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Preface

This document contains the PhD work carried out by Espen Steinseth Hamborg at the University of Twente from January 1st 2005 until December 31st 2007.

The document is divided into the following chapters:

1. `Introduction`. A general introduction to CO_2 absorption/desorption processes and the relation of this to the present document.

2. `Dissociation constants of amino acids used in CO2 absorption`. A description of the technique used to determine dissociation constant for amino acids used in CO_2 absorption and the experimental results.

3. `Diffusivities in Aqueous Piperazine and Aqueous Piperazine - MDEA Solutions`. A description of the technique used to determine liquid and gas diffusion in aqueous piperazine and aqueous piperazine - MDEA solutions and the experimental results.

4. `Diffusivities in Aqueous Amino Acid Salt Solutions`. Experimental results of liquid and gas diffusivities in aqueous amino acid salt solutions.

5. `Mass transfer in absorption and desorption processes`. Description of the work regarding absorption and desorption processes.

Chapter 1

Introduction

As of today, the three following processes are close to commercial operation of CO_2 capture from flue gases [1]

1. Post-combustion capture
2. Pre-combustion capture
3. Oxy-fuel

This document contains information about the use of different absorbents for use in post-combustion capture exclusively. More information about the pre-combustion capture and oxy-fuel process can be found elsewhere. [1]

1.1 Post-combustion capture

The development of post-combustion capture of CO_2 started in the 1930s with H_2S and CO_2 gas-treating of natural gas. Throughout the years, treating of flue gases have become important due to the increased level of CO_2 (and other greenhouse gases) in the atmosphere. The scientific community generally accepts that these emission lead to global warming and further dangers for the world. [1, 50]

Post-combustion capture are usually operated in the classical absorber/heat-exchanger/desorber configuration. [50] An absorbent, usually an amine or a mixture of different amines, are used to chemically capture CO_2 from the flue gas. The performance of a commercial CO_2 capture plant is closely related to the performance of the absorbent, i.e. reactivity, capacity, diffusivity, corrosion, degradation, etc. More detailed information about this is available elsewhere. [50] In recent years the use of amino acid salts as absorbents have gained increasing attention. [51] These type of absorbents have the nature of salts and also several advantages (and disadvantages). The salts are more stable towards oxidative degradation, have lower volatility, and higher surface tension than commercially available amines. The purpose of the work described in this document was to gain better understanding and description of the properties of amino acid salts as absorbents for CO_2 post-combustion capture. In each chapter the results described are discussed in terms of advantages/disadvantages for post-combustion CO_2 capture.

Chapter 2

Dissociation constants of amino acids used in CO_2 absorption

2.1 Introduction

Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating. [50] It has been widely reported that alkanolamines undergo degradation in oxygen atmosphere, usually encountered in the treatment of flue gases. Aqueous solutions of salts of amino acids might be an attractive alternative to alkanolamines. They have been found to have better resistance to degradation, and their reactivity with CO_2 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 higher surface tension than aqueous solutions of alkanolamines. [42, 70, 53]

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

2.2 Procedure

2.2.1 Amino acids

β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, and L-proline dissociate in aqueous solutions according to:

$$^{-}O_2C - R - NH_3^+ + H_2O \rightleftharpoons ^{-} O_2C - R - NH_2 + H_3O^+ \tag{2.1}$$

where 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.

(1) Failure to obey Nernst equation perfectly. This error arises due to the alkaline error and the asymmetry potential, which can vary with the change in the activity of H_3O^+ in the solution under investigation. In strong alkaline solutions, measurement errors may appear due to the potential contribution of alkaline ions (e.g. Na^+, K^+, etc.) and the measured activity of H_3O^+ appears to be higher than the actual.

(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 composition while continuously recording the potential. Measurements comparable to the accuracy of a system including the 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 in both cells, and the time periode between the two measurements should be as short as possible. [17] The standard potentials of the combined pH electrode are the same as a result of the matching temperature in the two cells. A combined pH electrode and a two cell system was used in order to determine dissociation constants:

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

and

$$\begin{aligned}&\text{Ag(s), AgCl(s)} \mid \text{3 M KCl(aq)} \parallel \text{NaOH(aq, }\bar{m}_{NaOH}\text{) ...}\\ &\qquad {}^{-}\text{O}_2\text{C-R-NH}_3^+ \text{ (aq, }\bar{m}_{^{-}O_2C-R-NH_3^+}\text{)} \parallel \text{Glass Electrode} \qquad \text{(II)}\end{aligned}$$

HCl was chosen to be used in cell I as a reference solution. A combined pH electrode can determine the activities of the compounds under investigation with a higher accuracy in an acidic solution, as compared to an alkaline solution as described above. As the activity of a pure solid is set to unity, the Nernst equation for cell I results in:

$$E_I = E^\circ (T_I) - \frac{RT_I}{F} \ln (a_{H_3O^+} a_{Cl^-})_I \tag{2.2}$$

and for cell II:

$$E_{II} = E^\circ (T_{II}) - \frac{RT_{II}}{F} \ln (a_{H_3O^+} a_{Cl^-})_{II} \tag{2.3}$$

As both cells are at the same temperature, $T_I = T_{II}$, they have the same standard potential, $E^\circ (T_I) = E^\circ (T_{II})$:

$$T_{II} \ln (a_{H_3O^+} a_{Cl^-})_{II} = \frac{F (E_I - E_{II})}{R} + T_I \ln (a_{H_3O^+} a_{Cl^-})_I \tag{2.4}$$

If exact temperature matching of the cells is achieved, the activity of the inner reference electrolyte of the pH electrode is identical througout the measurements, $(a_{Cl^-})_I = (a_{Cl^-})_{II}$. Hence, equation (2.4) reduces to:

$$\ln (a_{H_3O^+})_{II} = \frac{F (E_I - E_{II})}{RT} + \ln (a_{H_3O^+})_I \tag{2.5}$$

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:

$$\bar{n}_{^-O_2C-R-NH_3^+} = n_{^-O_2C-R-NH_3^+} + n_{^-O_2C-R-NH_2} \tag{2.6}$$

$$\bar{n}_{NaOH} = n_{Na^+} \tag{2.7}$$

$$\bar{n}_{H_2O} = n_{H_2O} + n_{H_3O^+} + n_{OH^-} \tag{2.8}$$

Electroneutrality results in:

$$n_{Na^+} + n_{H_3O^+} = n_{^-O_2C-R-NH_2} + n_{OH^-} \tag{2.9}$$

The chemical equilibrium conditions for both reactions present are:

$$K_w (T) = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}^2} \tag{2.10}$$

$$K (T) = \frac{a_{^-O_2C-R-NH_2} a_{H_3O^+}}{a_{^-O_2C-R-NH_3^+} a_{H_2O}} \tag{2.11}$$

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 [41] and Pabalan [68], 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 2.8. Activities of NaOH and the amino acid in Cell II are approximated using only 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 bara during further described calculations. The changes in the compositions of the electrolyte cells due to the outflow of KCl electrolyte from the electrode are neglected. The water dissociation constant, $K_W (T)$, is taken from Fisher [33]. With the given information equation (2.4) to equation (2.11) 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 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:

$$\lim_{\substack{\bar{m}_{NaOH,II}=\text{const.} \\ \bar{m}_{^-O_2C-R-NH_3^+}\to 0}} \left[K_{2,\text{exp}}\left(T, \bar{m}_{^-O_2C-R-NH_3^+}, \bar{m}_{NaOH,II}\right)\right] = K_{2,\text{exp}}\left(T, \bar{m}_{NaOH,II}\right) \quad (2.12)$$

$$\lim_{\bar{m}_{NaOH,II}\to 0} K_{2,\text{exp}}\left(T, \bar{m}_{NaOH,II}\right) = K_2\left(T\right) \quad (2.13)$$

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

2.2.2 Dicarboxylic amino acids

L-Glutamic acid and L-aspartic acid dissociates according to:

$$\substack{^-O_2C- \\ HO_2C-}R{-}NH_3^+ + H_2O \rightleftharpoons \substack{^-O_2C- \\ ^-O_2C-}R{-}NH_3^+ + H_3O^+ \quad (2.14)$$

$$\substack{^-O_2C- \\ ^-O_2C-}R{-}NH_3^+ + H_2O \rightleftharpoons \substack{^-O_2C- \\ ^-O_2C-}R{-}NH_2 + H_3O^+ \quad (2.15)$$

Measurements of the dissociation constants of L-glutamic acid and L-aspartic acid were performed in a similar manner as described above. However, equation (2.6) to equation (2.13) had to be adapted to describe the composition in the cell II to:

$$\bar{n}_{\substack{^-O_2C- \\ HO_2C-}R-NH_3^+} = n_{\substack{^-O_2C- \\ ^-O_2C-}R-NH_3^+} + n_{\substack{^-O_2C- \\ ^-O_2C-}R-NH_2} \quad (2.16)$$

$$\bar{n}_{NaOH} = n_{Na^+} \quad (2.17)$$

$$\bar{n}_{H_2O} = n_{H_2O} + n_{H_3O^+} + n_{OH^-} \quad (2.18)$$

Electroneutrality results in:

$$n_{Na^+} + n_{H_3O^+} = n_{\substack{^-O_2C- \\ ^-O_2C-}R-NH_3^+} + 2n_{\substack{^-O_2C- \\ ^-O_2C-}R-NH_2} + n_{OH^-} \quad (2.19)$$

The chemical equilibrium conditions for both reactions present are:

$$K_w\left(T\right) = \frac{a_{H_3O^+}a_{OH^-}}{a_{H_2O}^2} \quad (2.20)$$

$$K\left(T\right) = \frac{a_{\substack{^-O_2C- \\ ^-O_2C-}R-NH_2}\,a_{H_3O^+}}{a_{\substack{^-O_2C- \\ ^-O_2C-}R-NH_3^+}\,a_{H_2O}} \quad (2.21)$$

Since between one to two moles of sodium hydroxide have to be added to each initial mole of amino acid in this case, the extrapolation to zero ionic strength is performed according to:

$$\lim_{\substack{\bar{m}_{NaOH,II} \to 0 \\ \bar{m}_{\substack{^{-}O_2C- \\ HO_2C-}R-NH_3^+} \to 0}} \left[K_{3,\exp}\left(T, \bar{m}_{\substack{^{-}O_2C- \\ HO_2C-}R-NH_3^+}, \bar{m}_{NaOH,II}\right)\right] = K_3\left(T\right) \quad (2.22)$$

2.2.3 Alkanolamines

Measurements of the dissociation constant of protonated methyldiethanolamine (MDEA) were performed in order to validate the experimental setup. Protonated MDEA dissociates according to:

$$MDEAH^+ + H_2O \rightleftharpoons MDEA + H_3O^+ \quad (2.23)$$

However, HCl was used in cell II instead of NaOH, and consequently equation (2.6) to equation (2.13) were adapted to describe the composition of the cells:

$$\bar{n}_{MDEA} = n_{MDEA} + n_{MDEAH^+} \quad (2.24)$$

$$\bar{n}_{HCl} = n_{Cl^-} \quad (2.25)$$

$$\bar{n}_{H_2O} = n_{H_2O} + n_{H_3O^+} + n_{OH^-} \quad (2.26)$$

Electroneutrality results in:

$$n_{MDEAH^+} + n_{H_3O^+} = n_{Cl^-} + n_{OH^-} \quad (2.27)$$

The chemical equilibrium conditions for both reactions present are:

$$K_w\left(T\right) = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}^2} \quad (2.28)$$

$$K\left(T\right) = \frac{a_{MDEA} a_{H_3O^+}}{a_{MDEAH^+} a_{H_2O}} \quad (2.29)$$

The linear extrapolation to zero MDEA and HCl molalities were done as in equation (2.12) and (2.13):

$$\lim_{\substack{\bar{m}_{HCl,II} = \text{const.} \\ \bar{m}_{MDEA} \to 0}} \left[K_{1,\exp}\left(T, \bar{m}_{MDEA}, \bar{m}_{HCl,II}\right)\right] = K_{1,\exp}\left(T, \bar{m}_{HCl,II}\right) \quad (2.30)$$

$$\lim_{\bar{m}_{HCl,II} \to 0} K_{1,\exp}\left(T, \bar{m}_{HCl,II}\right) = K_1\left(T\right) \quad (2.31)$$

2.3 Thermodynamic relations

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

$$\Delta_r G_m = -RT \ln K \tag{2.32}$$

$$\Delta_r H_m = -R \frac{d \ln K}{d(1/T)} \tag{2.33}$$

$$\Delta_r S_m = \frac{(\Delta_r H_m - \Delta_r G_m)}{T} \tag{2.34}$$

$$\Delta_r C_{P,m} = \frac{d \Delta_r H_m}{dT} \tag{2.35}$$

and the change of standard state properties (T = T°= 298.15 K) for the dissociation of an amino acid in water are calculated from equation (2.32) to equation (2.35).

2.4 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 and placed in a temperature controlled water bath. The cells were sealed between each measurement. The experiments were performed under nitrogen atmosphere inside a glove box to prevent CO_2 from air absorbing into the electrolyte solutions. During each measurement the electromotive force (E) and the temperature in the cell (T) were recorded.

Measurements were performed from 293 K to 353 K at 10 K intervals and at 298.15 K. The overall molality of HCl in cell I and in cell II were held constant ($\bar{m}_{HCl,I} \approx \bar{m}_{HCl,II} \approx 0.01$ mol/kg) during measurements of the dissociation constants of protonated MDEA. The overall molality of MDEA was between 0.0455 mol/kg and 0.9033 mol/kg. 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 were held constant in all solutions ($\bar{m}_{HCl,I} \approx \bar{m}_{NaOH,II} \approx 0.01$ mol/kg) and the overall molality of the amino acids were between 0.0121 mol/kg and 0.8823 mol/kg. During measurements of L-glutamic and L-aspartic acid, the molality of the amino acids were between 0.0050 mol/kg and 0.0644 mol/kg, and the molality of sodium hydroxide was approximately 1.5 times of the amino acid. The overall molality of HCl in cell I was held constant ($\bar{m}_{HCl,I} \approx 0.01$ mol/kg). 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.

2.5 Chemicals

MDEA, β-Alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, L-proline, L-glutamic acid, L-aspartic acid, (Sigma-Aldrich) and NaOH and HCl (Merck) were used as supplied. NaOH and HCl were provided as 0.1 M standard solutions, and were diluted to the desired molalities and checked by means of titration. Water was demineralised and further purified by vacuum distillation.

2.6 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, L-proline, and the third dissociation constants of L-glutamic acid and L-aspartic acid are given in Table 2.1 with experimental uncertainties. The experimental uncertainties are due to inaccuracies in E_I and E_{II} of ± 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 provides insight of the accuracy of the linear extrapolation. The EMF measurement data are tabulated in Appendix 2.9 with corresponding 'Run no.'.

In Figure 2.1, $ln(K_{2,exp})$ is plotted as function of the dimensionless overall molality of β-alanine according to equation (2.12) and equation (2.13). 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 $ln(K_{2,exp})$, and $ln(K_{exp})$ for the case of MDEA. In Figure 2.2 $ln(K_3)$ of L-glutamic acid is plotted against the ionic strength of the solutions under investigation according to equation (2.22). The intercept at zero ionic strength is $ln(K_3)$. Figure 2.3 to Figure 2.13 shows the dissociation constants of protonated MDEA, the second dissociation constants of β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, L-proline and the third dissociation constants of L-glutamic acid and L-aspartic acid in comparison to literature values. [2, 65, 47, 56, 82, 60, 34, 28, 57, 13, 18, 49, 21, 84, 15, 69, 48, 67, 19, 44, 45, 85, 6, 3, 98, 7] Literature dissociation constants that are based on the molarity scale [65, 56, 82, 34, 28, 57, 44, 6, 3, 98] were converted to the molality scale by:

$$K = \frac{1}{\rho_W}\left(\frac{c^\circ}{m^\circ}\right)K_c \tag{2.36}$$

where ρ_W is the mass density of pure water taken from Saul [80], and K_c is the dissociation constant based on the molarity scale.

The results for protonated MDEA (i = 0), β-alanine, taurine, sarcosine, 6-aminohexanoic acid, DL-methionine, glycine, L-phenylalanine, L-proline (i = 2), L-aspartic acid and L-glutamic acid (i = 3) are correlated [32] by:

$$\ln K_i = \frac{A}{T} + B + C\ln(T) \tag{2.37}$$

The coefficients A, B, and C in equation (2.37) are given in Table 2.2, together with the average and maximum relative deviations between the values of the experimental determined dissociation constants and the fitted values.

In Table 2.3 to Table 2.13 correlated experimental results of the dissociation constants and the values of the standard state thermodynamic properties, given by equation (2.32) to equation (2.35), are given and compared to available literature values.

Table 2.1: Extrapolated experimental results of the dissociation constants

Run no. [-]	T [K]	ln(K) [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
The dissociation constants of protonated MDEA				
1	293.28	-19.92 ± 0.04	0.038	0.084
2	293.32	-19.93 ± 0.05	0.030	0.069
3	293.44	-19.95 ± 0.04	0.018	0.040
4	298.65	-19.68 ± 0.04	0.026	0.059
5	298.67	-19.69 ± 0.04	0.035	0.087
6	298.73	-19.70 ± 0.04	0.015	0.029
7	303.46	-19.45 ± 0.04	0.036	0.088
8	303.48	-19.46 ± 0.04	0.017	0.056
9	313.44	-19.06 ± 0.04	0.023	0.040
10	313.54	-19.02 ± 0.04	0.032	0.050
11	313.56	-19.05 ± 0.04	0.010	0.023
12	322.83	-18.58 ± 0.04	0.023	0.041
13	322.84	-18.59 ± 0.04	0.022	0.038
14	333.23	-18.15 ± 0.04	0.023	0.041
15	333.26	-18.14 ± 0.04	0.023	0.056
16	333.34	-18.16 ± 0.04	0.019	0.051
17	343.16	-17.78 ± 0.04	0.049	0.087
18	343.22	-17.76 ± 0.04	0.022	0.041
19	353.17	-17.38 ± 0.03	0.040	0.085
20	353.26	-17.39 ± 0.04	0.043	0.090
The second dissociation constants of β-alanine				
1	293.13	-24.10 ± 0.04	0.017	0.037
2	293.16	-24.11 ± 0.04	0.013	0.029
3	293.21	-24.11 ± 0.04	0.025	0.053
4	298.18	-23.78 ± 0.04	0.015	0.025
5	298.28	-23.77 ± 0.04	0.020	0.035
6	298.32	-23.77 ± 0.04	0.018	0.048
7	303.06	-23.47 ± 0.04	0.061	0.127
8	303.20	-23.46 ± 0.04	0.023	0.043
9	303.21	-23.47 ± 0.04	0.060	0.098
10	313.10	-22.88 ± 0.04	0.018	0.042
11	313.26	-22.88 ± 0.04	0.014	0.028
12	313.32	-22.88 ± 0.04	0.027	0.056
13	323.04	-22.34 ± 0.04	0.018	0.033
14	323.13	-22.33 ± 0.04	0.021	0.040
15	323.15	-22.34 ± 0.04	0.036	0.064
16	332.81	-21.83 ± 0.04	0.032	0.096
17	332.85	-21.82 ± 0.04	0.029	0.056

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Run no. [-]	T [K]	ln(K) [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
18	332.94	-21.79 ± 0.04	0.032	0.074
19	343.39	-21.32 ± 0.04	0.027	0.055
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
		The second dissociation constants of taurine		
1	293.22	-21.18 ± 0.04	0.016	0.026
2	293.64	-21.12 ± 0.04	0.048	0.094
3	293.65	-21.11 ± 0.04	0.028	0.059
4	298.47	-20.83 ± 0.04	0.056	0.088
5	298.55	-20.84 ± 0.04	0.042	0.061
6	303.12	-20.56 ± 0.04	0.027	0.039
7	303.45	-20.56 ± 0.04	0.036	0.060
8	313.13	-20.05 ± 0.04	0.037	0.073
9	313.14	-20.05 ± 0.04	0.034	0.046
10	323.39	-19.58 ± 0.04	0.025	0.058
11	323.55	-19.57 ± 0.04	0.036	0.077
12	333.22	-19.10 ± 0.04	0.023	0.030
13	333.24	-19.12 ± 0.04	0.048	0.107
14	333.24	-19.11 ± 0.04	0.039	0.082
15	343.16	-18.69 ± 0.04	0.050	0.088
16	349.86	-18.42 ± 0.04	0.064	0.155
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
		The second dissociation constants of sarcosine		
1	293.66	-23.76 ± 0.04	0.028	0.048
2	293.74	-23.76 ± 0.04	0.022	0.054
3	298.51	-23.48 ± 0.04	0.007	0.011
4	298.64	-23.47 ± 0.04	0.019	0.045
5	303.47	-23.23 ± 0.04	0.011	0.028
6	303.69	-23.21 ± 0.04	0.022	0.040
7	313.58	-22.71 ± 0.04	0.019	0.039
8	313.62	-22.72 ± 0.04	0.028	0.063
9	323.57	-22.25 ± 0.04	0.042	0.071
10	323.68	-22.25 ± 0.04	0.010	0.031
11	333.23	-21.82 ± 0.04	0.025	0.040
12	333.45	-21.82 ± 0.04	0.030	0.047
13	343.04	-21.41 ± 0.04	0.035	0.066
14	343.09	-21.42 ± 0.04	0.017	0.029

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Run no. [-]	T [K]	ln(K) [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
15	350.58	-21.11 ± 0.04	0.072	0.137
16	350.58	-21.11 ± 0.04	0.045	0.119
The second dissociation constants of 6-aminohexanoic acid				
1	293.82	-25.55 ± 0.04	0.015	0.025
2	293.83	-25.54 ± 0.04	0.012	0.025
3	293.87	-25.54 ± 0.04	0.028	0.036
4	298.64	-25.19 ± 0.04	0.014	0.026
5	298.69	-25.17 ± 0.04	0.011	0.028
6	298.73	-25.17 ± 0.04	0.028	0.040
7	303.59	-24.81 ± 0.04	0.017	0.035
8	303.64	-24.80 ± 0.04	0.015	0.034
9	303.65	-24.79 ± 0.04	0.023	0.053
10	313.08	-24.12 ± 0.04	0.040	0.085
11	313.27	-24.10 ± 0.04	0.027	0.049
12	313.32	-24.10 ± 0.04	0.043	0.088
13	322.46	-23.48 ± 0.04	0.031	0.071
14	322.49	-23.48 ± 0.04	0.040	0.079
15	322.74	-23.47 ± 0.04	0.019	0.051
16	334.14	-22.74 ± 0.04	0.027	0.055
17	334.15	-22.74 ± 0.04	0.051	0.102
18	343.83	-22.13 ± 0.04	0.068	0.149
19	343.86	-22.12 ± 0.04	0.066	0.152
20	353.16	-21.59 ± 0.04	0.029	0.051
21	353.24	-21.64 ± 0.04	0.063	0.113
The second dissociation constants of DL-methionine				
1	293.37	-21.70 ± 0.04	0.066	0.132
2	293.41	-21.70 ± 0.04	0.063	0.147
3	293.52	-21.68 ± 0.04	0.039	0.117
4	298.35	-21.41 ± 0.04	0.075	0.099
5	298.44	-21.38 ± 0.04	0.057	0.088
6	298.58	-21.40 ± 0.04	0.045	0.104
7	303.20	-21.13 ± 0.04	0.071	0.139
8	303.29	-21.13 ± 0.04	0.067	0.149
9	303.32	-21.14 ± 0.04	0.067	0.096
10	312.97	-20.61 ± 0.04	0.063	0.151
11	312.98	-20.61 ± 0.04	0.067	0.137
12	313.06	-20.61 ± 0.04	0.080	0.158
13	323.29	-20.08 ± 0.04	0.085	0.158
14	323.53	-20.07 ± 0.04	0.085	0.189
15	323.53	-20.08 ± 0.04	0.087	0.196
16	333.34	-19.59 ± 0.04	0.064	0.138
17	333.38	-19.60 ± 0.04	0.072	0.158

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Run no. [-]	T [K]	ln(K) [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
18	333.44	-19.60 ± 0.04	0.054	0.133
19	343.13	-19.17 ± 0.04	0.051	0.118
20	343.17	-19.16 ± 0.04	0.084	0.206
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
The second dissociation constants of glycine				
1	293.07	-22.86 ± 0.04	0.010	0.179
2	293.08	-22.80 ± 0.04	0.055	0.158
3	293.09	-22.85 ± 0.04	0.025	0.055
4	298.25	-22.49 ± 0.04	0.023	0.058
5	298.25	-22.48 ± 0.04	0.038	0.067
6	298.27	-22.44 ± 0.04	0.024	0.043
7	302.96	-22.19 ± 0.04	0.026	0.056
8	303.02	-22.20 ± 0.04	0.030	0.076
9	303.13	-22.22 ± 0.04	0.029	0.068
10	312.97	-21.71 ± 0.04	0.017	0.028
11	312.97	-21.66 ± 0.04	0.025	0.047
12	312.99	-21.69 ± 0.04	0.079	0.117
13	322.95	-21.17 ± 0.04	0.016	0.035
14	323.00	-21.16 ± 0.04	0.014	0.032
15	323.11	-21.17 ± 0.04	0.023	0.038
16	333.23	-20.69 ± 0.04	0.033	0.062
17	333.25	-20.68 ± 0.04	0.026	0.044
18	333.31	-20.69 ± 0.04	0.024	0.055
19	343.10	-20.27 ± 0.04	0.007	0.013
20	343.16	-20.22 ± 0.04	0.043	0.086
21	343.18	-20.26 ± 0.04	0.046	0.082
22	353.58	-19.82 ± 0.03	0.029	0.064
23	353.65	-19.84 ± 0.03	0.025	0.036
24	353.75	-19.82 ± 0.04	0.037	0.091
The second dissociation constants of L-phenylalanine				
1	292.83	-21.69 ± 0.04	0.056	0.137
2	293.21	-21.66 ± 0.04	0.083	0.201
3	298.07	-21.43 ± 0.04	0.077	0.166
4	298.26	-21.38 ± 0.04	0.049	0.096
5	298.42	-21.39 ± 0.04	0.111	0.173
6	302.88	-21.16 ± 0.04	0.090	0.175
7	302.95	-21.12 ± 0.04	0.029	0.049
8	303.12	-21.13 ± 0.04	0.157	0.265
9	312.99	-20.58 ± 0.04	0.137	0.247

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Run no. [-]	T [K]	ln(K) [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
10	313.06	-20.61 ± 0.04	0.073	0.161
11	313.11	-20.59 ± 0.04	0.045	0.105
12	322.79	-20.08 ± 0.04	0.133	0.234
13	322.85	-20.12 ± 0.04	0.070	0.153
14	322.92	-20.09 ± 0.04	0.058	0.117
15	332.79	-19.60 ± 0.04	0.116	0.239
16	332.95	-19.68 ± 0.04	0.069	0.115
17	333.05	-19.62 ± 0.04	0.068	0.146
18	342.99	-19.14 ± 0.04	0.127	0.246
19	343.02	-19.17 ± 0.03	0.023	0.039
20	343.16	-19.19 ± 0.04	0.051	0.101
21	353.12	-18.78 ± 0.04	0.054	0.105
22	353.20	-18.75 ± 0.03	0.100	0.189
23	353.29	-18.78 ± 0.03	0.072	0.147
		The second dissociation constants of L-proline		
1	292.66	-25.08 ± 0.04	0.049	0.095
2	292.81	-25.08 ± 0.04	0.063	0.193
3	292.91	-25.08 ± 0.04	0.073	0.172
4	298.06	-24.78 ± 0.04	0.084	0.230
5	298.13	-24.78 ± 0.04	0.069	0.162
6	298.20	-24.77 ± 0.04	0.051	0.127
7	303.14	-24.52 ± 0.04	0.082	0.186
8	303.23	-24.50 ± 0.04	0.114	0.267
9	303.29	-24.48 ± 0.04	0.039	0.075
10	313.14	-23.97 ± 0.04	0.129	0.294
11	313.20	-23.93 ± 0.04	0.143	0.313
12	313.36	-23.94 ± 0.04	0.021	0.051
13	323.03	-23.47 ± 0.04	0.059	0.163
14	323.06	-23.45 ± 0.04	0.099	0.300
15	323.07	-23.45 ± 0.04	0.090	0.266
16	333.24	-22.99 ± 0.04	0.097	0.200
17	333.27	-22.97 ± 0.04	0.124	0.377
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
		The third dissociation constants of L-glutamic acid		
1	293.02	-23.22 ± 0.04	0.343	0.680
2	293.04	-23.22 ± 0.04	0.258	0.569
3	298.14	-22.96 ± 0.04	0.329	0.640
4	298.15	-22.93 ± 0.04	0.380	0.565

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Run no. [-]	T [K]	ln(K) [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
5	298.22	-22.98 ± 0.04	0.265	0.582
6	303.12	-22.68 ± 0.04	0.367	0.623
7	303.14	-22.70 ± 0.04	0.300	0.668
8	312.95	-22.23 ± 0.04	0.335	0.592
9	312.97	-22.27 ± 0.04	0.293	0.595
10	313.12	-22.27 ± 0.04	0.287	0.617
11	323.34	-21.80 ± 0.04	0.315	0.533
12	323.35	-21.81 ± 0.04	0.234	0.491
13	333.15	-21.42 ± 0.04	0.236	0.415
14	343.29	-21.07 ± 0.04	0.180	0.318
15	343.45	-21.06 ± 0.04	0.199	0.365
16	353.23	-20.73 ± 0.04	0.271	0.562
17	353.25	-20.74 ± 0.04	0.230	0.446
The 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

Experimental results for the dissociation constants of protonated MDEA have been reported by several investigators, Kamps [2], Oscarson [65], Kim [47], Littel [56] and Schwabe [82]. The results are given in Table 2.3 and the correlated values from this work agree well with the results by Kamps [2] and Oscarson [65], 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 [2] and Oscarson [65], respectively. The results by Kim [47], Littel [56] and Schwabe [82] are within 0.46%, 1.76% and 0.58%, respectively. The values of $\Delta_r G^\circ_m$ and $\Delta_r H^\circ_m$ agree well with the literature values. The largest relative deviation in $\Delta_r G^\circ_m$ are from those of Schwabe [82] with 0.58%, and in $\Delta_r H^\circ_m$ from those of Kamps [2] with 2.65%. As expected, the largest relative deviation are in $\Delta_r S^\circ_m$ and $\Delta_r C^\circ_{P,m}$.

The correlated values for the second dissociation constants of β-alanine are

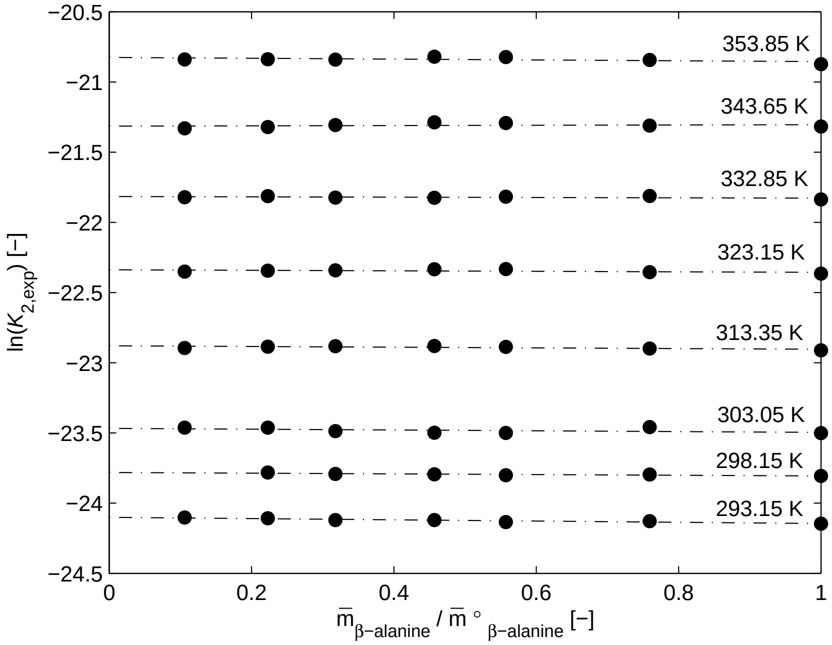

Figure 2.1: Influence of the dimensionless overall molality of β-alanine on $\ln(K_{2,exp})$: •, experimental values; -·-·, linear regression

in best agreement with the results by Boyd [13], with an average relative deviation (in $\ln(K_2)$) of 0.31%. The results by May [60], Gillespie [34], Dey [28] and Majumdar [57] deviates with 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 for protonated MDEA. May [60] did not take the activity coefficients of the chemical compound into account while calculating the second dissociation constants from the experimental data, and set the activity coefficients to unity for all species. If the activity coefficients are set to unity in this work, the correlated values from this work have an average relative deviation of 0.04% compared to May [60]. The results by Gillespie [34] differ with an average relative deviation of 1.24% from the correlated values of this work. Gillespie [34] determined $\Delta_r H_m^{\circ}$ experimentally by flow calorimetry and used a temperature specific value for $\ln(K_2)$ in order to derive values of $\ln(K_2)$ from the calorimetric data. By doing so, the accuracy of the results from the calorimetric data will follow the accuracy of the temperature specific value used. Gillespie [34] chose a temperature specific value from Christensen [18]. Christensen [18] fairly described the estimation of the activity coefficients by a succesive approximation of governing equations, and consequently it is difficult to explain the differences between the results of Gillespie [34] and Christensen [18] to the results of this work. In the work of Dey [28] and Majumdar [57] the activity coefficients are set to unity for all compounds. By applying this to this work, the determined second dissociation constants differ with 0.55% and 0.17%, respectively. Boyd [13] estimated the activity coefficients of the chemical com-

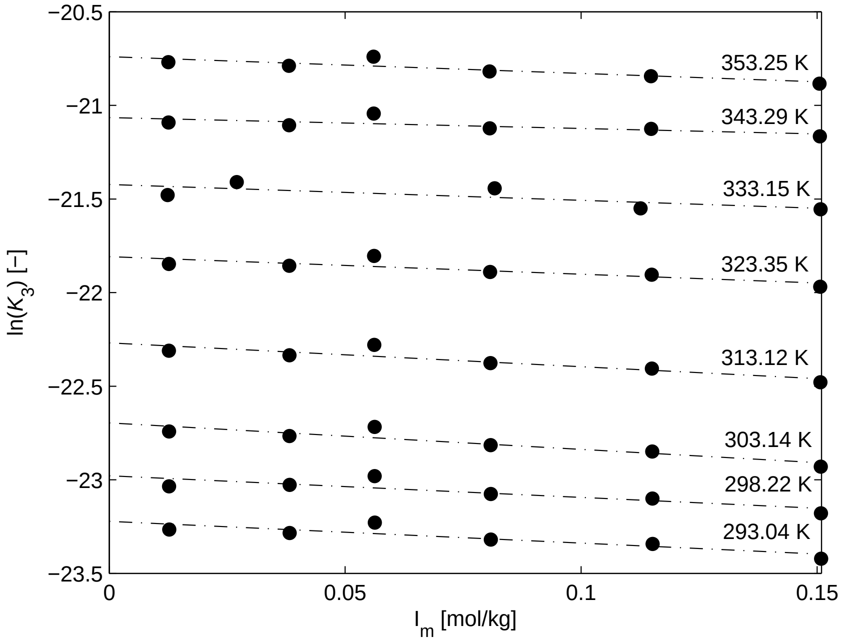

Figure 2.2: Influence of the ionic strength on $\ln(K_3)$ of L-glutamic acid: •, experimental values; -·-·, linear regression

pound using the Davies equation [24], a form the Debye-Hückel equation. By applying the Davis equation to this work, the correlated results have a relative average deviation of 0.19% compared Boyd [13]. Values for the thermodynamic properties of β-alanine are given by May [60], Gillespie [34] and Boyd [13]. The results by Boyd [13] are in the 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. The values of $\Delta_r S_m^\circ$ and $\Delta_r C_{P,m}^\circ$ have a larger relative difference.

Experimental values for the second dissociation constants of taurine are reported by King [49]. Correlated values from this work are in agreement with the results by King [49] 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, whereas $\Delta_r S_m^\circ$ and $\Delta_r C_{P,m}^\circ$ have larger relative difference.

Values for the second dissociation constants of sarcosine are reported by Datta [21]. The correlated values have an average relative deviation of 0.06% from the results by Datta [21]. Values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ given by Datta [22], have a relative deviation of 0.09% and 2.02% from the values of this work. The relative differences in $\Delta_r S_m^\circ$ and $\Delta_r C_{P,m}^\circ$ are larger.

