Dissociation Constants and Thermodynamic Properties of Amino Acids Used in CO₂ Absorption from (293 to 353) K

Espen S. Hamborg,[†] John P. M. Niederer,[‡] and Geert F. Versteeg*,[‡]

Department of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands, and Procede Group BV, P.O. Box 328, 7500 AH Enschede, The Netherlands

The second dissociation constants of the amino acids β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline and the third dissociation constants of L-glutamic acid and L-aspartic acid have been determined from electromotive force measurements at temperatures from (293 to 353) K. Experimental results are reported and compared to literature values. Values of the standard state thermodynamic properties are derived from the experimental results and compared to the values of commercially available amines used as absorbents for CO₂ capture.

1. Introduction

Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO₂ and H₂S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating.[1] It has been reported that alkanolamines undergo degradation in an oxygen atmosphere, usually encountered in the treatment of flue gases. Aqueous amino acid salt solutions might be an attractive alternative to alkanolamines. They have been found to have better resistance to degradation, and their reactivity with CO₂ is comparable to aqueous alkanolamines of related classes. Due to their ionic nature, aqueous solutions of salts of amino acids have negligible volatility and, among others, also have higher surface tension than aqueous solutions of alkanolamines.[2−4]

The second dissociation constants of β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline and the third dissociation constants of L-glutamic acid and L-aspartic acid have been determined from (293 to 353) K in this work by the use of electromotive force measurements. Parts of the results extend the temperature range of available literature data for the compounds under investigation.

2. Procedure

2.1. Amino Acids. β-Alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline dissociate in aqueous solutions according to

$$^-O_2C-R-NH_3{}^+ + H_2O \rightleftharpoons {}^-O_2C-R-NH_2 + H_3O^+ \quad (1)$$
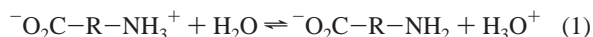
where the presence of the protonated amino acid zwitterion is neglected. The equilibrium constant can be determined by electromotive force (EMF) measurements using a combined glass pH electrode. A combined glass pH electrode has two well-known unpleasant properties.

* Corresponding author. E-mail: geert.versteeg@procede.nl.
† University of Twente.
‡ Procede Group BV.
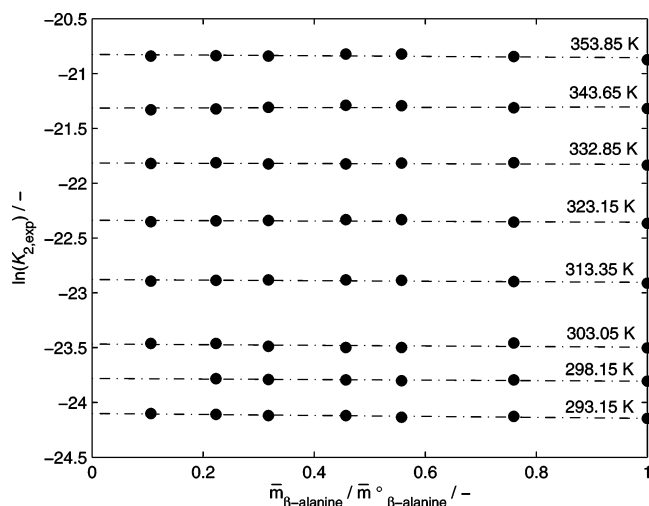
Figure 1. Influence of the dimensionless overall molality of β-alanine on $\ln(K_{2,\text{exptl}})$: ●, experimental values; -·-·, linear regression.

(1) Failure to obey the Nernst equation perfectly. This error arises due to the alkaline error and the asymmetry potential, which can vary with the change of the activity of H₃O⁺ in the solution under investigation. In strong alkaline solutions, errors may appear due to the contribution of alkaline ions (e.g., Na⁺, K⁺, etc.), and the measured activity of H₃O⁺ appears to be higher than the actual activity.

(2) A tendency to drift in potential by millivolts over periods of minutes to days. The standard potential of the electrode is not a constant in time.

To overcome the unpleasant properties described above, a combined glass pH electrode can be transferred back and forth between two solutions of different compositions while continuously recording the electrochemical potential. Measurements comparable to the accuracy of a system including a standard hydrogen electrode can be achieved if used with a noise-free voltmeter, proper shielding, and surrounding temperature matching of the solutions. The same electrode has to be used during both measurements, and the time period between the two measurements should be as short as possible.[5] A combined pH

Table 1. Comparison of Correlated Values of ln(K) and Thermodynamic Properties with Literature Data for Protonated MDEA

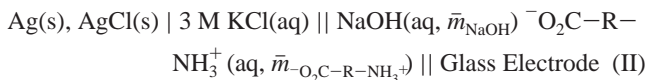| T/K	this work	Kamps[21]	Oscarson[10]	Kim[22]	Littel[11]	Schwabe[12]
			ln(K)			
293.00	-19.96^a	-19.93			-20.17	
298.15	-19.71	-19.69		-19.62		-19.60
298.20	-19.71		-19.71			
299.90	-19.63		-19.63			
303.00	-19.49	-19.47			-19.54	
308.15	-19.25					-19.13
311.00	-19.12		-19.11			
313.00	-19.03	-19.02				
318.15	-18.81					-18.69
323.00	-18.60	-18.60				
333.00	-18.18	-18.19			-19.06	
333.15	-18.17					-18.08
333.20	-18.17		-18.17		-18.38	
343.00	-17.77	-17.79				
353.00	-17.38	-17.41				
361.00	-17.08^a	-17.11	-17.09			
388.00	-16.11^a	-16.16	-16.14			
422.10	-15.00^a	-15.07	-15.06			
$\Delta_r G_m^\circ$/kJ·mol^{-1}	48.87	48.81	48.86	48.63		48.59
$\Delta_r H_m^\circ$/kJ·mol^{-1}	34.9	34.0	35.2	35.2		35.7

^{a} Extrapolated value.

electrode and a two-cell system were used to determine the dissociation constants

$$\text{Ag(s), AgCl(s)} \mid 3\text{ M KCl(aq)} \parallel \text{HCl(aq,} \bar{m}_{\text{HCl}}) \parallel$$
$$\text{Glass Electrode} \quad \text{(I)}$$

and

$$\text{Ag(s), AgCl(s)} \mid 3\text{ M KCl(aq)} \parallel \text{NaOH(aq, } \bar{m}_{\text{NaOH}}) \ ^-\text{O}_2\text{C}-\text{R}-$$
$$\text{NH}_3^+ \text{(aq, } \bar{m}_{-\text{O}_2\text{C}-\text{R}-\text{NH}_3^+}) \parallel \text{Glass Electrode} \quad \text{(II)}$$
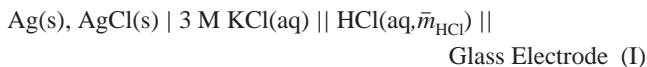
HCl was chosen to be used in cell I as a reference solution, since a combined pH electrode can determine the activity of H_3O^+ with a higher accuracy in an acidic solution than in a basic solution. As the activity of a pure solid is set to unity, the Nernst equation for cell I results in

$$E_I = E^\circ(T_I) - \frac{RT_I}{F} \ln(a_{\text{H}_3\text{O}^+} a_{\text{Cl}^-})_I \quad (2)$$

and for cell II results in

$$E_{II} = E^\circ(T_{II}) - \frac{RT_{II}}{F} \ln(a_{\text{H}_3\text{O}^+} a_{\text{Cl}^-})_{II} \quad (3)$$

As both cells are at the same temperature, $T_I = T_{II}$, the standard potential of the combined pH electrode is the same during both measurements, $E^\circ(T_I) = E^\circ(T_{II})$

$$T_{II} \ln(a_{\text{H}_3\text{O}^+} a_{\text{Cl}^-})_{II} = \frac{F(E_I - E_{II})}{R} + T_I \ln(a_{\text{H}_3\text{O}^+} a_{\text{Cl}^-})_I \quad (4)$$

In the case of exact temperature matching of the two cells, $T_I = T_{II} = T$, the activity of the inner reference electrolyte of the combined pH electrode is identical during both measurements, $(a_{\text{Cl}^-})_I = (a_{\text{Cl}^-})_{II}$

$$\ln(a_{\text{H}_3\text{O}^+})_{II} = \frac{F(E_I - E_{II})}{RT} + \ln(a_{\text{H}_3\text{O}^+})_I \quad (5)$$

As HCl is completely dissociated, the dissociation of water can be neglected in cell I. The mass balances for the amino acid, NaOH, and water in cell II are

$$\bar{n}_{-\text{O}_2\text{C}-\text{R}-\text{NH}_3^+} = n_{-\text{O}_2\text{C}-\text{R}-\text{NH}_3^+} + n_{-\text{O}_2\text{C}-\text{R}-\text{NH}_2} \quad (6)$$

$$\bar{n}_{\text{NaOH}} = n_{\text{Na}^+} \quad (7)$$

$$\bar{n}_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} + n_{\text{H}_3\text{O}^+} + n_{\text{OH}^-} \quad (8)$$

Electroneutrality results in

$$n_{\text{Na}^+} + n_{\text{H}_3\text{O}^+} = n_{-\text{O}_2\text{C}-\text{R}-\text{NH}_2} + n_{\text{OH}^-} \quad (9)$$

The chemical equilibrium conditions for both reactions present are

$$K_w(T) = \frac{a_{\text{H}_3\text{O}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}^2} \quad (10)$$

$$K(T) = \frac{a_{-\text{O}_2\text{C}-\text{R}-\text{NH}_2} a_{\text{H}_3\text{O}^+}}{a_{-\text{O}_2\text{C}-\text{R}-\text{NH}_3^+} a_{\text{H}_2\text{O}}} \quad (11)$$

For a given temperature and composition, the electromotive forces E_I and E_{II} and the temperature in each cell are measured.

