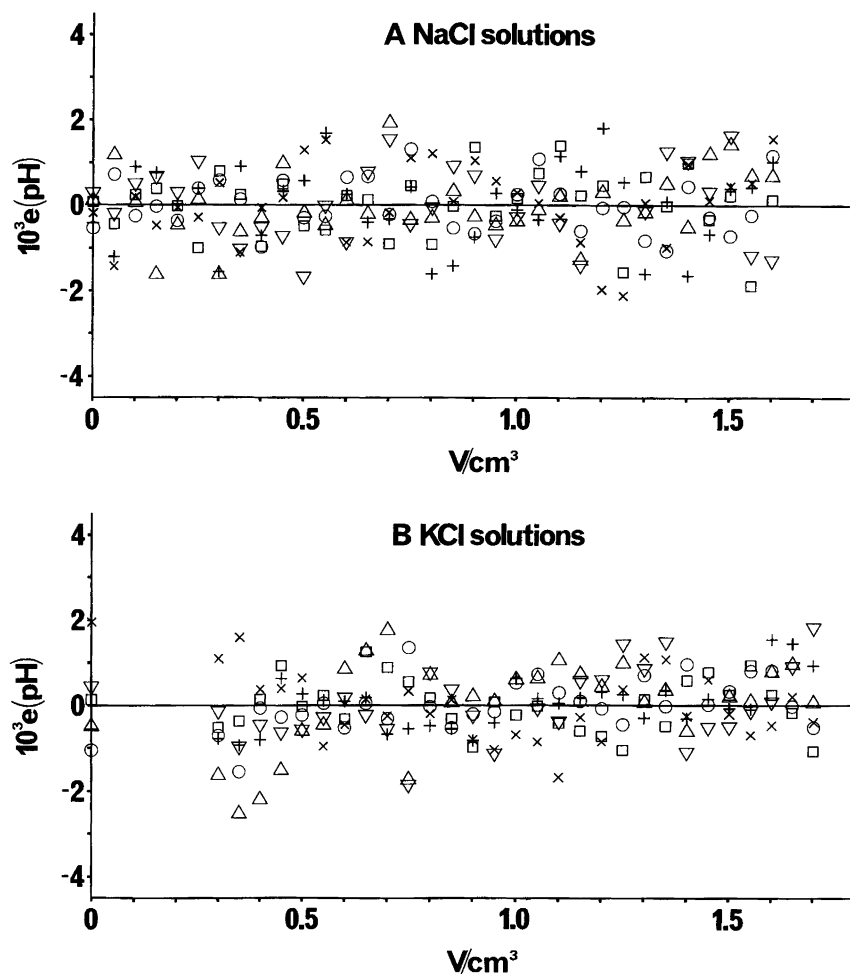
Fig. 1. The difference between the observed and predicted pH values as a function of the titrant volume in the titrations of bis(2,2-dimethyl-3-oxopropanol) amine hydrochloride solutions. Graph A contains the results of the titrations of this amino acid in NaCl solutions (Table 1) and graph B those in KCl solutions (Table 2). The observed pH values were corrected as described in Appendix of Ref. 5, and the predicted pH values were calculated by means of the new values of $K_{a,1}$ and $K_{a,2}$ for the acid and the new values for the ionic parameters in eqn. (1); for details see the text. Symbols for the ionic strengths (in mol kg^{-1}) of the titrations are as follows. (A) I_m ✕, 0.0595; +, 0.1191; △, 0.1789; ▽, 0.2388; □, 0.2988; ○, 0.3741; (B) I_m ✕, 0.0596; +, 0.1193; △, 0.1792; ▽, 0.2393; □, 0.2997; ○, 0.3754.

model agree with the experimental values almost always within 0.002, and the errors form in most cases a random pattern.

The K_a-values obtained in this study for the amino acid were also compared to the dissociation constants determined previously in the literature for similar sub-stances. The present understanding of the order of the K_a-values for iminodipropionic acid [$HOOC(CH_2)_2NH(CH_2)_2COOH$], which is close to the amino acid under consideration, can be based on the $K_{a,1}$-value for β-alanine [$H_2NCH_2CH_2COOH$] and on the K_a-values presented in Table 3 for pairs of the com-

Table 3. Thermodynamic dissociation constants at 298.15 K for pairs of the carboxylic acids of the following type: H–R$_1$–R$_2$–COOH (K_a) and HOOC–R$_2$–R$_1$–R$_2$–COOH ($K_{a,1}$ and $K_{a,2}$).

R$_1$	R$_2$	Monobasic acid	$10^5 K_a$	Ref.	Dibasic acid	$10^5 K_{a,1}$	$10^6 K_{a,2}$	Ref.
CH$_2$	CH$_2$CH$_2$	n-Butyric	1.52	9	Pimelic	3.3	3.8	10
CH$_2$	CH$_2$	Propionic	1.34	11	Glutaric	4.5	3.8	10
O	CH$_2$	Glycolic	14.8	12	Diglycolic	130[a]	93[a]	13
NH$_2^+$	CH$_2$	Glycine	447	14	Iminodiacetic		1050[b]	15

[a]Determined at the temperature of 303 K and at an ionic strength of 0.1 mol dm^{-3}; the K_a-values at 298 K are probably slightly smaller than these values. [b]Determined at 293 K; $K_{a,1}$ for this acid was so large that it was not determined.

pounds of the following type: $H-R_1-R_2-COOH$ and $HOOC-R_2-R_1-R_2-COOH$.

According to May and Felsing,[16] $K_{a,1}$ for β-alanine is 2.81×10^{-4}. On the basis of this value and the K_a-values presented in Table 3, it is quite possible that iminodipropionic acid has the dissociation constants that are of the following order: $K_{a,1} = 2.5 \times 10^{-3}$ and $K_{a,2} = 1.5 \times 10^{-4}$. The $K_{a,2}$-value is not fully supported by the value of 8×10^{-5} given by Chaberek and Martell[17] for $K_{c,2}$ of this acid at 303 K and at an ionic strength of 0.1 mol dm^{-3}. A possible reason for this slight disagreement can be the fact that these researchers omitted $K_{c,1}$ from their treatment.

In the amino acid studied here, there are two methyl substituents at the carbon atoms adjacent to the carbon atoms in the carboxyl groups. The effect of these substituents can be approximately predicted by comparing the K_a-values of, e.g., the following acids: propionic acid [CH_3CH_2COOH], $K_a = 1.34 \times 10^{-5}$ (Harned and Ehlers);[11] and trimethylacetic acid [$CH_3C(CH_3)_2COOH$], $K_a = 8.9 \times 10^{-6}$ (Dippy).[18] In the present study the values of $K_{a,1} = 2.0 \times 10^{-3}$ and $K_{a,2} = 1.02 \times 10^{-4}$ were obtained for $NH[CH_2C(CH_3)_2COOH]_2$, and they are reasonable on the basis of these K_a-values for propionic and trimethylacetic acid and the results deduced in the previous paragraph for iminodipropionic acid. As it is clear according to the treatment presented above, the comparison of the dissociation constants to the literature values can only be made on a semiquantitative level. According to our understanding, therefore, the K_a-values determined in the present study for the amino acid are most strongly supported by the titration results presented in Tables 1 and 2, which can be almost completely predicted by the model containing these values.

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