Smith [84], Gillespie [34] and Brandariz [15] reported values for the second dissociation constants of 6-aminohexanoic acid, and the values deviates with 1.29%, 1.32% and 0.36% (in $\ln(K_2)$) from this work. In the work of Smith [84], the activity coefficients for the amino acid are not estimated, and set to unity. By applying this assumption to the present work, the average relative

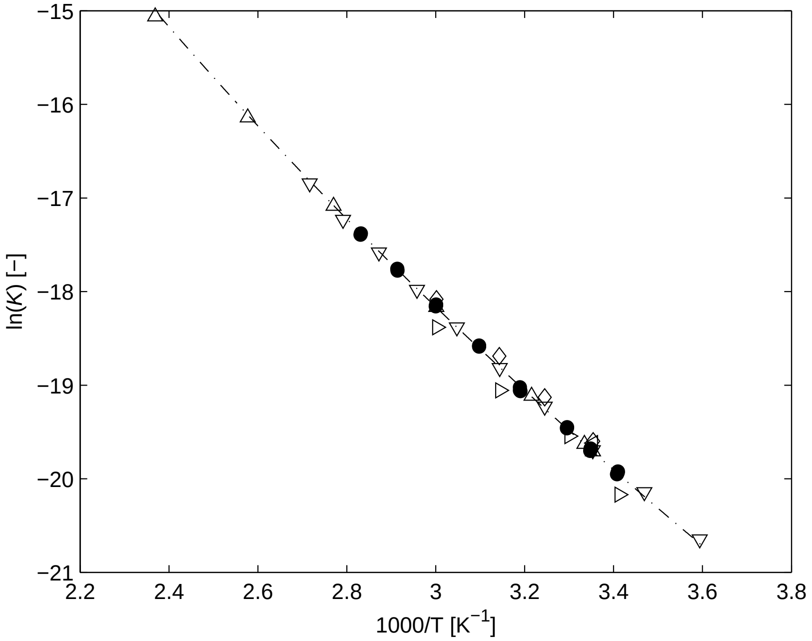

Figure 2.3: Dissociation constants of protonated MDEA: •, exp. results this work; -·-·, fit this work; ▽, Kamps [2]; △, Oscarson [65]; ◁, Kim [47]; ▷, Littel [56]; ◇, Schwabe [82]

deviation is 0.43%. Gillespie [34] measured $\Delta_r H_m^\circ$ by flow calorimetry, and used a temperature specific value of the dissociation constant from Smith [84]. With acitvity coefficients set to unity in this work, the relative difference is 0.12%. The relative difference between this work and the work of Brandariz [15] is 0.36%. Smith [84] 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. The relative differences in $\Delta_r S_m^\circ$ are larger.

Values for the second dissociation constants of DL-methionine are reported by Pelletier [69]. 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, and the deviations in $\Delta_r S_m^\circ$ are larger.

Values for the second dissociation constants of glycine have been reported by several investigators, Datta [21], King [48], Owen [67], Gillespie [34], Clarke [19] and Izatt [44]. 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 [22] and King [48] reported values with a relative deviation of 0.05% and 0.13% in $\Delta_r G_m^\circ$ and 0.45% and 0.45% in $\Delta_r H_m^\circ$, respectively. Owen [67] and Izatt [44] also reported values for $\Delta_r H_m^\circ$ with relative deviations of 2.95% and 0.11%. The relative deviation in the values of $\Delta_r S_m^\circ$ and $\Delta_r C_{P,m}^\circ$ reported by the authors are larger.

Izatt [45] reported values for the second dissociation constants of L-phenylalanine,

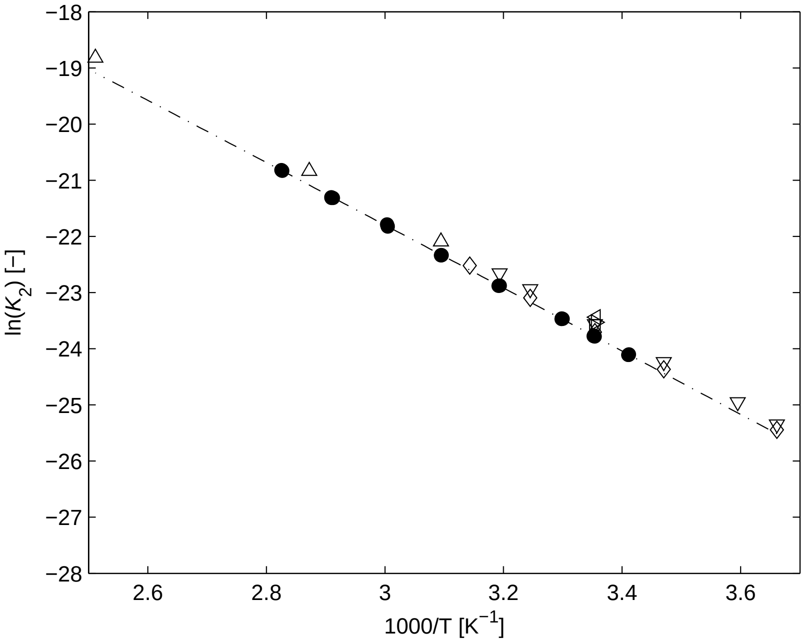

Figure 2.4: Dissociation constants of β-alanine: ●, exp. results this work; -·-·, fit this work; ▽, May [60]; △, Gillespie [34]; ◁, Dey [28]; ▷ Majumdar [57]; ◊ Boyd [13]; □, Christensen [18]

and the results deviates (in $\ln(K_2)$) with an average of 0.33% from the correlated values of this work. $\Delta_r H_m^\circ$ from Izatt [45] deviates with 2.6% from this work, and the relative deviations in $\Delta_r S_m^\circ$ are larger.

Values for the second dissociation constants of L-proline are reported by Smith [85] and Azab [6], 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 [85], the activity coefficients for each compound were set to unity. By applying so to this work, the values by Smith [85] have an average relative deviation of 0.15%. The values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ from Smith [85] have a relative deviation of 1.07% and 3.85%, whereas the value of $\Delta_r S_m^\circ$ from Smith [85] has a larger relative deviation.

Values for the third dissociation constants of L-glutamic acid have been reported by Albert [3] and Wilson [98] at 293.15 K and 298.15 K, and the results deviates with 1.59% and 0.31% (in $\ln(K_3)$) from the correlated results of this work. Albert [3] used a titration technique to determine the third dissociation constants without taking activity coefficients into consideration. However, the large relative deviation from this work can not be explained. In addition to the potentiometrically determined result at 298.15 K, Wilson [98] also carried out measurements of the third dissociation constants at elevated temperatures using a kinetic approach. Those results contains large uncertainties and are not compared to the results from this work.

Smith [84] and Batchelder [7] reported values for the third dissociation con-

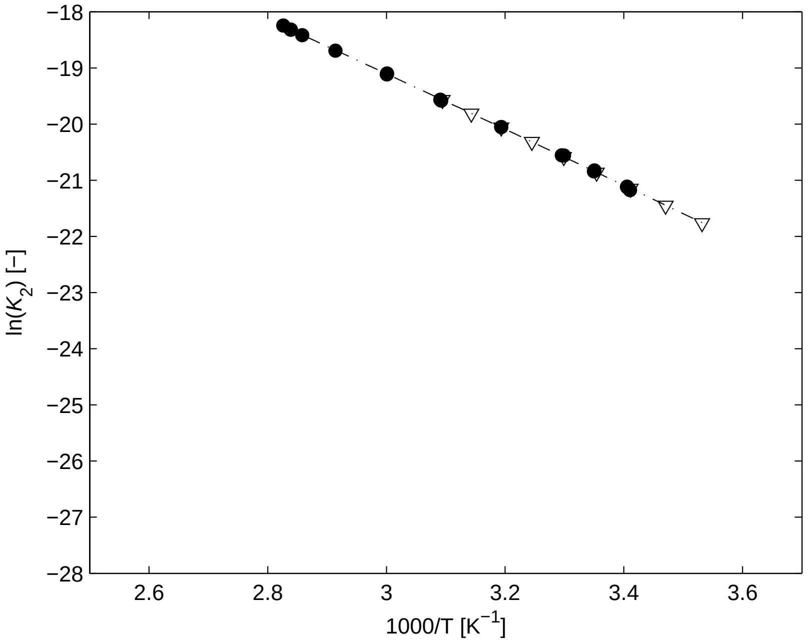

Figure 2.5: Dissociation constants of taurine: ●, exp. results this work; -·-·, fit this work; ▽, King [49]

stants of L-aspartic acid, and 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 [84] used the Debye-Hückel term, $log\left(\gamma^{(m)}\right) = -A_\phi z_i^2 \sqrt{I_m}$, to estimated the activity coefficients of the chemical compounds. By applying the term to the present work, the results by Smith [84] deviates with 1.08%. Batchelder [7] also used a version of the Debye-Hückel term to estimate the activity coefficients. Even though the estimation of the activity coefficients differs from the term used in this work, the large deviation can not be explained. Values of the thermodynamic properties for the third dissociation are reported by Smith [84], and the relative deviation from this work in $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ are 1.48% and 8.25%, whereas the relative deviation in $\Delta_r S_m^\circ$ is larger.

The results of the second and third dissociation constants in this work are in agreement with the above listed literature values. As shown, the value of the activity coefficients for the chemical compounds in the solutions under investigation have an influence on the final results. The results are in most cases in literature extrapolated to zero ionic strength after measurements at different ionic strength. The measurement at the lowest ionic strength are usually carried out at $I_m \approx 0.01$ mol/kg. A 1-1 salt with the molality of 0.01 mol/kg at 298.15 K and 1 bar has already an activity coefficient equal to 0.897 according to the modified Debye-Hückel term. Accurate estimations of the activity coefficients are important in order to achieve accurate results of the dissociation constants.

During the experiments described above, NaOH is used to deprotonate the amino acid and forming an amino acid salt. KOH and LiOH have also been

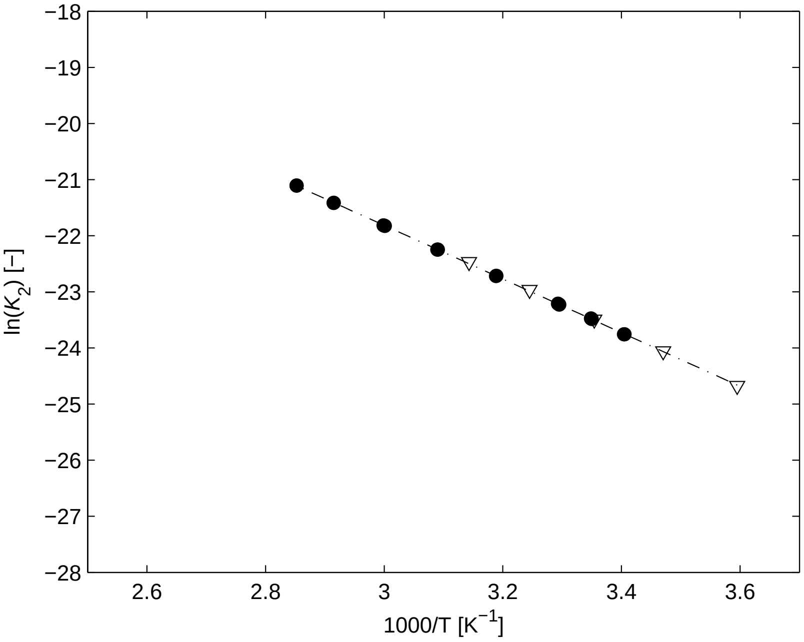

Figure 2.6: Dissociation constants of sarcosine: ●, exp. results this work; -·-·, fit this work; ▽, Datta [21]

used to form an amino acid salt in order to see the effect on the determined dissociation constants by having different counter ions. The second dissociation constants of taurine were determined at 293.15 K, 323.15 K and 353.15 K using the three different counter ions. The results with potassium and lithium as counter ions are compared in Table 2.14 to the correlated results given above. It shows that the results are all within the experimental errors, and there is no significant effect using the different counter ions. The experimental equilibrium data are given in Appendix 2.9. 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), and not on individual ionic molalities or other solute properties. [72] Since the ionic strength of the solutions under investigation here are low (e.g. $\bar{m}_{Na^+,\ K^+,\ Li^+} \leq \sim 0.01$ mol/kg), it can be concluded that the type of counter ion does not affect the determined dissociation constants. However, if measurements were to be done at higher ionic strength, the type of counter ion would most likely have an effect on the determined dissociation constants.

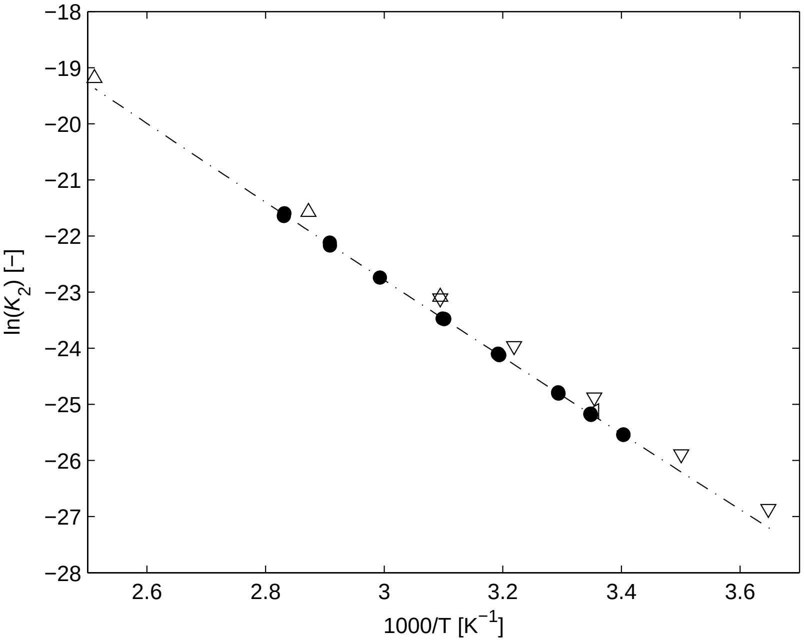

Figure 2.7: Dissociation constants of 6-aminohexanoic acid: ●, exp. results this work; -·-·, fit this work; ▽, Smith [84]; △, Gillespie [34]; ◁, Brandariz [15]

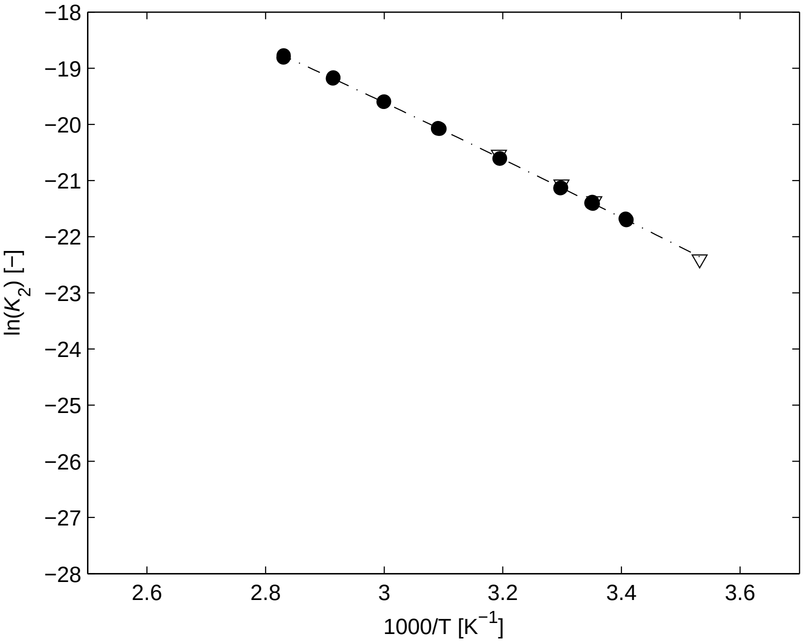

Figure 2.8: Dissociation constants of DL-methionine: ●, exp. results this work; -·-·, fit this work; ▽, Pelletier [69]

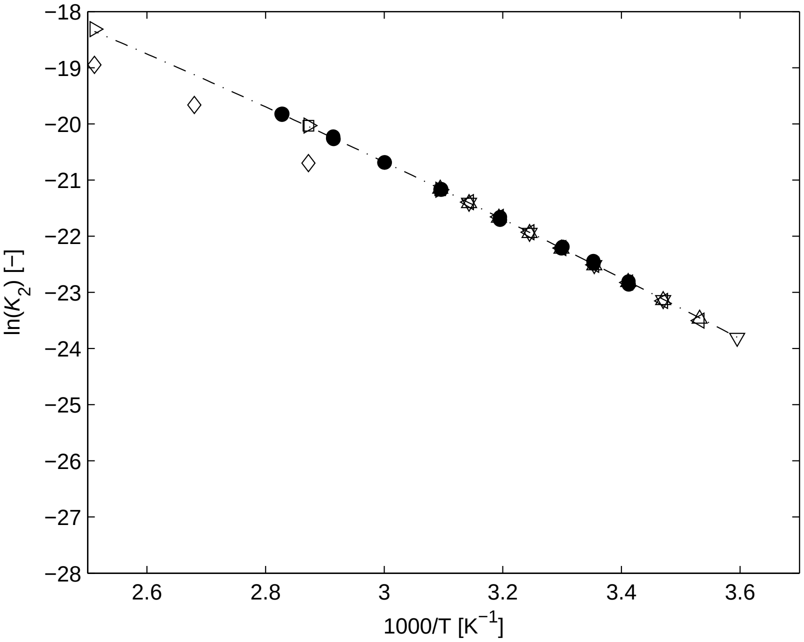

Figure 2.9: Dissociation constants of glycine: ●, exp. results this work; -·-·, fit this work; ▽, Datta [21]; △, King [48]; ◁, Owen [67]; ▷, Gillespie [34]; ◊, Clarke [19]; □, Izatt [44]

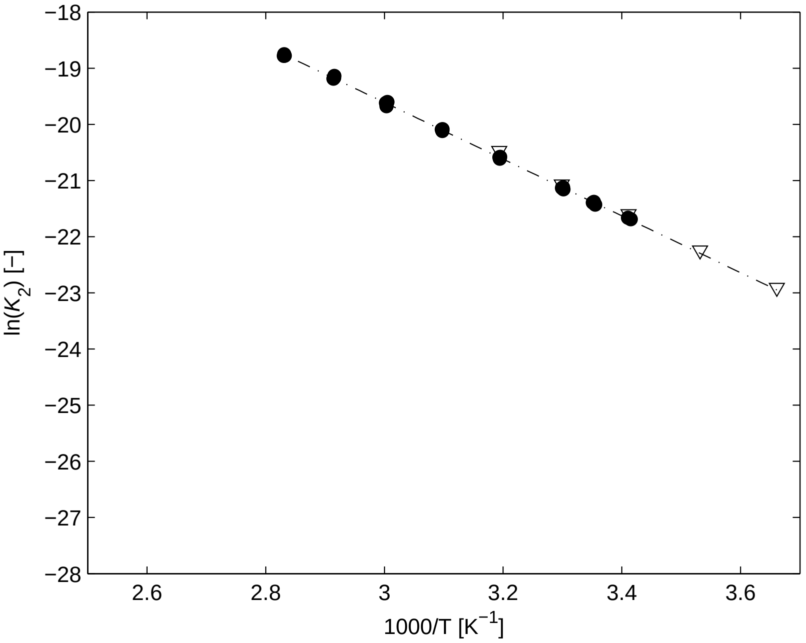

Figure 2.10: Dissociation constants of L-phenylalanine: ●, exp. results this work; -·-·, fit this work; ▽, Izatt [45]

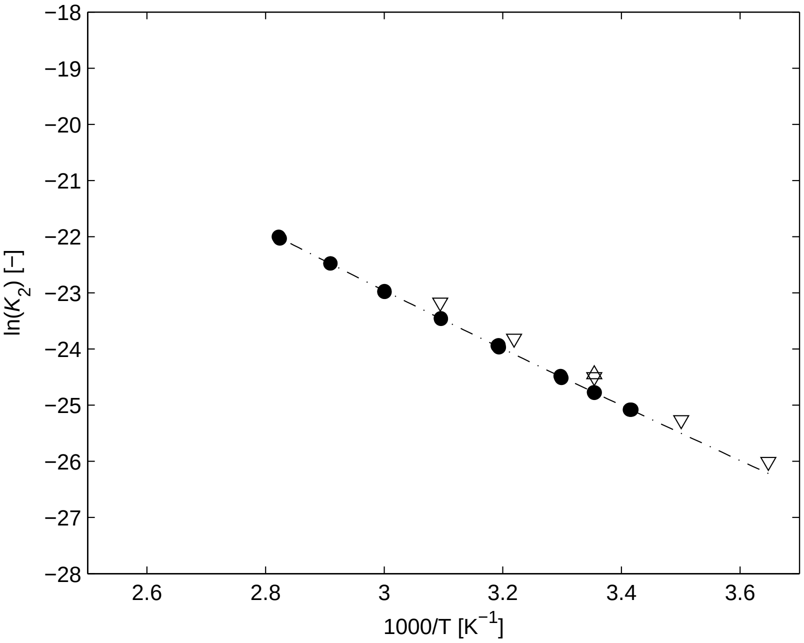

Figure 2.11: Dissociation constants of L-proline: •, exp. results this work; -·-·, fit this work; ▽, Smith [85]; △, Azab [6]

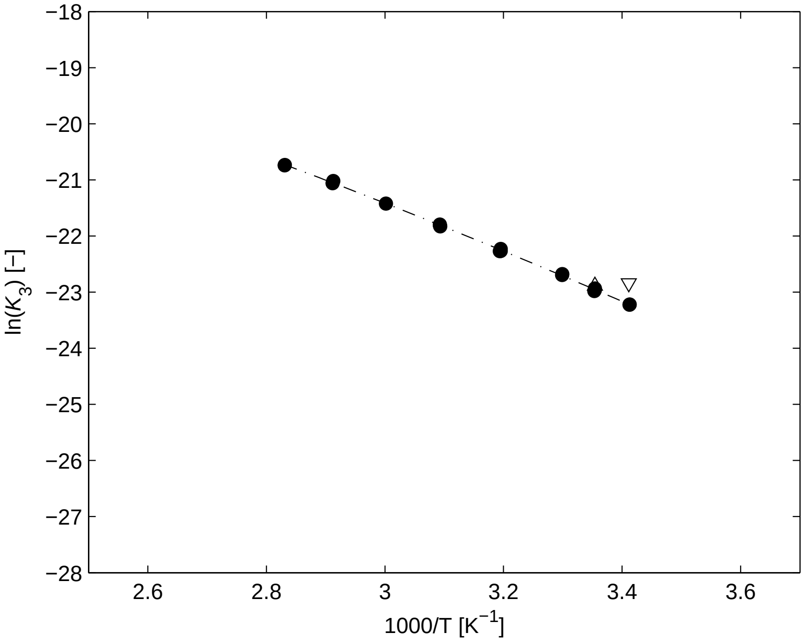

Figure 2.12: Dissociation constants of L-glutamic acid: •, exp. results this work; -·-·, fit this work; ▽, Albert [3]; △, Wilson [98]

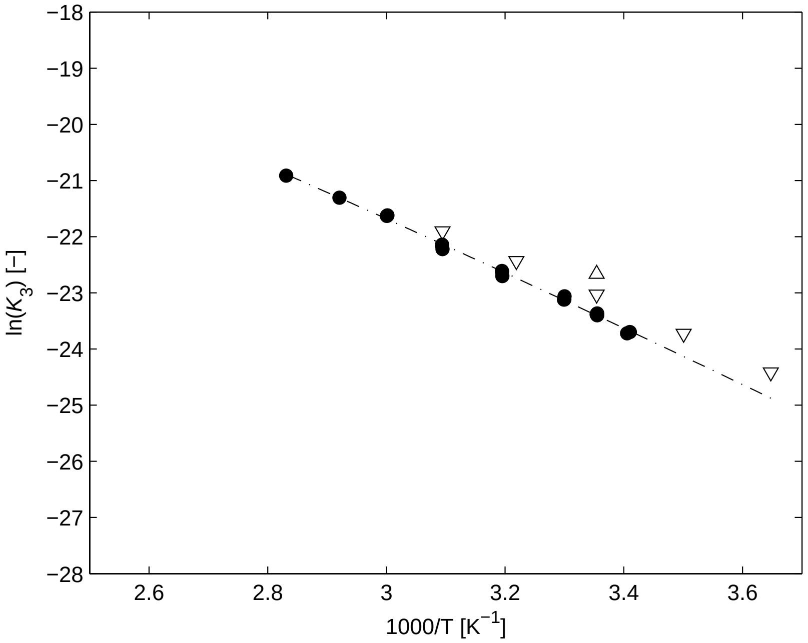

Figure 2.13: Dissociation constants of L-aspartic acid: •, exp. results this work; -·-·, fit this work; ▽, Smith [84]; △, Batchelder [7]

Table 2.2: Coefficients in equation (2.37)

	A [-]	B [-]	C [-]	Avg. rel. dev. [%]	Max. rel. dev. [%]
MDEA	-977.1	-77.882	10.7846	0.092	0.257
β-alanine	-5987.5	3.213	-1.2133	0.032	0.138
taurine	-5888.1	15.697	-2.9500	0.053	0.159
sarcosine	-4840.7	-6.123	-0.2016	0.019	0.038
6-aminohexanoic acid	-5871.3	-23.198	3.1031	0.041	0.156
DL-methionine	-7340.5	43.665	-7.1018	0.054	0.125
glycine	-7690.0	49.159	-8.0508	0.078	0.239
L-phenylalanine	-5070.7	-3.992	-0.0699	0.091	0.252
L-proline	-2865.5	-55.974	7.1627	0.039	0.118
L-glutamic acid	-7637.3	62.420	-10.4884	0.051	0.127
L-aspartic acid	-6623.7	30.801	-5.6139	0.151	0.393

Table 2.3: Comparison of correlated values of $ln(K)$ and thermodynamic properties with literature data for protonated MDEA

	this work	Kamps [2]	Oscarson [65]	Kim [47]	Littel [56]	Schwabe [82]
T [K]	$ln(K)$ [-]					
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[a]	-16.14			
422.10	-15.00[a]	-15.07[a]	-15.06			
$\Delta_r G_m^\circ$ [kJ/mol]	48.87	48.81	48.86	48.63		48.59
$\Delta_r H_m^\circ$ [kJ/mol]	34.9	34.0	35.2	35.2		35.7
$\Delta_r S_m^\circ$ [J/(mol K)]	-47.0	-49.6	-45.8	-45.1		-43.2
$\Delta_r C_{P,m}^\circ$ [J/(mol K)]	89.7	91.3	73.3			

---

[a] Extrapolated value

Table 2.4: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for β-alanine

	this work	May [60]	Gillespie [34]	Dey [28]	Majumdar [57]	Boyd [13]	Christensen [18]
T [K]	$ln(K_2)$ [-]						
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				
$\Delta_r G^\circ_m$ [kJ/mol]	58.95	58.41				58.77	
$\Delta_r H^\circ_m$ [kJ/mol]	46.8	47.5	47.3			46.9	
$\Delta_r S^\circ_m$ [J/(mol K)]	-40.9	-36.6	-37.7			-39.6	
$\Delta_r C^\circ_{P,m}$ [J/(mol K)]	-10.1	-59.8				-6.2	

---

[a] Extrapolated value

Table 2.5: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for taurine

		this work	King [49]
T [K]		$ln(K_2)$ [-]	
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]	51.71	51.76
$\Delta_r H_m^\circ$	[kJ/mol]	41.6	41.9
$\Delta_r S_m^\circ$	[J/(mol K)]	-33.8	-33.1
$\Delta_r C_{P,m}^\circ$	[J/(mol K)]	-24.5	-35.0

---

[a] Extrapolated value

Table 2.6: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for sarcosine

	this work	Datta [21, 22]
T [K]	$ln(K_2)$ [-]	
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]	58.27	58.22
$\Delta_r H_m^\circ$ [kJ/mol]	39.7	40.5
$\Delta_r S_m^\circ$ [J/(mol K)]	-62.1	-59.4
$\Delta_r C_{P,m}^\circ$ [J/(mol K)]	-1.7	-12.5

---

[a] Extrapolated value

Table 2.7: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for 6-aminohexanoic acid

	this work	Smith [84]	Gillespie [34]	Brandariz [15]
T [K]	$ln(K_2)$ [-]			
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	
$\Delta_r G^\circ_m$ [kJ/mol]	62.49	61.71		
$\Delta_r H^\circ_m$ [kJ/mol]	56.5	56.8		
$\Delta_r S^\circ_m$ [J/(mol K)]	-20.1	-16.7		
$\Delta_r C^\circ_{P,m}$ [J/(mol K)]	25.8			

---

[a] Extrapolated value

Table 2.8: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for DL-methionine

		this work	Pelletier [69]
T [K]		$ln(K_2)$ [-]	
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]	53.09	52.75
$\Delta_r H_m^\circ$	[kJ/mol]	43.4	43.5
$\Delta_r S_m^\circ$	[J/(mol K)]	-32.4	-31.4
$\Delta_r C_{P,m}^\circ$	[J/(mol K)]	-59.0	

---

[a] Extrapolated value

Table 2.9: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for glycine

	this work	Datta [21, 22]	King [48]	Owen [67]	Gillespie [34]	Clarke [19]	Izatt [44]
T [K]				$ln(K_2)$ [-]			
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]	55.78	55.81	55.85				
$\Delta_r H_m^\circ$ [kJ/mol]	44.0	44.2	44.2	45.3			43.95
$\Delta_r S_m^\circ$ [J/(mol K)]	-39.6	-38.9	-49.0				-39.1
$\Delta_r C_{P,m}^\circ$ [J/(mol K)]	-66.9	-44.9	-39.4				

---

[a] Extrapolated value

Table 2.10: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for L-phenylalanine

		this work	Izatt [45]
T [K]		$ln(K_2)$ [-]	
273.15^a		-22.95	-22.91
283.15^a		-22.29	-22.24
293.15^a		-21.69	-21.60
303.15		-21.12	-21.07
313.15		-20.59	-20.47
$\Delta_r G^\circ_m$	[kJ/mol]	53.04	
$\Delta_r H^\circ_m$	[kJ/mol]	42.0	43.1
$\Delta_r S^\circ_m$	[J/(mol K)]	-37.1	-32.7
$\Delta_r C^\circ_{P,m}$	[J/(mol K)]	-0.6	

---

[a] Extrapolated value

Table 2.11: Comparison of correlated values of $ln(K_2)$ and thermodynamic properties with literature values for L-proline

		this work	Smith [85]	Azab [6]
T [K]			$ln(K_2)$ [-]	
274.15[a]		-26.22	-26.01	
285.65[a]		-25.50	-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]	61.41	60.75	
$\Delta_r H_m^\circ$	[kJ/mol]	41.6	43.2	
$\Delta_r S_m^\circ$	[J/(mol K)]	-66.5	-59.0	
$\Delta_r C_{P,m}^\circ$	[J/(mol K)]	59.6		

---

[a] Extrapolated value

Table 2.12: Comparison of correlated values of $ln(K_3)$ and thermodynamic properties with literature values for L-glutamic acid

	this work	Albert [3]	Wilson [98]
T [K]		$ln(K_3)$ [-]	
293.15	-23.21	-22.84	
298.15	-22.95		-22.88
$\Delta_r G_m^\circ$ [kJ/mol]	56.90		
$\Delta_r H_m^\circ$ [kJ/mol]	37.5		
$\Delta_r S_m^\circ$ [J/(mol K)]	-65.1		
$\Delta_r C_{P,m}^\circ$ [J/(mol K)]	-87.2		

Table 2.13: Comparison of correlated values of $ln(K_3)$ and thermodynamic properties with literature values for L-aspartic acid

	this work	Smith [84]	Batchelder [7]
T [K]		$ln(K_3)$ [-]	
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]	58.01	57.15	
$\Delta_r H_m^\circ$ [kJ/mol]	41.2	37.8	
$\Delta_r S_m^\circ$ [J/(mol K)]	-56.5	-64.9	
$\Delta_r C_{P,m}^\circ$ [J/(mol K)]	-46.7		

Table 2.14: Comparison of the effect of different counter ions 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

Blauwhoff [11] and Versteeg [94, 95] related the basic strength of an absorbent to the CO_2 reaction rate constant by a Brønsted 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. Equation (2.32) relates $\Delta_r G_m^\circ$ to the dissociation constant, and also the basic strength. A high value of $\Delta_r G_m^\circ$ is favorable, and can indicate a high reactivity of the absorbent with CO_2. Even though, kinetic studies of the compounds have to be carried out before a definite conclusion can be drawn. During commercial post combustion CO_2 capture, an absorber is operated around 313 K and a desorber around 393 K depending on operating conditions. [50] From equation (2.33) it can be seen that 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. This might further lead to cost saving operations of CO_2 post combustion capture plants, since the temperature difference between the absorber and the desorber might be reduced. Table 2.15 shows $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ of commercially available CO_2 absorbents in comparison to the results from this work. The compounds are sorted with descending $\Delta_r G_m^\circ$ values. The values from this work are relisted in Table 2.15 for the convenience of the reader. As it can be seen, 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 $\Delta_r H_m^\circ$.

2.7 Conclusion

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

Based on the values for the standard state properties reported in this work, amino acid salts might be attractive compounds to be used as absorbents for

Table 2.15: Comparison of values of the standard state thermodynamic properties for commercially available absorbents to this work

Compound	Reference	$\Delta_r G_m^\circ$ [kJ/mol]	$\Delta_r H_m^\circ$ [kJ/mol]
6-aminohexanoic acid	this work	62.49	56.5
L-proline	this work	61.41	41.6
β-alanine	this work	58.95	46.8
sarcosine	this work	58.28	39.7
L-aspartic acid	this work	58.01	41.2
L-glutamic acid	this work	56.90	37.5
3-amino-1-Propanol (MPA)	[82]	56.85	53.6
glycine	this work	55.78	44.0
piperazine (PZ)	[40]	55.55	42.9
2-amino-2-methyl-1-propanol (AMP)	[56]	55.40	49.9
2-(diethylamino)ethanol (DEMEA)	[56]	54.92	47.8
monoethanolamine (MEA)	[9]	54.21	50.5
2-(2-aminoethoxy)ethanol (DGA)	[65]	53.74	50.2
DL-methionine	this work	53.09	43.4
L-phenylalanine	this work	53.04	42.0
taurine	this work	51.69	41.5
diisopropanolamine (DIPA)	[47]	50.69	42.7
diethanolamine (DEA)	[12]	50.68	42.4
methyldiethanolamine (MDEA)	this work	48.87	34.9
triethanolamine (TEA)	[8]	44.31	33.5

post-combustion CO_2 capture.