Activities of HCl and KCl are estimated using the excess energy model of Pitzer from Holmes[6] and Pabalan,[7] respectively. The activity of water follows from the Gibbs–Duhem equation. A very brief outline of the excess energy model of Pitzer used in this work is given in Appendix A. Activities of the compounds present in cell II are approximated using the modified Debye-Hückel term in Pitzer's equation, i.e., neglecting binary and ternary parameters. The activity coefficient of the zwitterion structure of the amino acid is set to unity for all molalities and temperatures. The influence of pressure on the chemical reactions is neglected, and it is set to 1 bar during the described calculations. The changes in the compositions of the electrolyte cells due to the outflow of the KCl electrolyte from the electrode are neglected. The water dissociation constant, $K_w(T)$, is taken from Fisher.[8] With the given information, eq 4 to eq 11 are solved iteratively to yield the "true" number of moles of each species present in cell II, as well as a preliminary value for the dissociation constant of the amino acid. This dissociation constant is called preliminary because it is calculated out of a set of equations in which for cell II the activities are not exactly known. The experiments are performed at

Table 2. Comparison of Correlated Values of ln(K₂) and Thermodynamic Properties with Literature Values for β-Alanine

T/K	this work	May[24]	Gillespie[13]	Dey[14]	Majumdar[15]	Boyd[23]	Christensen[25]
				ln(K_2)			
273.15	−25.51[a]	−25.35				−25.44	
278.15	−25.14[a]	−24.95					
288.15	−24.44[a]	−24.23				−24.37	
298.00	−23.79			−23.44	−23.53		
298.15	−23.78	−23.56				−23.71	−23.57
308.15	−23.17	−22.94				−23.09	
313.15	−22.88	−22.65					
318.15	−22.60					−22.52	
323.15	−22.33		−22.09				
348.15	−21.09		−20.84				
398.15	−19.09[a]		−18.82				
$\Delta_r G_m^\circ$/kJ·mol⁻¹	58.95	58.41				58.77	
$\Delta_r H_m^\circ$/kJ·mol⁻¹	46.8	47.5	47.3			46.9	

[a] Extrapolated value.

Table 3. Comparison of Correlated Values of ln(K₂) and Thermodynamic Properties with Literature Values for Taurine

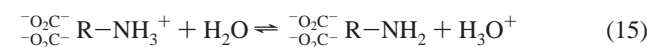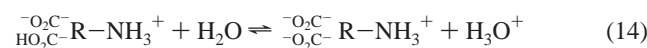| T/K	this work	King[27]
	ln(K_2)	
283.15	−21.75[a]	−21.76
288.15	−21.44[a]	−21.45
293.15	−21.15[a]	−21.15
298.15	−20.86	−20.86
303.15	−20.58	−20.59
308.15	−20.32	−20.32
313.15	−20.06	−20.06
318.15	−19.81	−19.81
323.15	−19.57	−19.57
$\Delta_r G_m^\circ$/kJ·mol⁻¹	51.71	51.76
$\Delta_r H_m^\circ$/kJ·mol⁻¹	41.6	41.9

[a] Extrapolated value.

different overall molalities of the amino acid, and the "true" equilibrium constant of the dissociation of the amino acid is determined in a two-step linear extrapolation procedure

$$\lim_{\substack{\bar{m}_{NaOH,II}=const. \\ \bar{m}_{-O_2C-R-NH_3^+}\to 0}} [K_{2,exptl}(T, \bar{m}_{-O_2C-R-NH_3^+}, \bar{m}_{NaOH,II})] =$$

$$K_{2,exptl}(T, \bar{m}_{NaOH,II}) \quad (12)$$

$$\lim_{\bar{m}_{NaOH,II}\to 0} K_{2,exptl}(T, \bar{m}_{NaOH,II}) = K_2(T) \quad (13)$$

However, if $\bar{m}_{NaOH,II}$ is small enough (e.g., $\bar{m}_{NaOH,II} \leq \sim 0.01$ mol·kg⁻¹), the second extrapolation is not necessary.

2.2. Dicarboxylic Amino Acids. L-Glutamic acid and L-aspartic acid dissociate according to

$$\begin{matrix} ^{-O_2C^-} \\ _{HO_2C^-} \end{matrix} R-NH_3^+ + H_2O \rightleftharpoons \begin{matrix} ^{-O_2C^-} \\ _{-O_2C^-} \end{matrix} R-NH_3^+ + H_3O^+ \quad (14)$$

$$\begin{matrix} ^{-O_2C^-} \\ _{-O_2C^-} \end{matrix} R-NH_3^+ + H_2O \rightleftharpoons \begin{matrix} ^{-O_2C^-} \\ _{-O_2C^-} \end{matrix} R-NH_2 + H_3O^+ \quad (15)$$

where the presence of the protonated amino acid zwitterion is neglected. Measurements of the third dissociation constants of L-glutamic acid and L-aspartic acid were performed in a manner similar to that described above. However, eq 6 to eq 13 had to be adapted to describe the composition in cell II

$$\bar{n}_{\substack{-O_2C^- \\ HO_2C^-}R-NH_3^+} = n_{-O_2C^-R-NH_3^+} + n_{-O_2C^-R-NH_2} \quad (16)$$

$$\bar{n}_{NaOH} = n_{Na^+} \quad (17)$$

Table 4. Comparison of Correlated Values of ln(K₂) and Thermodynamic Properties with Literature Values for Sarcosine

T/K	this work	Datta[28,29]
	ln(K_2)	
278.15	−24.66[a]	−24.67
288.15	−24.06[a]	−24.06
298.15	−23.51	−23.49
308.15	−22.99	−22.96
318.15	−22.50	−22.47
$\Delta_r G_m^\circ$/kJ·mol⁻¹	58.27	58.22
$\Delta_r H_m^\circ$/kJ·mol⁻¹	39.7	40.5

[a] Extrapolated value.

Table 5. Comparison of Correlated Values of ln(K₂) and Thermodynamic Properties with Literature Values for 6-Aminohexanoic Acid

T/K	this work	Smith[30]	Gillespie[13]	Brandariz[31]
	ln(K_2)			
274.15	−27.19[a]	−26.86		
285.65	−26.20[a]	−25.89		
298.15	−25.21	−24.88		−25.12
310.65	−24.29	−23.96		
323.15	−23.44	−23.11	−23.08	
348.15	−21.90		−21.57	
398.15	−19.37[a]		−19.19	
$\Delta_r G_m^\circ$/kJ·mol⁻¹	62.49	61.71		
$\Delta_r H_m^\circ$/kJ·mol⁻¹	56.5	56.8		

[a] Extrapolated value.

$$\bar{n}_{H_2O} = n_{H_2O} + n_{H_3O^+} + n_{OH^-} \quad (18)$$

Electroneutrality results in

$$n_{Na^+} + n_{H_3O^+} = n_{\substack{-O_2C^- \\ -O_2C^-}R-NH_3^+} + 2n_{\substack{-O_2C^- \\ -O_2C^-}R-NH_2} + n_{OH^-} \quad (19)$$

The chemical equilibrium conditions for both reactions present are

$$K_w(T) = \frac{a_{H_3O^+}a_{OH^-}}{a_{H_2O}^2} \quad (20)$$

$$K(T) = \frac{a_{\substack{-O_2C^- \\ -O_2C}R-NH_2}a_{H_3O^+}}{a_{\substack{-O_2C^- \\ -O_2C^-}R-NH_3^+}a_{H_2O}} \quad (21)$$

Because between one and two moles of NaOH have to be added to each initial mole of amino acid in this case, the

Table 6. Comparison of Correlated Values of ln(K_2) and Thermodynamic Properties with Literature Values for DL-Methionine

T/K	this work	Pelletier[32]
	ln(K_2)	
283.15	-22.36^a	-22.40
298.15	-21.42	-21.37
303.15	-21.13	-21.07
313.15	-20.59	-20.54
$\Delta_r G_m^\circ$/kJ·mol^{-1}	53.09	52.75
$\Delta_r H_m^\circ$/kJ·mol^{-1}	43.4	43.5

^{a} Extrapolated value.

extrapolation to zero ionic strength is performed according to

$$\lim_{\substack{\bar{m}_{NaOH,II} \to 0 \\ m_{\bar{m}^{-O_2C^-}_{HO_2C}R-NH_3^+} \to 0}} [K_{3,exptl}(T, \bar{m}_{HO_2C}^{-O_2C^-}{}_{R-NH_3^+}, \bar{m}_{NaOH,II})] = K_3(T) \tag{22}$$

2.3. Alkanolamines. Measurements of the dissociation constant of protonated methyldiethanolamine (MDEA) were performed to validate the experimental setup and technique. Protonated MDEA dissociates according to

$$MDEAH^+ + H_2O \rightleftharpoons MDEA + H_3O^+ \tag{23}$$

HCl was used in cell II instead of NaOH, and consequently eq 6 to eq 13 were adapted to describe the composition of the cell

$$\bar{n}_{MDEA} = n_{MDEA} + n_{MDEAH^+} \tag{24}$$

$$\bar{n}_{HCl} = n_{Cl^-} \tag{25}$$

$$\bar{n}_{H_2O} = n_{H_2O} + n_{H_3O^+} + n_{OH^-} \tag{26}$$

Electroneutrality results in

$$n_{MDEAH^+} + n_{H_3O^+} = n_{Cl^-} + n_{OH^-} \tag{27}$$

The chemical equilibrium conditions for both reactions present are

$$K_w(T) = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}^2} \tag{28}$$

$$K(T) = \frac{a_{MDEA} a_{H_3O^+}}{a_{MDEAH^+} a_{H_2O}} \tag{29}$$

The linear extrapolation to zero molalities was done as in eqs 12 and 13

$$\lim_{\substack{\bar{m}_{HCl,II}=const. \\ \bar{m}_{MDEA} \to 0}} [K_{exptl}(T, \bar{m}_{MDEA}, \bar{m}_{HCl,II})] = K_{exptl}(T, \bar{m}_{HCl,II}) \tag{30}$$

$$\lim_{\bar{m}_{HCl,II} \to 0} K_{exptl}(T, \bar{m}_{HCl,II}) = K(T) \tag{31}$$

3. Thermodynamic Relations

To the experimentally determined dissociation constants, the well-known thermodynamic relations are applied

$$\Delta_r G_m = -RT \ln K \tag{32}$$

$$\Delta_r H_m = -R \frac{d \ln K}{d(1/T)} \tag{33}$$

and the change of standard state properties ($T = T^\circ = 298.15$ K) for the dissociation of an amino acid in water are calculated from eq 32 to eq 33 by use of[9]

$$\ln K_i = \frac{A}{T} + B + C \ln(T) \tag{34}$$

where $i = 0$ for protonated MDEA, $i = 1$ for β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline, and $i = 2$ for L-aspartic acid and L-glutamic acid. The further thermodynamic relations can be calculated by the reader

$$\Delta_r S_m = \frac{(\Delta_r H_m - \Delta_r G_m)}{T} \tag{35}$$

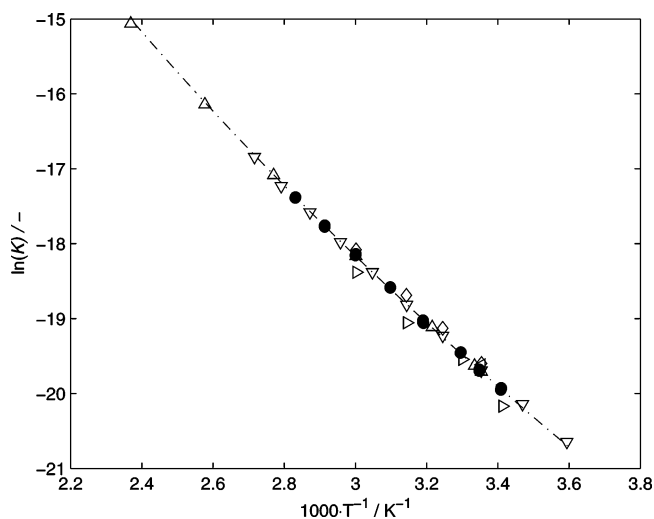$$\Delta_r C_{P,m} = \frac{d\Delta_r H_m}{dT} \tag{36}$$

4. Experimental

For the EMF measurements, a pH voltmeter (Metrohm 780) with a resolution of 0.1 mV and 0.1 K was used, together with a combined pH glass electrode (Metrohm 6.0258.010) with a 3 M KCl (Metrohm 6.2308.020) inner reference electrolyte and an integrated Pt1000 temperature sensor. When not in use, the electrode was stored in a storage solution (Metrohm 6.2323.000). Before each measurement, the electrode was carefully rinsed with distilled water and dried with paper tissue. The cells were completely filled with the electrolyte solutions, placed in a temperature controlled water bath, and sealed between each measurement. The experiments were performed under a nitrogen atmosphere inside a glovebox to prevent CO$_2$ from the air from absorbing into the electrolyte solutions. During each measurement the electromotive force (E/mV) and the temperature in the cell (T/K) were recorded.

Measurements were performed from (293 to 353) K at 10 K intervals and at 298.15 K. The overall molality of HCl in cell I and in cell II was held constant ($\bar{m}_{HCl,I} \approx \bar{m}_{HCl,II} \approx 0.01$ mol·kg^{-1}) during measurements of the dissociation constants of protonated MDEA. The overall molality of MDEA was between (0.0455 and 0.9033) mol·kg^{-1}. During measurements of β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline, the overall molality of HCl in cell I and NaOH in cell II was held constant in all solutions ($\bar{m}_{HCl,I} \approx \bar{m}_{NaOH,II} \approx 0.01$ mol·kg^{-1}). The overall molality of the amino acids was between (0.0121 and 0.8823) mol·kg^{-1}. During measurements of L-glutamic acid and L-aspartic acid, the molality of the amino acids was between 0.0050 mol·kg^{-1} and 0.0644 mol·kg^{-1}, and the molality of sodium hydroxide was approximately 1.5 times that of the amino acid. The overall molality of HCl in cell I was held constant ($\bar{m}_{HCl,I} \approx 0.01$ mol·kg^{-1}). Measurements where the temperature in cell I and in cell II deviated by more than ± 0.1 K were not considered in the described calculations.

5. Chemicals

MDEA [105-59-9], β-alanine [107-95-9], taurine [107-35-7], sarcosine [107-97-1], 6-aminohexanoic acid [60-32-2], DL-methionine [59-51-8], glycine [56-40-6], L-phenylalanine [63-91-2], L-proline [147-85-3], L-glutamic acid [56-86-0], L-aspartic acid [56-84-8] (Sigma-Aldrich), and NaOH [1310-73-2] and HCl [7647-01-0] (Merck) were used as supplied. NaOH and HCl were provided as 0.1 M standard solutions, diluted to the desired

Table 7. Comparison of Correlated Values of *ln(K₂)* and Thermodynamic Properties with Literature Values for Glycine

T/K	this work	Datta[28,29]	King[33]	Owen[34]	Gillespie[13]	Clarke[35]	Izatt[16]
				$\ln(K_2)$			
278.15	−23.80[a]	−23.81					
283.15	−23.45[a]		−23.47	−23.50			
288.15	−23.12[a]	−23.14	−23.14	−23.15			
293.15	−22.81		−22.82	−22.82			
298.15	−22.50	−22.51	−22.52	−22.51			
303.15	−22.21		−22.22	−22.21			
308.15	−21.93	−21.94	−21.94	−21.93			
313.15	−21.66		−21.67	−21.65			
318.15	−21.40	−21.40	−21.41	−21.39			
323.15	−21.16		−21.16		−21.17		−21.17
348.15	−20.05				−20.03	−20.70	−20.01
378.15	−18.96[a]					−19.66	
398.15	−18.35[a]				−18.31	−18.95	
$\Delta_r G_m^\circ$/kJ·mol^{-1}	55.78	55.81	55.85				
$\Delta_r H_m^\circ$/kJ·mol^{-1}	44.0	44.2	44.2	45.3			43.95

[a] Extrapolated value.