2.8 Outline of the model of Pitzer

A very brief outline of the model of Pitzer introduced by Pitzer [71] 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 [71] introduced the equation for the excess Gibbs energy:

$$\frac{G^{ex}}{RTw_S} = f\left(I_m\right) + \sum_i\sum_j m_i m_j B_{ij} + \sum_i\sum_j\sum_k m_i m_j m_k C_{ijk} + ... \tag{2.38}$$

Pitzer [71] further derived the expression for the activity coefficient. For the dissolved species $i : j$, the activity coefficients are estimated by:

$$ln\left(\gamma_{ij,m}\right) = -A_\phi\left[\frac{\sqrt{I_m}}{1+b\sqrt{I_m}} + \frac{2}{b}ln\left(1+b\sqrt{I_m}\right)\right] + mB_{ij} + 3m^2C_{ij} \tag{2.39}$$

where I_m is defined as:

$$I_m = \frac{1}{2}\sum_{x=i,j} m_x z_x^2 \tag{2.40}$$

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

$$A_\phi = \frac{1}{3}\sqrt{2\pi N_A \rho_W}\left(\frac{e^2}{4\pi\epsilon_0\epsilon_W kT}\right)^{1.5} \tag{2.41}$$

where the dielectric constant of water, ϵ_W, was taken from Bradley [14]. The second virial coefficient is given:

$$B_{ij} = 2\beta_{ij}^{(0)} + \left(\frac{2\beta_{ij}^{(1)}}{\alpha^2 I_m}\right)\left[1 - \left(1 + \alpha I_m^{1/2} - \frac{\alpha^2 I_m}{2}\right) exp\left(-\alpha I_m^{1/2}\right)\right] \tag{2.42}$$

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

$$ln\left(a_W\right) = \frac{M_W}{1000}\left\{2A_\phi\frac{I_m^{1.5}}{1+b\sqrt{I_m}} - \sum_{i\neq W} m_i\right\} \tag{2.43}$$

2.8.1 Interaction parameters for KCl in the model of Pitzer

The following section reports the temperature dependence of the ion interaction parameters for KCl given by Pabalan [68]. The interaction parameters are calculated from equation (2.44) and Table 2.16. 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 [80]. The pressure, P, was set to 1 bar. The pressure dependence of the thermodynamic properties are calculated from equation (2.45) and Table 2.17. A complete description of the equations below are given in Pabalan [68].

$$\begin{aligned}
f\left(T,P_r\right) = \frac{u_1T^2}{6} + \frac{u_2T}{2} + \frac{u_3T^2\left(\frac{ln(T)}{2}-\frac{5}{12}\right)}{3} + \frac{u_4T^3}{12} + \frac{u_5T^4}{20} \\
+ u_6\left[\frac{T}{2} + \frac{3\left(227\right)^2}{2T}\frac{227\left(T-227\right)ln\left(T-227\right)}{T}\right] \\
- u_7\left[\frac{2\left(647-T\right)ln\left(647-T\right)}{T} + ln\left(647-T\right)\right] \\
- \frac{K_1}{T} - f_L\left(T_r,P_r\right)\left(\frac{T_r^2}{T}\right) + K_2 + f_G\left(T_r,P_R\right) \quad (2.44)
\end{aligned}$$

Table 2.16: Parameters for equation (2.44)

parameter	$\beta^{(0)}_{KCl}$ [kg mol^{-1}]	$\beta^{(1)}_{KCl}$ [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
$f_L\left(T_r, 1\text{bar}\right)$	6.77136e-4	9.67854e-4	-4.12364e-5
$f_L\left(T_r, P_r\right)$	6.56838e-4	9.67854e-4	-4.12364e-5
$f_G\left(T_r, 1\text{bar}\right)$	4.8080e-2	2.18752e-1	-3.94e-4
$f_G\left(T_r, P_r\right)$	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

$$\begin{aligned}
&ln\gamma_{\pm}\left(P_2\right) - ln\gamma_{\pm}\left(P_1\right) = \\
&- \left[A_{\phi}\left(P_2\right) - A_{\phi}\left(P_1\right)\right]\left(\frac{I_m^{1/2}}{1+bI_m^{1/2}} + \frac{2}{b}ln\left(1+bI_m^{1/2}\right)\right) + \int_{P_1}^{P_2}\left\{2m\left(\frac{\partial\beta^{(0)}_{ij}}{\partial P}\right)_T\right. \\
&+ \frac{2m}{\alpha^2 I_m}\left(\frac{\partial\beta^{(1)}_{ij}}{\partial P}\right)_T\left[1-\left(1+\alpha I_m^{1/2}-\frac{\alpha^2 I_m}{2}\right)exp\left(-\alpha I_m^{1/2}\right)\right] \\
&\left. + 3m^2\left(\frac{\partial C_{ij}}{\partial P}\right)_T\right\}dP \quad (2.45)
\end{aligned}$$

where $\left(\frac{\partial \beta_{ij}^{(0)}}{\partial P}\right)_T = B_{ij}^V$ and B_{ij}^V is calculated from equation (2.46). Further, in this case, $\left(\frac{\partial \beta_{ij}^{(1)}}{\partial P}\right)_T = 0$ and $\left(\frac{\partial C_{ij}}{\partial P}\right)_T = 0$.

$$\begin{aligned} f_V\left(T,P\right) = q_1 + \frac{q_2}{T} + q_3 T + q_4 T^2 + \frac{q_5}{647-T} \\ + P\left[q_6 + \frac{q_7}{T} + q_8 T + q_9 T^2 + \frac{q_{10}}{(647-T)}\right] \\ + P^2\left[q_{11} + \frac{q_{12}}{T} + q_{13} T + q_{14} T^2 + \frac{q_{15}}{(647-T)}\right] \end{aligned} \tag{2.46}$$

Table 2.17: Parameters for equation (2.46)

parameter	B_{KCl}^V [kg mol^{-1} 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

2.8.2 Interaction parameters for HCl in the model of Pitzer

The following section reports the density, pressure and temperature dependence on the ion interaction parameters for HCl given by Holmes [41]. The ion interaction parameters are given by equation (2.48) and Table 2.18. T is the temperature in Kelvin, T^* is 1 K, P^* is 1 MPa and ρ^* 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 reference density. For HCl, the interaction parameter, C in equation (2.39), is defined:

$$C = \frac{1}{2} C_{HCl} \tag{2.47}$$

$$f\left(\rho,P,T\right) = q_1 + q_2 ln\left(\frac{\rho}{\rho_R}\right) + q_3\frac{(\rho-\rho_R)}{\rho^*} + q_4\frac{(T-T_R)}{T^*} + q_5\frac{(P-P_R)}{P^*} \tag{2.48}$$

Table 2.18: Parameters for equation (2.48)

parameter	$\beta^{(0)}_{HCl}$ [kg mol^{-1}]	$\beta^{(1)}_{HCl}$ [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

2.9 Experimental equilibrium data

2.9.1 MDEA

Table 2.19: Experimental equilibrium data for MDEA measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{MDEA}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.25	0.0099	293.25	0.0099	0.0481	-421.9	-19.9530
293.25	0.0099	293.35	0.0099	0.1314	-452.8	-20.0161
293.25	0.0099	293.35	0.0099	0.2153	-466.7	-20.0441
293.25	0.0099	293.25	0.0099	0.3047	-476.3	-20.0739
293.25	0.0099	293.25	0.0099	0.3594	-480.5	-20.0722
293.25	0.0099	293.35	0.0099	0.4595	-486.8	-20.0661
293.25	0.0099	293.35	0.0099	0.7509	-499.3	-20.0726
Run no. 2						
293.35	0.0099	293.35	0.0099	0.0895	-442.0	-20.0113
293.35	0.0099	293.25	0.0099	0.1636	-459.4	-20.0517
293.35	0.0099	293.25	0.0099	0.2097	-466.9	-20.0883
293.35	0.0099	293.25	0.0099	0.2952	-476.0	-20.0957
293.35	0.0099	293.35	0.0099	0.4612	-487.7	-20.0997
293.35	0.0099	293.25	0.0099	0.5889	-493.6	-20.0966
Run no. 3						
293.45	0.0099	293.55	0.0099	0.0770	-437.7	-19.9992
293.45	0.0099	293.45	0.0099	0.1314	-453.6	-20.0428
293.45	0.0099	293.45	0.0099	0.2206	-468.1	-20.0694
293.45	0.0099	293.45	0.0099	0.2964	-476.4	-20.0937
293.45	0.0099	293.45	0.0099	0.3711	-482.4	-20.1025
293.45	0.0099	293.35	0.0099	0.4705	-488.4	-20.1086
293.45	0.0099	293.35	0.0099	0.6627	-496.9	-20.1040
Run no. 4						
298.65	0.0099	298.75	0.0099	0.0895	-443.4	-19.7492
298.65	0.0099	298.75	0.0099	0.1636	-461.2	-19.7858
298.65	0.0099	298.65	0.0099	0.2097	-468.5	-19.8168
298.65	0.0099	298.55	0.0099	0.2952	-478.0	-19.8413
298.65	0.0099	298.55	0.0099	0.3604	-483.5	-19.8526
298.65	0.0099	298.65	0.0099	0.4612	-489.9	-19.8461
298.65	0.0099	298.65	0.0099	0.5889	-496.4	-19.8558
Run no. 5						
298.65	0.0099	298.55	0.0099	0.0481	-423.5	-19.7203
298.65	0.0099	298.75	0.0099	0.1314	-454.9	-19.7749
298.65	0.0099	298.75	0.0099	0.2153	-469.4	-19.8172
298.65	0.0099	298.75	0.0099	0.3047	-478.4	-19.8095
298.65	0.0099	298.65	0.0099	0.3594	-483.0	-19.8283
298.65	0.0099	298.65	0.0099	0.4595	-489.4	-19.8301
298.65	0.0099	298.75	0.0099	0.7509	-501.8	-19.8180
Run no. 6						
298.75	0.0099	298.75	0.0099	0.0770	-439.0	-19.7502
298.75	0.0099	298.75	0.0099	0.1314	-455.2	-19.7876
298.75	0.0099	298.75	0.0099	0.2206	-470.0	-19.8165
298.75	0.0099	298.75	0.0099	0.2964	-478.2	-19.8315
298.75	0.0099	298.65	0.0099	0.4705	-490.5	-19.8506
298.75	0.0099	298.65	0.0099	0.6627	-499.1	-19.8451
Run no. 7						
303.45	0.0099	303.55	0.0099	0.0895	-444.6	-19.5233
303.45	0.0099	303.55	0.0099	0.1636	-462.9	-19.5687
303.45	0.0099	303.35	0.0099	0.2097	-470.4	-19.6101
303.45	0.0099	303.35	0.0099	0.2952	-479.9	-19.6221
303.45	0.0099	303.35	0.0099	0.3604	-485.4	-19.6305
303.45	0.0099	303.55	0.0099	0.4612	-492.3	-19.6330
303.45	0.0099	303.55	0.0099	0.5889	-499.0	-19.6474
Run no. 8						
303.45	0.0099	303.45	0.0099	0.0481	-424.7	-19.4996

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{MDEA}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
303.45	0.0099	303.55	0.0099	0.1314	-456.4	-19.5537
303.45	0.0099	303.55	0.0099	0.2153	-471.4	-19.6070
303.45	0.0099	303.55	0.0099	0.3047	-481.0	-19.6177
303.45	0.0099	303.45	0.0099	0.3594	-485.7	-19.6378
303.45	0.0099	303.45	0.0099	0.4595	-492.4	-19.6481
303.45	0.0099	303.55	0.0099	0.7509	-504.3	-19.6108
Run no. 9						
313.45	0.0099	313.35	0.0099	0.0770	-442.7	-19.0955
313.45	0.0099	313.45	0.0099	0.1314	-459.7	-19.1279
313.45	0.0099	313.45	0.0099	0.2206	-474.8	-19.1427
313.45	0.0099	313.45	0.0099	0.2964	-483.4	-19.1592
313.45	0.0099	313.45	0.0099	0.3711	-490.1	-19.1812
313.45	0.0099	313.45	0.0099	0.4705	-496.4	-19.1781
313.45	0.0099	313.45	0.0099	0.6627	-505.5	-19.1792
Run no. 10						
313.55	0.0099	313.45	0.0099	0.0481	-426.6	-19.0536
313.55	0.0099	313.55	0.0099	0.1314	-459.6	-19.1189
313.55	0.0099	313.55	0.0099	0.2153	-474.5	-19.1513
313.55	0.0099	313.55	0.0099	0.3047	-484.4	-19.1627
313.55	0.0099	313.55	0.0099	0.3594	-489.2	-19.1743
313.55	0.0099	313.55	0.0099	0.4595	-495.8	-19.1737
313.55	0.0099	313.55	0.0099	0.7509	-508.6	-19.1668
Run no. 11						
313.55	0.0099	313.55	0.0099	0.0895	-447.8	-19.1022
313.55	0.0099	313.55	0.0099	0.1636	-466.5	-19.1414
313.55	0.0099	313.65	0.0099	0.2097	-474.0	-19.1534
313.55	0.0099	313.55	0.0099	0.2952	-483.8	-19.1728
313.55	0.0099	313.55	0.0099	0.3604	-489.4	-19.1790
313.55	0.0099	313.55	0.0099	0.4612	-496.2	-19.1852
313.55	0.0099	313.55	0.0099	0.5889	-502.4	-19.1737
Run no. 12						
322.85	0.0099	322.85	0.0099	0.0481	-425.8	-18.5642
322.85	0.0099	322.85	0.0099	0.1314	-457.8	-18.5645
322.85	0.0099	322.85	0.0099	0.2153	-472.0	-18.5553
322.85	0.0099	322.75	0.0099	0.3047	-481.7	-18.5551
322.85	0.0099	322.85	0.0099	0.3594	-486.3	-18.5474
322.85	0.0099	322.75	0.0099	0.4595	-492.7	-18.5385
322.85	0.0099	322.75	0.0099	0.7509	-505.1	-18.5014
Run no. 13						
322.85	0.0099	322.75	0.0099	0.0895	-446.3	-18.5774
322.85	0.0099	322.85	0.0099	0.1636	-464.4	-18.5686
322.85	0.0099	322.85	0.0099	0.2097	-471.6	-18.5684
322.85	0.0099	322.85	0.0099	0.2952	-481.3	-18.5666
322.85	0.0099	322.85	0.0099	0.3604	-486.5	-18.5519
322.85	0.0099	322.75	0.0099	0.4612	-493.1	-18.5496
322.85	0.0099	322.85	0.0099	0.5889	-499.3	-18.5240
Run no. 14						
333.25	0.0099	333.35	0.0099	0.0481	-427.4	-18.1372
333.25	0.0099	333.25	0.0099	0.1314	-460.2	-18.1362
333.25	0.0099	333.25	0.0099	0.2153	-474.8	-18.1260
333.25	0.0099	333.15	0.0099	0.3047	-484.7	-18.1224
333.25	0.0099	333.15	0.0099	0.3594	-489.3	-18.1167
333.25	0.0099	333.15	0.0099	0.4595	-495.7	-18.0947
Run no. 15						
333.25	0.0099	333.25	0.0099	0.0770	-442.9	-18.1235
333.25	0.0099	333.25	0.0099	0.1314	-459.9	-18.1254
333.25	0.0099	333.25	0.0099	0.2206	-474.9	-18.1040
333.25	0.0099	333.25	0.0099	0.2964	-483.4	-18.0984
333.25	0.0099	333.25	0.0099	0.3711	-489.9	-18.0987
333.25	0.0099	333.25	0.0099	0.4705	-496.0	-18.0748
333.25	0.0099	333.35	0.0099	0.6627	-505.0	-18.0457
Run no. 16						
333.35	0.0099	333.25	0.0099	0.0895	-448.5	-18.1496
333.35	0.0099	333.25	0.0099	0.1636	-467.0	-18.1415

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{MDEA}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
333.35	0.0099	333.35	0.0099	0.2097	-474.3	-18.1310
333.35	0.0099	333.35	0.0099	0.2952	-484.1	-18.1225
333.35	0.0099	333.35	0.0099	0.3604	-489.7	-18.1167
333.35	0.0099	333.35	0.0099	0.4612	-496.7	-18.1154
333.35	0.0099	333.35	0.0099	0.5889	-502.8	-18.0869
Run no. 17						
343.15	0.0099	343.15	0.0099	0.0895	-450.0	-17.7494
343.15	0.0099	343.15	0.0099	0.1636	-469.5	-17.7575
343.15	0.0099	343.15	0.0099	0.2097	-477.1	-17.7565
343.15	0.0099	343.15	0.0099	0.2952	-487.3	-17.7528
343.15	0.0099	343.25	0.0099	0.3604	-492.6	-17.7253
343.15	0.0099	343.15	0.0099	0.4612	-499.6	-17.7238
343.15	0.0099	343.15	0.0099	0.5889	-505.7	-17.6899
Run no. 18						
343.25	0.0099	343.25	0.0099	0.0455	-426.3	-17.7437
343.25	0.0099	343.15	0.0099	0.1632	-468.7	-17.7342
343.25	0.0099	343.15	0.0099	0.2119	-476.7	-17.7327
343.25	0.0099	343.25	0.0099	0.3260	-489.3	-17.7148
343.25	0.0099	343.15	0.0099	0.9033	-516.0	-17.6254
Run no. 19						
353.15	0.0099	353.25	0.0099	0.0455	-427.0	-17.3578
353.15	0.0099	353.05	0.0099	0.1632	-470.9	-17.3635
353.15	0.0099	353.15	0.0099	0.2119	-478.7	-17.3423
353.15	0.0099	353.25	0.0099	0.3260	-491.4	-17.3163
353.15	0.0099	353.25	0.0099	0.6627	-510.7	-17.2515
Run no. 20						
353.25	0.0099	353.25	0.0099	0.0895	-451.6	-17.3676
353.25	0.0099	353.15	0.0099	0.1636	-471.4	-17.3728
353.25	0.0099	353.25	0.0099	0.2097	-478.8	-17.3524
353.25	0.0099	353.25	0.0099	0.2952	-489.1	-17.3424
353.25	0.0099	353.35	0.0099	0.3604	-494.3	-17.3068
353.25	0.0099	353.35	0.0099	0.4612	-501.5	-17.2994
353.25	0.0099	353.35	0.0099	0.5889	-508.3	-17.2838

2.9.2 β-alanine

Table 2.20: Experimental equilibrium data for β-alanine measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{\beta-alanine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.15	0.0102	293.15	0.0100	0.0750	-440.2	-24.0732
293.15	0.0102	293.15	0.0100	0.1573	-419.7	-24.0776
293.15	0.0102	293.05	0.0100	0.2244	-410.4	-24.0908
293.15	0.0102	293.05	0.0100	0.3224	-400.9	-24.0907
293.15	0.0102	293.05	0.0100	0.3933	-396.1	-24.1052
293.15	0.0102	293.15	0.0100	0.5359	-388.1	-24.0981
293.15	0.0102	293.15	0.0100	0.7056	-381.5	-24.1164
Run no. 2						
293.15	0.0102	293.15	0.0100	0.0732	-441.2	-24.0853
293.15	0.0102	293.15	0.0100	0.1515	-420.8	-24.0809
293.15	0.0102	293.15	0.0100	0.2280	-410.1	-24.0889
293.15	0.0102	293.15	0.0100	0.3004	-402.9	-24.0906
293.15	0.0102	293.15	0.0100	0.3801	-396.9	-24.0954
293.15	0.0102	293.15	0.0100	0.5277	-388.3	-24.0903
293.15	0.0102	293.25	0.0100	0.7116	-381.2	-24.1068
Run no. 3						
293.25	0.0102	293.15	0.0100	0.0733	-441.2	-24.0882
293.25	0.0102	293.15	0.0100	0.1621	-419.4	-24.0987
293.25	0.0102	293.15	0.0100	0.2312	-409.9	-24.0966
293.25	0.0102	293.15	0.0100	0.3147	-401.7	-24.0923
293.25	0.0102	293.25	0.0100	0.3737	-397.4	-24.0923
293.25	0.0102	293.15	0.0100	0.5269	-389.0	-24.1176
293.25	0.0102	293.15	0.0100	0.6945	-382.3	-24.1331
Run no. 4						
298.15	0.0102	298.25	0.0100	0.1573	-418.6	-23.7513
298.15	0.0102	298.15	0.0100	0.2244	-409.1	-23.7628
298.15	0.0102	298.15	0.0100	0.3224	-399.5	-23.7652
298.15	0.0102	298.15	0.0100	0.3933	-394.4	-23.7712
298.15	0.0102	298.25	0.0100	0.5359	-386.3	-23.7659
298.15	0.0102	298.25	0.0100	0.7056	-379.4	-23.7769
Run no. 5						
298.25	0.0102	298.35	0.0100	0.0732	-440.3	-23.7467
298.25	0.0102	298.35	0.0100	0.1515	-419.3	-23.7329
298.25	0.0102	298.25	0.0100	0.2280	-408.3	-23.7430
298.25	0.0102	298.25	0.0100	0.3004	-401.1	-23.7495
298.25	0.0102	298.25	0.0100	0.3801	-394.8	-23.7466
298.25	0.0102	298.35	0.0100	0.5277	-386.4	-23.7490
298.25	0.0102	298.35	0.0100	0.7116	-379.0	-23.7650
Run no. 6						
298.35	0.0102	298.35	0.0102	0.0733	-440.4	-23.7534
298.35	0.0102	298.35	0.0102	0.1621	-418.0	-23.7555
298.35	0.0102	298.25	0.0102	0.2312	-408.5	-23.7664
298.35	0.0102	298.25	0.0102	0.3147	-400.4	-23.7715
298.35	0.0102	298.35	0.0102	0.3737	-395.8	-23.7630
298.35	0.0102	298.25	0.0102	0.5269	-387.4	-23.7937
298.35	0.0102	298.25	0.0102	0.6945	-380.3	-23.7982
Run no. 7						
303.05	0.0102	303.15	0.0100	0.0750	-438.4	-23.4320
303.05	0.0102	303.15	0.0100	0.1573	-417.1	-23.4323
303.05	0.0102	303.05	0.0100	0.2244	-407.8	-23.4572
303.05	0.0102	302.95	0.0100	0.3224	-398.1	-23.4680
303.05	0.0102	302.95	0.0100	0.3933	-392.8	-23.4695
303.05	0.0102	303.15	0.0100	0.5359	-383.8	-23.4289
303.05	0.0102	303.15	0.0100	0.7056	-377.6	-23.4711
Run no. 8						
303.15	0.0102	303.25	0.0100	0.0732	-439.5	-23.4412
303.15	0.0102	303.25	0.0100	0.1515	-418.2	-23.4290
303.15	0.0102	303.25	0.0100	0.2280	-407.1	-23.4357

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{\beta-alanine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
303.15	0.0102	303.25	0.0100	0.3004	-399.4	-23.4277
303.15	0.0102	303.25	0.0100	0.3801	-393.3	-23.4365
303.15	0.0102	303.25	0.0100	0.5277	-384.9	-23.4504
303.15	0.0102	303.25	0.0100	0.7116	-376.7	-23.4404
Run no. 9						
303.25	0.0102	303.25	0.0100	0.0733	-439.6	-23.4479
303.25	0.0102	303.05	0.0100	0.1621	-417.2	-23.4767
303.25	0.0102	303.25	0.0100	0.2312	-406.9	-23.4437
303.25	0.0102	303.15	0.0100	0.3147	-399.1	-23.4716
303.25	0.0102	303.25	0.0100	0.3737	-394.2	-23.4546
303.25	0.0102	303.25	0.0100	0.5269	-385.3	-23.4654
303.25	0.0102	302.95	0.0100	0.6945	-378.8	-23.5151
Run no. 10						
313.05	0.0102	313.15	0.0100	0.0733	-437.9	-22.8558
313.05	0.0102	313.15	0.0100	0.1621	-414.3	-22.8542
313.05	0.0102	313.15	0.0100	0.2312	-404.0	-22.8464
313.05	0.0102	313.15	0.0100	0.3147	-395.6	-22.8553
313.05	0.0102	313.15	0.0100	0.3737	-391.1	-22.8653
313.05	0.0102	313.15	0.0100	0.5269	-381.8	-22.8719
313.05	0.0102	313.15	0.0100	0.6945	-374.3	-22.8747
Run no. 11						
313.25	0.0102	313.35	0.0100	0.0732	-438.1	-22.8513
313.25	0.0102	313.25	0.0100	0.1515	-416.2	-22.8489
313.25	0.0102	313.25	0.0100	0.2280	-404.7	-22.8543
313.25	0.0102	313.25	0.0100	0.3004	-397.1	-22.8594
313.25	0.0102	313.25	0.0100	0.3801	-390.4	-22.8534
313.25	0.0102	313.25	0.0100	0.5277	-381.6	-22.8627
313.25	0.0102	313.25	0.0100	0.7116	-373.8	-22.8776
Run no. 12						
313.35	0.0102	313.25	0.0100	0.0750	-437.5	-22.8640
313.35	0.0102	313.35	0.0100	0.1573	-415.4	-22.8546
313.35	0.0102	313.35	0.0100	0.2244	-405.2	-22.8514
313.35	0.0102	313.35	0.0100	0.3224	-395.0	-22.8497
313.35	0.0102	313.25	0.0100	0.3933	-389.5	-22.8562
313.35	0.0102	313.25	0.0100	0.5359	-381.3	-22.8686
313.35	0.0102	313.25	0.0100	0.7056	-374.1	-22.8813
Run no. 13						
323.05	0.0102	323.05	0.0100	0.0732	-436.5	-22.3119
323.05	0.0102	323.05	0.0100	0.1515	-414.1	-22.3097
323.05	0.0102	323.05	0.0100	0.2280	-402.2	-22.3135
323.05	0.0102	323.05	0.0100	0.3004	-394.0	-22.3056
323.05	0.0102	323.05	0.0100	0.3801	-387.4	-22.3107
323.05	0.0102	322.95	0.0100	0.5277	-378.1	-22.3173
323.05	0.0102	322.95	0.0100	0.7116	-370.0	-22.3301
Run no. 14						
323.15	0.0102	323.15	0.0100	0.0733	-436.5	-22.3088
323.15	0.0102	323.15	0.0100	0.1621	-412.1	-22.3053
323.15	0.0102	323.05	0.0100	0.2312	-401.4	-22.3005
323.15	0.0102	323.05	0.0100	0.3147	-392.6	-22.3045
323.15	0.0102	323.15	0.0100	0.3737	-387.7	-22.2998
323.15	0.0102	323.05	0.0100	0.5269	-378.2	-22.3152
323.15	0.0102	323.15	0.0100	0.6945	-370.7	-22.3212
Run no. 15						
323.15	0.0102	323.15	0.0100	0.0750	-436.1	-22.3202
323.15	0.0102	323.15	0.0100	0.1573	-413.2	-22.3130
323.15	0.0102	323.15	0.0100	0.2244	-402.7	-22.3104
323.15	0.0102	323.15	0.0100	0.3224	-392.0	-22.3022
323.15	0.0102	323.15	0.0100	0.3933	-386.3	-22.3020
323.15	0.0102	323.15	0.0100	0.5359	-378.1	-22.3236
323.15	0.0102	323.15	0.0100	0.7056	-370.6	-22.3337
Run no. 16						
332.85	0.0102	332.75	0.0100	0.0732	-435.1	-21.8114
332.85	0.0102	332.85	0.0100	0.1515	-411.8	-21.7957
332.85	0.0102	332.85	0.0100	0.2280	-399.0	-21.7807

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{\beta-alanine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
332.85	0.0102	332.75	0.0100	0.3004	-391.3	-21.8041
332.85	0.0102	332.75	0.0100	0.3801	-384.6	-21.8127
332.85	0.0102	332.75	0.0100	0.5277	-375.0	-21.8132
332.85	0.0102	332.75	0.0100	0.7116	-366.4	-21.8171
Run no. 17						
332.85	0.0102	332.95	0.0100	0.0750	-434.0	-21.7890
332.85	0.0102	332.95	0.0100	0.1573	-410.4	-21.7815
332.85	0.0102	332.85	0.0100	0.2244	-399.8	-21.7920
332.85	0.0102	332.75	0.0100	0.3224	-388.9	-21.7932
332.85	0.0102	332.75	0.0100	0.3933	-382.8	-21.7849
332.85	0.0102	332.95	0.0100	0.5359	-373.9	-21.7804
332.85	0.0102	332.75	0.0100	0.7056	-366.3	-21.8050
Run no. 18						
332.95	0.0102	332.95	0.0100	0.0733	-434.3	-21.7749
332.95	0.0102	332.95	0.0100	0.1621	-409.0	-21.7657
332.95	0.0102	332.85	0.0100	0.2312	-398.2	-21.7685
332.95	0.0102	332.85	0.0100	0.3147	-389.3	-21.7783
332.95	0.0102	333.05	0.0100	0.3737	-384.2	-21.7669
332.95	0.0102	332.95	0.0100	0.5269	-374.7	-21.7922
332.95	0.0102	332.85	0.0100	0.6945	-367.2	-21.8165
Run no. 19						
343.35	0.0102	343.35	0.0100	0.0733	-433.6	-21.2976
343.35	0.0102	343.45	0.0100	0.1621	-407.6	-21.2862
343.35	0.0102	343.35	0.0100	0.2312	-396.3	-21.2832
343.35	0.0102	343.45	0.0100	0.3147	-387.3	-21.2942
343.35	0.0102	343.45	0.0100	0.3737	-382.0	-21.2919
343.35	0.0102	343.45	0.0100	0.5269	-372.2	-21.3120
343.35	0.0102	343.45	0.0100	0.6945	-363.9	-21.3122
Run no. 20						
343.65	0.0102	343.65	0.0100	0.0750	-433.2	-21.2972
343.65	0.0102	343.65	0.0100	0.1573	-408.8	-21.2882
343.65	0.0102	343.65	0.0100	0.2244	-397.3	-21.2744
343.65	0.0102	343.65	0.0100	0.3224	-385.6	-21.2552
343.65	0.0102	343.65	0.0100	0.3933	-379.7	-21.2605
343.65	0.0102	343.75	0.0100	0.5359	-371.0	-21.2779
343.65	0.0102	343.65	0.0100	0.7056	-362.8	-21.2853
Run no. 21						
343.75	0.0102	343.75	0.0100	0.0732	-433.5	-21.2757
343.75	0.0102	343.75	0.0100	0.1515	-409.6	-21.2711
343.75	0.0102	343.65	0.0100	0.2280	-397.0	-21.2821
343.75	0.0102	343.65	0.0100	0.3004	-388.4	-21.2783
343.75	0.0102	343.65	0.0100	0.3801	-381.3	-21.2807
343.75	0.0102	343.65	0.0100	0.5277	-371.8	-21.2952
Run no. 22						
353.75	0.0102	353.75	0.0100	0.0732	-431.5	-20.8011
353.75	0.0102	353.75	0.0100	0.1515	-406.7	-20.7898
353.75	0.0102	353.65	0.0100	0.2280	-394.2	-20.8159
353.75	0.0102	353.65	0.0100	0.3004	-385.4	-20.8138
353.75	0.0102	353.85	0.0100	0.3801	-377.9	-20.8005
Run no. 23						
353.85	0.0102	353.95	0.0100	0.0750	-431.1	-20.8063
353.85	0.0102	353.95	0.0100	0.1573	-406.2	-20.8050
353.85	0.0102	353.85	0.0100	0.2244	-394.7	-20.8073
353.85	0.0102	353.85	0.0100	0.3224	-382.6	-20.7864
353.85	0.0102	353.95	0.0100	0.3933	-376.6	-20.7894
353.85	0.0102	353.95	0.0100	0.5359	-367.6	-20.8105
353.85	0.0102	353.75	0.0100	0.7056	-359.7	-20.8399
Run no. 24						
353.95	0.0102	354.05	0.0100	0.0733	-431.4	-20.7864
353.95	0.0102	353.85	0.0100	0.1621	-405.1	-20.8069
353.95	0.0102	353.85	0.0100	0.2312	-393.8	-20.8101
353.95	0.0102	353.95	0.0100	0.3147	-384.6	-20.8238
353.95	0.0102	353.95	0.0100	0.3737	-379.7	-20.8399
353.95	0.0102	353.95	0.0100	0.5269	-369.4	-20.8534

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{\beta-alanine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
353.95	0.0102	353.95	0.0100	0.6945	-361.1	-20.8620

2.9.3 Taurine

Table 2.21: Experimental equilibrium data for taurine measurements

T_I [K]	$\tilde{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\tilde{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\tilde{m}_{taurine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.25	0.0102	293.25	0.0100	0.0544	-376.4	21.1808
293.25	0.0102	293.15	0.0100	0.1414	-348.8	21.1785
293.25	0.0102	293.15	0.0100	0.2070	-338.9	21.1918
293.25	0.0102	293.15	0.0100	0.2842	-330.5	21.1901
293.25	0.0102	293.25	0.0100	0.3412	-325.8	21.1872
293.25	0.0102	293.15	0.0100	0.4143	-320.9	21.1984
Run no. 2						
293.65	0.0082	293.65	0.0087	0.0632	-361.6	-21.1136
293.65	0.0082	293.65	0.0087	0.1379	-340.5	-21.1440
293.65	0.0082	293.65	0.0087	0.2106	-329.6	-21.1595
293.65	0.0082	293.65	0.0087	0.2479	-324.6	-21.1315
293.65	0.0082	293.55	0.0087	0.3301	-317.3	-21.1438
293.65	0.0082	293.55	0.0087	0.4705	-308.7	-21.1661
293.65	0.0082	293.65	0.0087	0.5369	-305.3	-21.1607
Run no. 3						
293.65	0.0082	293.65	0.0087	0.0378	-377.3	-21.1083
293.65	0.0082	293.55	0.0087	0.1283	-341.8	-21.1234
293.65	0.0082	293.65	0.0087	0.2081	-329.4	-21.1391
293.65	0.0082	293.75	0.0087	0.2696	-322.4	-21.1259
293.65	0.0082	293.65	0.0087	0.4242	-310.7	-21.1343
293.65	0.0082	293.65	0.0087	0.4314	-310.6	-21.1475
293.65	0.0082	293.65	0.0087	0.5947	-302.4	-21.1500
Run no. 4						
298.45	0.0082	298.55	0.0087	0.0632	-360.0	-20.8174
298.45	0.0082	298.45	0.0087	0.1379	-338.6	-20.8554
298.45	0.0082	298.55	0.0087	0.4705	-305.9	-20.8522
298.45	0.0082	298.45	0.0087	0.5369	-302.8	-20.8711
Run no. 5						
298.55	0.0082	298.55	0.0087	0.0378	-376.6	-20.8381
298.55	0.0082	298.45	0.0087	0.1283	-340.7	-20.8605
298.55	0.0082	298.55	0.0087	0.2081	-327.5	-20.8532
298.55	0.0082	298.65	0.0087	0.2696	-320.5	-20.8448
298.55	0.0082	298.65	0.0087	0.4242	-308.7	-20.8515
298.55	0.0082	298.45	0.0087	0.4314	-308.6	-20.8751
Run no. 6						
303.05	0.0082	303.15	0.0100	0.0798	-356.0	-20.5738
303.05	0.0082	303.25	0.0100	0.1490	-338.0	-20.5671
303.05	0.0082	303.25	0.0100	0.2085	-328.8	-20.5715
303.05	0.0082	303.25	0.0100	0.2891	-320.4	-20.5909
303.05	0.0082	303.05	0.0100	0.3210	-317.4	-20.5945
Run no. 7						
303.45	0.0082	303.45	0.0100	0.0830	-354.8	-20.5601
303.45	0.0082	303.45	0.0100	0.1396	-340.2	-20.5754
303.45	0.0082	303.45	0.0100	0.2138	-327.9	-20.5577
303.45	0.0082	303.45	0.0100	0.3688	-313.8	-20.5840
Run no. 8						
313.15	0.0082	313.15	0.0100	0.0798	-353.7	-20.0585
313.15	0.0082	313.15	0.0100	0.1490	-335.1	-20.0570
313.15	0.0082	313.05	0.0100	0.2085	-326.1	-20.0850
313.15	0.0082	313.05	0.0100	0.3210	-313.7	-20.0742
Run no. 9						
313.15	0.0082	313.05	0.0100	0.0830	-352.5	-20.0639
313.15	0.0082	313.25	0.0100	0.1396	-337.0	-20.0525
313.15	0.0082	313.15	0.0100	0.2138	-325.1	-20.0695
313.15	0.0082	313.15	0.0100	0.4125	-306.6	-20.0642
313.15	0.0082	313.05	0.0100	0.5588	-298.7	-20.0862
Run no. 10						
323.35	0.0102	323.35	0.0100	0.0544	-370.4	19.5915

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{taurine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
323.35	0.0102	323.45	0.0100	0.1414	-339.8	19.5724
323.35	0.0102	323.45	0.0100	0.2070	-328.4	19.5685
323.35	0.0102	323.45	0.0100	0.2842	-319.4	19.5765
323.35	0.0102	323.45	0.0100	0.3412	-314.2	19.5786
323.35	0.0102	323.45	0.0100	0.4143	-308.5	19.5738
323.35	0.0102	323.45	0.0100	0.5598	-300.0	19.5762
Run no. 11						
323.55	0.0082	323.45	0.0100	0.1396	-334.2	-19.5652
323.55	0.0082	323.45	0.0100	0.2138	-321.3	-19.5551
323.55	0.0082	323.55	0.0100	0.2699	-314.4	-19.5458
323.55	0.0082	323.55	0.0100	0.3688	-306.0	-19.5670
323.55	0.0082	323.65	0.0100	0.4125	-302.2	-19.5411
323.55	0.0082	323.65	0.0100	0.5588	-293.7	-19.5463
Run no. 12						
333.25	0.0082	333.25	0.0099	0.0652	-355.3	-19.1023
333.25	0.0082	333.25	0.0099	0.1258	-333.7	-19.0906
333.25	0.0082	333.15	0.0099	0.2807	-309.2	-19.0902
333.25	0.0082	333.15	0.0099	0.3683	-301.0	-19.0851
333.25	0.0082	333.15	0.0099	0.4508	-295.3	-19.0935
Run no. 13						
333.25	0.0082	333.15	0.0099	0.0816	-348.1	-19.1160
333.25	0.0082	333.25	0.0099	0.1891	-321.1	-19.0872
333.25	0.0082	333.15	0.0099	0.2035	-319.8	-19.1241
333.25	0.0082	333.25	0.0099	0.2887	-308.6	-19.0942
333.25	0.0082	333.25	0.0099	0.3528	-302.4	-19.0851
333.25	0.0082	333.25	0.0099	0.4363	-296.3	-19.0908
333.25	0.0082	333.25	0.0099	0.5706	-288.4	-19.0894
Run no. 14						
333.25	0.0082	333.25	0.0099	0.0793	-349.0	-19.1110
333.25	0.0082	333.25	0.0099	0.1205	-335.8	-19.1163
333.25	0.0082	333.25	0.0099	0.1879	-321.8	-19.1054
333.25	0.0082	333.25	0.0099	0.3105	-306.3	-19.0895
333.25	0.0082	333.25	0.0099	0.3885	-299.5	-19.0833
333.25	0.0082	333.25	0.0099	0.4498	-295.4	-19.0906
333.25	0.0082	333.15	0.0099	0.5301	-290.9	-19.1057
Run no. 15						
343.15	0.0082	343.15	0.0099	0.0793	-347.0	-18.6976
343.15	0.0082	343.15	0.0099	0.1205	-333.0	-18.6892
343.15	0.0082	343.15	0.0099	0.1879	-318.4	-18.6720
343.15	0.0082	343.25	0.0099	0.3105	-302.6	-18.6574
343.15	0.0082	343.25	0.0099	0.3885	-295.7	-18.6547
343.15	0.0082	343.15	0.0099	0.4498	-291.3	-18.6601
343.15	0.0082	343.15	0.0099	0.5301	-286.7	-18.6721
Run no. 16						
349.85	0.0095	349.85	0.0092	0.0735	-349.3	-18.4075
349.85	0.0095	349.85	0.0092	0.1755	-319.9	-18.3821
349.85	0.0095	349.85	0.0092	0.1944	-317.5	-18.4099
349.85	0.0095	349.95	0.0092	0.2519	-310.0	-18.4276
349.85	0.0095	349.85	0.0092	0.4377	-291.4	-18.3833
349.85	0.0095	349.85	0.0092	0.5504	-284.0	-18.3712
Run no. 17						
352.25	0.0082	352.15	0.0099	0.0793	-344.5	-18.3214
352.25	0.0082	352.25	0.0099	0.1205	-330.4	-18.3174
352.25	0.0082	352.25	0.0099	0.1879	-314.3	-18.2636
352.25	0.0082	352.25	0.0099	0.3105	-297.0	-18.2175
352.25	0.0082	352.25	0.0099	0.3885	-290.2	-18.2240
352.25	0.0082	352.25	0.0099	0.4498	-285.7	-18.2259
352.25	0.0082	352.25	0.0099	0.5301	-281.2	-18.2452
Run no. 18						
352.25	0.0082	352.25	0.0099	0.0816	-343.2	-18.3056
352.25	0.0082	352.35	0.0099	0.1891	-314.7	-18.2789
352.25	0.0082	352.35	0.0099	0.2035	-312.7	-18.2906
352.25	0.0082	352.35	0.0099	0.2887	-302.0	-18.3028
352.25	0.0082	352.35	0.0099	0.3528	-294.3	-18.2560

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{taurine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 19						
353.85	0.0102	353.85	0.0100	0.0544	-363.8	18.2453
353.85	0.0102	353.85	0.0100	0.1414	-330.3	18.2305
353.85	0.0102	353.75	0.0100	0.2070	-317.6	18.2233
353.85	0.0102	353.75	0.0100	0.2842	-307.7	18.2294
353.85	0.0102	353.85	0.0100	0.3412	-301.7	18.2172
353.85	0.0102	353.75	0.0100	0.4143	-295.4	18.2141
353.85	0.0102	353.75	0.0100	0.5598	-285.7	18.2033

2.9.4 Sarcosine

Table 2.22: Experimental equilibrium data for sarcosine measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{sarcosine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.65	0.0082	293.45	0.0100	0.1091	-416.3	-23.7579
293.65	0.0082	293.75	0.0100	0.1751	-403.6	-23.7455
293.65	0.0082	293.65	0.0100	0.2248	-397.0	-23.7540
293.65	0.0082	293.75	0.0100	0.3094	-388.2	-23.7316
293.65	0.0082	293.65	0.0100	0.3955	-381.9	-23.7417
293.65	0.0082	293.75	0.0100	0.5151	-374.8	-23.7252
293.65	0.0082	293.65	0.0100	0.6832	-367.6	-23.7339
Run no. 2						
293.75	0.0082	293.75	0.0100	0.0709	-429.0	-23.7553
293.75	0.0082	293.75	0.0100	0.1707	-404.7	-23.7630
293.75	0.0082	293.75	0.0100	0.2338	-396.3	-23.7622
293.75	0.0082	293.65	0.0100	0.3198	-387.8	-23.7575
293.75	0.0082	293.75	0.0100	0.4159	-380.9	-23.7488
293.75	0.0082	293.75	0.0100	0.5461	-374.5	-23.7740
293.75	0.0082	293.75	0.0100	0.7186	-367.2	-23.7645
Run no. 3						
298.55	0.0082	298.55	0.0100	0.1657	-405.0	-23.4876
298.55	0.0082	298.45	0.0100	0.2172	-397.4	-23.4844
298.55	0.0082	298.45	0.0100	0.3188	-387.3	-23.4901
298.55	0.0082	298.45	0.0100	0.4011	-381.2	-23.4892
Run no. 4						
298.65	0.0082	298.55	0.0100	0.0709	-428.6	-23.4704
298.65	0.0082	298.55	0.0100	0.1707	-404.1	-23.4856
298.65	0.0082	298.75	0.0100	0.2338	-395.5	-23.4697
298.65	0.0082	298.65	0.0100	0.3198	-387.1	-23.4744
298.65	0.0082	298.65	0.0100	0.4159	-380.2	-23.4764
Run no. 5						
303.45	0.0082	303.55	0.0100	0.1657	-404.8	-23.2214
303.45	0.0082	303.45	0.0100	0.2172	-397.1	-23.2190
303.45	0.0082	303.45	0.0100	0.3188	-386.5	-23.2121
303.45	0.0082	303.45	0.0100	0.4011	-380.5	-23.2189
303.45	0.0082	303.55	0.0100	0.5964	-369.6	-23.2012
303.45	0.0082	303.55	0.0100	0.6840	-366.0	-23.2027
Run no. 6						
303.65	0.0082	303.65	0.0100	0.1091	-416.5	-23.2143
303.65	0.0082	303.75	0.0100	0.1751	-402.9	-23.1977
303.65	0.0082	303.75	0.0100	0.2248	-396.0	-23.1968
303.65	0.0082	303.75	0.0100	0.3094	-387.1	-23.1884
303.65	0.0082	303.65	0.0100	0.3955	-380.7	-23.2025
303.65	0.0082	303.75	0.0100	0.5151	-373.4	-23.1879
303.65	0.0082	303.75	0.0100	0.6832	-365.7	-23.1808
Run no. 7						
313.55	0.0082	313.55	0.0100	0.1091	-416.5	-22.7160
313.55	0.0082	313.65	0.0100	0.1751	-402.5	-22.7011
313.55	0.0082	313.65	0.0100	0.2248	-395.3	-22.6974
313.55	0.0082	313.65	0.0100	0.3094	-386.1	-22.6886
313.55	0.0082	313.55	0.0100	0.3955	-379.2	-22.6916
313.55	0.0082	313.55	0.0100	0.5151	-371.9	-22.6916
313.55	0.0082	313.65	0.0100	0.6832	-363.9	-22.6772
Run no. 8						
313.65	0.0082	313.55	0.0100	0.0709	-429.7	-22.7211
313.65	0.0082	313.55	0.0100	0.1707	-403.5	-22.7182
313.65	0.0082	313.65	0.0100	0.2338	-394.6	-22.7138
313.65	0.0082	313.65	0.0100	0.3198	-385.3	-22.6944
313.65	0.0082	313.65	0.0100	0.4159	-378.1	-22.6982
313.65	0.0082	313.55	0.0100	0.5461	-370.6	-22.7042
313.65	0.0082	313.55	0.0100	0.7186	-363.1	-22.7055
Run no. 9						

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{sarcosine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
323.55	0.0082	323.55	0.0100	0.1657	-404.4	-22.2604
323.55	0.0082	323.65	0.0100	0.2172	-396.0	-22.2392
323.55	0.0082	323.65	0.0100	0.3188	-384.8	-22.2359
323.55	0.0082	323.65	0.0100	0.4011	-378.1	-22.2319
323.55	0.0082	323.45	0.0100	0.6840	-363.1	-22.2485
Run no. 10						
323.65	0.0082	323.75	0.0100	0.1707	-403.2	-22.2391
323.65	0.0082	323.65	0.0100	0.2338	-393.8	-22.2385
323.65	0.0082	323.75	0.0100	0.3198	-384.5	-22.2242
323.65	0.0082	323.65	0.0100	0.4159	-376.9	-22.2273
323.65	0.0082	323.65	0.0100	0.5461	-369.0	-22.2220
323.65	0.0082	323.75	0.0100	0.7186	-361.1	-22.2124
Run no. 11						
333.25	0.0082	333.15	0.0100	0.1091	-416.6	-21.8233
333.25	0.0082	333.25	0.0100	0.1751	-402.0	-21.8182
333.25	0.0082	333.25	0.0100	0.2248	-394.2	-21.8092
333.25	0.0082	333.25	0.0100	0.3094	-384.3	-21.7959
333.25	0.0082	333.25	0.0100	0.3955	-376.9	-21.7908
333.25	0.0082	333.15	0.0100	0.5151	-369.0	-21.7909
333.25	0.0082	333.15	0.0100	0.6832	-360.7	-21.7889
Run no. 12						
333.45	0.0082	333.45	0.0100	0.1657	-403.8	-21.8137
333.45	0.0082	333.35	0.0100	0.2172	-395.3	-21.8088
333.45	0.0082	333.55	0.0100	0.3188	-383.6	-21.7893
333.45	0.0082	333.45	0.0100	0.4011	-376.5	-21.7836
333.45	0.0082	333.45	0.0100	0.5964	-364.9	-21.7848
333.45	0.0082	333.45	0.0100	0.6840	-360.9	-21.7847
Run no. 13						
343.05	0.0082	342.95	0.0100	0.1657	-403.5	-21.4204
343.05	0.0082	342.95	0.0100	0.2172	-394.5	-21.4014
343.05	0.0082	343.15	0.0100	0.3188	-382.8	-21.3938
343.05	0.0082	343.15	0.0100	0.4011	-375.5	-21.3830
343.05	0.0082	343.05	0.0100	0.5964	-363.6	-21.3902
343.05	0.0082	342.95	0.0100	0.6840	-359.4	-21.3920
Run no. 14						
343.05	0.0082	343.05	0.0100	0.0709	-431.1	-21.4150
343.05	0.0082	343.15	0.0100	0.1707	-402.2	-21.3978
343.05	0.0082	343.15	0.0100	0.2338	-392.1	-21.3869
343.05	0.0082	343.05	0.0100	0.3198	-382.4	-21.3885
343.05	0.0082	343.15	0.0100	0.4159	-374.0	-21.3695
343.05	0.0082	343.15	0.0100	0.5461	-365.6	-21.3633
343.05	0.0082	343.15	0.0100	0.7186	-356.8	-21.3445
Run no. 15						
350.55	0.0082	350.55	0.0100	0.1657	-403.5	-21.1272
350.55	0.0082	350.65	0.0100	0.2172	-394.0	-21.0934
350.55	0.0082	350.65	0.0100	0.3188	-381.3	-21.0712
350.55	0.0082	350.55	0.0100	0.4011	-373.9	-21.0672
350.55	0.0082	350.65	0.0100	0.5964	-362.2	-21.0801
350.55	0.0082	350.65	0.0100	0.6840	-358.4	-21.0934
Run no. 16						
350.55	0.0082	350.65	0.0100	0.1091	-415.8	-21.0794
350.55	0.0082	350.65	0.0100	0.1751	-401.8	-21.1249
350.55	0.0082	350.65	0.0100	0.2248	-393.2	-21.1027
350.55	0.0082	350.55	0.0100	0.3094	-383.2	-21.1081
350.55	0.0082	350.65	0.0100	0.3955	-375.3	-21.0943
350.55	0.0082	350.65	0.0100	0.5151	-367.0	-21.0898
350.55	0.0082	350.45	0.0100	0.6832	-357.9	-21.0848

2.9.5 6-Aminohexanoic acid

Table 2.23: Experimental equilibrium data for 6-aminohexanoic acid measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{6-amhex.\ acid_{II}}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.85	0.0102	293.75	0.0099	0.0745	-477.5	-25.3319
293.85	0.0102	293.85	0.0099	0.1523	-457.5	-25.3181
293.85	0.0102	293.75	0.0099	0.2039	-449.7	-25.3248
293.85	0.0102	293.85	0.0099	0.2857	-440.7	-25.3130
293.85	0.0102	293.75	0.0099	0.3473	-435.5	-25.3156
293.85	0.0102	293.75	0.0099	0.4128	-431.1	-25.3188
293.85	0.0102	293.85	0.0099	0.5800	-422.3	-25.3111
Run no. 2						
293.85	0.0102	293.85	0.0099	0.0701	-479.1	-25.3176
293.85	0.0102	293.85	0.0099	0.1150	-465.3	-25.3244
293.85	0.0102	293.85	0.0099	0.1981	-450.4	-25.3149
293.85	0.0102	293.85	0.0099	0.2750	-441.7	-25.3129
293.85	0.0102	293.75	0.0099	0.3582	-434.8	-25.3198
293.85	0.0102	293.75	0.0099	0.4250	-430.3	-25.3171
293.85	0.0102	293.75	0.0099	0.5141	-425.5	-25.3217
Run no. 3						
293.85	0.0102	293.95	0.0099	0.0462	-491.7	-25.3126
293.85	0.0102	293.85	0.0099	0.1357	-460.9	-25.3281
293.85	0.0102	293.85	0.0099	0.2010	-450.3	-25.3259
293.85	0.0102	293.85	0.0099	0.2892	-440.8	-25.3289
293.85	0.0102	293.95	0.0099	0.3466	-435.8	-25.3111
293.85	0.0102	293.95	0.0099	0.4220	-430.7	-25.3114
293.85	0.0102	293.85	0.0099	0.5765	-422.7	-25.3202
Run no. 4						
298.65	0.0102	298.65	0.0099	0.0701	-477.7	-24.9593
298.65	0.0102	298.65	0.0099	0.1150	-463.6	-24.9631
298.65	0.0102	298.55	0.0099	0.1981	-448.6	-24.9661
298.65	0.0102	298.55	0.0099	0.2750	-439.7	-24.9617
298.65	0.0102	298.65	0.0099	0.3582	-432.6	-24.9515
298.65	0.0102	298.65	0.0099	0.4250	-427.9	-24.9439
298.65	0.0102	298.65	0.0099	0.5141	-422.9	-24.9438
Run no. 5						
298.65	0.0102	298.75	0.0099	0.1523	-455.5	-24.9420
298.65	0.0102	298.75	0.0099	0.2039	-447.6	-24.9427
298.65	0.0102	298.75	0.0099	0.2857	-438.4	-24.9361
298.65	0.0102	298.65	0.0099	0.3473	-433.3	-24.9457
298.65	0.0102	298.75	0.0099	0.4128	-428.7	-24.9374
298.65	0.0102	298.75	0.0099	0.5800	-419.6	-24.9306
Run no. 6						
298.75	0.0102	298.65	0.0099	0.0462	-490.3	-24.9558
298.75	0.0102	298.65	0.0099	0.1357	-458.9	-24.9596
298.75	0.0102	298.75	0.0099	0.2010	-447.9	-24.9416
298.75	0.0102	298.75	0.0099	0.2892	-438.1	-24.9390
298.75	0.0102	298.75	0.0099	0.3466	-433.4	-24.9431
298.75	0.0102	298.75	0.0099	0.4220	-428.3	-24.9467
298.75	0.0102	298.65	0.0099	0.5765	-420.2	-24.9565
Run no. 7						
303.55	0.0102	303.55	0.0099	0.0745	-474.1	-24.5907
303.55	0.0102	303.65	0.0099	0.1523	-453.3	-24.5724
303.55	0.0102	303.65	0.0099	0.2039	-445.4	-24.5780
303.55	0.0102	303.65	0.0099	0.2857	-436.1	-24.5734
303.55	0.0102	303.55	0.0099	0.3473	-430.9	-24.5822
303.55	0.0102	303.65	0.0099	0.4128	-426.2	-24.5731
303.55	0.0102	303.65	0.0099	0.5800	-417.0	-24.5682
Run no. 8						
303.65	0.0102	303.65	0.0099	0.0701	-475.7	-24.5771

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{6-amhex.\ acid_{II}}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
303.65	0.0102	303.65	0.0099	0.1150	-461.4	-24.5824
303.65	0.0102	303.65	0.0099	0.1981	-446.1	-24.5765
303.65	0.0102	303.65	0.0099	0.2750	-437.1	-24.5742
303.65	0.0102	303.55	0.0099	0.3582	-429.9	-24.5780
303.65	0.0102	303.65	0.0099	0.4250	-425.2	-24.5669
303.65	0.0102	303.55	0.0099	0.5141	-420.3	-24.5803
Run no. 9						
303.65	0.0102	303.65	0.0099	0.0462	-488.3	-24.5640
303.65	0.0102	303.65	0.0099	0.1357	-456.5	-24.5731
303.65	0.0102	303.65	0.0099	0.2010	-445.7	-24.5767
303.65	0.0102	303.65	0.0099	0.2892	-435.6	-24.5689
303.65	0.0102	303.75	0.0099	0.3466	-430.7	-24.5617
303.65	0.0102	303.65	0.0099	0.4220	-425.6	-24.5750
303.65	0.0102	303.55	0.0099	0.5765	-417.5	-24.5897
Run no. 10						
313.05	0.0102	312.95	0.0099	0.0745	-470.6	-23.9173
313.05	0.0102	313.15	0.0099	0.1523	-448.9	-23.8836
313.05	0.0102	313.15	0.0099	0.2039	-440.6	-23.8836
313.05	0.0102	313.15	0.0099	0.2857	-431.1	-23.8824
313.05	0.0102	313.05	0.0099	0.3473	-425.8	-23.8932
313.05	0.0102	313.15	0.0099	0.4128	-421.4	-23.9011
313.05	0.0102	313.15	0.0099	0.5800	-411.7	-23.8883
Run no. 11						
313.25	0.0102	313.35	0.0099	0.0701	-471.9	-23.8719
313.25	0.0102	313.35	0.0099	0.1150	-457.3	-23.8833
313.25	0.0102	313.35	0.0099	0.1981	-441.2	-23.8660
313.25	0.0102	313.15	0.0099	0.2750	-432.3	-23.8906
313.25	0.0102	313.25	0.0099	0.3582	-424.8	-23.8790
313.25	0.0102	313.35	0.0099	0.4250	-420.2	-23.8775
313.25	0.0102	313.25	0.0099	0.5141	-415.1	-23.8889
Run no. 12						
313.35	0.0102	313.45	0.0099	0.0462	-485.1	-23.8602
313.35	0.0102	313.25	0.0099	0.1357	-452.5	-23.8913
313.35	0.0102	313.25	0.0099	0.2010	-441.3	-23.8928
313.35	0.0102	313.25	0.0099	0.2892	-430.9	-23.8857
313.35	0.0102	313.35	0.0099	0.3466	-425.4	-23.8624
313.35	0.0102	313.25	0.0099	0.4220	-420.5	-23.8887
313.35	0.0102	313.25	0.0099	0.5765	-412.0	-23.8917
Run no. 13						
322.45	0.0102	322.55	0.0099	0.0745	-466.8	-23.2582
322.45	0.0102	322.55	0.0099	0.1523	-444.6	-23.2438
322.45	0.0102	322.35	0.0099	0.2039	-435.7	-23.2433
322.45	0.0102	322.55	0.0099	0.2857	-425.8	-23.2260
322.45	0.0102	322.45	0.0099	0.3473	-420.3	-23.2350
322.45	0.0102	322.35	0.0099	0.4128	-415.6	-23.2488
322.45	0.0102	322.45	0.0099	0.5800	-405.9	-23.2407
Run no. 14						
322.45	0.0102	322.45	0.0099	0.0701	-468.6	-23.2605
322.45	0.0102	322.55	0.0099	0.1150	-453.3	-23.2559
322.45	0.0102	322.55	0.0099	0.1981	-437.0	-23.2487
322.45	0.0102	322.55	0.0099	0.2750	-427.3	-23.2414
322.45	0.0102	322.55	0.0099	0.3582	-419.9	-23.2477
322.45	0.0102	322.55	0.0099	0.4250	-415.0	-23.2465
322.45	0.0102	322.55	0.0099	0.5141	-410.4	-23.2752
Run no. 15						
322.75	0.0102	322.75	0.0099	0.0462	-482.1	-23.2349
322.75	0.0102	322.65	0.0099	0.1357	-448.2	-23.2479
322.75	0.0102	322.75	0.0099	0.2010	-436.4	-23.2340
322.75	0.0102	322.75	0.0099	0.2892	-425.5	-23.2203
322.75	0.0102	322.75	0.0099	0.3466	-420.5	-23.2273
322.75	0.0102	322.65	0.0099	0.4220	-414.7	-23.2262
322.75	0.0102	322.75	0.0099	0.5765	-405.9	-23.2219
Run no. 16						
334.15	0.0102	334.05	0.0099	0.0462	-478.0	-22.5054

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{6-amhex.\ acid_{II}}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
334.15	0.0102	334.05	0.0099	0.1357	-442.6	-22.5027
334.15	0.0102	334.15	0.0099	0.2010	-430.8	-22.5039
334.15	0.0102	334.15	0.0099	0.2892	-419.5	-22.4898
334.15	0.0102	334.15	0.0099	0.3466	-413.8	-22.4786
334.15	0.0102	334.15	0.0099	0.4220	-408.1	-22.4823
334.15	0.0102	334.15	0.0099	0.5765	-399.2	-22.4912
Run no. 17						
334.15	0.0102	334.15	0.0099	0.0701	-464.0	-22.5092
334.15	0.0102	334.15	0.0099	0.1150	-448.3	-22.5168
334.15	0.0102	334.15	0.0099	0.1981	-431.3	-22.5058
334.15	0.0102	334.15	0.0099	0.2750	-421.0	-22.4898
334.15	0.0102	334.15	0.0099	0.3582	-412.9	-22.4811
334.15	0.0102	334.15	0.0099	0.4250	-408.3	-22.4965
334.15	0.0102	334.15	0.0099	0.5141	-403.5	-22.5241
Run no. 18						
343.85	0.0102	343.75	0.0099	0.0701	-459.2	-21.8970
343.85	0.0102	343.85	0.0099	0.1150	-443.4	-21.9115
343.85	0.0102	343.75	0.0099	0.1981	-425.4	-21.8891
343.85	0.0102	343.75	0.0099	0.2750	-415.1	-21.8833
343.85	0.0102	343.85	0.0099	0.3582	-406.5	-21.8604
343.85	0.0102	343.85	0.0099	0.4250	-402.1	-21.8871
343.85	0.0102	343.85	0.0099	0.5141	-397.4	-21.9228
Run no. 19						
343.85	0.0102	343.75	0.0099	0.0462	-474.0	-21.8996
343.85	0.0102	343.85	0.0099	0.1357	-437.1	-21.8771
343.85	0.0102	343.95	0.0099	0.2010	-424.6	-21.8669
343.85	0.0102	343.95	0.0099	0.2892	-412.9	-21.8506
343.85	0.0102	343.85	0.0099	0.3466	-408.7	-21.9009
343.85	0.0102	343.85	0.0099	0.4220	-402.3	-21.8866
343.85	0.0102	343.85	0.0099	0.5765	-393.4	-21.9043
Run no. 20						
353.15	0.0102	353.15	0.0099	0.0462	-470.6	-21.3590
353.15	0.0102	353.15	0.0099	0.1357	-433.3	-21.3634
353.15	0.0102	353.15	0.0099	0.2010	-421.2	-21.3830
353.15	0.0102	353.15	0.0099	0.2892	-409.7	-21.3836
353.15	0.0102	353.25	0.0099	0.3466	-404.2	-21.3847
353.15	0.0102	353.25	0.0099	0.4220	-398.6	-21.4025
353.15	0.0102	353.15	0.0099	0.5765	-389.8	-21.4363
Run no. 21						
353.25	0.0102	353.25	0.0099	0.0701	-456.6	-21.3928
353.25	0.0102	353.25	0.0099	0.1150	-440.4	-21.4144
353.25	0.0102	353.25	0.0099	0.1981	-422.6	-21.4096
353.25	0.0102	353.25	0.0099	0.2750	-412.0	-21.4033
353.25	0.0102	353.15	0.0099	0.3582	-402.8	-21.3787
353.25	0.0102	353.25	0.0099	0.4250	-397.9	-21.3879
353.25	0.0102	353.25	0.0099	0.5141	-393.2	-21.4278

2.9.6 DL-methionine

Table 2.24: Experimental equilibrium data for DL-methionine measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{DL-methionine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.35	0.0099	293.45	0.0097	0.0128	-455.8	-21.7227
293.35	0.0099	293.35	0.0097	0.0278	-410.3	-21.6721
293.35	0.0099	293.35	0.0097	0.0579	-385.8	-21.6821
293.35	0.0099	293.35	0.0097	0.0719	-378.5	-21.6493
293.35	0.0099	293.45	0.0097	0.1293	-362.2	-21.6514
293.35	0.0099	293.45	0.0097	0.1771	-353.6	-21.6477
Run no. 2						
293.35	0.0099	293.55	0.0097	0.0121	-462.4	-21.7243
293.35	0.0099	293.45	0.0097	0.0187	-428.1	-21.6740
293.35	0.0099	293.45	0.0097	0.0227	-418.7	-21.6663
293.35	0.0099	293.45	0.0097	0.0292	-408.4	-21.6661
293.35	0.0099	293.45	0.0097	0.0458	-392.7	-21.6597
293.35	0.0099	293.45	0.0097	0.0663	-381.1	-21.6516
Run no. 3						
293.55	0.0099	293.55	0.0097	0.0178	-431.8	-21.7031
293.55	0.0099	293.45	0.0097	0.0208	-422.6	-21.6670
293.55	0.0099	293.55	0.0097	0.0297	-407.8	-21.6628
293.55	0.0099	293.45	0.0097	0.0359	-401.1	-21.6729
293.55	0.0099	293.45	0.0097	0.0546	-387.4	-21.6702
293.55	0.0099	293.45	0.0097	0.0841	-374.8	-21.6770
Run no. 4						
298.35	0.0099	298.45	0.0097	0.0128	-455.9	-21.4289
298.35	0.0099	298.35	0.0097	0.0278	-409.8	-21.3826
298.35	0.0099	298.15	0.0097	0.0579	-384.9	-21.4054
298.35	0.0099	298.25	0.0097	0.0719	-377.9	-21.3829
298.35	0.0099	298.55	0.0097	0.1293	-360.8	-21.3531
298.35	0.0099	298.35	0.0097	0.1771	-352.4	-21.3743
Run no. 5						
298.45	0.0099	298.55	0.0097	0.0178	-431.2	-21.3951
298.45	0.0099	298.35	0.0097	0.0208	-422.6	-21.3947
298.45	0.0099	298.55	0.0097	0.0297	-406.9	-21.3586
298.45	0.0099	298.45	0.0097	0.0359	-399.9	-21.3613
298.45	0.0099	298.35	0.0097	0.0546	-386.5	-21.3855
298.45	0.0099	298.35	0.0097	0.0841	-373.4	-21.3810
Run no. 6						
298.55	0.0099	298.65	0.0097	0.0121	-462.1	-21.4066
298.55	0.0099	298.55	0.0097	0.0187	-427.4	-21.3610
298.55	0.0099	298.55	0.0097	0.0227	-418.1	-21.3634
298.55	0.0099	298.45	0.0097	0.0292	-407.5	-21.3647
298.55	0.0099	298.65	0.0097	0.0458	-391.4	-21.3407
298.55	0.0099	298.75	0.0097	0.0663	-379.6	-21.3268
Run no. 7						
303.15	0.0099	303.25	0.0097	0.0128	-455.9	-21.1523
303.15	0.0099	303.25	0.0097	0.0278	-409.2	-21.1029
303.15	0.0099	303.25	0.0097	0.0579	-383.7	-21.1061
303.15	0.0099	303.25	0.0097	0.0719	-376.5	-21.0866
303.15	0.0099	303.25	0.0097	0.1293	-359.1	-21.0736
303.15	0.0099	303.25	0.0097	0.1771	-350.6	-21.0847
Run no. 8						
303.25	0.0099	303.25	0.0097	0.0121	-462.2	-21.1443
303.25	0.0099	303.35	0.0097	0.0187	-427.2	-21.0915
303.25	0.0099	303.35	0.0097	0.0227	-417.6	-21.0880
303.25	0.0099	303.35	0.0097	0.0292	-406.9	-21.0855
303.25	0.0099	303.35	0.0097	0.0458	-390.4	-21.0687
303.25	0.0099	303.35	0.0097	0.0663	-378.5	-21.0640
Run no. 9						
303.35	0.0099	303.35	0.0097	0.0178	-431.4	-21.1411
303.35	0.0099	303.05	0.0097	0.0208	-422.5	-21.1404

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{DL-methionine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
303.35	0.0099	303.35	0.0097	0.0297	-406.8	-21.1077
303.35	0.0099	303.25	0.0097	0.0359	-399.6	-21.1068
303.35	0.0099	303.35	0.0097	0.0546	-385.6	-21.1041
303.35	0.0099	303.35	0.0097	0.0841	-372.5	-21.1079
Run no. 10						
312.95	0.0099	313.05	0.0097	0.0121	-462.9	-20.6267
312.95	0.0099	313.05	0.0097	0.0187	-426.8	-20.5751
312.95	0.0099	312.95	0.0097	0.0227	-416.8	-20.5738
312.95	0.0099	312.95	0.0097	0.0292	-405.8	-20.5726
312.95	0.0099	312.95	0.0097	0.0458	-389.1	-20.5675
312.95	0.0099	313.05	0.0097	0.0663	-376.9	-20.5601
Run no. 11						
312.95	0.0099	313.05	0.0097	0.0128	-456.4	-20.6335
312.95	0.0099	312.95	0.0097	0.0278	-408.0	-20.5785
312.95	0.0099	312.95	0.0097	0.0579	-381.8	-20.5857
312.95	0.0099	312.95	0.0097	0.0719	-374.7	-20.5784
312.95	0.0099	313.15	0.0097	0.1293	-356.6	-20.5494
312.95	0.0099	313.05	0.0097	0.1771	-347.6	-20.5575
Run no. 12						
313.05	0.0099	313.05	0.0097	0.0178	-431.0	-20.6198
313.05	0.0099	312.95	0.0097	0.0208	-421.6	-20.5976
313.05	0.0099	313.15	0.0097	0.0297	-405.5	-20.5756
313.05	0.0099	313.05	0.0097	0.0359	-398.1	-20.5755
313.05	0.0099	313.05	0.0097	0.0546	-383.8	-20.5843
313.05	0.0099	313.15	0.0097	0.0841	-369.8	-20.5648
Run no. 13						
323.25	0.0099	323.25	0.0097	0.0178	-430.5	-20.1031
323.25	0.0099	323.35	0.0097	0.0208	-420.4	-20.0544
323.25	0.0099	323.35	0.0097	0.0297	-404.2	-20.0596
323.25	0.0099	323.35	0.0097	0.0359	-396.4	-20.0479
323.25	0.0099	323.35	0.0097	0.0546	-381.5	-20.0520
323.25	0.0099	323.35	0.0097	0.0841	-367.3	-20.0473
Run no. 14						
323.55	0.0099	323.45	0.0097	0.0121	-463.2	-20.0988
323.55	0.0099	323.55	0.0097	0.0187	-426.2	-20.0467
323.55	0.0099	323.55	0.0097	0.0227	-415.8	-20.0367
323.55	0.0099	323.55	0.0097	0.0292	-404.5	-20.0379
323.55	0.0099	323.45	0.0097	0.0458	-387.3	-20.0405
323.55	0.0099	323.45	0.0097	0.0663	-375.0	-20.0497
Run no. 15						
323.55	0.0099	323.55	0.0097	0.0128	-456.9	-20.1127
323.55	0.0099	323.55	0.0097	0.0278	-407.0	-20.0519
323.55	0.0099	323.55	0.0097	0.0579	-379.7	-20.0513
323.55	0.0099	323.55	0.0097	0.0719	-372.1	-20.0347
323.55	0.0099	323.45	0.0097	0.1293	-354.1	-20.0470
323.55	0.0099	323.45	0.0097	0.1771	-344.7	-20.0461
Run no. 16						
333.35	0.0099	333.35	0.0097	0.0121	-463.4	-19.6200
333.35	0.0099	333.35	0.0097	0.0187	-425.7	-19.5851
333.35	0.0099	333.35	0.0097	0.0227	-415.1	-19.5789
333.35	0.0099	333.35	0.0097	0.0292	-403.7	-19.5884
333.35	0.0099	333.35	0.0097	0.0458	-386.1	-19.5897
333.35	0.0099	333.25	0.0097	0.0663	-373.6	-19.6100
Run no. 17						
333.35	0.0099	333.35	0.0097	0.0178	-430.0	-19.6230
333.35	0.0099	333.45	0.0097	0.0208	-419.6	-19.5748
333.35	0.0099	333.45	0.0097	0.0297	-402.7	-19.5730
333.35	0.0099	333.45	0.0097	0.0359	-395.1	-19.5767
333.35	0.0099	333.45	0.0097	0.0546	-379.9	-19.5865
333.35	0.0099	333.35	0.0097	0.0841	-364.8	-19.5709
Run no. 18						
333.45	0.0099	333.45	0.0097	0.0128	-456.6	-19.6228
333.45	0.0099	333.45	0.0097	0.0278	-405.6	-19.5747
333.45	0.0099	333.45	0.0097	0.0579	-377.7	-19.5822

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{DL-methionine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
333.45	0.0099	333.35	0.0097	0.0719	-370.2	-19.5821
333.45	0.0099	333.45	0.0097	0.1293	-351.5	-19.5791
333.45	0.0099	333.45	0.0097	0.1771	-341.7	-19.5744
Run no. 19						
343.15	0.0099	343.05	0.0097	0.0121	-464.0	-19.1943
343.15	0.0099	343.15	0.0097	0.0187	-425.6	-19.1641
343.15	0.0099	343.15	0.0097	0.0227	-414.7	-19.1581
343.15	0.0099	343.15	0.0097	0.0292	-402.9	-19.1652
343.15	0.0099	343.05	0.0097	0.0458	-384.9	-19.1753
343.15	0.0099	343.05	0.0097	0.0663	-371.7	-19.1792
Run no. 20						
343.15	0.0099	343.25	0.0097	0.0178	-430.0	-19.1958
343.15	0.0099	343.25	0.0097	0.0208	-418.9	-19.1395
343.15	0.0099	343.25	0.0097	0.0297	-401.6	-19.1409
343.15	0.0099	343.15	0.0097	0.0359	-393.3	-19.1334
343.15	0.0099	343.15	0.0097	0.0546	-377.4	-19.1345
343.15	0.0099	343.05	0.0097	0.0841	-362.6	-19.1436
Run no. 21						
343.25	0.0099	343.25	0.0097	0.0128	-457.3	-19.2008
343.25	0.0099	343.25	0.0097	0.0278	-405.4	-19.1702
343.25	0.0099	343.25	0.0097	0.0579	-376.5	-19.1714
343.25	0.0099	343.25	0.0097	0.0719	-368.9	-19.1704
343.25	0.0099	343.15	0.0097	0.1293	-349.6	-19.1753
343.25	0.0099	343.15	0.0097	0.1771	-339.4	-19.1667
Run no. 22						
353.25	0.0099	353.35	0.0097	0.0208	-419.7	-18.7671
353.25	0.0099	353.35	0.0097	0.0297	-402.0	-18.7717
353.25	0.0099	353.35	0.0097	0.0359	-393.6	-18.7639
353.25	0.0099	353.35	0.0097	0.0546	-377.5	-18.7738
353.25	0.0099	353.35	0.0097	0.0841	-361.7	-18.7598
Run no. 23						
353.35	0.0099	353.25	0.0097	0.0121	-466.1	-18.8218
353.35	0.0099	353.25	0.0097	0.0187	-426.6	-18.7929
353.35	0.0099	353.25	0.0097	0.0227	-414.9	-18.7708
353.35	0.0099	353.25	0.0097	0.0292	-402.8	-18.7794
353.35	0.0099	353.25	0.0097	0.0458	-384.4	-18.7887
353.35	0.0099	353.25	0.0097	0.0663	-370.7	-18.7890
Run no. 24						
353.35	0.0099	353.25	0.0097	0.0128	-458.9	-18.8260
353.35	0.0099	353.35	0.0097	0.0278	-405.9	-18.8007
353.35	0.0099	353.35	0.0097	0.0579	-375.5	-18.7804
353.35	0.0099	353.35	0.0097	0.0719	-367.9	-18.7867
353.35	0.0099	353.25	0.0097	0.1293	-347.9	-18.7870
353.35	0.0099	353.25	0.0097	0.1771	-337.4	-18.7784