Table 8. Comparison of Correlated Values of ln(K₂) and Thermodynamic Properties with Literature Values for L-Phenylalanine

T/K	this work	Izatt[36]
	$\ln(K_2)$	
273.15	−22.95[a]	−22.91
283.15	−22.29[a]	−22.24
293.15	−21.69[a]	−21.60
303.15	−21.12	−21.07
313.15	−20.59	−20.47
$\Delta_r G_m^\circ$/kJ·mol^{-1}	53.04	
$\Delta_r H_m^\circ$/kJ·mol^{-1}	42.0	43.1

[a] Extrapolated value.

Table 9. Comparison of Correlated Values of ln(K₂) and Thermodynamic Properties with Literature Values for L-Proline

T/K	this work	Smith[37]	Azab[17]
		$\ln(K_2)$	
274.15	−26.22[a]	−26.01	
285.65	−25.50[a]	−25.26	
298.15	−24.77	−24.50	−24.45
310.65	−24.09	−23.81	
323.15	−23.45	−23.17	
$\Delta_r G_m^\circ$/kJ·mol^{-1}	61.41	60.75	
$\Delta_r H_m^\circ$/kJ·mol^{-1}	41.6	43.2	

[a] Extrapolated value.

Table 10. Comparison of Correlated Values of ln(K₃) and Thermodynamic Properties with Literature Values for L-Glutamic Acid

T/K	this work	Albert[18]	Wilson[19]
		$\ln(K_3)$	
293.15	−23.21	−22.84	
298.15	−22.95		−22.88
$\Delta_r G_m^\circ$/kJ·mol^{-1}	56.90		
$\Delta_r H_m^\circ$/kJ·mol^{-1}	37.5		

molalities, and checked by means of titration. Water was demineralized and further purified by vacuum distillation.

6. Results and Discussion

Experimental results at averaged temperatures for the dissociation constants of protonated MDEA, the second dissociation constants of β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline, and the third dissociation constants of L-glutamic acid and L-aspartic acid are given in Appendix B with experimental uncertainties. The experimental uncertainties are due to inaccuracies in E_I and E_{II} of $\pm$ 0.5 mV. The results are also given with the average and maximum relative deviation between the experimental data and the values from the linear fit. These numbers provide insight into the accuracy of the linear extrapolation. The experimental equilibrium data are given as Supporting Information with "Run no." corresponding to Appendix B.

In Figure 1, $\ln(K_{2,\text{exptl}})$ is plotted as function of the dimensionless overall molality of β-alanine according to eq 12 and eq 13. The extrapolations to zero amino acid molality were done by linear regression for MDEA, β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline. The intercept at zero amino acid molality is ln-$(K_{2,\text{exptl}})$ and $\ln(K_{\text{exptl}})$ in the case of MDEA. For L-glutamic acid and L-aspartic acid, a linear extrapolation yields $\ln(K_3)$ at the intercept of zero ionic strength according to eq 22.

In Table 1 to Table 11, correlated experimental results of the dissociation constants and the values of the standard state thermodynamic properties are given and compared to available literature values. Literature dissociation constants that are based on the molarity scale[10−19] were converted to the molality scale by

$$K = \frac{1}{\rho_w}\left(\frac{c^\circ}{m^\circ}\right)K_c \qquad (37)$$

where ρ_w is the mass density of pure water taken from Saul[20] and K_c is the dissociation constant based on the molarity scale.

Experimental results of the dissociation constants of protonated MDEA have been reported by Kamps,[21] Oscarson,[10] Kim,[22] Littel,[11] and Schwabe.[12] The results are given in Table 1 and Figure 2. The correlated values from this work agree well with the results by Kamps[21] and Oscarson,[10] with an average relative deviation (in $\ln(K)$) of 0.01 % and 0.03 %, respectively. The values extrapolated to higher temperatures are within 0.08 % and 0.21 % of the results by Kamps[21] and Oscarson,[10] respectively. The results by Kim,[22] Littel,[11] and Schwabe[12] are within 0.46 %, 1.76 %, and 0.58 %, respectively. The values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ agree well with the literature values. The largest relative deviations in $\Delta_r G_m^\circ$ are from those of Schwabe[12] with 0.58 % and in $\Delta_r H_m^\circ$ are from those of Kamps[21] with 2.65 %.

The correlated values of the second dissociation constants of β-alanine are in the best agreement with the results by Boyd,[23] with an average relative deviation (in $\ln(K_2)$) of 0.31 %. The results by May,[24] Gillespie,[13] Dey,[14] and Majumdar[15] deviate by 0.87 %, 1.24 %, 1.49 %, and 1.10 %, respectively. The differences between the correlated values of this work and the litterature values for β-alanine are larger than those of protonated MDEA. May[24] did not take activity coefficients of the compounds into consideration when determining the second dissociation constants from experimental data; hence, the activity coefficients were set to unity for all species. If the activity

Figure 2. Dissociation constants of protonated MDEA: ●, exptl results this work; -·- ·, fit this work; ▽, Kamps;[21] △, Oscarson;[10] open triangle pointing left, Kim;[22] open triangle pointing right, Littel;[11] ◇, Schwabe.[12]

Table 11. Comparison of Correlated Values of ln(K_3) and Thermodynamic Properties with Literature Values for L-Aspartic Acid

T/K	this work	Smith[30]	Batchelder[38]
		ln(K_3)	
274.15	−24.87	−24.42	
285.65	−24.13	−23.73	
298.15	−23.40	−23.03	−22.66
310.65	−22.74	−22.43	
323.15	−22.13	−21.90	
$\Delta_r G_m^\circ$/kJ·mol^{-1}	58.01	57.15	
$\Delta_r H_m^\circ$/kJ·mol^{-1}	41.2	37.8	

coefficients are set to unity in the present work, the correlated values from this work have an average relative deviation of 0.04 % compared to May.[24] The results by Gillespie[13] differ with an average relative deviation of 1.24 % from the correlated values of this work. Gillespie[13] determined $\Delta_r H_m^\circ$ experimentally by flow calorimetry and used a temperature specific value of ln-(K_2) to derive temperature-dependent values of ln(K_2). By this, the accuracy of the results from the calorimetric data will follow the accuracy of the temperature specific value of ln(K_2) used. Gillespie[13] chose a value from Christensen.[25] Christensen[25] described the estimation of the activity coefficients inadequately, and consequently, it is difficult to explain the differences between the results of Gillespie,[13] Christensen,[25] and this work. In the work of Dey[14] and Majumdar,[15] the activity coefficients were set to unity for all compounds. By applying this to the present work, the second dissociation constants differ by 0.55 % and 0.17 %, respectively. Boyd[23] estimated the activity coefficients of the compounds using the Davies equation,[26] a form of the Debye−Hückel equation. By applying the Davies equation to this work, the correlated results have a relative average deviation of 0.19 % compared to Boyd.[23] Values of the thermodynamic properties of β-alanine are given by May,[24] Gillespie,[13] and Boyd.[23] The results by Boyd[23] are in best agreement with the results from this work, with a deviation of 0.30 % and 0.21 % in $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$, respectively.

Experimental values of the second dissociation constants of taurine are reported by King.[27] Correlated values from this work are in agreement with the results by King[27] with an average relative deviation (in ln(K_2)) of 0.02 %. The thermodynamic values are also in agreement, with a relative deviation of 0.10 % and 0.72 % in $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$, respectively.

Values of the second dissociation constants of sarcosine are reported by Datta.[28] The correlated values have an average relative deviation of 0.06 % from the results by Datta.[28] Values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ given by Datta[29] have a relative deviation of 0.09 % and 2.02 % from the values of this work.

Smith,[30] Gillespie,[13] and Brandariz[31] reported values for the second dissociation constants of 6-aminohexanoic acid, and the values deviate by 1.29 %, 1.32 %, and 0.36 % (in ln(K_2)) from this work, respectively. In the work of Smith,[30] the activity coefficients of the amino acid are set to unity. By applying this to the present work, the average relative deviation is 0.43 %. Gillespie[13] measured $\Delta_r H_m^\circ$ by flow calorimetry and used a temperature specific value of the dissociation constant from Smith.[30] With activity coefficients set to unity in this work, the relative difference is 0.12 %. The relative difference between this work and the work of Brandariz[31] is 0.36 %. Smith[30] reported values for $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$, and the values have a relative deviation of 1.24 % and 0.53 % from this work, respectively.

Values of the second dissociation constants of DL-methionine are reported by Pelletier.[32] The results have an average relative deviation of 0.15 % (in ln(K_2)) from the correlated values of this work. The values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ have a relative deviation of 0.64 % and 0.23 %, respectively.