2.9.7 Glycine

Table 2.25: Experimental equilibrium data for glycine measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{glycine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.05	0.0099	293.15	0.0100	0.0393	-427.5	-22.8246
293.05	0.0099	293.05	0.0100	0.0660	-411.8	-22.8559
293.05	0.0099	293.05	0.0100	0.0824	-406.5	-22.9020
293.05	0.0099	293.05	0.0100	0.1597	-388.5	-22.9145
293.05	0.0099	293.05	0.0100	0.2407	-377.7	-22.9194
293.05	0.0099	293.15	0.0100	0.3471	-368.0	-22.9082
293.05	0.0099	293.15	0.0100	0.4049	-364.0	-22.9080
Run no. 2						
293.05	0.0099	293.15	0.0100	0.0411	-425.4	-22.7987
293.05	0.0099	293.15	0.0100	0.0647	-411.4	-22.8084
293.05	0.0099	293.15	0.0100	0.0879	-402.7	-22.8177
293.05	0.0099	293.05	0.0100	0.1589	-387.6	-22.8738
293.05	0.0099	293.05	0.0100	0.2519	-375.1	-22.8638
293.05	0.0099	293.05	0.0100	0.3355	-367.9	-22.8753
293.05	0.0099	293.15	0.0100	0.4179	-362.4	-22.8773
Run no. 3						
293.05	0.0099	293.15	0.0100	0.0429	-425.2	-22.8471
293.05	0.0099	293.15	0.0100	0.0653	-412.7	-22.8706
293.05	0.0099	293.15	0.0100	0.0865	-404.7	-22.8790
293.05	0.0099	293.15	0.0100	0.1649	-387.3	-22.8947
293.05	0.0099	293.15	0.0100	0.2341	-378.2	-22.9037
293.05	0.0099	293.05	0.0100	0.3455	-368.6	-22.9334
293.05	0.0099	293.15	0.0100	0.4023	-365.3	-22.9531
Run no. 4						
298.25	0.0099	298.25	0.0100	0.0429	-423.4	-22.4924
298.25	0.0099	298.25	0.0100	0.0653	-410.2	-22.4971
298.25	0.0099	298.25	0.0100	0.0865	-402.1	-22.5069
298.25	0.0099	298.15	0.0100	0.1649	-384.5	-22.5328
298.25	0.0099	298.35	0.0100	0.2341	-375.1	-22.5242
298.25	0.0099	298.25	0.0100	0.3455	-365.3	-22.5525
298.25	0.0099	298.25	0.0100	0.4023	-361.7	-22.5688
Run no. 5						
298.25	0.0099	298.25	0.0100	0.0393	-425.9	-22.4761
298.25	0.0099	298.25	0.0100	0.0660	-409.7	-22.4918
298.25	0.0099	298.25	0.0100	0.0824	-403.6	-22.5104
298.25	0.0099	298.25	0.0100	0.1597	-385.1	-22.5159
298.25	0.0099	298.15	0.0100	0.2407	-374.5	-22.5420
298.25	0.0099	298.25	0.0100	0.3471	-365.0	-22.5454
298.25	0.0099	298.35	0.0100	0.4049	-361.1	-22.5460
Run no. 6						
298.25	0.0099	298.25	0.0100	0.0411	-423.7	-22.4477
298.25	0.0099	298.25	0.0100	0.0647	-409.4	-22.4552
298.25	0.0099	298.35	0.0100	0.0879	-400.3	-22.4484
298.25	0.0099	298.25	0.0100	0.1589	-384.2	-22.4758
298.25	0.0099	298.35	0.0100	0.2519	-371.8	-22.4724
298.25	0.0099	298.25	0.0100	0.3355	-364.7	-22.4987
298.25	0.0099	298.35	0.0100	0.4179	-359.1	-22.5008
Run no. 7						
302.95	0.0099	302.85	0.0100	0.0411	-423.7	-22.2005
302.95	0.0099	302.95	0.0100	0.0647	-409.0	-22.1946
302.95	0.0099	303.05	0.0100	0.0879	-399.7	-22.1859
302.95	0.0099	302.95	0.0100	0.1589	-383.2	-22.2075
302.95	0.0099	302.95	0.0100	0.2519	-370.9	-22.2212
302.95	0.0099	302.95	0.0100	0.3355	-363.3	-22.2267
302.95	0.0099	303.05	0.0100	0.4179	-357.5	-22.2247
Run no. 8						
303.05	0.0099	303.05	0.0100	0.0393	-425.2	-22.1889
303.05	0.0099	303.05	0.0100	0.0660	-408.6	-22.1991

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T_I	$\bar{m}_{HCl_I}$	T_{II}	$\bar{m}_{NaOH_{II}}$	$\bar{m}_{glycine}$	$(E_I - E_{II})$	$ln(K_{2,exp})$
[K]	[mol kg^{-1}]	[K]	[mol kg^{-1}]	[mol kg^{-1}]	[mV]	[-]
303.05	0.0099	302.95	0.0100	0.0824	-402.4	-22.2238
303.05	0.0099	302.95	0.0100	0.1597	-383.3	-22.2175
303.05	0.0099	302.95	0.0100	0.2407	-372.4	-22.2325
303.05	0.0099	302.95	0.0100	0.3471	-362.7	-22.2399
303.05	0.0099	303.05	0.0100	0.4049	-358.8	-22.2431
Run no. 9						
303.15	0.0099	303.15	0.0100	0.0429	-423.2	-22.2205
303.15	0.0099	303.15	0.0100	0.0653	-409.9	-22.2296
303.15	0.0099	303.05	0.0100	0.0865	-401.5	-22.2392
303.15	0.0099	303.05	0.0100	0.1649	-383.6	-22.2583
303.15	0.0099	303.25	0.0100	0.2341	-373.9	-22.2444
303.15	0.0099	303.05	0.0100	0.3455	-363.9	-22.2767
303.15	0.0099	303.05	0.0100	0.4023	-360.3	-22.2953
Run no. 10						
312.95	0.0099	312.95	0.0100	0.0429	-423.2	-21.7177
312.95	0.0099	312.95	0.0100	0.0653	-409.4	-21.7240
312.95	0.0099	313.05	0.0100	0.0865	-400.6	-21.7167
312.95	0.0099	313.05	0.0100	0.1649	-381.9	-21.7279
312.95	0.0099	313.05	0.0100	0.2341	-372.1	-21.7338
312.95	0.0099	312.95	0.0100	0.3455	-361.6	-21.7536
312.95	0.0099	312.95	0.0100	0.4023	-357.7	-21.7653
Run no. 11						
312.95	0.0099	312.95	0.0100	0.0411	-423.5	-21.6726
312.95	0.0099	313.05	0.0100	0.0647	-408.1	-21.6590
312.95	0.0099	313.05	0.0100	0.0879	-398.6	-21.6604
312.95	0.0099	313.05	0.0100	0.1589	-381.4	-21.6702
312.95	0.0099	312.95	0.0100	0.2519	-368.6	-21.6861
312.95	0.0099	312.95	0.0100	0.3355	-360.8	-21.6934
312.95	0.0099	312.95	0.0100	0.4179	-354.7	-21.6930
Run no. 12						
313.05	0.0099	313.05	0.0100	0.0393	-425.1	-21.6697
313.05	0.0099	313.05	0.0100	0.0660	-408.1	-21.6851
313.05	0.0099	312.85	0.0100	0.0824	-401.8	-21.7192
313.05	0.0099	312.85	0.0100	0.1597	-382.4	-21.7248
313.05	0.0099	312.75	0.0100	0.2407	-371.0	-21.7400
313.05	0.0099	312.95	0.0100	0.3471	-360.4	-21.7148
313.05	0.0099	312.95	0.0100	0.4049	-356.4	-21.7247
Run no. 13						
322.95	0.0099	323.05	0.0100	0.0411	-423.2	-21.1746
322.95	0.0099	322.95	0.0100	0.0647	-407.5	-21.1795
322.95	0.0099	322.95	0.0100	0.0879	-397.6	-21.1772
322.95	0.0099	322.95	0.0100	0.1589	-379.8	-21.1849
322.95	0.0099	322.95	0.0100	0.2519	-366.2	-21.1811
322.95	0.0099	322.95	0.0100	0.3355	-358.2	-21.1902
322.95	0.0099	322.85	0.0100	0.4179	-352.2	-21.2055
Run no. 14						
322.95	0.0099	323.05	0.0100	0.0429	-421.4	-21.1660
322.95	0.0099	323.05	0.0100	0.0653	-406.8	-21.1594
322.95	0.0099	323.05	0.0100	0.0865	-397.8	-21.1609
322.95	0.0099	323.05	0.0100	0.1649	-378.4	-21.1684
322.95	0.0099	323.05	0.0100	0.2341	-368.4	-21.1784
322.95	0.0099	323.05	0.0100	0.3455	-357.1	-21.1760
322.95	0.0099	323.05	0.0100	0.4023	-352.8	-21.1779
Run no. 15						
323.15	0.0099	323.05	0.0100	0.0393	-424.6	-21.1700
323.15	0.0099	323.05	0.0100	0.0660	-406.9	-21.1796
323.15	0.0099	323.15	0.0100	0.0824	-399.9	-21.1783
323.15	0.0099	323.15	0.0100	0.1597	-379.5	-21.1708
323.15	0.0099	323.05	0.0100	0.2407	-367.4	-21.1740
323.15	0.0099	323.05	0.0100	0.3471	-357.3	-21.1902
323.15	0.0099	323.05	0.0100	0.4049	-353.0	-21.1939
Run no. 16						
333.25	0.0099	333.25	0.0100	0.0411	-422.3	-20.6843
333.25	0.0099	333.15	0.0100	0.0647	-406.6	-20.7061

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{glycine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
333.25	0.0099	333.25	0.0100	0.0879	-396.4	-20.6989
333.25	0.0099	333.25	0.0100	0.1589	-377.7	-20.6950
333.25	0.0099	333.25	0.0100	0.2519	-363.8	-20.6958
333.25	0.0099	333.15	0.0100	0.3355	-355.7	-20.7152
333.25	0.0099	333.15	0.0100	0.4179	-349.5	-20.7250
Run no. 17						
333.25	0.0099	333.25	0.0100	0.0429	-420.9	-20.6917
333.25	0.0099	333.25	0.0100	0.0653	-405.7	-20.6801
333.25	0.0099	333.25	0.0100	0.0865	-396.3	-20.6775
333.25	0.0099	333.25	0.0100	0.1649	-376.3	-20.6853
333.25	0.0099	333.25	0.0100	0.2341	-365.5	-20.6784
333.25	0.0099	333.25	0.0100	0.3455	-353.9	-20.6780
333.25	0.0099	333.25	0.0100	0.4023	-349.8	-20.6917
Run no. 18						
333.35	0.0099	333.25	0.0100	0.0393	-424.1	-20.6910
333.35	0.0099	333.35	0.0100	0.0660	-405.7	-20.6901
333.35	0.0099	333.25	0.0100	0.0824	-398.4	-20.6970
333.35	0.0099	333.25	0.0100	0.1597	-377.1	-20.6803
333.35	0.0099	333.25	0.0100	0.2407	-364.9	-20.6879
333.35	0.0099	333.25	0.0100	0.3471	-354.4	-20.7013
333.35	0.0099	333.25	0.0100	0.4049	-349.8	-20.6992
Run no. 19						
343.15	0.0099	343.05	0.0100	0.0411	-422.4	-20.2742
343.15	0.0099	343.05	0.0100	0.0647	-405.7	-20.2722
343.15	0.0099	343.05	0.0100	0.0879	-395.2	-20.2704
343.15	0.0099	343.05	0.0100	0.1589	-376.2	-20.2748
343.15	0.0099	343.05	0.0100	0.2519	-361.9	-20.2759
343.15	0.0099	343.05	0.0100	0.3355	-353.3	-20.2816
Run no. 20						
343.15	0.0099	343.15	0.0100	0.0429	-419.9	-20.2403
343.15	0.0099	343.15	0.0100	0.0653	-403.9	-20.2168
343.15	0.0099	343.05	0.0100	0.0865	-393.9	-20.2084
343.15	0.0099	343.15	0.0100	0.1649	-373.4	-20.2144
343.15	0.0099	343.15	0.0100	0.2341	-363.0	-20.2318
343.15	0.0099	343.25	0.0100	0.3455	-350.7	-20.2148
343.15	0.0099	343.25	0.0100	0.4023	-346.2	-20.2190
Run no. 21						
343.15	0.0099	343.25	0.0100	0.0393	-424.2	-20.2673
343.15	0.0099	343.25	0.0100	0.0660	-405.2	-20.2699
343.15	0.0099	343.25	0.0100	0.0824	-397.5	-20.2653
343.15	0.0099	343.25	0.0100	0.1597	-375.6	-20.2498
343.15	0.0099	343.15	0.0100	0.2407	-362.8	-20.2543
343.15	0.0099	343.15	0.0100	0.3471	-352.6	-20.2883
343.15	0.0099	343.15	0.0100	0.4049	-347.7	-20.2807
Run no. 22						
353.55	0.0099	353.55	0.0100	0.0429	-419.8	-19.8253
353.55	0.0099	353.55	0.0100	0.0653	-403.7	-19.8143
353.55	0.0099	353.55	0.0100	0.0865	-393.6	-19.8075
353.55	0.0099	353.65	0.0100	0.1649	-372.6	-19.8179
353.55	0.0099	353.65	0.0100	0.2341	-361.7	-19.8293
353.55	0.0099	353.65	0.0100	0.3455	-348.9	-19.8128
353.55	0.0099	353.65	0.0100	0.4023	-344.1	-19.8117
Run no. 23						
353.65	0.0099	353.65	0.0100	0.0411	-422.2	-19.8443
353.65	0.0099	353.65	0.0100	0.0647	-404.8	-19.8361
353.65	0.0099	353.65	0.0100	0.0879	-393.8	-19.8285
353.65	0.0099	353.65	0.0100	0.1589	-373.9	-19.8226
353.65	0.0099	353.65	0.0100	0.2519	-359.3	-19.8283
Run no. 24						
353.75	0.0099	353.75	0.0100	0.0393	-423.5	-19.8259
353.75	0.0099	353.75	0.0100	0.0660	-404.2	-19.8376
353.75	0.0099	353.75	0.0100	0.0824	-396.0	-19.8243
353.75	0.0099	353.75	0.0100	0.1597	-373.8	-19.8210
353.75	0.0099	353.75	0.0100	0.2407	-360.3	-19.8105

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{glycine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
353.75	0.0099	353.75	0.0100	0.3471	-349.5	-19.8352
353.75	0.0099	353.75	0.0100	0.4049	-344.8	-19.8392

2.9.8 L-phenylalanine

Table 2.26: Experimental equilibrium data for L-phenylalanine measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-phenylalanine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
292.85	0.0098	292.85	0.0099	0.0263	-412.2	-21.6633
292.85	0.0098	292.85	0.0099	0.0321	-405.8	-21.7146
292.85	0.0098	292.85	0.0099	0.0492	-390.8	-21.6886
292.85	0.0098	292.85	0.0099	0.0833	-374.6	-21.6721
292.85	0.0098	292.75	0.0099	0.1067	-367.6	-21.6776
292.85	0.0098	292.75	0.0099	0.1700	-355.0	-21.6814
Run no. 2						
293.25	0.0098	293.15	0.0099	0.0387	-398.3	-21.6606
293.25	0.0098	293.15	0.0099	0.0437	-393.5	-21.6307
293.25	0.0098	293.25	0.0099	0.0632	-381.9	-21.6216
293.25	0.0098	293.15	0.0099	0.0876	-372.3	-21.6246
293.25	0.0098	293.15	0.0099	0.1366	-359.3	-21.5982
Run no. 3						
298.05	0.0098	298.05	0.0099	0.0222	-421.3	-21.4475
298.05	0.0098	298.15	0.0099	0.0387	-397.7	-21.3746
298.05	0.0098	298.15	0.0099	0.0607	-382.7	-21.3566
298.05	0.0098	298.05	0.0099	0.0892	-371.2	-21.3600
298.05	0.0098	298.05	0.0099	0.1028	-366.9	-21.3512
298.05	0.0098	298.05	0.0099	0.1237	-361.5	-21.3439
Run no. 4						
298.25	0.0098	298.35	0.0099	0.0321	-404.6	-21.3724
298.25	0.0098	298.25	0.0099	0.0492	-389.7	-21.3675
298.25	0.0098	298.35	0.0099	0.0653	-380.3	-21.3393
298.25	0.0098	298.25	0.0099	0.0833	-372.8	-21.3353
298.25	0.0098	298.15	0.0099	0.1067	-365.8	-21.3456
298.25	0.0098	298.25	0.0099	0.1227	-361.7	-21.3329
Run no. 5						
298.45	0.0098	298.45	0.0099	0.0263	-412.5	-21.3708
298.45	0.0098	298.45	0.0099	0.0387	-398.1	-21.3737
298.45	0.0098	298.35	0.0099	0.0437	-394.4	-21.3963
298.45	0.0098	298.35	0.0099	0.0632	-382.0	-21.3702
298.45	0.0098	298.35	0.0099	0.0876	-371.9	-21.3541
298.45	0.0098	298.35	0.0099	0.1366	-359.0	-21.3406
Run no. 6						
302.85	0.0098	302.85	0.0099	0.0222	-420.9	-21.1743
302.85	0.0098	302.95	0.0099	0.0387	-396.8	-21.0968
302.85	0.0098	302.95	0.0099	0.0607	-381.6	-21.0804
302.85	0.0098	302.95	0.0099	0.0892	-369.7	-21.0695
302.85	0.0098	302.85	0.0099	0.1028	-365.5	-21.0730
302.85	0.0098	302.95	0.0099	0.1237	-360.0	-21.0595
Run no. 7						
302.95	0.0098	303.05	0.0099	0.0321	-404.0	-21.1073
302.95	0.0098	302.95	0.0099	0.0492	-388.8	-21.0996
302.95	0.0098	302.95	0.0099	0.0653	-379.6	-21.0908
302.95	0.0098	302.85	0.0099	0.0833	-372.2	-21.0950
302.95	0.0098	302.85	0.0099	0.1067	-364.7	-21.0843
302.95	0.0098	303.05	0.0099	0.1227	-360.5	-21.0647
Run no. 8						
303.15	0.0098	303.05	0.0099	0.0263	-412.2	-21.1189
303.15	0.0098	303.15	0.0099	0.0387	-397.1	-21.0973
303.15	0.0098	303.05	0.0099	0.0437	-393.4	-21.1219
303.15	0.0098	303.05	0.0099	0.0632	-380.8	-21.0957
303.15	0.0098	303.05	0.0099	0.0876	-370.4	-21.0742
303.15	0.0098	303.15	0.0099	0.1366	-357.2	-21.0513
Run no. 9						
312.95	0.0098	313.05	0.0099	0.0263	-410.9	-20.5686
312.95	0.0098	313.05	0.0099	0.0387	-395.4	-20.5566
312.95	0.0098	313.05	0.0099	0.0437	-391.4	-20.5685

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-phenylalanine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
312.95	0.0098	313.05	0.0099	0.0632	-378.4	-20.5427
312.95	0.0098	312.95	0.0099	0.0876	-367.9	-20.5357
312.95	0.0098	313.05	0.0099	0.1366	-354.4	-20.5180
312.95	0.0098	313.05	0.0099	0.1700	-347.8	-20.5076
Run no. 10						
313.05	0.0098	313.05	0.0099	0.0222	-420.2	-20.6276
313.05	0.0098	313.05	0.0099	0.0387	-395.5	-20.5637
313.05	0.0098	313.05	0.0099	0.0607	-379.8	-20.5474
313.05	0.0098	313.05	0.0099	0.0892	-367.5	-20.5364
313.05	0.0098	313.05	0.0099	0.1028	-362.8	-20.5208
313.05	0.0098	313.15	0.0099	0.1237	-357.2	-20.5107
313.05	0.0098	313.15	0.0099	0.1470	-352.3	-20.5149
Run no. 11						
313.15	0.0098	313.05	0.0099	0.0321	-403.1	-20.5864
313.15	0.0098	313.05	0.0099	0.0492	-387.0	-20.5578
313.15	0.0098	313.15	0.0099	0.0653	-377.4	-20.5399
313.15	0.0098	313.05	0.0099	0.0833	-369.6	-20.5381
313.15	0.0098	313.05	0.0099	0.1067	-361.9	-20.5294
313.15	0.0098	313.05	0.0099	0.1227	-357.9	-20.5338
313.15	0.0098	313.15	0.0099	0.1524	-351.2	-20.5141
Run no. 12						
322.75	0.0098	322.85	0.0099	0.0263	-409.9	-20.0749
322.75	0.0098	322.75	0.0099	0.0387	-394.0	-20.0713
322.75	0.0098	322.85	0.0099	0.0437	-389.7	-20.0714
322.75	0.0098	322.75	0.0099	0.0632	-376.4	-20.0548
322.75	0.0098	322.85	0.0099	0.0876	-365.6	-20.0379
322.75	0.0098	322.85	0.0099	0.1366	-351.7	-20.0265
322.75	0.0098	322.85	0.0099	0.1700	-345.0	-20.0200
Run no. 13						
322.85	0.0098	322.85	0.0099	0.0222	-419.4	-20.1308
322.85	0.0098	322.85	0.0099	0.0387	-394.1	-20.0728
322.85	0.0098	322.85	0.0099	0.0607	-377.8	-20.0525
322.85	0.0098	322.85	0.0099	0.0892	-365.1	-20.0410
322.85	0.0098	322.85	0.0099	0.1028	-360.3	-20.0271
322.85	0.0098	322.85	0.0099	0.1237	-354.4	-20.0179
322.85	0.0098	322.85	0.0099	0.1470	-349.3	-20.0203
Run no. 14						
322.95	0.0098	322.85	0.0099	0.0321	-402.1	-20.1014
322.95	0.0098	322.95	0.0099	0.0492	-385.4	-20.0638
322.95	0.0098	322.95	0.0099	0.0653	-375.4	-20.0480
322.95	0.0098	322.95	0.0099	0.0833	-367.4	-20.0423
322.95	0.0098	322.85	0.0099	0.1067	-359.4	-20.0367
322.95	0.0098	322.85	0.0099	0.1227	-355.3	-20.0420
322.95	0.0098	322.85	0.0099	0.1524	-348.5	-20.0315
Run no. 15						
332.75	0.0098	332.85	0.0099	0.0263	-408.8	-19.5989
332.75	0.0098	332.75	0.0099	0.0387	-392.2	-19.5877
332.75	0.0098	332.85	0.0099	0.0437	-388.1	-19.5996
332.75	0.0098	332.85	0.0099	0.0632	-374.3	-19.5746
332.75	0.0098	332.85	0.0099	0.0876	-363.0	-19.5573
332.75	0.0098	332.85	0.0099	0.1366	-348.7	-19.5469
332.75	0.0098	332.85	0.0099	0.1700	-342.2	-19.5546
Run no. 16						
332.95	0.0098	332.95	0.0099	0.0222	-419.2	-19.6718
332.95	0.0098	332.95	0.0099	0.0387	-393.0	-19.6097
332.95	0.0098	332.95	0.0099	0.0607	-376.1	-19.5862
332.95	0.0098	332.95	0.0099	0.0892	-362.7	-19.5641
332.95	0.0098	332.95	0.0099	0.1028	-358.0	-19.5589
Run no. 17						
333.05	0.0098	332.95	0.0099	0.0321	-401.1	-19.6332
333.05	0.0098	333.15	0.0099	0.0492	-383.7	-19.5844
333.05	0.0098	333.15	0.0099	0.0653	-373.7	-19.5796
333.05	0.0098	333.05	0.0099	0.0833	-365.3	-19.5737
333.05	0.0098	333.05	0.0099	0.1067	-357.1	-19.5647

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T_I	$\bar{m}_{HCl_I}$	T_{II}	$\bar{m}_{NaOH_{II}}$	$\bar{m}_{L-phenylalanine}$	$(E_I - E_{II})$	$ln(K_{2,exp})$
[K]	[mol kg^{-1}]	[K]	[mol kg^{-1}]	[mol kg^{-1}]	[mV]	[-]
333.05	0.0098	332.95	0.0099	0.1227	-352.9	-19.5758
333.05	0.0098	333.05	0.0099	0.1524	-346.1	-19.5679
Run no. 18						
342.95	0.0098	343.05	0.0099	0.0263	-407.1	-19.1230
342.95	0.0098	342.95	0.0099	0.0387	-390.8	-19.1389
342.95	0.0098	343.05	0.0099	0.0437	-385.7	-19.1214
342.95	0.0098	343.05	0.0099	0.0632	-372.2	-19.1208
342.95	0.0098	343.05	0.0099	0.0876	-360.4	-19.0983
342.95	0.0098	343.05	0.0099	0.1366	-345.5	-19.0824
342.95	0.0098	342.95	0.0099	0.1700	-338.6	-19.0878
Run no. 19						
343.05	0.0098	343.15	0.0099	0.0387	-391.6	-19.1594
343.05	0.0098	342.95	0.0099	0.0607	-374.5	-19.1563
343.05	0.0098	342.95	0.0099	0.0892	-360.8	-19.1376
343.05	0.0098	342.95	0.0099	0.1028	-356.1	-19.1372
343.05	0.0098	342.95	0.0099	0.1237	-349.8	-19.1268
343.05	0.0098	342.95	0.0099	0.1470	-344.5	-19.1332
Run no. 20						
343.15	0.0098	343.15	0.0099	0.0321	-400.1	-19.1880
343.15	0.0098	343.15	0.0099	0.0492	-382.2	-19.1506
343.15	0.0098	343.15	0.0099	0.0653	-371.9	-19.1457
343.15	0.0098	343.25	0.0099	0.0833	-363.2	-19.1285
343.15	0.0098	343.25	0.0099	0.1067	-354.6	-19.1145
343.15	0.0098	343.25	0.0099	0.1227	-350.1	-19.1150
343.15	0.0098	343.05	0.0099	0.1524	-342.8	-19.1111
Run no. 21						
353.15	0.0098	353.05	0.0099	0.0387	-390.9	-18.773
353.15	0.0098	353.15	0.0099	0.0607	-373.3	-18.7553
353.15	0.0098	353.15	0.0099	0.0892	-358.7	-18.7204
353.15	0.0098	353.15	0.0099	0.1028	-354.0	-18.7246
353.15	0.0098	353.05	0.0099	0.1237	-347.7	-18.7248
353.15	0.0098	352.95	0.0099	0.1470	-342.1	-18.7308
Run no. 22						
353.15	0.0098	353.25	0.0099	0.0263	-407.7	-18.7510
353.15	0.0098	353.25	0.0099	0.0387	-390.1	-18.7349
353.15	0.0098	353.25	0.0099	0.0437	-385.5	-18.7438
353.15	0.0098	353.25	0.0099	0.0632	-371.1	-18.7268
353.15	0.0098	353.25	0.0099	0.1366	-344.4	-18.7144
353.15	0.0098	353.25	0.0099	0.1700	-337.2	-18.7122
Run no. 23						
353.25	0.0098	353.25	0.0099	0.0321	-399.5	-18.7872
353.25	0.0098	353.35	0.0099	0.0492	-380.7	-18.7327
353.25	0.0098	353.25	0.0099	0.0653	-370.2	-18.7359
353.25	0.0098	353.35	0.0099	0.0833	-361.0	-18.7109
353.25	0.0098	353.35	0.0099	0.1067	-352.3	-18.7019
353.25	0.0098	353.35	0.0099	0.1227	-348.0	-18.7133
353.25	0.0098	353.35	0.0099	0.1524	-340.3	-18.6943

2.9.9 L-proline

Table 2.27: Experimental equilibrium data for L-proline measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-proline}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
292.65	0.0099	292.65	0.0096	0.0199	-506.6	-24.8468
292.65	0.0099	292.65	0.0096	0.0408	-480.9	-24.8796
292.65	0.0099	292.75	0.0096	0.0855	-458.4	-24.8563
292.65	0.0099	292.65	0.0096	0.2688	-426.3	-24.8139
292.65	0.0099	292.65	0.0096	0.4335	-413.5	-24.7976
292.65	0.0099	292.65	0.0096	0.6366	-403.0	-24.7724
292.65	0.0099	292.75	0.0096	0.8823	-394.6	-24.7633
Run no. 2						
292.85	0.0099	292.85	0.0096	0.0169	-513.8	-24.8107
292.85	0.0099	292.75	0.0096	0.0408	-481.1	-24.8825
292.85	0.0099	292.75	0.0096	0.0814	-460.1	-24.8716
292.85	0.0099	292.75	0.0096	0.2420	-429.8	-24.8392
292.85	0.0099	292.75	0.0096	0.4049	-415.9	-24.8185
292.85	0.0099	292.75	0.0096	0.6369	-403.4	-24.7845
292.85	0.0099	292.75	0.0096	0.8792	-394.6	-24.7620
Run no. 3						
292.95	0.0099	292.95	0.0096	0.0164	-515.4	-24.8141
292.95	0.0099	292.85	0.0096	0.0417	-480.6	-24.8837
292.95	0.0099	292.85	0.0096	0.0801	-460.7	-24.8700
292.95	0.0099	292.85	0.0096	0.2608	-428.0	-24.8397
292.95	0.0099	292.95	0.0096	0.4176	-415.1	-24.8060
292.95	0.0099	292.85	0.0096	0.6446	-403.3	-24.7872
292.95	0.0099	292.85	0.0096	0.8666	-395.6	-24.7818
Run no. 4						
298.05	0.0099	298.15	0.0096	0.0169	-514.7	-24.4932
298.05	0.0099	298.15	0.0096	0.0408	-481.9	-24.5680
298.05	0.0099	298.05	0.0096	0.0814	-460.8	-24.5743
298.05	0.0099	298.05	0.0096	0.2420	-429.9	-24.5392
298.05	0.0099	297.95	0.0096	0.4049	-415.7	-24.5232
298.05	0.0099	298.15	0.0096	0.6369	-403.0	-24.4771
298.05	0.0099	298.05	0.0096	0.8792	-394.3	-24.4711
Run no. 5						
298.15	0.0099	298.05	0.0096	0.0164	-516.4	-24.5167
298.15	0.0099	298.15	0.0096	0.0417	-481.4	-24.5771
298.15	0.0099	298.15	0.0096	0.0801	-461.5	-24.5764
298.15	0.0099	298.05	0.0096	0.2608	-427.9	-24.5401
298.15	0.0099	298.25	0.0096	0.4176	-414.8	-24.5012
298.15	0.0099	298.05	0.0096	0.6446	-403.1	-24.5007
298.15	0.0099	298.05	0.0096	0.8666	-395.0	-24.4850
Run no. 6						
298.15	0.0099	298.25	0.0096	0.0199	-507.6	-24.5150
298.15	0.0099	298.15	0.0096	0.0408	-481.8	-24.5651
298.15	0.0099	298.15	0.0096	0.0855	-459.0	-24.5525
298.15	0.0099	298.15	0.0096	0.2688	-426.5	-24.5101
298.15	0.0099	298.25	0.0096	0.4335	-413.3	-24.4810
298.15	0.0099	298.35	0.0096	0.6366	-402.6	-24.4494
298.15	0.0099	298.45	0.0096	0.8823	-393.7	-24.4274
Run no. 7						
303.15	0.0099	303.05	0.0096	0.0164	-517.5	-24.2389
303.15	0.0099	303.05	0.0096	0.0417	-482.3	-24.3118
303.15	0.0099	303.15	0.0096	0.0801	-461.9	-24.2962
303.15	0.0099	303.15	0.0096	0.2608	-427.8	-24.2551
303.15	0.0099	303.25	0.0096	0.4176	-414.3	-24.2160
303.15	0.0099	303.15	0.0096	0.6446	-402.3	-24.2050
Run no. 8						
303.25	0.0099	303.35	0.0096	0.0169	-515.8	-24.2028
303.25	0.0099	303.15	0.0096	0.0408	-483.0	-24.3052
303.25	0.0099	303.15	0.0096	0.0814	-461.4	-24.2974

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T_I	$\bar{m}_{HCl_I}$	T_{II}	$\bar{m}_{NaOH_{II}}$	$\bar{m}_{L-proline}$	$(E_I - E_{II})$	$ln(K_{2,exp})$
[K]	[mol kg^{-1}]	[K]	[mol kg^{-1}]	[mol kg^{-1}]	[mV]	[-]
303.25	0.0099	303.25	0.0096	0.4049	-415.3	-24.2239
303.25	0.0099	303.25	0.0096	0.6369	-402.6	-24.1992
303.25	0.0099	303.15	0.0096	0.8792	-393.8	-24.1949
Run no. 9						
303.25	0.0099	303.25	0.0096	0.0199	-508.6	-24.2359
303.25	0.0099	303.35	0.0096	0.0408	-482.3	-24.2633
303.25	0.0099	303.35	0.0096	0.0855	-459.3	-24.2573
303.25	0.0099	303.35	0.0096	0.2688	-426.3	-24.2169
303.25	0.0099	303.35	0.0096	0.4335	-413.0	-24.1992
303.25	0.0099	303.35	0.0096	0.6366	-401.7	-24.1580
303.25	0.0099	303.35	0.0096	0.8823	-392.7	-24.1442
Run no. 10						
313.15	0.0099	313.25	0.0096	0.0164	-519.0	-23.6640
313.15	0.0099	313.05	0.0096	0.0417	-483.6	-23.7735
313.15	0.0099	313.05	0.0096	0.0801	-462.7	-23.7693
313.15	0.0099	313.15	0.0096	0.2608	-427.6	-23.7251
313.15	0.0099	313.25	0.0096	0.4176	-413.5	-23.6805
313.15	0.0099	313.15	0.0096	0.6446	-401.1	-23.6689
313.15	0.0099	313.05	0.0096	0.8666	-393.2	-23.6816
Run no. 11						
313.15	0.0099	313.25	0.0096	0.0169	-516.6	-23.6209
313.15	0.0099	313.25	0.0096	0.0408	-483.6	-23.7318
313.15	0.0099	313.25	0.0096	0.0814	-461.5	-23.7304
313.15	0.0099	313.25	0.0096	0.6369	-400.3	-23.6211
313.15	0.0099	313.25	0.0096	0.8792	-391.2	-23.6103
Run no. 12						
313.35	0.0099	313.25	0.0096	0.0199	-510.5	-23.6988
313.35	0.0099	313.45	0.0096	0.0408	-483.4	-23.7128
313.35	0.0099	313.45	0.0096	0.0855	-459.8	-23.7108
313.35	0.0099	313.35	0.0096	0.2688	-425.8	-23.6794
313.35	0.0099	313.35	0.0096	0.4335	-411.9	-23.6557
313.35	0.0099	313.35	0.0096	0.6366	-400.5	-23.6245
313.35	0.0099	313.35	0.0096	0.8823	-390.9	-23.5994
Run no. 13						
323.05	0.0099	323.05	0.0096	0.0199	-512.1	-23.1908
323.05	0.0099	323.05	0.0096	0.0408	-485.1	-23.2465
323.05	0.0099	323.05	0.0096	0.0855	-460.9	-23.2469
323.05	0.0099	323.05	0.0096	0.2688	-425.8	-23.2063
323.05	0.0099	322.95	0.0096	0.4335	-411.5	-23.1892
323.05	0.0099	322.95	0.0096	0.6366	-400.0	-23.1670
323.05	0.0099	322.95	0.0096	0.8823	-390.5	-23.1560
Run no. 14						
323.05	0.0099	323.05	0.0096	0.0164	-520.3	-23.1410
323.05	0.0099	323.05	0.0096	0.0417	-484.1	-23.2375
323.05	0.0099	323.05	0.0096	0.0801	-462.7	-23.2381
323.05	0.0099	323.05	0.0096	0.2608	-426.6	-23.2038
323.05	0.0099	323.05	0.0096	0.4176	-412.6	-23.1848
323.05	0.0099	323.15	0.0096	0.6446	-399.7	-23.1576
323.05	0.0099	323.05	0.0096	0.8666	-390.6	-23.1359
Run no. 15						
323.05	0.0099	323.05	0.0096	0.0169	-519.1	-23.1495
323.05	0.0099	323.05	0.0096	0.0408	-485.1	-23.2466
323.05	0.0099	323.15	0.0096	0.0814	-462.2	-23.2330
323.05	0.0099	323.15	0.0096	0.2420	-428.8	-23.1994
323.05	0.0099	323.15	0.0096	0.4049	-413.3	-23.1726
323.05	0.0099	323.05	0.0096	0.6369	-400.1	-23.1654
323.05	0.0099	323.05	0.0096	0.8792	-390.3	-23.1396
Run no. 16						
333.25	0.0099	333.25	0.0096	0.0199	-513.8	-22.6945
333.25	0.0099	333.35	0.0096	0.0408	-486.5	-22.7582
333.25	0.0099	333.15	0.0096	0.0855	-461.6	-22.7715
333.25	0.0099	333.25	0.0096	0.2688	-425.2	-22.7175
333.25	0.0099	333.15	0.0096	0.4335	-410.8	-22.7123
Run no. 17						

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-proline}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
333.25	0.0099	333.35	0.0096	0.0164	-522.1	-22.6359
333.25	0.0099	333.25	0.0096	0.0417	-485.6	-22.7600
333.25	0.0099	333.35	0.0096	0.0801	-463.5	-22.7523
333.25	0.0099	333.25	0.0096	0.2608	-426.5	-22.7316
333.25	0.0099	333.35	0.0096	0.4176	-411.7	-22.6945
333.25	0.0099	333.25	0.0096	0.6446	-398.6	-22.6856
333.25	0.0099	333.25	0.0096	0.8666	-389.4	-22.6647
Run no. 18						
333.35	0.0099	333.25	0.0096	0.0169	-521.0	-22.6576
333.35	0.0099	333.35	0.0096	0.0408	-486.7	-22.7666
333.35	0.0099	333.25	0.0096	0.0814	-463.2	-22.7682
333.35	0.0099	333.25	0.0096	0.2420	-428.7	-22.7319
333.35	0.0099	333.25	0.0096	0.4049	-412.6	-22.7010
333.35	0.0099	333.25	0.0096	0.6369	-399.1	-22.6920
333.35	0.0099	333.25	0.0096	0.8792	-389.1	-22.6700
Run no. 19						
343.65	0.0099	343.65	0.0096	0.0164	-522.9	-22.1199
343.65	0.0099	343.75	0.0096	0.0417	-486.1	-22.2601
343.65	0.0099	343.75	0.0096	0.0801	-463.5	-22.2645
343.65	0.0099	343.75	0.0096	0.2608	-425.1	-22.2296
343.65	0.0099	343.75	0.0096	0.4176	-410.3	-22.2137
343.65	0.0099	343.75	0.0096	0.6446	-396.5	-22.1895
343.65	0.0099	343.75	0.0096	0.8666	-387.1	-22.1717
Run no. 20						
343.75	0.0099	343.65	0.0096	0.0169	-521.2	-22.1123
343.75	0.0099	343.75	0.0096	0.0408	-487.0	-22.2648
343.75	0.0099	343.65	0.0096	0.0814	-463.1	-22.2771
343.75	0.0099	343.75	0.0096	0.2420	-427.7	-22.2411
343.75	0.0099	343.75	0.0096	0.4049	-411.5	-22.2239
343.75	0.0099	343.75	0.0096	0.6369	-397.4	-22.2090
343.75	0.0099	343.75	0.0096	0.8792	-386.9	-22.1807
Run no. 21						
354.15	0.0099	354.25	0.0096	0.0169	-522.5	-21.6251
354.15	0.0099	354.05	0.0096	0.0408	-488.0	-21.8213
354.15	0.0099	354.05	0.0096	0.0814	-463.9	-21.8445
354.15	0.0099	354.05	0.0096	0.2420	-427.8	-21.8257
354.15	0.0099	354.05	0.0096	0.4049	-411.0	-21.8047
354.15	0.0099	354.15	0.0096	0.6369	-396.3	-21.7790
354.15	0.0099	354.05	0.0096	0.8792	-385.9	-21.7692
Run no. 22						
354.35	0.0099	354.45	0.0096	0.0164	-524.0	-21.6144
354.35	0.0099	354.45	0.0096	0.0417	-486.9	-21.7914
354.35	0.0099	354.35	0.0096	0.0801	-464.0	-21.8144
354.35	0.0099	354.35	0.0096	0.4176	-409.5	-21.7745
354.35	0.0099	354.25	0.0096	0.6446	-395.8	-21.7724
354.35	0.0099	354.25	0.0096	0.8666	-385.9	-21.7476

2.9.10 L-glutamic acid

Table 2.28: Experimental equilibrium data for L-glutamic acid measurements

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-glutamicacid}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.05	0.0101	292.95	0.0092	0.0057	-471.4	-23.3020
293.05	0.0101	293.05	0.0279	0.0165	-471.9	-23.2384
293.05	0.0101	292.95	0.0564	0.0314	-482.8	-23.3064
293.05	0.0101	292.95	0.0796	0.0560	-442.4	-23.4516
293.05	0.0101	293.05	0.1042	0.0636	-462.9	-23.4944
Run no. 2						
293.05	0.0101	293.05	0.0092	0.0055	-473.9	-23.2656
293.05	0.0101	293.05	0.0279	0.0174	-464.0	-23.2841
293.05	0.0101	293.05	0.0394	0.0224	-478.3	-23.2285
293.05	0.0101	292.95	0.0564	0.0317	-480.1	-23.3193
293.05	0.0101	293.05	0.0796	0.0438	-484.1	-23.3424
293.05	0.0101	293.05	0.1042	0.0574	-483.2	-23.4216
Run no. 3						
298.15	0.0101	298.05	0.0092	0.0057	-472.7	-23.0483
298.15	0.0101	298.15	0.0279	0.0165	-472.8	-22.9640
298.15	0.0101	298.15	0.0564	0.0314	-484.0	-23.0315
298.15	0.0101	298.15	0.0796	0.0560	-442.6	-23.1618
298.15	0.0101	298.15	0.1042	0.0636	-463.4	-23.2109
Run no. 4						
298.15	0.0101	298.15	0.0092	0.0058	-467.7	-23.0324
298.15	0.0101	298.15	0.0196	0.0119	-468.1	-22.8900
298.15	0.0101	298.15	0.0564	0.0306	-490.6	-23.0031
298.15	0.0101	298.15	0.0796	0.0462	-473.1	-23.1264
298.15	0.0101	298.15	0.1042	0.0573	-484.6	-23.1398
Run no. 5						
298.25	0.0101	298.15	0.0092	0.0055	-475.7	-23.0349
298.25	0.0101	298.25	0.0279	0.0174	-465.4	-23.0275
298.25	0.0101	298.15	0.0394	0.0224	-479.9	-22.9806
298.25	0.0101	298.25	0.0564	0.0317	-482.2	-23.0756
298.25	0.0101	298.15	0.0796	0.0438	-485.9	-23.0998
298.25	0.0101	298.15	0.1042	0.0574	-485.0	-23.1794
Run no. 6						
303.15	0.0101	303.25	0.0092	0.0058	-468.2	-22.7553
303.15	0.0101	303.05	0.0196	0.0119	-469.6	-22.6647
303.15	0.0101	303.05	0.0564	0.0306	-492.0	-22.7653
303.15	0.0101	303.05	0.0796	0.0462	-474.2	-22.8829
303.15	0.0101	303.05	0.1042	0.0573	-486.1	-22.9071
Run no. 7						
303.15	0.0101	303.25	0.0092	0.0055	-475.9	-22.7415
303.15	0.0101	303.15	0.0279	0.0174	-466.0	-22.7663
303.15	0.0101	303.15	0.0394	0.0224	-480.8	-22.7176
303.15	0.0101	303.15	0.0564	0.0317	-483.0	-22.8147
303.15	0.0101	303.05	0.0796	0.0438	-487.0	-22.8494
303.15	0.0101	303.05	0.1042	0.0574	-486.1	-22.9295
Run no. 8						
312.95	0.0101	313.05	0.0092	0.0058	-470.2	-22.2933
312.95	0.0101	312.85	0.0196	0.0119	-472.3	-22.2237
312.95	0.0101	312.85	0.0564	0.0306	-494.9	-22.3166
312.95	0.0101	313.05	0.0796	0.0462	-476.6	-22.4132
312.95	0.0101	312.95	0.1042	0.0573	-488.7	-22.4421
Run no. 9						
312.95	0.0101	312.95	0.0092	0.0057	-475.9	-22.3341
312.95	0.0101	312.95	0.0279	0.0165	-476.9	-22.2797
312.95	0.0101	312.95	0.0564	0.0314	-488.2	-22.3377
312.95	0.0101	313.05	0.0796	0.0560	-444.7	-22.4477
312.95	0.0101	313.05	0.1042	0.0636	-466.3	-22.4930
Run no. 10						
313.15	0.0101	313.15	0.0092	0.0055	-478.8	-22.3109

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-glutamicacid}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
313.15	0.0101	313.05	0.0279	0.0174	-469.0	-22.3345
313.15	0.0101	313.15	0.0394	0.0224	-484.1	-22.2796
313.15	0.0101	313.05	0.0564	0.0317	-486.2	-22.3771
313.15	0.0101	313.05	0.0796	0.0438	-490.3	-22.4062
313.15	0.0101	313.05	0.1042	0.0574	-489.2	-22.4793
Run no. 11						
323.35	0.0101	323.35	0.0092	0.0058	-473.0	-21.8688
323.35	0.0101	323.35	0.0196	0.0119	-475.0	-21.7749
323.35	0.0101	323.35	0.0564	0.0306	-497.5	-21.8480
323.35	0.0101	323.25	0.0796	0.0462	-478.9	-21.9666
323.35	0.0101	323.35	0.1042	0.0573	-491.0	-21.9731
Run no. 12						
323.35	0.0101	323.35	0.0092	0.0055	-480.6	-21.8471
323.35	0.0101	323.35	0.0279	0.0174	-470.6	-21.8571
323.35	0.0101	323.35	0.0394	0.0224	-485.9	-21.8041
323.35	0.0101	323.35	0.0564	0.0317	-487.9	-21.8895
323.35	0.0101	323.35	0.0796	0.0438	-491.7	-21.9050
323.35	0.0101	323.35	0.1042	0.0574	-490.3	-21.9691
Run no. 13						
333.15	0.0101	333.15	0.0092	0.0058	-475.4	-21.4795
333.15	0.0101	333.15	0.0196	0.0119	-478.2	-21.4099
333.15	0.0101	333.15	0.0564	0.0306	-500.0	-21.4433
333.15	0.0101	333.15	0.0796	0.0462	-480.9	-21.5506
333.15	0.0101	333.15	0.1042	0.0573	-493.0	-21.5550
Run no. 14						
343.25	0.0101	343.35	0.0092	0.0055	-486.0	-21.0912
343.25	0.0101	343.35	0.0279	0.0174	-476.2	-21.1061
343.25	0.0101	343.35	0.0394	0.0224	-491.8	-21.0442
343.25	0.0101	343.25	0.0564	0.0317	-493.5	-21.1224
343.25	0.0101	343.35	0.0796	0.0438	-497.2	-21.1260
343.25	0.0101	343.35	0.1042	0.0574	-495.0	-21.1660
Run no. 15						
343.45	0.0101	343.55	0.0092	0.0058	-478.4	-21.1075
343.45	0.0101	343.45	0.0196	0.0119	-481.7	-21.0558
343.45	0.0101	343.35	0.0564	0.0306	-503.0	-21.0649
343.45	0.0101	343.55	0.0796	0.0462	-483.3	-21.1528
343.45	0.0101	343.35	0.1042	0.0573	-495.8	-21.1750
Run no. 16						
353.25	0.0101	353.25	0.0092	0.0058	-480.9	-20.7720
353.25	0.0101	353.25	0.0196	0.0119	-485.5	-20.7567
353.25	0.0101	353.25	0.0564	0.0306	-507.8	-20.7883
353.25	0.0101	353.15	0.0796	0.0462	-488.0	-20.8974
353.25	0.0101	353.15	0.1042	0.0573	-501.0	-20.9201
Run no. 17						
353.25	0.0101	353.35	0.0092	0.0055	-489.3	-20.7697
353.25	0.0101	353.25	0.0279	0.0174	-479.5	-20.7888
353.25	0.0101	353.25	0.0394	0.0224	-495.7	-20.7398
353.25	0.0101	353.25	0.0564	0.0317	-497.6	-20.8185
353.25	0.0101	353.15	0.0796	0.0438	-501.6	-20.8439
353.25	0.0101	353.25	0.1042	0.0574	-499.5	-20.8839

2.9.11 L-aspartic acid

Table 2.29: Experimental equilibrium data for L-aspartic acid measurements

T_I [K]	$\tilde{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\tilde{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\tilde{m}_{L-asparticacid}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.15	0.0099	293.15	0.0196	0.0102	-516.7	-23.9397
293.15	0.0099	293.55	0.0279	0.0150	-502.1	-23.5699
293.15	0.0099	293.15	0.0564	0.0297	-506.5	-23.5526
293.15	0.0099	293.25	0.0796	0.0415	-509.1	-23.5766
293.15	0.0099	293.55	0.1042	0.0644	-471.8	-23.9204
Run no. 2						
293.65	0.0099	293.65	0.0279	0.0142	-522.7	-23.7787
293.65	0.0099	293.65	0.0394	0.0198	-528.9	-23.6920
293.65	0.0099	293.65	0.0564	0.0305	-502.6	-23.786
293.65	0.0099	293.55	0.0796	0.0408	-520.7	-23.6998
293.65	0.0099	293.65	0.1042	0.0572	-494.8	-23.8241
Run no. 3						
298.05	0.0099	298.05	0.0279	0.0143	-519.7	-23.4643
298.05	0.0099	298.05	0.0564	0.0306	-499.3	-23.4118
298.05	0.0099	298.05	0.0796	0.0429	-499.9	-23.4486
298.05	0.0099	298.05	0.1042	0.0598	-483.4	-23.5408
Run no. 4						
298.05	0.0099	298.05	0.0090	0.0053	-485.7	-23.3550
298.05	0.0099	298.05	0.0279	0.0150	-504.6	-23.4092
298.05	0.0099	298.05	0.0564	0.0297	-508.8	-23.3466
298.05	0.0099	298.05	0.0796	0.0415	-512.0	-23.4043
Run no. 5						
298.15	0.0099	298.15	0.0279	0.0142	-521.6	-23.4305
298.15	0.0099	298.15	0.0394	0.0198	-528.7	-23.4065
298.15	0.0099	298.15	0.0564	0.0305	-503.4	-23.5338
298.15	0.0099	298.05	0.0796	0.0408	-519.9	-23.3711
298.15	0.0099	298.05	0.1042	0.0572	-495.5	-23.5761
Run no. 6						
303.05	0.0099	303.05	0.0196	0.0105	-506.4	-23.0902
303.05	0.0099	302.95	0.0279	0.0143	-519.9	-23.1827
303.05	0.0099	302.95	0.0394	0.0203	-517.4	-23.0797
303.05	0.0099	302.95	0.0564	0.0306	-500.6	-23.1666
303.05	0.0099	303.05	0.0796	0.0429	-501.1	-23.1909
303.05	0.0099	303.05	0.1042	0.0598	-484.5	-23.2849
Run no. 7						
303.05	0.0099	303.05	0.0090	0.0053	-486.6	-23.0989
303.05	0.0099	303.05	0.0279	0.0150	-505.8	-23.1593
303.05	0.0099	302.95	0.0564	0.0297	-510.0	-23.1004
303.05	0.0099	303.05	0.0796	0.0415	-512.9	-23.1352
Run no. 8						
303.15	0.0099	303.05	0.0279	0.0142	-522.4	-23.1919
303.15	0.0099	303.15	0.0394	0.0198	-528.8	-23.1175
303.15	0.0099	303.15	0.0564	0.0305	-504.5	-23.2720
303.15	0.0099	303.05	0.0796	0.0408	-521.2	-23.1293
303.15	0.0099	303.05	0.1042	0.0572	-496.7	-23.3189
Run no. 9						
312.95	0.0099	312.85	0.0090	0.0053	-489.8	-22.6883
312.95	0.0099	313.05	0.0279	0.0150	-508.9	-22.7162
312.95	0.0099	313.05	0.0564	0.0297	-513.0	-22.6374
312.95	0.0099	313.05	0.0796	0.0415	-515.9	-22.6767
Run no. 10						
313.05	0.0099	313.05	0.0196	0.0105	-509.1	-22.6457
313.05	0.0099	312.95	0.0279	0.0143	-522.0	-22.7259
313.05	0.0099	312.95	0.0394	0.0203	-520.0	-22.6331
313.05	0.0099	312.85	0.0564	0.0306	-503.6	-22.7116
313.05	0.0099	313.05	0.0796	0.0429	-504.1	-22.7270
313.05	0.0099	312.95	0.1042	0.0598	-487.0	-22.8184
Run no. 11						

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T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{NaOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{L-asparticacid}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
313.05	0.0099	312.95	0.0090	0.0050	-497.7	-22.6376
313.05	0.0099	313.05	0.0279	0.0142	-523.6	-22.6843
313.05	0.0099	313.15	0.0394	0.0198	-529.6	-22.5914
313.05	0.0099	313.05	0.0564	0.0305	-506.6	-22.7769
313.05	0.0099	312.95	0.0796	0.0408	-523.1	-22.6383
313.05	0.0099	312.95	0.1042	0.0572	-498.7	-22.8217
Run no. 12						
323.15	0.0099	323.15	0.0090	0.0053	-491.4	-22.2049
323.15	0.0099	323.25	0.0279	0.0150	-510.6	-22.2271
323.15	0.0099	323.25	0.0564	0.0297	-514.7	-22.1434
323.15	0.0099	323.05	0.0796	0.0415	-517.1	-22.1721
Run no. 13						
323.25	0.0099	323.25	0.0196	0.0105	-511.6	-22.2067
323.25	0.0099	323.25	0.0279	0.0143	-523.7	-22.2446
323.25	0.0099	323.25	0.0394	0.0203	-522.1	-22.1644
323.25	0.0099	323.15	0.0564	0.0306	-506.1	-22.2429
323.25	0.0099	323.15	0.0796	0.0429	-507.4	-22.3032
323.25	0.0099	323.15	0.1042	0.0598	-489.9	-22.3821
Run no. 14						
323.25	0.0099	323.35	0.0090	0.0050	-499.6	-22.1670
323.25	0.0099	323.15	0.0279	0.0142	-525.3	-22.2239
323.25	0.0099	323.25	0.0394	0.0198	-531.3	-22.1397
323.25	0.0099	323.25	0.0564	0.0305	-509.2	-22.3184
323.25	0.0099	323.25	0.0796	0.0408	-525.3	-22.1655
323.25	0.0099	323.25	0.1042	0.0572	-501.0	-22.3471
Run no. 15						
333.15	0.0099	333.15	0.0196	0.0105	-511.6	-21.6810
333.15	0.0099	333.15	0.0279	0.0143	-522.5	-21.6334
333.15	0.0099	333.15	0.0564	0.0306	-506.2	-21.7240
333.15	0.0099	333.15	0.0796	0.0429	-506.8	-21.7579
Run no. 16						
333.25	0.0099	333.35	0.0090	0.0050	-500.5	-21.6947
333.25	0.0099	333.35	0.0279	0.0142	-523.9	-21.5730
333.25	0.0099	333.15	0.0564	0.0305	-510.1	-21.8367
333.25	0.0099	333.15	0.0796	0.0408	-525.1	-21.6218
333.25	0.0099	333.25	0.1042	0.0572	-501.5	-21.8538
Run no. 17						
342.25	0.0099	342.35	0.0090	0.0052	-497.3	-21.3416
342.25	0.0099	342.35	0.0196	0.0107	-508.6	-21.2770
342.25	0.0099	342.65	0.0796	0.0417	-516.0	-21.2120
342.25	0.0099	342.65	0.1042	0.0565	-504.1	-21.3373
Run no. 18						
353.25	0.0099	353.15	0.0090	0.0052	-500.1	-20.9625
353.25	0.0099	353.15	0.0196	0.0107	-511.2	-20.8777
353.25	0.0099	353.25	0.0796	0.0417	-517.4	-20.7727
353.25	0.0099	353.25	0.1042	0.0565	-507.1	-20.9679

2.9.12 Taurine with K^+ and Li^+ as counter ions

Table 2.30: Experimental equilibrium data for taurine measurements using different counter ions

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{KOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{taurine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.15	0.0102	293.25	0.0101	0.0644	-371.8	21.1928
293.15	0.0102	293.25	0.0101	0.1324	-351.1	21.1852
293.15	0.0102	293.25	0.0101	0.2056	-339.3	21.1870
293.15	0.0102	293.15	0.0101	0.2641	-332.3	21.1772
293.15	0.0102	293.05	0.0101	0.3446	-326.0	21.2088
293.15	0.0102	293.25	0.0101	0.4205	-320.6	21.1886
293.15	0.0102	293.15	0.0101	0.5611	-313.2	21.1956
Run no. 2						
323.65	0.0102	323.55	0.0101	0.0644	-365.1	19.5896
323.65	0.0102	323.55	0.0101	0.1324	-342.4	19.5869
323.65	0.0102	323.55	0.0101	0.2056	-329.3	19.5857
323.65	0.0102	323.65	0.0101	0.2641	-321.7	19.5701
323.65	0.0102	323.55	0.0101	0.3446	-313.9	19.5706
323.65	0.0102	323.55	0.0101	0.4205	-308.5	19.5813
323.65	0.0102	323.55	0.0101	0.5611	-300.3	19.5818
Run no. 3						
353.75	0.0102	353.85	0.0101	0.0644	-359.1	18.2851
353.75	0.0102	353.85	0.0101	0.1324	-333.7	18.2635
353.75	0.0102	353.75	0.0101	0.2056	-319.0	18.2542
353.75	0.0102	353.85	0.0101	0.2641	-311.1	18.2527
353.75	0.0102	353.85	0.0101	0.3446	-301.7	18.2198
353.75	0.0102	353.75	0.0101	0.4205	-296.3	18.2511
353.75	0.0102	353.75	0.0101	0.5611	-286.7	18.2307

T_I [K]	$\bar{m}_{HCl_I}$ [mol kg^{-1}]	T_{II} [K]	$\bar{m}_{LiOH_{II}}$ [mol kg^{-1}]	$\bar{m}_{taurine}$ [mol kg^{-1}]	$(E_I - E_{II})$ [mV]	$ln(K_{2,exp})$ [-]
Run no. 1						
293.15	0.0102	293.15	0.0103	0.0434	-384.1	21.1748
293.15	0.0102	293.25	0.0103	0.1248	-352.4	21.1544
293.15	0.0102	293.25	0.0103	0.1953	-340.3	21.1558
293.15	0.0102	293.15	0.0103	0.2789	-331.0	21.1658
293.15	0.0102	293.25	0.0103	0.3280	-326.7	21.1580
293.15	0.0102	293.15	0.0103	0.4049	-321.3	21.1667
Run no. 2						
323.65	0.0102	323.55	0.0103	0.0434	-379.2	19.5845
323.65	0.0102	323.55	0.0103	0.1248	-344.2	19.5693
323.65	0.0102	323.55	0.0103	0.1953	-330.8	19.5689
323.65	0.0102	323.55	0.0103	0.2789	-320.3	19.5648
323.65	0.0102	323.55	0.0103	0.3280	-315.8	19.5712
323.65	0.0102	323.55	0.0103	0.4049	-309.5	19.5622
323.65	0.0102	323.55	0.0103	0.5532	-300.8	19.5690
Run no. 3						
353.75	0.0102	353.75	0.0103	0.0434	-374.2	18.2742
353.75	0.0102	353.65	0.0103	0.1248	-336.2	18.2719
353.75	0.0102	353.65	0.0103	0.1953	-321.8	18.2795
353.75	0.0102	353.65	0.0103	0.2789	-309.9	18.2615

Chapter 3

Diffusivities in Aqueous Piperazine and Aqueous (Piperazine + MDEA) Solutions

3.1 Introduction

Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating. [50] Recently, blends of a primary or secondary (alkanol)amine with an aqueous solution of a tertiary (alkanol)amine has found application in the removal and absorption of CO_2 due to higher reaction rates and lower heats of regeneration in the desorber section. There is a growing interest in the use of piperazine (PZ) blended with aqueous solutions of N-methyldiethanolamine (MDEA) as a tertiary alkanolamine for gas treating processes. This type of solution is also called the activated MDEA solvent. PZ is known as the activator or promotor and enhances the reactivity towards CO_2, whereas MDEA contributes to the lower heats of regeneration. In these solvents, the concentration of MDEA is usually kept at about (3 to 4) $\text{kmol}\cdot\text{m}^{-3}$ and typically a maximum PZ concentration of about 1.0 $\text{kmol}\cdot\text{m}^{-3}$ is applied. [27, 10, 99, 100, 25]

Accurate design of gas-liquid contactors requires knowledge on the mass transfer coefficients and diffusion coefficients. As the mass transfer coefficients are related to the diffusion coefficients, knowledge of the diffusion coefficients is necessary to make the design of this equipment more reliable. They are also essential for a correct and accurate interpretation of many (lab scale) absorption rate experiments, as e.g. the experiments aimed at the determination of the intrinsic kinetics in a gas-liquid process. [20, 94] In the past, several studies have reported experimental diffusivities of carbon dioxide and various (alkanol)amines in systems relevant for acid gas absorption. [96, 86] In this work, liquid and gas diffusivities are presented to extend the existing experimental database of absorbent properties.

Liquid diffusivities in aqueous PZ solutions and aqueous (PZ + MDEA) solutions and gas diffusivities in aqueous PZ are reported at various concentrations and temperatures. The diffusivities have been determined using the Taylor dispersion technique.

3.2 Theory and experimental procedures

3.2.1 Taylor Dispersion Technique - liquid diffusivities

The diffusivities were determined using the Taylor dispersion technique. A square pulse of a solute solution is injected into a solvent solution showing laminar flow through a capillary tube. The solute contains the same components as the solvent, but with a slightly higher concentration of the component of which diffusivities are to be determined (an addition of approx. 0.05 kmol·m^{-3}). As an example; for measurements of liquid diffusivity of PZ in aqueous PZ solution at about 1.0 kmol·m^{-3}, the solvent solution would contain 1.00 kmol·m^{-3} PZ. The solute solution would contain 1.05 kmol·m^{-3} PZ, and a square pulse of this solution would be injected into the flowing solvent solution. The combined action of axial convection and radial and axial molecular diffusion will eventually change the shape of the solute pulse (the excess number of moles of PZ injected) into a gaussian shaped curve. The theory and mathematical description of such measurements have been described in detail by Taylor [89, 90] and Aris [5]. The mathematical description of a measurement is described by:

$$C_m = \frac{N_{inj,A}}{2\pi R^2 \sqrt{\pi K_A t}} exp\left(-\frac{(L-ut)^2}{4K_A t}\right) \tag{3.1}$$

$$K_A = \frac{u^2 R^2}{48 D_A} + D_A \tag{3.2}$$

where C_m is the measured gaussian concentration profile, $N_{inj,A}$ is the excess number of moles of amine injected, t is the time, and D_A is the binary molecular diffusion coefficient. The subscript A refers to the amine. The other parameters are defined in Table 3.1. $N_{inj,A}$, u and D_A are the independent parameters used to curvefit equation (3.1) and (3.2) to the experimentally recorded results. Since the concentration of the solute pulse decreases because of dispersion while the solute pulse is traversing with the solvent through the tubing, an average concentration value has to be determined. Alizadeh et al. [4] referred to this as the reference concentration C_{ref} given by:

$$C_{ref} = C_{solv} + \frac{N_{inj,A}\left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}}\right)}{\pi R^2 \sqrt{2K_A \dot{t}}} \tag{3.3}$$

where C_{solv} is the solvent concentration and $\dot{t}$ is the time at which the measurement ends.

The experimental setup used is shown schematically in Figure 3.1. Two vessels containing the solute solution and solvent solution are kept under a constant 5 bar pressure of saturated helium in order to create a constant flow of the solute solution and the solvent solution. Introduction of a square solute pulse is done by switching an air actuated six way valve back and forth within a few seconds. The capillary tube is elliptical coiled and placed in a water bath for temperature control. The flow velocity is controlled with mass flow controllers (Rosemount Flowmega 5881), located behind the refractive index (RI) detector (Varian 350 RI) and the six way pulse valve in order to obtain a constant pulsation-free solute and solvent solution flow throughout the measurement. In order to avoid bubble formation inside the tubing and a disturbance of the laminar fluid flow profile, especially at higher temperatures, pressure reducers are located behind the RI detector and the six-way pulse valve. These reducers pressurizes the fluids inside the tubing to 4 bar. The influence of the pressure on the diffusion coefficients can be neglected for the pressure applied. [31, 59] Prior to each experiment, both the solute and the solvent solution were degassed by applying vacuum for a while, and further the RI detector was calibrated. The RI detector showed a linear response to concentration changes of the amines investigated. A computer is connected to the setup for control and data acquisition. The output signal from the RI detector is recorded as a function of time and used to determine the molecular diffusion coefficients as aforementioned. The dimensions of the experimental setup and the flow conditions are given in Table 3.1.

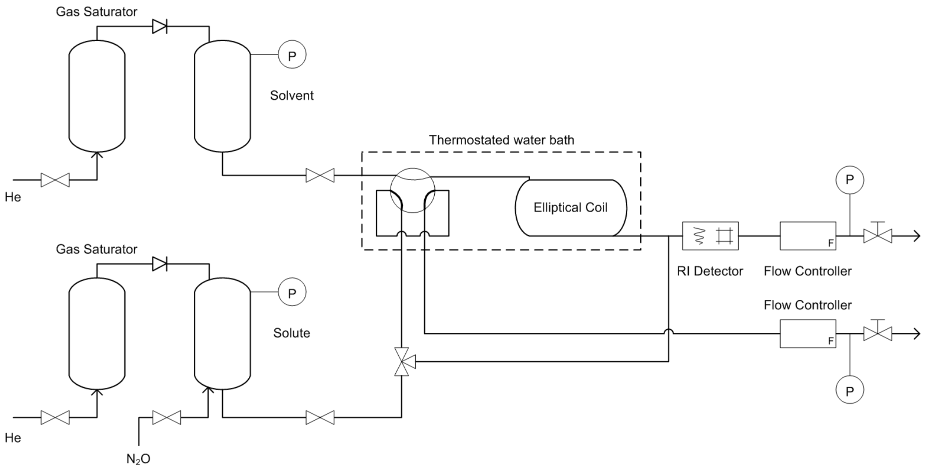

Figure 3.1: Schematic representation of the Taylor dispersion setup

Table 3.1: Dimensions of the experimental setup and flow conditions

Length of the coil	L	14.92 m
Inner radius of the coil	R	$5.14{\cdot}10^{-4}$ m
Radius of the coil	R_C	0.1 m
Injection volume	V_{inj}	(2.5 to 4.1)$\cdot 10^{-8}$ m^3
Liquid flow velocity	u	(2 to 6)$\cdot 10^{-3}$ $m{\cdot}s^{-1}$

A disturbance of the laminar fluid flow profile can occur due to the elliptic coiling of the tube. The varying path lengths traversed by the fluid at different radial positions inside the capillary tube and the secondary flows present in the flow can contribute additionally to the dispersion process. This topic has been extensively discussed by Alizadeh et al. [4] and Snijder et al. [86]. In order to avoid this disturbance, the critical $(De)^2Sc$ was determined for each system. The dimensionless $(De)^2Sc$ number is defined as:

$$De = Re \left(\frac{R_C}{R} \right)^{-1/2} \tag{3.4}$$

$$Sc = \frac{\mu}{\rho D} \tag{3.5}$$

where Re is the well-known Reynolds number and μ and ρ are the solvent viscosity and density. The other parameters are defined in Table 3.1. The measurements had to be carried out at a value of $(De)^2Sc$ lower than the critical one.

3.2.2 Taylor Dispersion Technique - gas diffusivities

A square pulse of a solute solution is injected into a solvent solution showing laminar flow through a capillary tube. The solute solution contains the same amounts of liquid components as the solvent, but with additional N_2O gas absorbed. As an example; for measurements of N_2O diffusivity in an aqueous PZ solution of 1.0 kmol·m^{-3}, the solute and solvent solution would contain 1.0 kmol·m^{-3} PZ. The solute solution would additionally contain N_2O gas absorbed, and a square pulse of this solution would be injected into the flowing solvent solution. The combined action of axial convection and radial and axial molecular diffusion will eventually change the shape of the solute pulse into a gaussian shaped curve. The theory and mathematical description of such a measurement have been in detail described by Taylor [89, 90] and Aris [5].

Diffusion of N_2O in H_2O

Figure 3.2 shows a typical experimental result from a pulse recorded using the Taylor dispersion technique. The figure shows a dimensionless result from a N_2O/H_2O system. The recorded pulse is the response from absorbed N_2O in the solution flowing through the RI detector. The experimental result of the diffusion coefficient from this typical experiment is derived from curve fitting equation (3.6) and (3.7) [89, 90, 5] to the experimental data where N_{inj,N_2O}, u and D_{N_2O} are the independent variables.

$$C_m = \frac{N_{inj,N_2O}}{2\pi R^2 \sqrt{\pi K_{N_2O} t}} exp\left(-\frac{(L-ut)^2}{4K_{N_2O}t} \right) \tag{3.6}$$

$$K_{N_2O} = \frac{u^2 R^2}{48 D_{N_2O}} + D_{N_2O} \tag{3.7}$$

In equation (3.6) and (3.7), C_m is the measured concentration profile, t is the time, N_{inj,N_2O} is the number of moles of N_2O injected and D_{N_2O} is the molecular diffusion coefficient of N_2O. The other parameters are defined in Table 3.1.

Diffusion of N_2O in ($PZ + H_2O$)

Figure 3.3 shows a dimensionless recorded experimental result from a N_2O/(PZ + H_2O) system. It is shown that a combination of two pulses appears. The degassed solvent and solute solutions used were prepared containing a specific and equal concentration of PZ. N_2O was further absorbed into the solute solution as aforementioned. As N_2O is absorbed into the solution, a small liquid volume increase takes place because of the volume occupied by the N_2O molecules. Consequently, the concentration of PZ is decreased in the solute solution, as compared to the solvent solution. The 'negative' peak in Figure 3.3 must be attributed to this phenomena. The 'positive' peak is the effect of the N_2O present in the solution.

A RI detector shows a higher sensitivity towards concentration changes of liquid compounds than concentration changes of absorbed gas compounds in the fluid under investigation. The concentration peak responsible for the 'negative' pulse in Figure 3.3 was found to be in the order of 10^{-6} kmol·m^{-3} after calibration of a PZ/H_2O system, whereas the 'positive' peak was found to be in the order of 10^{-3} kmol·m^{-3}. Since the concentration differences between the 'negative' and 'positive' peak is in the order of 10^3 kmol·m^{-3}, ternary diffusion effects such as cross diffusion can be neglected, i.e. the concentration gradients of PZ is much lower than the concentration gradients of N_2O in the solute pulse as it is traversing and dispersing in the capillary tube. As the dispersion of the 'positive' and 'negative' puls are unequal, molecular diffusion coefficients can be determined from the recorded experimental data by the principle of superposition. The total response of the RI detector is the sum of two separate gaussian curves.

The experimental measured result was curve fitted to equation (3.8) to (3.10):

$$C_m = \frac{N_{inj,N_2O}}{2\pi R^2\sqrt{\pi K_{N_2O} t}} exp\left(-\frac{(L-ut)^2}{4K_{N_2O}t}\right) + \frac{N_{inj,PZ}}{2\pi R^2\sqrt{\pi K_{PZ} t}} exp\left(-\frac{(L-ut)^2}{4K_{PZ}t}\right) \tag{3.8}$$

$$K_{N_2O} = \frac{u^2R^2}{48D_{N_2O}} + D_{N_2O} \tag{3.9}$$

$$K_{PZ} = \frac{u^2R^2}{48D_{PZ}} + D_{PZ} \tag{3.10}$$

where C_m is the measured concentration profile, t is the time, N_{inj,N_2O} and $N_{inj,PZ}$ are the respective number of moles of N_2O and excess number of moles of PZ injected. The fluid flow, u, is identical for both N_2O and PZ. D_{N_2O} and D_{PZ} are the respective molecular binary diffusion coefficients of N_2O and PZ. The parameters N_{inj,N_2O}, $N_{inj,PZ}$, u and D_{N_2O} in equation (3.8) to (3.10) are the independent variables used to fit the equations to the experimental data. D_{PZ} is taken from Derks [25], and the influence of N_2O present in the current work on this value is neglected. The value of D_{PZ} represents the dispersion of the 'negative' pulse in Figure 3.3 through equation (3.10). The other parameters are defined in Table 3.1.