Values of the second dissociation constants of glycine have been reported by Datta,[28] King,[33] Owen,[34] Gillespie,[13] Clarke,[35] and Izatt.[16] The results by the authors have a relative deviation (in ln(K_2)) of 0.04 %, 0.05 %, 0.04 %, 0.09 %, 3.40 %, and 0.08 % from this work, respectively. Datta[29] and King[33] reported values with a relative deviation of 0.05 % and 0.13 % in $\Delta_r G_m^\circ$ and of 0.45 % and 0.45 % in $\Delta_r H_m^\circ$, respectively. Owen[34] and Izatt[16] also reported values for $\Delta_r H_m^\circ$ with relative deviations of 2.95 % and 0.11 %.

Izatt[36] reported values of the second dissociation constants of L-phenylalanine, and the results deviate (in ln(K_2)) with an average of 0.33 % from the correlated values of this work. $\Delta_r H_m^\circ$ from Izatt[36] deviates by 2.6 % from this work.

Values of the second dissociation constants of L-proline are reported by Smith[37] and Azab,[17] and the values have an average relative deviation of 1.04 % and 1.29 % (in ln(K_2)) from the correlated values of this work. In the work of Smith,[37] the activity coefficients of each compound were set to unity. By applying so to this work, the values by Smith[37] have an average relative deviation of 0.15 %. The values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ from Smith[37] have a relative deviation of 1.07 % and 3.85 %.

Values of the third dissociation constants of L-glutamic acid have been reported by Albert[18] and Wilson[19] at (293.15 and 298.15) K, and the results deviate by 1.59 % and 0.31 % (in ln(K_3)) from the correlated results of this work. Albert[18] used a titration technique to determine the third dissociation constants without taking activity coefficients into consideration. However, the large relative deviation from this work cannot be explained. In addition to the potentiometrically determined result at 298.15 K, Wilson[19] also carried out measurements of the third dissociation constants at elevated temperatures using a kinetic approach. Those results contain large uncertainties and are not compared to the results from this work.

Smith[30] and Batchelder[38] have reported values of the third dissociation constants of L-aspartic acid. The results by these authors have a relative deviation of 1.49 % and 3.16 % (in ln-(K_3)), respectively, from the correlated results of this work. Smith[30] used the Debye−Hückel term, $\log (\gamma^{(m)}) = -A_\phi z_i^2 \sqrt{I_m}$, to estimate the activity coefficients of the compounds. By applying the term to the present work, the results by Smith[30]

Table 12. Comparison of Values of the Standard State Thermodynamic Properties for Commercially Available absorbents to this work

compound	ref	$\Delta_r G_m^\circ/\text{kJ·mol}^{-1}$	pK_a	$\Delta_r H_m^\circ/\text{kJ·mol}^{-1}$
6-aminohexanoic acid	this work	62.49	10.95	56.5
L-proline	this work	61.41	10.76	41.6
β-alanine	this work	58.95	10.33	46.8
sarcosine	this work	58.28	10.21	39.7
L-aspartic acid	this work	58.01	10.16	41.2
L-glutamic acid	this work	56.90	9.97	37.5
3-amino-1-propanol (MPA)	[12]	56.85	9.96	53.6
glycine	this work	55.78	9.77	44.0
piperazine (PZ)	[43]	55.55	9.73	42.9
2-amino-2-methyl-1-propanol (AMP)	[11]	55.40	9.71	49.9
monoethanolamine (MEA)	[44]	54.21	9.50	50.5
2-(2-aminoethoxy)ethanol (DGA)	[10]	53.74	9.42	50.2
DL-methionine	this work	53.09	9.30	43.4
L-phenylalanine	this work	53.04	9.29	42.0
taurine	this work	51.69	9.06	41.5
diisopropanolamine (DIPA)	[22]	50.69	8.88	42.7
diethanolamine (DEA)	[45]	50.68	8.88	42.4
methyldiethanolamine (MDEA)	this work	48.87	8.56	34.9

Table 13. Parameters for Equation 44

parameter	$\beta_{KCl}^{(0)}$ kg·mol^{-1}	$\beta_{KCl}^{(1)}$ kg·mol^{-1}	C_{KCl} kg^2·mol^{-2}
u_1	−2.10289e−2	2.20813e−1	0.0
u_2	6.03967e−1	−4.61849	7.64891e−4
u_3	3.67768e−3	−4.10116e−2	0.0
u_4	−7.05537e−6	1.10445e−4	−1.12131e−8
u_5	1.97968e−9	−4.73196e−8	1.72256e−11
u_6	−2.47588e−3	−2.74120e−2	0.0
u_7	1.44160e−1	3.32883e−1	−5.71188e−3
$f_L(T_r, 1\text{ bar})$	6.77136e−4	9.67854e−4	−4.12364e−5
$f_L(T_r, P_r)$	6.56838e−4	9.67854e−4	−4.12364e−5
$f_G(T_r, 1\text{ bar})$	4.8080e−2	2.18752e−1	−3.94e−4
$f_G(T_r, P_r)$	5.0038e−2	2.18752e−1	−3.94e−4
K_1	−2931.268116	6353.355434	28.172180
K_2	−33.953143	193.004059	−0.125567

Table 14. Parameters for Equation 46

parameter	$B_{KCl}^V/\text{kg·(mol·bar)}^{-1}$
q_1	0.0
q_2	0.0
q_3	9.45015e−8
q_4	−2.90741e−10
q_5	3.26205e−3
q_6	8.39662e−7
q_7	0.0
q_8	−4.41638e−9
q_9	6.71235e−12
q_{10}	−4.42327e−5
q_{11}	−7.97437e−10
q_{12}	0.0
q_{13}	4.12771e−12
q_{14}	−6.24996e−15
q_{15}	4.16221e−8

Table 15. Parameters for Equation 48

parameter	$\beta_{HCl}^{(0)}$ kg·mol^{-1}	$\beta_{HCl}^{(1)}$ kg·mol^{-1}	C_{HCl} kg^2·mol^{-2}
q_1	0.17690	0.2973	0.362e−3
q_2	−0.09140	16.147	0.0
q_3	0.0	−17.631e−3	0.0
q_4	−4.034e−4	0.0	−3.036e−5
q_5	0.620e−4	7.20e−4	0.0

estimations of the activity coefficients are important to achieve accurate results of the dissociation constants.

During the measurements described, NaOH is used to deprotonate the amino acids and form an amino acid salt. KOH and LiOH have also been used to form amino acid salts to see the effect on the determined dissociation constants by having different counterions. The second dissociation constants of taurine were determined at (293.15, 323.15, and 353.15) K using the three different counterions. The results with sodium, potassium, and lithium as counterions are given and compared in Appendix B. It shows that the results are all within the experimental uncertainties, and there are no significant effects using the different counterions. The experimental equilibrium data are given as Supporting Information. According to electrolyte thermodynamics, activity coefficients are only dependent on the ionic strength in dilute solutions (e.g., $I_m \leq \sim 0.01$ mol·kg^{-1}) and not on individual ionic molalities or other solute properties.[39] Since the ionic strengths of the solutions under investigation are low (e.g., $\bar{m}_{Na+}$, K$^+$, Li$^+$ ≤ ∼0.01 mol·kg^{-1}), it can be concluded that the type of counterion does not affect the determined dissociation constants. However, if measurements were to be done at higher ionic strength, the type of counterion would most likely have an effect on the determined dissociation constants.

Table 12 shows $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ of primary and secondary amines used as commercial CO$_2$ absorbents in comparison to the results from this work. The pK_a value of each compound is also listed for the convenience of the reader. The compounds are sorted with descending $\Delta_r G_m^\circ$ and pK_a values. The thermodynamic values from this work are relisted in Table 12 for the convenience of the reader.

Blauwhoff[40] and Versteeg[41,42] related the basic strength of an absorbent to the CO$_2$ reaction rate constant by a Brønsted

deviate by 1.08 %. Batchelder[38] also estimated the activity coefficients by a Debye−Hückel term. Even though the estimation of the activity coefficients differs from the term used in this work, the large deviation cannot be explained. Values of the thermodynamic properties of the third dissociation are reported by Smith,[30] and the relative deviations from this work in $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ are 1.48 % and 8.25 %.