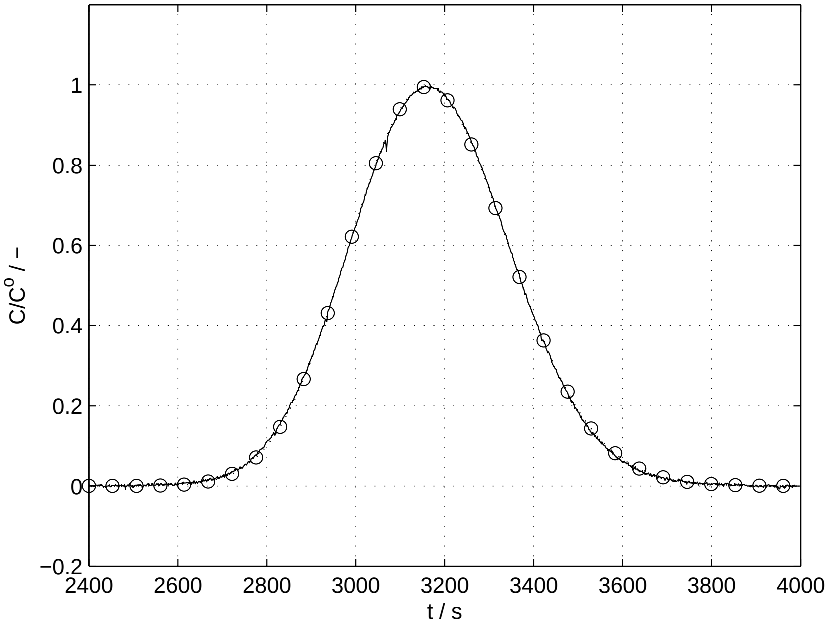

Figure 3.2: Typical result from a N_2O/H_2O system: −, exp. result; · · ○ · ·, fit

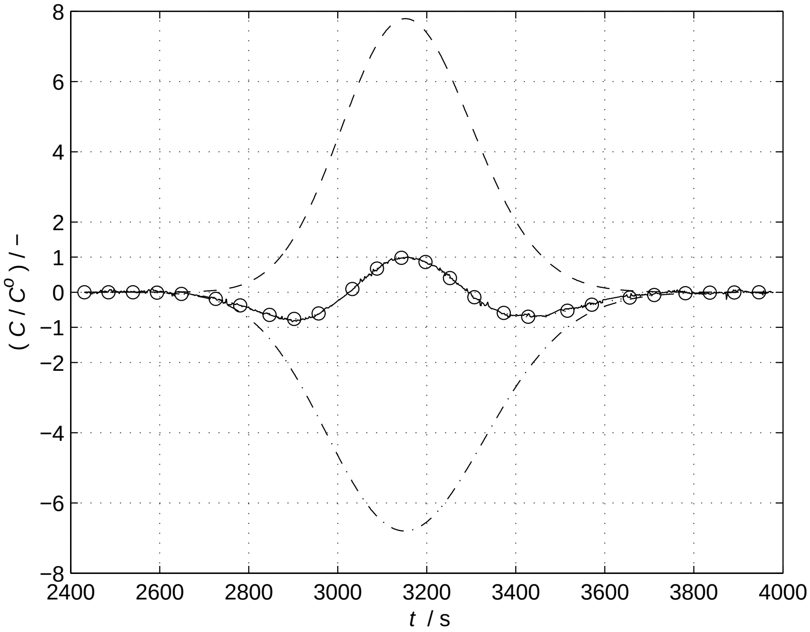

Figure 3.3: Typical result from a $N_2O/(PZ + H_2O)$ system: −, exp. result; · · ○ · ·, fit; −−, N_2O response; -·-·, PZ response

3.2.3 Chemicals

The amine solutions were prepared by dissolving known amounts of PZ [110-85-0] (purity 99%, Aldrich) and/or MDEA [105-59-9] (purity 98%, Aldrich) in double distilled water. The actual amine concentrations in the prepared solution were measured (at T = 293 K) by means of a volumetric titration with 1.0 mol·L^{-1} HCl. The experimentally determined PZ and MDEA concentrations were accurate to within 1.0% of the concentrations as determined by the weight ratios of the components. The methanol [67-56-1] (purity 99%, Aldrich) solutions in water, used in validation experiments, were prepared in a similar manner. The helium gas [7440-59-7] used was supplied by Hoekloos.

3.3 Results and discussion

3.3.1 Validation

The diffusion coefficients of the binary system methanol-water were determined in order to validate the experimental setup. The critical (De)^{2}Sc number was determined to be about 150 for this system. The experimentally obtained diffusion coefficients measured at different composition and temperature are listed in Table 3.2 and 3.3, and a graphical comparison of the present data with literature data [92, 54, 31, 58] is given in Figure 3.4 and 3.5. It can be concluded that the newly obtained experimental diffusivity data are very well in line with the experimental data available in the literature.

Table 3.2: Diffusion coefficient, D_{methanol}, of methanol in water at 308.15 K as a function of mole fraction, x_{methanol}.

x_{methanol}	D_{methanol} / 10^{-9}·m^2·s^{-1}
0.00	1.89
0.01	1.81
0.10	1.51
0.20	1.31
0.30	1.26
0.40	1.18
0.50	1.27
0.60	1.36
0.80	1.91
1.00	2.62

Table 3.3: Infinite dilution diffusion coefficient, $D_{0,\mathrm{methanol}}$, of methanol in water as a function of temperature T

T / K	$D_{0,\mathrm{methanol}}$ / 10^{-9}·m^2·s^{-1}
298.15	1.55
313.15	2.39
333.15	3.58
353.15	4.68
363.15	5.39

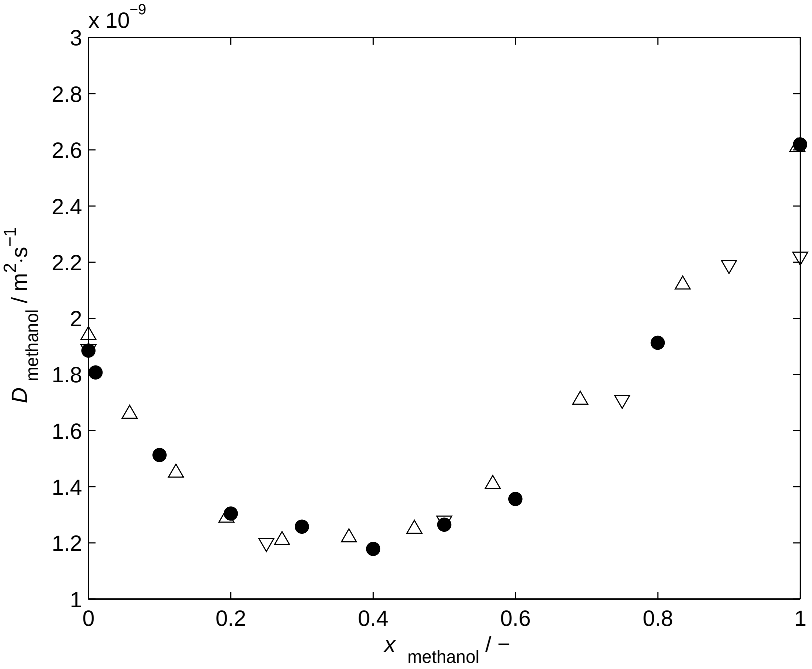

Figure 3.4: Diffusion coefficient, D_{methanol}, of methanol in water at 308.15 K as a function of mole fraction, x_{methanol}. ●, this work; △, van de Ven-Lucassen et al. [92]; ▽, Lee & Li [54]

3.3.2 Liquid diffusivities in aqueous PZ solutions

Liquid diffusivities in aqueous PZ solution were measured over a concentration range of (0 to 1.4) kmol·m^{-3} PZ and temperatures between (293.15 and 368.15) K. The results (averaged over at least three experiments) are listed in Table 3.4. The critical (De)^{2}Sc was 150 for this system.

As in the work of Snijder et al. [86], all experimental diffusion coefficients were correlated using one equation accounting for the influence of both temperature (T in K) and concentration (C_{PZ} in mol·m^{-3}). The resulting relation is given in Eq. (3.11), which was able to correlate all experimental data with an average deviation of less than 4% (maximum deviation 9%).

$$ln(D) = -13.672 + \frac{-2160.9}{T} - 19.263 \cdot 10^{-5} \cdot C_{PZ} \tag{3.11}$$

Versteeg & Van Swaaij [96] suggested a modified Stokes-Einstein relation to estimate the amine diffusion coefficient from the solution's viscosity according to Eq. (3.12). Snijder et al. [86] showed in their work that this relation is able to predict the diffusion coefficients of various alkanolamines (MEA, DEA, MDEA and DIPA) in aqueous solution over a wide range of temperatures and concentrations.

$$\frac{D}{D_0} = \left(\frac{\mu_0}{\mu}\right)^{0.6} \tag{3.12}$$

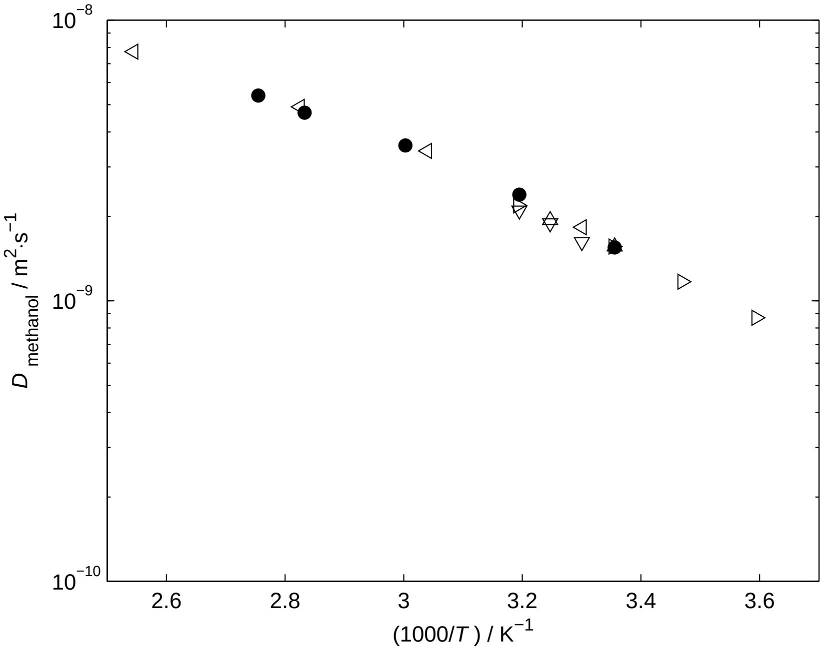

Figure 3.5: Infinite dilution diffusion coefficient, $D_{0,\text{methanol}}$, of methanol in water as a function of temperature T. ●, this work; △, van de Ven-Lucassen et al. [92]; ▽, Lee & Li [54]; ▷, Easteal & Woolf [31]; ◁, Matthews & Akgerman [58]

where μ_0 is the viscosity of pure water, μ is the viscosity of the solution and D_0 is the diffusion coefficient at infinite dilution. Measuring viscosities are usually very straightforward, whereas the experimental determination of D_0 is a more laborious task. In the literature, several correlations have been proposed to estimate the diffusion coefficient at infinite dilution. In the present work, six of these estimation methods are compared and evaluated on their ability to predict the infinitely dilute diffusion coefficient of PZ in water. An important parameter in all methods is the molar volume of PZ at the normal boiling point, which was estimated using the method of Le Bas [73]. This value (0.1052 m^3·kmol^{-1}) was compared to the result obtained with an extrapolation relation given by Steele et al. [87] in their study on PZ's critical constants. As both methods yielded a similar value, the value of Le Bas [73] was found reliable to use in the diffusion coefficient estimations. The values calculated with the estimation methods are compared to the experimental diffusion coefficients at infinite dilution, taken from Table 3.4 at $C_{ref,PZ}$ in the order of 10^{-3} kmol·m^{-3}, and the results are listed in Table 3.5 and shown graphically in Figure 3.6.

Both Table 3.5 and Figure 3.6 clearly illustrate that only the prediction method of Othmer & Thakar [66] is able to predict the piperazine diffusion coefficient at infinite dilution in water within 10% over the complete temperature range. Also the Hayduk & Laudie [38] equation seems to be a suitable prediction method, although it consistently overpredicts the experimental value with

Table 3.4: Diffusion of PZ in aqueous PZ solutions

T / K	$C_{ref,PZ}$ / kmol·m^{-3}	D / 10^{-9}·m^2·s^{-1}
293.15	$0.8\cdot10^{-3}$	0.757
	0.284	0.660
	0.602	0.617
	0.907	0.560
	1.46	0.511
298.15	$0.8\cdot10^{-3}$	0.889
	0.285	0.762
	0.602	0.714
	0.908	0.666
	1.46	0.607
303.15	$0.9\cdot10^{-3}$	1.01
	0.285	0.870
	0.602	0.799
	0.908	0.754
	1.46	0.715
313.15	$1.0\cdot10^{-3}$	1.27
	0.285	1.11
	0.603	1.05
	0.910	0.972
	1.46	0.948
333.15	$1.2\cdot10^{-3}$	1.83
	0.285	1.66
	0.604	1.59
	0.913	1.52
	1.47	1.41
353.15	$1.4\cdot10^{-3}$	2.47
	0.287	2.36
	0.605	2.24
	0.915	2.15
	1.47	2.01
368.15	$1.6\cdot10^{-3}$	3.06
	0.287	2.89
	0.606	2.82
	0.917	2.60
	1.48	2.59

about 10%. Both the method of Scheibel [81] and the modified Wilke-Chang [38] relation provide satisfactory results up to a temperature of 313.15 K, but with increasing temperature the agreement between prediction and experiment gradually deteriorates. In the study of Snijder et al. [86] on the diffusion of MEA, DEA, MDEA and DIPA in aqueous solution, the method of Othmer & Thakar [66] was also found to give the best prediction results (together with the modified Wilke-Chang correlation).

Next, the applicability of the modified Stokes-Einstein relation (Eq. (3.12)) was evaluated for the diffusion of PZ, using the experimental viscosity data reported by Derks et al. [26] and the experimental diffusion coefficients from

Table 3.5: Methods to estimate the diffusion coefficient of PZ at infinite dilution in water

Method	Reference	Symbol in Figure 3.6	Avg. dev. / %
Othmer-Thakar	[66]	○	5.6
Wilke-Chang	[97]	△	20
Hayduk-Minas	[39]	▽	20
Scheibel	[81]	▷	12
Hayduk-Laudie	[38]	◁	11
Modified Wilke-Chang[a]	[38]	□	12

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[a] Hayduk-Laudie [38] recommended to adjust the water association parameter in the Wilke-Chang relation from 2.6 to a value of 2.26.

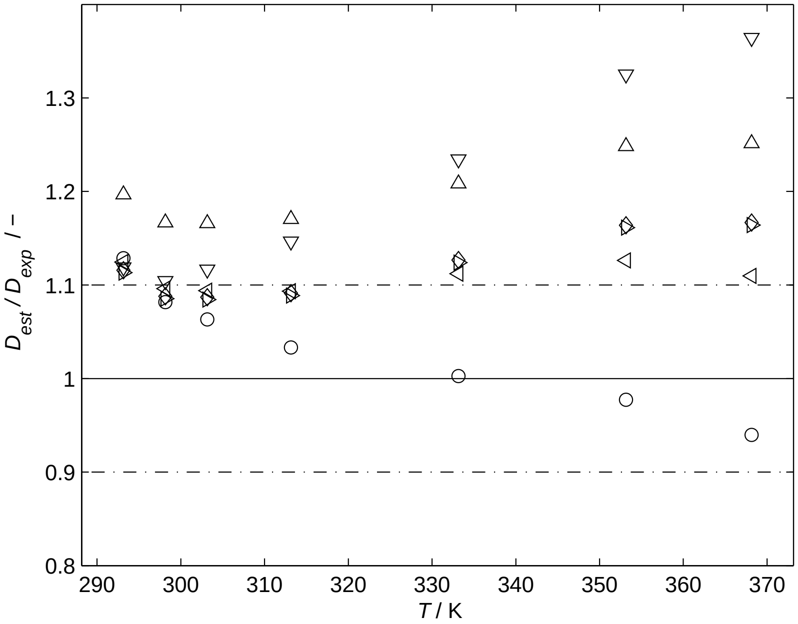

Figure 3.6: Comparison between the experimental infinitely dilute diffusion coefficient and the estimated value according to the estimation methods applied. ○, Othmer - Thakar; △, Wilke - Chang; ▽, Hayduk - Minas; ▷, Scheibel; ◁, Hayduk - Laudie; □, modified Wilke - Chang. References are given in Table 3.5

Table 3.4. For this purpose, a double logarithmic plot of Eq. (3.12) is shown in Figure 8. Despite the fact there seems to be a small offset between some of the experimental data and the solid line representing Eq. (3.7), it may still be concluded that the modified Stokes-Einstein relation can be used for estimating PZ diffusivities in aqueous PZ systems (at concentrations < 1.5 kmol·m^{-3}) satisfactorily, as the deviation is always within about 10%.

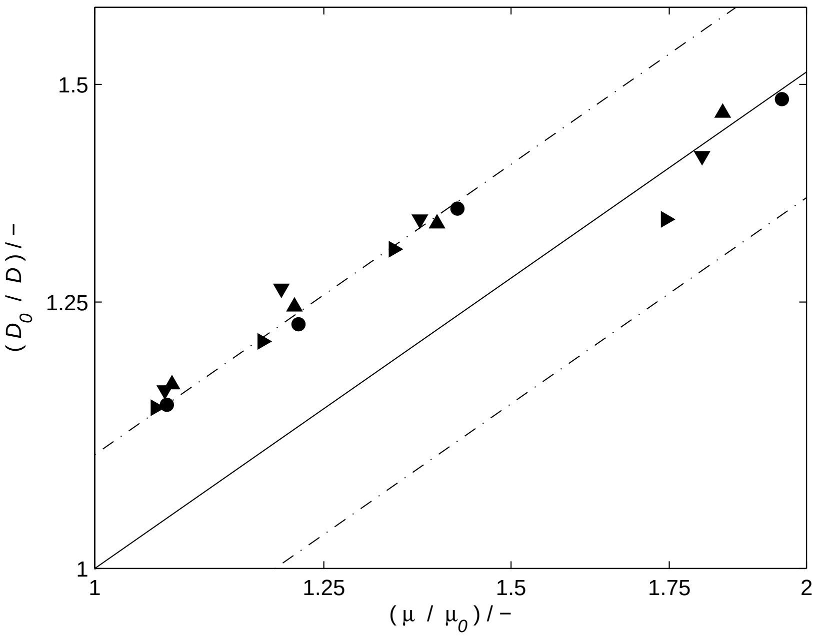

Figure 3.7: Stokes-Einstein plot for the diffusion coefficient of PZ in aqueous PZ solutions: ●, 293 K; ▲, 298.15 K; ▼, 303.15 K; ▶, 313.15 K; The solid line represents Eq. (3.12) and the dashed lines represents ±10%

3.3.3 Liquid diffusivities in aqueous (PZ + MDEA) solutions

Diffusivities in ternary (and multicomponent) systems have, in a large part, been determined by the use of interferometry at ambient temperatures. Amongst others, Miller [62, 63] has conducted extensive work on this subject. Lately, the Taylor dispersion technique has also been used to determine diffusivities in ternary liquid systems. [35] In kinetic models describing aqueous solutions of (PZ + MDEA) as possible CO_2 absorbents, apparent diffusivities are used [10, 99, 100, 25] and multi-component diffusion effects such as cross diffusion are thus neglected. The purpose of the present work is to determine diffusivities in the aqueous (PZ + MDEA) system to give insight into apparent diffusivities used in absorption models for these ternary systems.

The apparent diffusion coefficients of both PZ and MDEA in aqueous solutions containing 4.0 kmol·m^{-3} MDEA and (0, 0.5 or 1.0) kmol·m^{-3} PZ were measured at temperatures between (298.15 and 368.15) K. During measurements of PZ diffusivities in aqueous (PZ + MDEA) solutions, the concentration of MDEA was kept at a constant 4.0 kmol·m^{-3} concentration in both the solute and the solvent, e.g. no concentration gradient of MDEA in the fluid traversing through the capillary coil. The solute contained a slightly higher concentration of PZ than the solvent, e.g. an addition of approx. 0.05 kmol·m^{-3}. Cross diffusion effects present in ternary systems are neglected in these measurements.

During measurements of MDEA diffusivities in aqueous (PZ + MDEA) solutions, the concentration of PZ was kept constant in both the solute and the solvent as described whereas the solute contained a slightly higher concentration of MDEA (an addition of approx 0.05 kmol·m^{-3}) than the solvent. The results (averaged over at least three experiments) are listed in Table 3.6. All experiments were carried out with (De)^{2}Sc < 47.

Similarly to the results obtained for the aqueous PZ system, the experimentally obtained results listed in Table 3.6 are compared to predictions made with the modified Stokes-Einstein equation (Eq. (3.12)). The MDEA diffusion coefficient at infinite dilution was taken from the work of Snijder et al. [86]. Due to a lack of viscosity data, this comparison is limited to the conditions of which the viscosity data are listed in this work and by Rinker et al. [76]. Figure 3.8 shows that an agreement exists between the experimentally obtained PZ and MDEA diffusivities and the values obtained using the modified Stokes-Einstein equation.

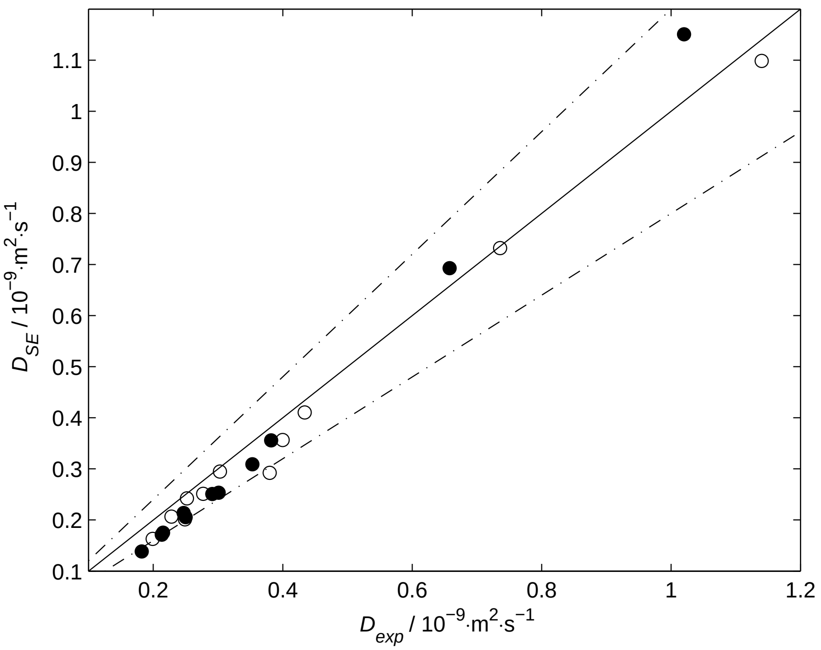

Figure 3.8: Comparison between the experimentally determined diffusion coefficients,D_{exp}, and the values estimated with the Stokes-Einstein equation, D_{SE}: •, PZ; ◦, MDEA ; The dashed lines represents ±20%

3.3.4 Diffusivity of N_2O in H_2O

Measurements were conducted on the system N_2O/H_2O from (293 to 368) K to evaluate the accuracy of the equipment used. The critical (De)^{2}Sc number was found to be 130 for this system. Figure 3.9 shows the experimental results of N_2O diffusion in H_2O, and the results are tabulated in Table 3.7. The values are the average value of at least three measurements, and the results of the present study are in agreement with the results reported by previous authors using different experimental techniques. [23, 29, 37, 78, 46, 96, 91, 79]

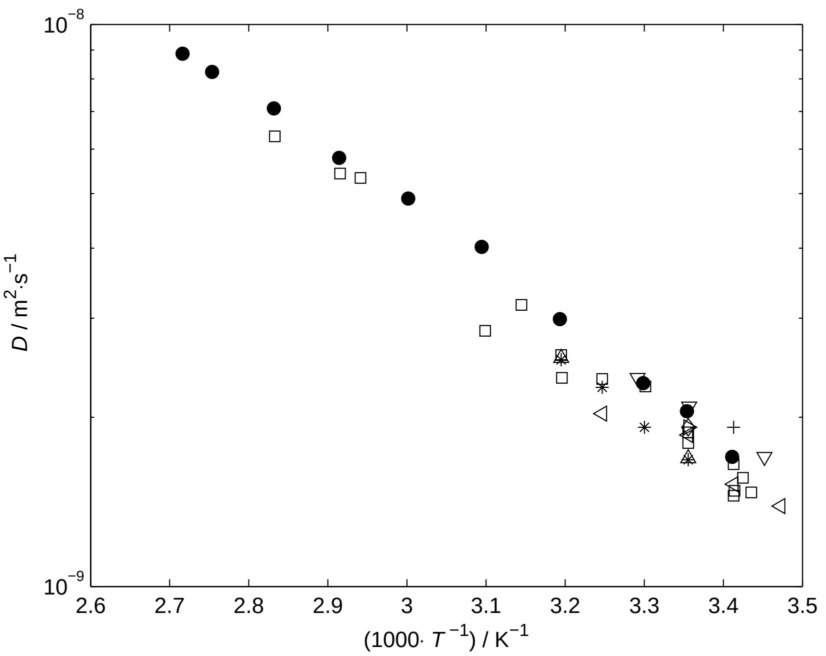

Figure 3.9: Experimental results of N_2O diffusion in H_2O: ●, exp. results this work; ▽, Davidson & Cullen [23]; △, Duda & Vrentas [29]; ◁, Haimour & Sandall [37]; ▷, Sada et al. [78]; ◊, Joosten & Danckwerts [46]; □, Versteeg & Van Swaaij [96]; +, Thomas & Adams [91]; ∗, Samanta et al. [79]

Table 3.6: Diffusion coefficients of PZ and MDEA in aqueous (PZ + MDEA) solutions

$\frac{T}{\text{K}}$	$\frac{C_{MDEA}}{\text{kmol} \cdot \text{m}^{-3}}$	$\frac{C_{ref,PZ}}{\text{kmol} \cdot \text{m}^{-3}}$	$\frac{D_{PZ}}{10^{-9} \cdot \text{m}^2 \cdot \text{s}^{-1}}$	$\frac{C_{PZ}}{\text{kmol} \cdot \text{m}^{-3}}$	$\frac{C_{ref,MDEA}}{\text{kmol} \cdot \text{m}^{-3}}$	$\frac{D_{MDEA}}{10^{-9} \cdot \text{m}^2 \cdot \text{s}^{-1}}$
298.15	4.0	$0.6 \cdot 10^{-3}$	0.252	0	3.99	0.250
	4.0	0.504	0.228	0.5	3.96	0.215
	4.0	1.00	0.199	1.0	4.02	0.182
303.15	4.0	$0.6 \cdot 10^{-3}$	0.303	0	3.99	0.291
	4.0	0.504	0.277	0.5	3.96	0.247
	4.0	1.01	0.249	1.0	4.02	0.213
313.15	4.0	$0.7 \cdot 10^{-3}$	0.434	0	3.99	0.382
	4.0	0.506	0.400	0.5	3.96	0.353
	4.0	1.01	0.380	1.0	4.02	0.301
333.15	4.0	$1.0 \cdot 10^{-3}$	0.736	0	4.00	0.658
	4.0	0.509	0.716	0.5	3.98	0.610
	4.0	1.01	0.662	1.0	4.03	0.538
353.15	4.0	$1.2 \cdot 10^{-3}$	1.14	0	4.01	1.02
	4.0	0.516	1.10	0.5	3.99	0.964
	4.0	1.02	1.12	1.0	4.04	0.886
368.15	4.0	$1.3 \cdot 10^{-3}$	1.48	0	4.02	1.34
	4.0	0.519	1.46	0.5	3.99	1.27
	4.0	1.02	1.47	1.0	4.05	1.16

Table 3.7: Diffusivity of N_2O in H_2O at various temperatures

T / K	D / 10^{-9}·m^2·s^{-1}	Reference		Method[a]
288.00	1.39	Haimour & Sandall	[37]	LLJ
289.70	1.70	Davidson & Cullen	[23]	WWA
291.10	1.47	Versteeg & Van Swaaij	[96]	DC
292.00	1.56	Versteeg & Van Swaaij	[96]	DC
292.90	1.48	Versteeg & Van Swaaij	[96]	DC
293.00	1.52	Haimour & Sandall	[37]	LLJ
293.00	1.92	Thomas & Adams	[91]	LLJ
293.00	1.45	Versteeg & Van Swaaij	[96]	DC
293.00	1.65	Versteeg & Van Swaaij	[96]	DC
293.15	1.70	this work		TDT
297.90	2.09	Davidson & Cullen	[23]	WWA
298.00	1.86	Haimour & Sandall	[37]	LLJ
298.00	1.69	Duda & Vrentas	[29]	LLJ
298.00	1.92	Joosten & Danckwerts	[46]	LLJ
298.00	1.78	Sada et al.	[78]	LLJ
298.00	1.88	Versteeg & Van Swaaij	[96]	DC
298.00	1.80	Versteeg & Van Swaaij	[96]	DC
298.00	1.68	Samanta et al.	[79]	WWA
298.15	2.05	this work		TDT
302.90	2.27	Versteeg & Van Swaaij	[96]	DC
303.00	1.92	Samanta et al.	[79]	WWA
303.15	2.30	this work		TDT
303.80	2.35	Davidson & Cullen	[23]	WWA
308.00	2.03	Haimour & Sandall	[37]	LLJ
308.00	2.34	Versteeg & Van Swaaij	[96]	DC
308.00	2.26	Samanta et al.	[79]	WWA
312.90	2.35	Versteeg & Van Swaaij	[96]	DC
313.00	2.55	Duda & Vrentas	[29]	LLJ
313.00	2.58	Versteeg & Van Swaaij	[96]	DC
313.00	2.53	Samanta et al.	[79]	WWA
313.15	2.99	this work		TDT
318.00	3.17	Versteeg & Van Swaaij	[96]	DC
322.70	2.85	Versteeg & Van Swaaij	[96]	DC
323.15	4.02	this work		TDT
333.15	4.90	this work		TDT
340.00	5.33	Versteeg & Van Swaaij	[96]	DC
343.00	5.43	Versteeg & Van Swaaij	[96]	DC
343.15	5.79	this work		TDT
353.00	6.32	Versteeg & Van Swaaij	[96]	DC
353.15	7.09	this work		TDT

continued on next page

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[a] LLJ = laminar liquid jet; DC = diaphragm cell; WWA = wetted wall absorber; TDT = Taylor dispersion technique

continued from previous page

T / K	D / 10^{-9}·m^2·s^{-1}	Reference	Method[a]
363.15	8.23	this work	TDT
368.15	8.87	this work	TDT

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[a] LLJ = laminar liquid jet; DC = diaphragm cell; WWA = wetted wall absorber; TDT = Taylor dispersion technique

3.3.5 Diffusivity of N_2O in aqueous PZ solutions

The experimental determined diffusivities of N_2O in (PZ + H_2O) were measured and averaged over at least three measurements from (293 to 333) K and (0.3 to 1.4) kmol·m^{-3}. These results are presented in Table 3.8. The critical (De)^{2}Sc number was found to be 80 for this system. The diffusivities were also calculated at different temperatures and concentration with the modified Stokes-Einstein relation [96]:

$$\frac{D_{N_2O \text{ in PZ sol.}}}{D_{N_2O \text{ in } \mathrm{H_2O}}} = \left(\frac{\mu_{H_2O}}{\mu_{PZ \text{ sol.}}}\right)^{0.8} = \text{constant} \tag{3.13}$$

where the viscosities μ_{H_2O} and $\mu_{PZ \text{ sol.}}$ were taken from Lide [55] and Derks et al. [26], respectively. The viscosities from Derks et al. [26] were extrapolated to 333.15 K. The diffusivity of N_2O in H_2O was calculated by the equation presented by Versteeg & Van Swaaij [96]:

$$D_{N_2O \text{ in } \mathrm{H_2O}} = 5.07 \cdot 10^{-6} exp\left(\frac{-2371}{T}\right) \tag{3.14}$$

A Stokes-Einstein logarithmic plot for the diffusivity of N_2O in aqueous PZ solutions is shown in Figure 3.10. The modified Stokes-Einstein relation can be used to calculate N_2O diffusivities in aqueous PZ solutions satisfactorily from (293 to 333) K and up to approximately 1.4 kmol·m^{-3}. The average and maximum absolute relative deviation between the experimental determined values and the calculated values are 3.0 % and 6.4 %, respectively. The diffusivity of CO_2 in an aqueous PZ solution can be estimated by the "N_2O analogy". [96]

Table 3.8: Diffusivity of N_2O in aqueous PZ solutions at various temperatures and solvent concentrations

C_{PZ} / kmol · m^{-3}	T / K					
	293.15	298.15	303.15	313.15	323.15	333.15
	D_{N_2O} / 10^{-9}·m^2·s^{-1}					
0.295	1.44	1.60	1.83	2.41	2.99	3.61
0.629	1.24	1.46	1.70	2.10	2.69	3.31
1.067	1.13	1.32	1.54	2.00	2.47	3.00
1.368	1.02	1.24	1.37	1.76	2.19	2.85

Diffusivities of N_2O in aqueous PZ solutions have been reported by Samanta et al. [79] and Sun et al. [88] at 303 K and 313 K. These data are compared to the results from the present work at 303.15 K and 313.15 K in Figure 3.11 and the calculated values from the modified Stokes-Einstein relation. The values from the present work have a relative absolute average deviation of 2.4 % and 2.8 % from the calculated values at 303.15 K and 313.15 K, respectively. The

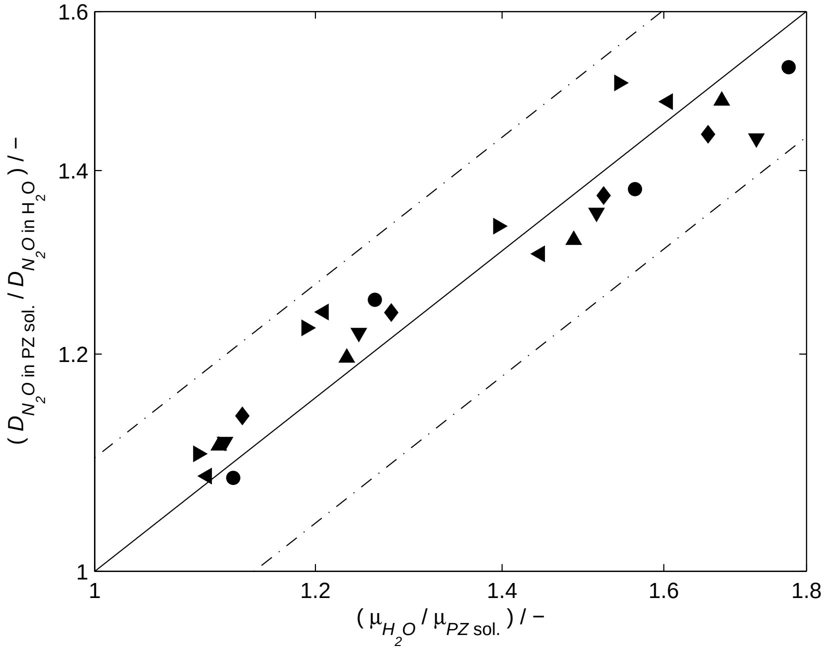

Figure 3.10: Stokes-Einstein plot for D_{N_2O} in aqueous PZ solutions: ●, T = 293.15 K; ▼, T = 298.15 K; ▲, T = 303.15 K; ◀, T = 313.15 K; ▶, T = 323.15 K; ♦, T = 333.15 K; The solid line represents equation (3.13) and the dashed lines represent ±10%

values from Samanta et al. [79] deviates with 1.9 % and 5.6 % at 303 K and 313 K and the values of Sun et al. [88] deviates with 5.2 % and 3.0 %, respectively, from the calculated values. Samanta et al. [79] and Sun et al. [88] both used a wetted wall absorber to determine the diffusivities. Figure 3.11 shows that the method developed and described in the present work can be used to determine gas diffusivities in binary liquid systems with sufficient accuracy.

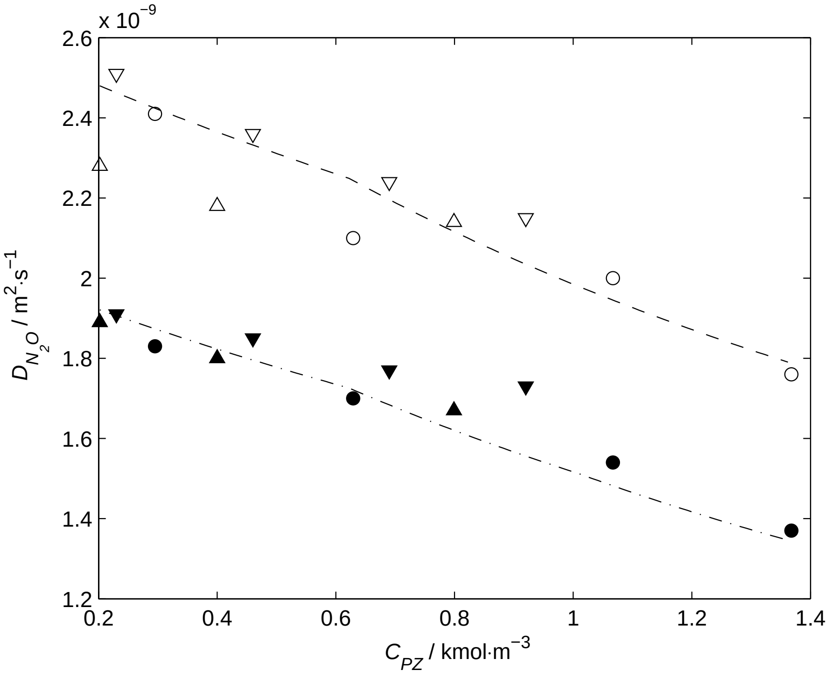

Figure 3.11: Comparison of D_{N_2O} to literature sources: ●, T = 303.15 K present work; ▼, T = 303 K Sun et. al [88]; ▲, T = 303 K Samanta et al. [79]; -·-·, T = 303.15 K modified Stokes-Einstein; ○, T = 313.15 K present work; ▽, T = 313 K Sun et al. [88]; △, T = 313 K Samanta et al. [79]; - - -, T = 313.15 K modified Stokes-Einstein

3.4 Conclusion

The diffusion coefficient of piperazine in aqueous PZ solutions was measured at different PZ concentrations and temperatures using the Taylor dispersion technique. It was found that the modified Stokes-Einstein equation was able to predict the experimental diffusivities with an average deviation of less than 10 %. The diffusivities of MDEA and PZ were determined for an aqueous 4.0 kmol m^{-3} MDEA solution blended with 0, 0.5 and 1.0 kmol m^{-3} PZ at temperatures ranging from 298.15 to 338.15 K.