The results of the dissociation constants presented in this work are in agreement with the above listed literature values. As shown, the values of the estimated activity coefficients of the compounds have an influence on the final results. Accurate

Table 16. Extrapolated Experimental Results of the Dissociation Constants

run no.	T/K	$\ln(K)$	avg. rel. dev./%	max. rel. dev./%	run no.	T/K	$\ln(K)$	avg. rel. dev./%	max. rel. dev./%
		Dissociation Constants of Protonated MDEA					Second Dissociation Constants of β-Alanine		
1	293.28	-19.92 ± 0.04	0.038	0.084	1	293.13	-24.10 ± 0.04	0.017	0.037
2	293.32	-19.93 ± 0.05	0.030	0.069	2	293.16	-24.11 ± 0.04	0.013	0.029
3	293.44	-19.95 ± 0.04	0.018	0.040	3	293.21	-24.11 ± 0.04	0.025	0.053
4	298.65	-19.68 ± 0.04	0.026	0.059	4	298.18	-23.78 ± 0.04	0.015	0.025
5	298.67	-19.69 ± 0.04	0.035	0.087	5	298.28	-23.77 ± 0.04	0.020	0.035
6	298.73	-19.70 ± 0.04	0.015	0.029	6	298.32	-23.77 ± 0.04	0.018	0.048
7	303.46	-19.45 ± 0.04	0.036	0.088	7	303.06	-23.47 ± 0.04	0.061	0.127
8	303.48	-19.46 ± 0.04	0.017	0.056	8	303.20	-23.46 ± 0.04	0.023	0.043
9	313.44	-19.06 ± 0.04	0.023	0.040	9	303.21	-23.47 ± 0.04	0.060	0.098
10	313.54	-19.02 ± 0.04	0.032	0.050	10	313.10	-22.88 ± 0.04	0.018	0.042
11	313.56	-19.05 ± 0.04	0.010	0.023	11	313.26	-22.88 ± 0.04	0.014	0.028
12	322.83	-18.58 ± 0.04	0.023	0.041	12	313.32	-22.88 ± 0.04	0.027	0.056
13	322.84	-18.59 ± 0.04	0.022	0.038	13	323.04	-22.34 ± 0.04	0.018	0.033
14	333.23	-18.15 ± 0.04	0.023	0.041	14	323.13	-22.33 ± 0.04	0.021	0.040
15	333.26	-18.14 ± 0.04	0.023	0.056	15	323.15	-22.34 ± 0.04	0.036	0.064
16	333.34	-18.16 ± 0.04	0.019	0.051	16	332.81	-21.83 ± 0.04	0.032	0.096
17	343.16	-17.78 ± 0.04	0.049	0.087	17	332.85	-21.82 ± 0.04	0.029	0.056
18	343.22	-17.76 ± 0.04	0.022	0.041	18	332.94	-21.79 ± 0.04	0.032	0.074
19	353.17	-17.38 ± 0.03	0.040	0.085	19	343.39	-21.32 ± 0.04	0.027	0.055
20	353.26	-17.39 ± 0.04	0.043	0.090	20	343.66	-21.31 ± 0.04	0.057	0.104
					21	343.72	-21.30 ± 0.04	0.018	0.020
					22	353.74	-20.83 ± 0.03	0.024	0.046
					23	353.87	-20.82 ± 0.04	0.058	0.092
					24	353.94	-20.82 ± 0.04	0.039	0.059
		Second Dissociation Constants of Taurine					Second Dissociaion Constants of Sarcosine		
1	293.22	-21.18 ± 0.04	0.016	0.026	1	293.66	-23.76 ± 0.04	0.028	0.048
2	293.64	-21.12 ± 0.04	0.048	0.094	2	293.74	-23.76 ± 0.04	0.022	0.054
3	293.65	-21.11 ± 0.04	0.028	0.059	3	298.51	-23.48 ± 0.04	0.007	0.011
4	298.47	-20.83 ± 0.04	0.056	0.088	4	298.64	-23.47 ± 0.04	0.019	0.045
5	298.55	-20.84 ± 0.04	0.042	0.061	5	303.47	-23.23 ± 0.04	0.011	0.028
6	303.12	-20.56 ± 0.04	0.027	0.039	6	303.69	-23.21 ± 0.04	0.022	0.040
7	303.45	-20.56 ± 0.04	0.036	0.060	7	313.58	-22.71 ± 0.04	0.019	0.039
8	313.13	-20.05 ± 0.04	0.037	0.073	8	313.62	-22.72 ± 0.04	0.028	0.063
9	313.14	-20.05 ± 0.04	0.034	0.046	9	323.57	-22.25 ± 0.04	0.042	0.071
10	323.39	-19.58 ± 0.04	0.025	0.058	10	323.68	-22.25 ± 0.04	0.010	0.031
11	323.55	-19.57 ± 0.04	0.036	0.077	11	333.23	-21.82 ± 0.04	0.025	0.040
12	333.22	-19.10 ± 0.04	0.023	0.030	12	333.45	-21.82 ± 0.04	0.030	0.047
13	333.24	-19.12 ± 0.04	0.048	0.107	13	343.04	-21.41 ± 0.04	0.035	0.066
14	333.24	-19.11 ± 0.04	0.039	0.082	14	343.09	-21.42 ± 0.04	0.017	0.029
15	343.16	-18.69 ± 0.04	0.050	0.088	15	350.58	-21.11 ± 0.04	0.072	0.137
16	349.86	-18.42 ± 0.04	0.064	0.155	16	350.58	-21.11 ± 0.04	0.045	0.119
17	352.24	-18.32 ± 0.03	0.116	0.212					
18	352.29	-18.32 ± 0.03	0.058	0.133					
19	353.82	-18.24 ± 0.03	0.018	0.033					
		Second Dissociation Constants of 6-Aminohexanoic Acid					Second Dissociation Constants of DL-Methionine		
1	293.82	-25.55 ± 0.04	0.015	0.025	1	293.37	-21.70 ± 0.04	0.066	0.132
2	293.83	-25.54 ± 0.04	0.012	0.025	2	293.41	-21.70 ± 0.04	0.063	0.147
3	293.87	-25.54 ± 0.04	0.028	0.036	3	293.52	-21.68 ± 0.04	0.039	0.117
4	298.64	-25.19 ± 0.04	0.014	0.026	4	298.35	-21.41 ± 0.04	0.075	0.099
5	298.69	-25.17 ± 0.04	0.011	0.028	5	298.44	-21.38 ± 0.04	0.057	0.088
6	298.73	-25.17 ± 0.04	0.028	0.040	6	298.58	-21.40 ± 0.04	0.045	0.104
7	303.59	-24.81 ± 0.04	0.017	0.035	7	303.20	-21.13 ± 0.04	0.071	0.139
8	303.64	-24.80 ± 0.04	0.015	0.034	8	303.29	-21.13 ± 0.04	0.067	0.149
9	303.65	-24.79 ± 0.04	0.023	0.053	9	303.32	-21.14 ± 0.04	0.067	0.096
10	313.08	-24.12 ± 0.04	0.040	0.085	10	312.97	-20.61 ± 0.04	0.063	0.151
11	313.27	-24.10 ± 0.04	0.027	0.049	11	312.98	-20.61 ± 0.04	0.067	0.137
12	313.32	-24.10 ± 0.04	0.043	0.088	12	313.06	-20.61 ± 0.04	0.080	0.158
13	322.46	-23.48 ± 0.04	0.031	0.071	13	323.29	-20.08 ± 0.04	0.085	0.158
14	322.49	-23.48 ± 0.04	0.040	0.079	14	323.53	-20.07 ± 0.04	0.085	0.189
15	322.74	-23.47 ± 0.04	0.019	0.051	15	323.53	-20.08 ± 0.04	0.087	0.196
16	334.14	-22.74 ± 0.04	0.027	0.055	16	333.34	-19.59 ± 0.04	0.064	0.138
17	334.15	-22.74 ± 0.04	0.051	0.102	17	333.38	-19.60 ± 0.04	0.072	0.158
18	343.83	-22.13 ± 0.04	0.068	0.149	18	333.44	-19.60 ± 0.04	0.054	0.133
19	343.86	-22.12 ± 0.04	0.066	0.152	19	343.13	-19.17 ± 0.04	0.051	0.118
20	353.16	-21.59 ± 0.04	0.029	0.051	20	343.17	-19.16 ± 0.04	0.084	0.206
21	353.24	-21.64 ± 0.04	0.063	0.113	21	343.23	-19.18 ± 0.04	0.042	0.092
					22	353.30	-18.77 ± 0.03	0.034	0.053
					23	353.30	-18.80 ± 0.04	0.062	0.139
					24	353.32	-18.81 ± 0.03	0.050	0.102