The diffusivities of N_2O in aqueous PZ solutions have been determined from (293 to 333) K and (0.3 to 1.4) kmol·m^{-3}. The diffusivity of N_2O and CO_2 can be calculated and estimated respectively with a modified Stokes-Einstein relation.

Gas diffusivities can be measured by the taylor dispersion technique in a binary liquid system.

Chapter 4

Diffusivities in Aqueous Amino Acid Salt Solutions

4.1 Introduction

Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating. Alkanolamines can undergo degradation in oxygen atmosphere, usually encountered in the treatment of flue gases. The relative high volatility of alkanolamines also leads to losses of the compound during commercial operation of CO_2 capture plants. Aqueous amino acid salts solutions might be an attractive alternative to alkanolamines. They have been found to have better resistance to oxidative degradation, and their reactivity with CO_2 is comparable to aqueous alkanolamines of related classes. The ionic nature of aqueous amino acid salt solutions result in a negligible volatility. [50, 42, 70, 53, 93]

Knowledge of diffusion coefficients is neede for the design of absorbers and desorbers in a commercial CO_2 capture plant, as they are related to the mass transfer coefficients. They are also essential for a correct and accurate interpretation of many (lab scale) absorption rate experiments, e.g. experiments aimed to determine the intrinsic kinetics in a gas-liquid process. The liquid diffusivities in the aqueous solutions of the potassium salt of taurine, sarcosine, L-proline and glycine determined by the Taylor dispersion technique at temperatures from (293 to 368) K and concentration ranges from (0 to 3.0) $\text{kmol}\cdot\text{m}^{-3}$ are presented in this work. The diffusivities of N_2O in the same solutions determined with the same technique at temperatures from (293 to 333) K and concentration range from (1.0 to 3.0) $\text{kmol}\cdot\text{m}^{-3}$ are also presented. The results are correlated and compared to literature values.

The visocisoties of the potassium salt of sarcosine and L-proline have been determined from (298 to 333) K and from (0.5 to 3.0) $\text{kmol}\cdot\text{m}^{-3}$ for the potassium salt of sarcosine sarcosine and to 3.5 $\text{kmol}\cdot\text{m}^{-3}$ for the potassium salt of L-proline.[1] The liquid diffusivities in the aqueous solutions of the potassium salt of taurine, sarcosine, L-proline and glycine have been determined by the taylor

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[1] This work was carried out by Jacco van Holst. The results are given here for the convenience of the reader only.

dispersion technique at temperatures from (293 to 368) K and concentration ranges from (0 to 3.0) kmol·m^{-3}. The diffusivities of N_2O in the same solutions have been determined with the same technique at temperatures from (293 to 333) K and concentration range from (1.0 to 3.0) kmol·m^{-3}. The results are presented and correlated in the this work.

4.2 Theory and experimental procedures

4.2.1 Amino acid salt preparation

The respective aqueous amino acid salt solutions were prepared by adding equimolar amounts of the amino acid and KOH. The aqueous amino acid zwitterion will be deprotonated according to:

$$^{-}OOC - R - NH_3^+ + KOH \rightarrow K^+ +^- OOC - R - NH_2 + H_2O \qquad (4.1)$$

and form a potassium amino acid salt. The concentration of the amino acid salt was checked by means of titration.

4.2.2 Viscositiy

The viscosities were measured using a PSL Ubbelohde viscometer (type ASTM-IP, size 0), submerged in a thermostatbath for temperature control within ±0.1 K. [1]

4.2.3 General theory of the Taylor dispersion technique

The diffusivities were determined using the Taylor dispersion technique. A square pulse of a solute solution is injected into a solvent solution showing laminar flow through a capillary tube. The solute solution contains the same components as the solvent solution, but with a slightly higher concentration of the compound of which diffusivities are to be determined (an addition of approx. 0.05 kmol·m^{-3}). In the case of gas measurements; the solute solution contains the same amounts of liquid components as the solvent solution, but with additional N_2O gas absorbed. As an example of liquid measurements; for measurements of diffusivities in a approx. 1.00 kmol·m^{-3} of K^+taurine, the solvent solution would contain 1.00 kmol·m^{-3} K^+taurine. The solute solution would contain 1.05 kmol·m^{-3} K^+taurine, and a square pulse of this solution would be injected into the flowing solvent solution. For gas measurements at 1.00 kmol·m^{-3} of K^+taurine, both the solvent and solute solution would contain 1.00 kmol·m^{-3} of K^+taurine. The solute solution would contain additional absorbed N_2O, and a square pulse of this solution would be injected into the flowing solvent. The combined action of axial convection and radial and axial molecular diffusion will eventually change the pulse into a gaussian curve. The theory, mathematical description and procedure of such diffusivity measurements have been described in detail by Taylor [89, 90], Aris [5] and in section 3.2.

The experimental setup used is shown schematically in Figure 4.1. Two vessels containing the solute solution and the solvent solution are kept under a

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[1] This work was carried out by Jacco van Holst. The results are given here for the convenience of the reader only.

constant 5 bar pressure of saturated helium in order to create a constant flow of the solute and the solvent. Saturated helium is used in order to prevent any concentration changes in the solute and solvent solution as the liquid level in the two closed vessels containing the solutions decrease during a measurement due to the solution outflow. Introduction of a solute pulse is done by switching an air actuated six way valve back and forth within a few seconds. The capillary tube is elliptical coiled and placed in a water bath for temperature control. The flow velocity is controlled with mass flow controllers (Rosemount Flowmega 5881), located behind the refractive index (RI) detector (Varian 350 RI) and the six way pulse valve in order to obtain a constant pulsation-free solute and solvent solution flow throughout the measurement. In order to avoid bubble formation inside the tubing and a disturbance of the laminar fluid flow profile, especially at higher temperatures and/or during gas diffusion measurements, pressure reducers are located behind the RI detector and the six-way pulse valve. These reducers pressurizes the fluids inside the tubing to 4 bara. The influence of the pressure on the diffusion coefficients can be neglected for the pressure applied. [31, 59] Prior to each experiment, both the solute and solvent solution were degassed by applying vacuum for a while, and further the RI detector was calibrated. For gas diffusion measurements, N_2O was absorbed into the solute solution by bubbling the gas up to 1.5 bara into a closed vessel containing the solution. A computer is connected to the setup for control and data acquisition. The output signal from the RI detector is recorded as a function of time and used to determine the molecular diffusion coefficients. The RI detector showed a linear response to concentration changes of the potassium amino acid salts and N_2O in the solutions investigated. The dimensions of the experimental setup and the flow conditions are given in Table 4.1.

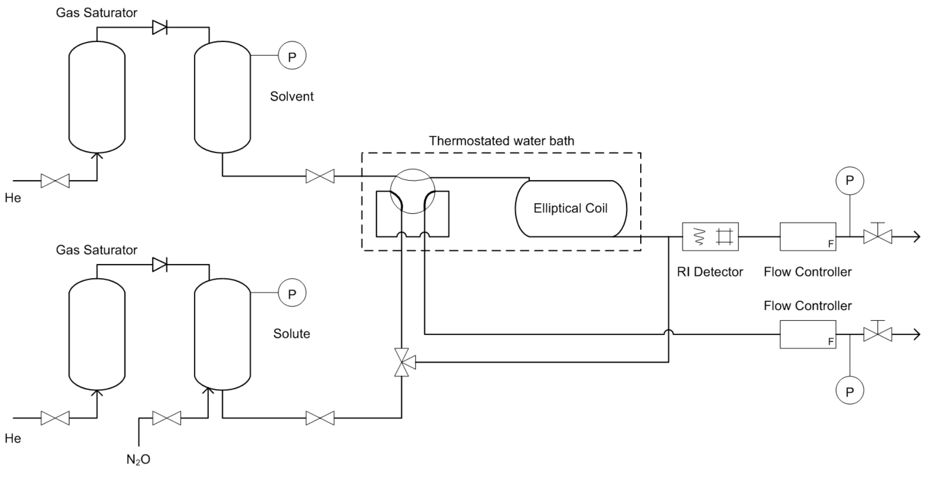

Figure 4.1: Schematic representation of the Taylor dispersion setup

A disturbance of the laminar fluid flow profile can occur due to the elliptic coiling of the tube. The varying path lengths traversed by the fluid at different radial positions in the tube and the secondary flows present in the flow can contribute additionally to the dispersion process. This topic has been extensively discussed by Alizadeh et al. [4] and Snijder et al. [86]. In order to avoid

Table 4.1: Dimensions of the experimental setup and flow conditions

Length of the capillary tube	L	14.92 m
Inner radius of the capillary tube	R	$5.14 \cdot 10^{-4}$ m
Radius of the helical coil	R_C	0.1 m
Injection volume	V_{inj}	$(2.5 \text{ to } 4.1) \cdot 10^{-8}$ m^3
Liquid flow velocity	u	$(2 \text{ to } 6) \cdot 10^{-3}$ m$\cdot$s^{-1}

this disturbance, the critical $(\mathrm{De})^2\mathrm{Sc}$ was determined for each system. The dimensionless $(\mathrm{De})^2\mathrm{Sc}$ number is defined as:

$$De = Re\left(\frac{R_C}{R}\right)^{-1/2} \tag{4.2}$$

$$Sc = \frac{\mu}{\rho D} \tag{4.3}$$

where Re is the well-known Reynolds number and μ and ρ are the solvent viscosity and density. The other parameters are defined in Table 4.1. The measurements had to be carried out at a value of $(\mathrm{De})^2\mathrm{Sc}$ lower than the critical one.

4.2.4 Liquid diffusivities

The results of liquid diffusivity measurements can be described by: [89, 90, 5]

$$C_m = \frac{N_{inj,AAS}}{2\pi R^2\sqrt{\pi K_{AAS} t}} exp\left(-\frac{(L-ut)^2}{4K_{AAS}t}\right) \tag{4.4}$$

$$K_{AAS} = \frac{u^2 R^2}{48 D_{AAS}} + D_{AAS} \tag{4.5}$$

where C_m is the measured concentration profile at the end of the capillary tube, $N_{inj,AAS}$ is the excess number of moles of amino acid salt injected, t is the time, and D_{AAS} is the binary molecular diffusion coefficient. The subscript AAS refers to the aqueous amino acid salt. $N_{inj,AAS}$, u and D_{AAS} are the independent parameters used to curvefit equation (4.4) and (4.5) to the experimentally recorded results. The other parameters are defined in Table 4.1. Since the concentration of the solute pulse decreases because of dispersion while the solute pulse is traversing with the solvent through the tubing, an average concentration value has to be determined. Alizadeh et al. [4] referred to this as the reference concentration C_{ref} given by:

$$C_{ref} = C_{solv} + \frac{N_{inj,AAS}\left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}}\right)}{\pi R^2\sqrt{2K_{AAS}\dot{t}}} \tag{4.6}$$

where C_{solv} is the solvent concentration and $\dot{t}$ is the time at which the measurement ends.

4.2.5 Gas diffusivity

The experimental procedure used to determine N_2O diffusivities in aqueous solutions by the Taylor dispersion technique has been given in detail in section 3.2. The recorded pulses are described by equation (4.7) to (4.9):

$$C_m = \frac{N_{inj,N_2O}}{2\pi R^2\sqrt{\pi K_{N_2O}t}} exp\left(-\frac{(L-ut)^2}{4K_{N_2O}t}\right) + \frac{N_{inj,AAS}}{2\pi R^2\sqrt{\pi K_{AAS}t}} exp\left(-\frac{(L-ut)^2}{4K_{AAS}t}\right) \tag{4.7}$$

$$K_{N_2O} = \frac{u^2R^2}{48D_{N_2O}} + D_{N_2O} \tag{4.8}$$

$$K_{AAS} = \frac{u^2R^2}{48D_{AAS}} + D_{AAS} \tag{4.9}$$

where C_m is the measured concentration profile, N_{inj,N_2O} and $N_{inj,AAS}$ are the respective numbers of moles of N_2O and excess number of moles of potassium amino acid salt injected, t is the time and D_{N_2O} and D_{AAS} are the respective molecular diffusion coefficients of N_2O and potassium amino acid salt in the aqueous potassium amino acid salt solution. The other parameters are defined in Table 4.1. The parameters N_{inj,N_2O}, $N_{inj,AAS}$, u and D_{N_2O} are the independent variables used to fit the equations to the experimental data. The value of D_{AAS} is from the previous measurement as aforementioned, and the influence of N_2O present in the current measurement on this value is neglected.

4.2.6 Chemicals

Taurine [107-35-7], sarcosine [107-97-1], glycine [56-40-6], L-proline [147-85-3], KOH [1310-58-3] (Sigma-Aldrich), N_2O [10024-97-2] and helium [7440-59-7] (Linde Gas) were used as supplied. Water was demineralized and further purified by vacuum distillation.

4.3 Results and discussion

4.3.1 Viscosity

Experimentally determined values of the viscosities of potassium salt of sarcosine and L-proline at temperatures from (298.18 to 333.15) K and concentrations from (0.5 to 3.0) kmol · m^{-3} for aqueous potassium salt of sarcosine and from (0.5 to 3.5) kmol · m^{-3} for aqueous potassium salt of L-proline are listed in Table 4.2.[1] The experimental error is estimated to ±1%.

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[1] These experimental values are measured by Jacco van Holst. The results are given here for the convenience of the reader only.

Table 4.2: Viscosities of aqueous potassium salts of sarcosine and L-proline

	T / K				
	298.15	303.15	313.15	323.15	333.15
$C_{\mathrm{K^+sarcosine}}$ / kmol · m^{-3}	$\mu_{K^+sarcosine}$ / mPa · s				
0.51	1.045	0.935	0.762	0.636	0.543
1.02	1.246	1.112	0.915	0.789	0.635
1.53	1.518	1.346	1.076	0.887	0.745
2.02	1.833	1.611	1.291	1.055	0.880
2.44	2.201	1.913	1.514	1.220	1.016
2.99	2.868	2.508	1.967	1.588	1.264
$C_{\mathrm{K^+L\text{-}proline}}$ / kmol · m^{-3}	$\mu_{\mathrm{K^+L\text{-}proline}}$ / mPa · s				
0.51	1.107	0.986	0.799	0.664	0.565
1.01	1.400	1.242	0.992	0.816	0.685
1.52	1.811	1.590	1.251	1.017	0.846
2.01	2.365	2.061	1.599	1.286	1.061
2.52	3.163	2.721	2.076	1.636	1.331
2.98	4.112	3.516	2.664	2.068	1.658
3.45	5.732	4.837	3.587	2.767	2.181

4.3.2 Liquid diffusivity

Values of the liquid diffusivities in aqueous potassium salt solutions of taurine, sarcosine, L-proline and glycine were measured and averaged over at least three measurements from (293 to 368) K and (0 to 3.0) kmol·m^{-3}. The results are presented in Table 4.4. The critical (De)^{2}Sc number was found to be 100 for these system.

The theory of diffusion of aqueous salts at low concentration is well developed. [73] For dilute solutions of a single salt, the diffusion coefficient can be estimated by the Nernst-Haskell equation:

$$D^0 = \frac{RT\left[(1/z_+) + (1/z_-)\right]}{F^2\left[(1/\lambda_+^0) + (1/\lambda_-^0)\right]} \tag{4.10}$$

where D^0 is the diffusion coefficient at infinite dilution, R is the gas constant, T is the temperature, F is the faraday constant, λ_+^0 and λ_-^0 are the limiting ionic conductivities and z_+ and z_- are the respective valences of the cation and anion. In the case of the potassium salt of glycine at 298.15 K; limiting ionic conductivities have been reported by D'yachkova et al. [30], Miyamoto & Schmidt [64] and Mehl & Schmidt [61] for deprotonated glycine (anion structure). These values are listed in Table 4.3. The limiting ionic conductivity of the potassium ion is reported by Poling et al. [73] to be 73.5 cm^2 · Ω^{-1}·mol^{-1}. By the use of these values and equation (4.10), the respective estimated diffusivities

Table 4.3: Limiting ionic conductivities estimated diffusivities

	λ_-^0 / cm^2 · Ω^{-1} · mol^{-1}	$D_{\mathrm{est,K^+glycine}}$ / 10^{-9} · m^2 · s^{-1}	$D_{\mathrm{K^+glycine}}$ / 10^{-9} · m^2 · s^{-1}	rel. dev. / %
D'yachkova et al. [30]	24.5	0.979	1.11	-11.8
Miyamoto & Schmidt [64]	30.0	1.13	1.11	-1.8
Mehl & Schmidt [61]	39.2	1.36	1.11	22.5

at infinite dilution, $D_{\mathrm{est,K^+glycine}}$, are calculated and listed in Table 4.3. From Table 4.4; the experimentally determined value, $D_{\mathrm{K^+glycine}}$, is $1.11 \cdot 10^{-9}$ $\mathrm{m^2 \cdot s^{-1}}$. The relative deviation between the estimated and the experimental values are listed in Table 4.3. The limiting ionic conductivity of 39.2 $\mathrm{cm^2 \cdot \Omega^{-1} \cdot mol^{-1}}$ from Mehl & Schmidt [61] is most likely too high [77] for an ion of the size of deprotonated glycine. This can explain the relative deviation of 22.5 %. In the absence of limiting ionic conductivities of deprotonated taurine, sarcosine and L-proline ions, diffusivities at infinite dilutione are not estimated for these salts. At higher concentrations, salt diffusivities can be estimated [73] by the additional use of viscosities, solvent partial molar volume and molar density and mean ionic activity coefficients. As some of these properties are not readily available for the considered salts, such estimations are not further investigated in the present work.

Table 4.4: Liquid diffusion coefficients in aqueous amino acid salt solutions at various temperatures and concentrations

$\frac{T}{\mathrm{K}}$	$\frac{D_{\mathrm{K^+taurine}}}{10^{-9} \cdot \mathrm{m^2 \cdot s^{-1}}}$	$\frac{C_{\mathrm{ref,K^+taurine}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{D_{\mathrm{K^+sarcosine}}}{10^{-9} \cdot \mathrm{m^2 \cdot s^{-1}}}$	$\frac{C_{\mathrm{ref,K^+sarcosine}}}{\mathrm{kmol \cdot m^{-3}}}$
293.15	1.01	$0.3 \cdot 10^{-3}$	0.961	$0.9 \cdot 10^{-3}$
	0.975	0.937	0.945	0.970
	0.936	1.87	0.893	1.99
	0.884	2.71	0.865	2.91
298.15	1.13	$0.3 \cdot 10^{-3}$	1.10	$0.1 \cdot 10^{-2}$
	1.11	0.938	1.04	0.970
	1.07	1.87	0.993	1.99
	1.00	2.72	0.982	2.91
303.15	1.26	$0.4 \cdot 10^{-3}$	1.23	$0.1 \cdot 10^{-2}$
	1.24	0.938	1.19	0.971
	1.20	1.87	1.18	1.99
	1.14	2.72	1.11	2.91
313.15	1.56	$0.4 \cdot 10^{-3}$	1.54	$0.1 \cdot 10^{-2}$
	1.53	0.939	1.50	0.971
	1.48	1.88	1.45	1.99
	1.40	2.72	1.39	2.91
323.15	1.92	$0.4 \cdot 10^{-3}$	1.89	$0.1 \cdot 10^{-2}$
	1.89	0.939	1.85	0.972
	1.80	1.88	1.80	1.99
	1.71	2.72	1.73	2.91
333.15	2.29	$0.5 \cdot 10^{-3}$	2.34	$0.2 \cdot 10^{-2}$
	2.25	0.940	2.27	0.972
	2.16	1.88	2.18	1.99
	2.05	2.72	2.08	2.91
343.15	2.71	$0.5 \cdot 10^{-3}$	2.71	$0.2 \cdot 10^{-2}$
	2.65	0.94	2.66	0.973
	2.54	1.89	2.52	1.99

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	2.41	2.73	2.44	2.92
353.15	3.17	$0.6{\cdot}10^{-3}$	3.13	$0.2{\cdot}10^{-2}$
	3.05	0.940	3.09	0.974
	2.95	1.89	2.93	1.99
	2.79	2.73	2.86	2.92
363.15	3.66	$0.6{\cdot}10^{-3}$	3.56	$0.2{\cdot}10^{-2}$
	3.48	0.942	3.53	0.974
	3.36	1.90	3.38	1.99
	3.19	2.73	3.27	2.92
368.15	3.93	$0.6{\cdot}10^{-3}$	3.85	$0.3{\cdot}10^{-2}$
	3.73	0.942	3.77	0.975
	3.59	1.90	3.64	1.99
	3.40	2.73	3.49	2.92

$\frac{T}{\mathrm{K}}$	$\frac{D_{\mathrm{K^{+}L\text{-}proline}}}{10^{-9}\cdot\mathrm{m}^{2}\cdot\mathrm{s}^{-1}}$	$\frac{C_{\mathrm{ref,K^{+}L\text{-}proline}}}{\mathrm{kmol}\cdot\mathrm{m}^{-3}}$	$\frac{D_{\mathrm{K^{+}glycine}}}{10^{-9}\cdot\mathrm{m}^{2}\cdot\mathrm{s}^{-1}}$	$\frac{C_{\mathrm{ref,K^{+}glycine}}}{\mathrm{kmol}\cdot\mathrm{m}^{-3}}$
293.15	0.924	$0.4{\cdot}10^{-1}$	0.999	$0.5{\cdot}10^{-3}$
	0.840	1.03	1.05	1.07
	0.760	1.95	1.07	2.02
	0.605	2.97	1.04	3.09
298.15	1.04	$0.5{\cdot}10^{-1}$	1.11	$0.5{\cdot}10^{-3}$
	0.959	1.04	1.20	1.07
	0.870	1.96	1.25	2.02
	0.719	2.97	1.18	3.09
303.15	1.17	$0.5{\cdot}10^{-1}$	1.25	$0.6{\cdot}10^{-3}$
	1.08	1.04	1.37	1.07
	0.988	1.96	1.41	2.02
	0.819	2.97	1.37	3.09
313.15	1.48	$0.5{\cdot}10^{-1}$	1.56	$0.6{\cdot}10^{-3}$
	1.35	1.04	1.70	1.07
	1.25	1.96	1.72	2.03
	1.05	2.97	1.68	3.09
323.15	1.81	$0.6{\cdot}10^{-1}$	1.91	$0.7{\cdot}10^{-3}$
	1.68	1.04	2.11	1.07
	1.56	1.96	2.13	2.03
	1.34	2.97	2.11	3.09
333.15	2.18	$0.6{\cdot}10^{-1}$	2.28	$0.8{\cdot}10^{-3}$
	2.02	1.04	2.50	1.07
	1.88	1.96	2.53	2.03
	1.63	2.98	2.44	3.09
343.15	2.55	$0.7{\cdot}10^{-1}$	2.70	$0.9{\cdot}10^{-3}$
	2.39	1.04	2.93	1.07
	2.22	1.96	2.94	2.03
	1.94	2.98	2.88	3.09
353.15	2.93	$0.8{\cdot}10^{-1}$	3.11	$0.9{\cdot}10^{-3}$

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	2.78	1.05	3.36	1.07
	2.59	1.97	3.40	2.03
	2.28	2.98	3.30	3.09
363.15	3.42	$0.8\cdot10^{-1}$	3.56	$0.1\cdot10^{-2}$
	3.18	1.05	3.88	1.07
	2.98	1.97	3.86	2.03
	2.64	2.98	3.73	3.09
368.15	3.66	$0.9\cdot10^{-1}$	3.82	$0.1\cdot10^{-2}$
	3.42	1.05	4.14	1.07
	3.19	1.97	4.11	2.03
	2.84	2.99	3.95	3.09

4.3.3 Gas diffusivity

The experimental determined diffusivities of N_2O in aqueous potassium salt solutions of taurine, sarcosine, L-proline and glycine were measured and averaged over at least three measurements each from (293 to 333) K and (1.0 to 3.0) kmol·m^{-3}. These results are presented in Table 4.5. The critical $(\mathrm{De})^2\mathrm{Sc}$ number was found to be 80 for these systems.

Several investigators have correlated the diffusion of an inert gas in an aqueous salt solution to the viscosity or the salt concentration. [75, 36, 43, 16, 52] Ratcliff & Holdcroft [75], Brilman et al. [16] and Kumar et al. [52] correlated the diffusivities to the viscosities by a modified Stokes-Einstein relation:

$$\frac{D_{N_2O\ \mathrm{in\ AAS}}}{D_{N_2O\ \mathrm{in\ H_2O}}} = \left(\frac{\mu_{H_2O}}{\mu_{AAS}}\right)^{\alpha} = \text{constant} \tag{4.11}$$

where α is a constant. Ratcliff & Holdcroft [75] found this value to be 0.637, whereas Brilman et al. [16] found it to be 0.6. Kumar et al. [52] found the value to be 0.74. A α value of 0.6 was found to predict the diffusivities within an average and maximum absolute relative deviation of 5.7 % and 15.1 %, respectively. The viscosities were taken from Kumar et al. [52], Portugal et al. [74], Lide [55] and Table 4.2. The diffusivity of N_2O in H_2O was taken from Versteeg & van Swaaij [96]. The correlation is presented in Figure 4.2 for the aqueous amino acid salt solutions. Diffusivities of CO_2 in aqueous amino acid salt solutions can be estimated by the "N_2O analogy" [96].

Kumar et al. [52] reported diffusivities of N_2O in aqueous solutions of the potassium salt of taurine at 293 K. The results [52] are compared to the results from the present work at 293.15 K in Figure 4.3 and the estimated values from the modified Stokes-Einstein relation at 293.15 K. The values from the present work have an absolute average and maximum deviation of 4.55 % and 6.11 % from the calculated values from the modified Stokes-Einstein relation at 293.15 K, respectively. The values of Kumar et al. [52] deviates by 4.77 % and 10.48 %.

4.4 Conclusion

Liquid diffusivities of aqueous potassium salts of taurine, sarcosine, L-proline and glycine have been determined from (293 to 368) K and (0 to 3.0) kmol·m^{-3}.

Table 4.5: Diffusivity of N_2O in aqueous amino acid salt solutions at various temperatures and solvent concentrations

	T / K					
	293.15	298.15	303.15	313.15	323.15	333.15
$C_{\mathrm{K^+taurine}}$ / kmol·m^{-3}	D_{N_2O} / 10^{-9}·m^2·s^{-1}					
0.920	1.49	1.65	1.80	2.21	2.73	3.43
1.87	1.24	1.35	1.51	1.87	2.38	2.73
2.78	1.01	1.10	1.23	1.54	1.87	2.24
$C_{\mathrm{K^+sarcosine}}$ / kmol·m^{-3}	D_{N_2O} / 10^{-9}·m^2·s^{-1}					
0.953	1.42	1.57	1.76	2.20	2.59	3.13
1.94	1.18	1.28	1.40	1.73	2.14	2.57
2.98	0.889	1.02	1.21	1.51	1.81	2.25
$C_{\mathrm{K^+L\text{-}proline}}$ / kmol·m^{-3}	D_{N_2O} / 10^{-9}·m^2·s^{-1}					
1.05	1.22	1.35	1.56	1.93	2.47	2.92
2.05	0.896	0.999	1.16	1.45	1.76	2.23
3.03	0.689	0.792	0.907	1.14	1.49	1.75
$C_{\mathrm{K^+glycine}}$ / kmol·m^{-3}	D_{N_2O} / 10^{-9}·m^2·s^{-1}					
1.08	1.49	1.62	1.79	2.19	2.66	3.19
2.09	1.32	1.44	1.65	1.92	2.30	2.83
3.10	1.13	1.25	1.44	1.77	2.22	2.57

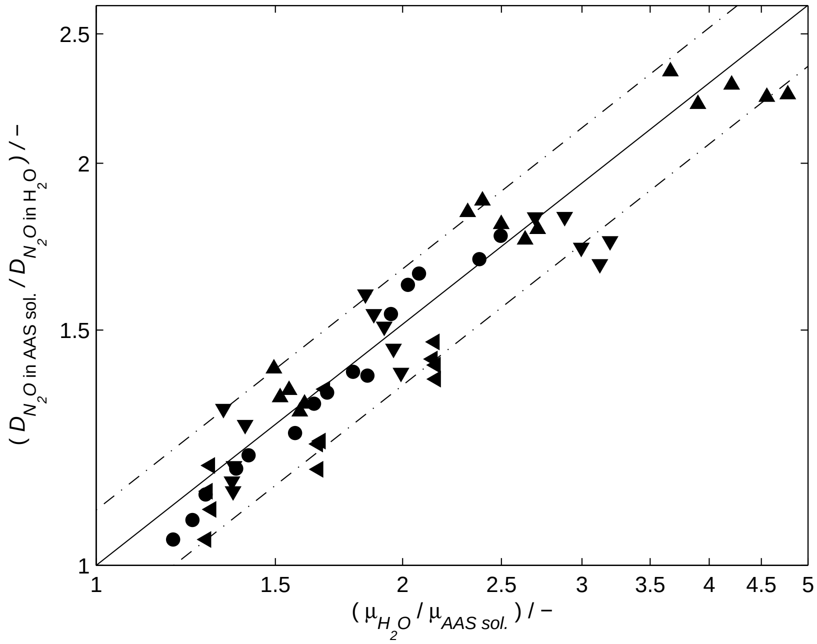

Figure 4.2: Stokes-Einstein plot for D_{N_2O} in aqueous amino acid salt solutions: ●, K$^+$taurine; ▼, K$^+$sarcosine; ▲, K$^+$L-proline; ◀, K$^+$glycine; The solid line represents equation (4.11) with $\alpha = 0.6$ and the dashed lines represents ±10%

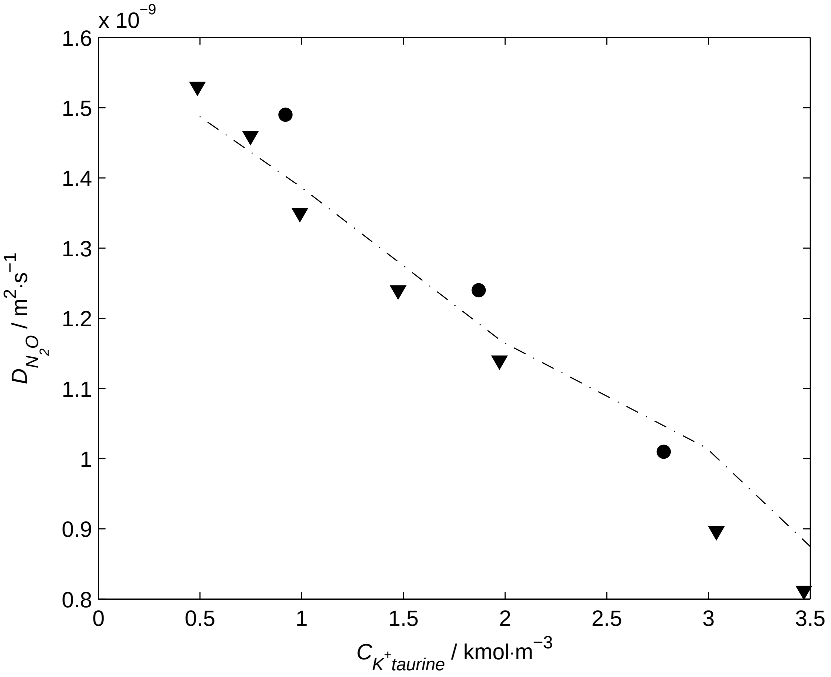

Figure 4.3: Comparison of D_{N_2O} in aqueous potassium taurine salt to literature values at 293.15 K: ●, present work; ▼, Kumar et al. [52]; -·-·, modified Stokes-Einstein relation

The diffusivities at infinite dilution can be estimated by the Nernst-Haskell equation if limiting ionic conductivity data are available.

Diffusivities of N_2O in aqueous amino acid salt solutions of taurine, sarcosine, L-proline and glycine have been determined from (293 to 333) K and (1.0 to 3.0) $\mathrm{kmol \cdot m^{-3}}$. The diffusivities are in agreement with available litterature values. The diffusivities can be estimated using a modified Stokes-Einstein relation, and the diffusivities of CO_2 in these solutions can be further calculated.

Chapter 5

Mass transfer in absorption and desorption processes

5.1 Summary

A post-combustion capture plant is in its design depended on absorption and desorption processes of CO_2 and/or H_2S gas. As most attention in research has been given to the absorption stage of such a plant, important and useful research results can be gained by focusing research about the desorption stage. As opposite to absorption, desorption takes place at higher temperatures and not necessarily atmospheric pressure. [50] This is due to the thermodynamic conditions needed for parts of the gas compound to leave the liquid phase and enter the gas phase. [83]

The purpose of this research was to investigate absorption and desorption processes at the same operating conditions, e.g. temperature, pressure, etc., to see if these processes are mirror processes of each other.

A stirred cell setup has been built. All parameters and conditions involved in the mass transfer can be kept constant, e.g. surface area, liquid volume and flow, gas volume and flow, etc. Preliminary results from this setup is reported below. Because of a significant delay of the construction of the setup there are no more experimental results available. The author of this report disclaim the responsibility of this delay as it was caused by interference outside of the control of the author.

5.2 Preliminary results

In order to be familiar with the stirred cell reactor, mass transfer coefficients (k_L) have to be determined a different stirrer speeds and liquid level, and it is shown in Figure 5.1. The reactor dimensions are given in Table 5.1.

Table 5.1: Dimension of reactor

Rector volume V	4.276 dm^3
Reactor diameter d	1.389 dm

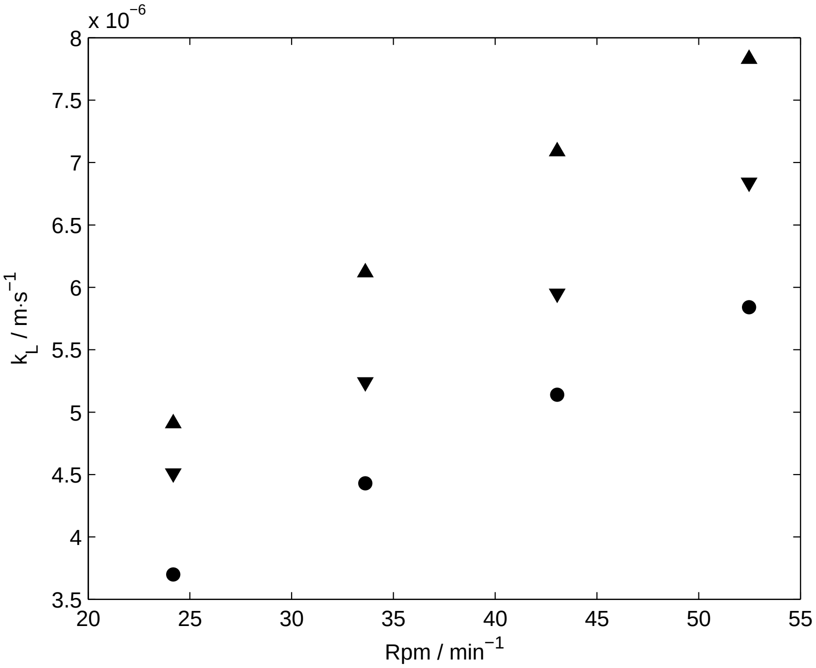

Figure 5.1: Mass transfer coefficient as a function of reactor liquid level and stirrer speed. ●, high liquid level V_{liq} = 2.38 dm^3; ▼, medium liquid level V_{liq} = 2.17 dm^3; ▲, low liquid level V_{liq} = 1.98 dm^3;

The 'm' value for CO_2 in water was also determined in order to check the performance of the stirred cell. This is important since these types of stirred cells are operated at underpressure. The 'm' value was measured to be 0.82, and this is well in line with values of Versteeg & Van Swaaij [96].

Final conclusion

In the present report values are reported for dissociation constant and liquid and gas diffusion constant of amino acid selected as potential CO_2 absorbents. The dissociation constants are reported as a function of temperature, and further thermodynamic properties are derived. Diffusion coefficients are reported as a function of temperature and concentration. These values give insight into the use of amino acid salts as CO_2 absorbents. Additionally, liquid and gas diffusion coefficients are reported for the aqueous PZ and (PZ + MDEA) solutions. The report also gives a short summary of the work carried out regarding absorption and desorption processes.

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Enschede, 31.12.2007

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