Table 16. (Continued)

run no.	T/K	ln(K)	avg. rel. dev./%	max. rel. dev./%	run no.	T/K	ln(K)	avg. rel. dev./%	max. rel. dev./%
	Second Dissociation Constants of Glycine					Second Dissociation Constants of L-Phenylalanine			
1	293.07	−22.86 ± 0.04	0.010	0.179	1	292.83	−21.69 ± 0.04	0.056	0.137
2	293.08	−22.80 ± 0.04	0.055	0.158	2	293.21	−21.66 ± 0.04	0.083	0.201
3	293.09	−22.85 ± 0.04	0.025	0.055	3	298.07	−21.43 ± 0.04	0.077	0.166
4	298.25	−22.49 ± 0.04	0.023	0.058	4	298.26	−21.38 ± 0.04	0.049	0.096
5	298.25	−22.48 ± 0.04	0.038	0.067	5	298.42	−21.39 ± 0.04	0.111	0.173
6	298.27	−22.44 ± 0.04	0.024	0.043	6	302.88	−21.16 ± 0.04	0.090	0.175
7	302.96	−22.19 ± 0.04	0.026	0.056	7	302.95	−21.12 ± 0.04	0.029	0.049
8	303.02	−22.20 ± 0.04	0.030	0.076	8	303.12	−21.13 ± 0.04	0.157	0.265
9	303.13	−22.22 ± 0.04	0.029	0.068	9	312.99	−20.58 ± 0.04	0.137	0.247
10	312.97	−21.71 ± 0.04	0.017	0.028	10	313.06	−20.61 ± 0.04	0.073	0.161
11	312.97	−21.66 ± 0.04	0.025	0.047	11	313.11	−20.59 ± 0.04	0.045	0.105
12	312.99	−21.69 ± 0.04	0.079	0.117	12	322.79	−20.08 ± 0.04	0.133	0.234
13	322.95	−21.17 ± 0.04	0.016	0.035	13	322.85	−20.12 ± 0.04	0.070	0.153
14	323.00	−21.16 ± 0.04	0.014	0.032	14	322.92	−20.09 ± 0.04	0.058	0.117
15	323.11	−21.17 ± 0.04	0.023	0.038	15	332.79	−19.60 ± 0.04	0.116	0.239
16	333.23	−20.69 ± 0.04	0.033	0.062	16	332.95	−19.68 ± 0.04	0.069	0.115
17	333.25	−20.68 ± 0.04	0.026	0.044	17	333.05	−19.62 ± 0.04	0.068	0.146
18	333.31	−20.69 ± 0.04	0.024	0.055	18	342.99	−19.14 ± 0.04	0.127	0.246
19	343.10	−20.27 ± 0.04	0.007	0.013	19	343.02	−19.17 ± 0.03	0.023	0.039
20	343.16	−20.22 ± 0.04	0.043	0.086	20	343.16	−19.19 ± 0.04	0.051	0.101
21	343.18	−20.26 ± 0.04	0.046	0.082	21	353.12	−18.78 ± 0.04	0.054	0.105
22	353.58	−19.82 ± 0.03	0.029	0.064	22	353.20	−18.75 ± 0.03	0.100	0.189
23	353.65	−19.84 ± 0.03	0.025	0.036	23	353.29	−18.78 ± 0.03	0.072	0.147
24	353.75	−19.82 ± 0.04	0.037	0.091					
	Second Dissociation Constants of L-Proline					Third Dissociation Constants of L-Glutamic Acid			
1	292.66	−25.08 ± 0.04	0.049	0.095	1	293.02	−23.22 ± 0.04	0.343	0.680
2	292.81	−25.08 ± 0.04	0.063	0.193	2	293.04	−23.22 ± 0.04	0.258	0.569
3	292.91	−25.08 ± 0.04	0.073	0.172	3	298.14	−22.96 ± 0.04	0.329	0.640
4	298.06	−24.78 ± 0.04	0.084	0.230	4	298.15	−22.93 ± 0.04	0.380	0.565
5	298.13	−24.78 ± 0.04	0.069	0.162	5	298.22	−22.98 ± 0.04	0.265	0.582
6	298.20	−24.77 ± 0.04	0.051	0.127	6	303.12	−22.68 ± 0.04	0.367	0.623
7	303.14	−24.52 ± 0.04	0.082	0.186	7	303.14	−22.70 ± 0.04	0.300	0.668
8	303.23	−24.50 ± 0.04	0.114	0.267	8	312.95	−22.23 ± 0.04	0.335	0.592
9	303.29	−24.48 ± 0.04	0.039	0.075	9	312.97	−22.27 ± 0.04	0.293	0.595
10	313.14	−23.97 ± 0.04	0.129	0.294	10	313.12	−22.27 ± 0.04	0.287	0.617
11	313.20	−23.93 ± 0.04	0.143	0.313	11	323.34	−21.80 ± 0.04	0.315	0.533
12	313.36	−23.94 ± 0.04	0.021	0.051	12	323.35	−21.81 ± 0.04	0.234	0.491
13	323.03	−23.47 ± 0.04	0.059	0.163	13	333.15	−21.42 ± 0.04	0.236	0.415
14	323.06	−23.45 ± 0.04	0.099	0.300	14	343.29	−21.07 ± 0.04	0.180	0.318
15	323.07	−23.45 ± 0.04	0.090	0.266	15	343.45	−21.06 ± 0.04	0.199	0.365
16	333.24	−22.99 ± 0.04	0.097	0.200	16	353.23	−20.73 ± 0.04	0.271	0.562
17	333.27	−22.97 ± 0.04	0.124	0.377	17	353.25	−20.74 ± 0.04	0.230	0.446
18	333.31	−22.98 ± 0.04	0.110	0.335					
19	343.69	−22.47 ± 0.04	0.150	0.453					
20	343.74	−22.48 ± 0.04	0.168	0.508					
21	354.12	−22.03 ± 0.04	0.237	0.691					
22	354.35	−22.00 ± 0.04	0.229	0.583					
	Third Dissociation Constants of L-Aspartic Acid								
1	293.24	−23.70 ± 0.06	0.726	1.017					
2	293.64	−23.72 ± 0.08	0.220	0.343					
3	298.05	−23.40 ± 0.07	0.196	0.427					
4	298.05	−23.37 ± 0.05	0.115	0.171					
5	298.13	−23.38 ± 0.08	0.303	0.606					
6	303.03	−23.06 ± 0.06	0.294	0.624					
7	303.04	−23.12 ± 0.05	0.101	0.175					
8	303.12	−23.12 ± 0.08	0.326	0.624					
9	312.97	−22.70 ± 0.05	0.106	0.238					
10	313.01	−22.62 ± 0.06	0.265	0.573					
11	313.03	−22.61 ± 0.07	0.309	0.664					
12	323.16	−22.22 ± 0.05	0.130	0.277					
13	323.23	−22.14 ± 0.08	0.323	0.682					
14	323.25	−22.15 ± 0.07	0.301	0.626					
15	333.15	−21.62 ± 0.06	0.238	0.399					
16	333.25	−21.63 ± 0.06	0.481	0.807					
17	342.38	−21.30 ± 0.05	0.225	0.403					
18	353.23	−20.91 ± 0.05	0.337	0.622					

plot. According to the authors, there are linear correlations between the logarithm of the forward second-order reaction rate constant and the basic strength. A higher basic strength can indicate a faster reaction between the absorbent and CO_2. A high value of $\Delta_r G_m^\circ$ or pK_a can indicate a high reactivity of the absorbent with CO_2; however, kinetic studies of the compounds have to be carried out before definite conclusions can be drawn. In commercial CO_2 capture, an absorber is operated around 313 K and a desorber around 393 K depending on operating conditions.[1] A high value of $\Delta_r H_m^\circ$ will lead to a favorable shift of the dissociation reaction at absorber and desorber temperature conditions, given by eq 33. This might further lead to cost saving

Table 17. Comparison of the Effect of Different Counterions on the Determined Dissociation Constants of Taurine

run no.	T/K	$\ln(K_2)$	$\ln(K_2)$
		K^+	Na^+
1	293.17	-21.19 ± 0.04	-21.15
2	323.61	-19.59 ± 0.04	-19.55
3	353.78	-18.28 ± 0.03	-18.26
		Li^+	Na^+
1	293.18	-21.16 ± 0.04	-21.14
2	323.60	-19.58 ± 0.04	-19.55
3	353.71	-18.28 ± 0.03	-18.26

operations of CO_2 capture plants, since the temperature difference between the absorber and the desorber might be reduced. From Table 12, 6-aminohexanoic acid has higher values of both $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ than the commercially available amines listed. L-Proline, β-alanine, sarcosine, L-aspartic acid, and L-glutamic acid have a higher value of $\Delta_r G_m^\circ$ than the commercially available amines but not necessarily a higher value of $\Delta_r H_m^\circ$.

7. Conclusion

The dissociation constants of protonated MDEA, the second dissociation constants of β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline, and the third dissociation constants of L-glutamic acid and L-aspartic acid have been determined from electromotive force measurements from (293 to 353) K. Parts of the results extend the temperature range of available literature data of the investigated compounds. The experimental results agree with results previously reported in the literature.

The values of the dissociation constants and the thermodynamic relations presented in this work give information about the use of amino acid salts as possible absorbents for CO_2 capture.

Appendix A: Outline of the Pitzer Model

A very brief outline of the Pitzer model introduced by Pitzer[46] is given for a 1:1 aqueous electrolyte solution. For an electrolyte solution containing w_S kilograms of solvent, with molalities m_i, m_j, ..., of solute spices i, j, ..., Pitzer[46] introduced the equation for the excess Gibbs energy

$$\frac{G^{ex}}{RTw_S} = f(I_m) + \sum_i \sum_j m_i m_j B_{ij} + \sum_i \sum_j \sum_k m_i m_j m_k C_{ijk} + \dots \quad (38)$$

Pitzer[46] further derived the expression for the activity coefficient. For the dissolved species i:j, the activity coefficients are estimated by

$$\ln(\gamma_{ij,m}) = -A_\phi \left[\frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b} \ln(1 + b\sqrt{I_m}) \right] + mB_{ij} + 3m^2 C_{ij} \quad (39)$$

where I_m is defined as

$$I_m = \frac{1}{2} \sum_{x=i,j} m_x z_x^2 \quad (40)$$

and $b = 1.2$ $kg^{1/2} \cdot mol^{-1/2}$. The Debye–Hückel term is given

$$A_\phi = \frac{1}{3} \sqrt{2\pi N_A \rho_w} \left(\frac{e^2}{4\pi\epsilon_0 \epsilon_w kT} \right)^{1.5} \quad (41)$$

where the dielectric constant of water, ϵ_w, was taken from Bradley.[47] The second virial coefficient is given

$$B_{ij} = 2\beta_{ij}^{(0)} + \left(\frac{2\beta_{ij}^{(1)}}{\alpha^2 I_m} \right) \left[1 - \left(1 + \alpha I_m^{1/2} - \frac{\alpha^2 I_m}{2} \right) \exp(-\alpha I_m^{1/2}) \right] \quad (42)$$

where $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, and C_{ij} are salt specific interaction parameters. For the case considered here, $\alpha = 2.0$ $kg^{1/2} \cdot mol^{-1/2}$. In the case where interaction parameters are neglected, the activity of water follows from the Gibbs–Duhem equation in the form of

$$\ln(a_w) = \frac{M_w}{1000} \left\{ 2A_\phi \frac{I_m^{1.5}}{1 + b\sqrt{I_m}} - \sum_{i \neq w} m_i \right\} \quad (43)$$

A.1. Interaction Parameters for KCl in the Pitzer Model. The following section reports the temperature dependence of the ion interaction parameters for KCl given by Pabalan.[7] The interaction parameters are calculated from eq 44 and Table 13. T is the temperature in Kelvin; T_R is 298.15 K; P is the pressure in bar; and P_R is 179 bar. The density of water, ρ_w, was taken from Saul.[20] The pressure, P, was set to 1 bar. The pressure dependence of the thermodynamic properties are calculated from eq 45 and Table 14. A complete description of the equations below are given in Pabalan's work.[7]

$$f(T, P_r) = \frac{u_1 T^2}{6} + \frac{u_2 T}{2} + \frac{u_3 T^2 \left(\frac{\ln(T)}{2} - \frac{5}{12} \right)}{3} + \frac{u_4 T^3}{12} + \frac{u_5 T^4}{20} + u_6 \left[\frac{T}{2} + \frac{3(227)^2}{2T} \frac{227(T - 227) \ln(T - 227)}{T} \right] - u_7 \left[\frac{2(647 - T) \ln(647 - T)}{T} + \ln(647 - T) \right] - \frac{K_1}{T} - f_L(T_r, P_r) \left(\frac{T_r^2}{T} \right) + K_2 + f_G(T_r, P_R) \quad (44)$$

$$\ln \gamma_\pm(P_2) - \ln \gamma_\pm(P_1) - [A_\phi(P_2) - A_\phi(P_1)] \left(\frac{I_m^{1/2}}{1 + bI_m^{1/2}} + \frac{2}{b} \ln(1 + bI_m^{1/2}) \right) + \int_{P_1}^{P_2} \left\{ 2m \left(\frac{\partial\beta_{ij}^{(0)}}{\partial P} \right)_T + \frac{2m}{\alpha^2 I_m} \left(\frac{\partial\beta_{ij}^{(1)}}{\partial P} \right)_T \left[1 - \left(1 + \alpha I_m^{1/2} - \frac{\alpha^2 I_m}{2} \right) \times \exp(-\alpha I_m^{1/2}) \right] + 3m^2 \left(\frac{\partial C_{ij}}{\partial P} \right)_T \right\} dP \quad (45)$$

where $((\partial\beta_{ij}^{(0)}/\partial P))_T = B_{ij}^V$ and B_{ij}^V is calculated from eq 46. Further, in this case, $((\partial\beta_{ij}^{(1)}/\partial P))_T = 0$ and $((\partial C_{ij}/\partial P))_T = 0$.

$$f_V(T, P) = q_1 + \frac{q_2}{T} + q_3 T + q_4 T^2 + \frac{q_5}{647 - T} + P \left[q_6 + \frac{q_7}{T} + q_8 T + q_9 T^2 + \frac{q_{10}}{(647 - T)} \right] + P^2 \left[q_{11} + \frac{q_{12}}{T} + q_{13} T + q_{14} T^2 + \frac{q_{15}}{(647 - T)} \right] \quad (46)$$

A.2. Interaction Parameters for HCl in the Pitzer Model. The following section reports the density, pressure, and temperature dependence on the ion interaction parameters for HCl given by Holmes.[6] The ion interaction parameters are given by equation 48 and Table 15. T is the temperature in Kelvin; T^* is

1 K; $P*$ is 1 MPa; and $P*$ is 1 kg·m^{-3}. T_R, P_R, and ρ_R are the reference temperature, pressure, and density and are set to 298.15 K, 0.101325 MPa, and 997.062 kg·m^{-3}, respectively. The pressure and density, P and ρ, are set equal to the reference pressure and the reference density. For HCl, the interaction parameter, C in equation 39, is defined

$$C = \frac{1}{2} C_{\mathrm{HCl}} \qquad (47)$$

$$f(\rho,P,T) = q_1 +$$
$$q_2 \ln\!\left(\frac{\rho}{\rho_R}\right) + q_3 \frac{(\rho - \rho_R)}{\rho*} + q_4 \frac{(T - T_R)}{T*} + q_5 \frac{(P - P_R)}{P*} \quad (48)$$

B. Experimental Results. Tables 16 and 17 contain the experimental results.

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Nomenclature

Nomenclature
$\bar{m}_i$/mol·kg^{-1} = overall molality of component i
$\bar{n}_i$/mol = overall number of moles of component i
ρ/kg·m^{-3} = density
a_i = activity of component i
A_ϕ/kg$^{1/2}$·mol$^{-1/2}$ = Debye–Hückel constant
b/kg$^{1/2}$·mol$^{-1/2}$ = constant in the modified Debye–Hückel term
$B_{i,j}$ = second virial coefficient in Pitzer's equation
$c°$/1 mol·L^{-1} = reference molarity
C_P/J·(mol·kg)$^{-1}$ = heat capacity
C_{ijk} = third virial coefficient in Pitzer's equation
E/mV = electromotive force
e/C = charge of electron
$E°$/mV = standard potential
F/C·mol^{-1} = Faradays constant
f = modified Debye–Hückel term
G/kJ·mol^{-1} = Gibbs energy
H/kJ·mol^{-1} = enthalpy
I_m/mol·kg^{-1} = ionic strength
K = dissociation constant
k/J·K^{-1} = Boltzmann constant
K_w = dissociation constant of water
$m°$/1 mol·kg^{-1} = reference molality
N_A/mol^{-1} = Avogadro constant
n_i/mol = number of moles of component i
S/J·(mol·K)$^{-1}$ = entropy
T/K = temperature
w_s/kg = number of kilograms of solvent
z_i = number of charges of component i
Greek Letters
α/kg$^{1/2}$·mol$^{-1/2}$ = constant in Pitzer's equation
$\beta_{ij}^{(0)}$/kg·mol^{-1} = binary interaction parameter in Pitzer's equation
$\beta_{ij}^{(1)}$/kg·mol^{-1} = binary interaction parameter in Pitzer's equation
Δ = difference
ϵ_0/C^2·N^{-1}·m^{-2} = permittivity of a vacuum
ϵ_w = relative dielectric constant of water
$\gamma^{(m)}$ = activity coefficient based on molality
γ_{ij} = mean activity coefficient of i:j salt
Susperscripts
$°$ = standard state

ex = excess
Subscripts
I,II = cell I, cell II
2 = second dissociation constant
3 = third dissociation constant
c = on molarity scale
ij = components i, j
ijk = components i, j, k
m = on molality scale
r = reaction
Abbreviations
aq = in aqueous solution
s = solid
exptl = experimental
w = water

Supporting Information Available:

Experimental equilibrium data with "Run no." corresponding to Appendix B. This material is available free of charge via the Internet at http://pubs.acs.org.

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