

Determination of dissociation constants of CO₂ absorbents between 293 K – 353 K using electromotive force measurements

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Abstract

The second dissociation constants of the amino acids β-alanine, taurine, sarcosine, 6-aminohexanoic acid, and the dissociation constant of protonated methyldiethanolamine have been determined from electromotive force measurements at temperatures from 293 K to 353 K. Experimental results are reported and compared to literature values.

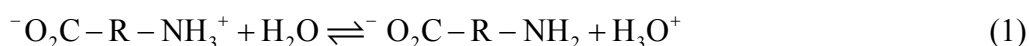
Keywords: dissociation constants, absorbents, salts of amino acids

Introduction

Aqueous solutions of amines are extensively used for the removal of acid gases, such as CO₂ and H₂S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely used in gas treating. [1] It has been widely reported that alkanolamines undergo degradation in oxygen rich atmosphere, usually encountered in the treatment of flue gases. Aqueous solutions of salts of amino acids might be an attractive alternative to alkanolamines. They were found to have better resistance to degradation, and their reactivity with CO₂ is comparable to aqueous alkanolamines of related classes. Due to their ionic nature, aqueous solutions of salts of amino acids have negligible volatility and higher surface tension than aqueous solutions of alkanolamines. [2] [3] [4]

Procedure

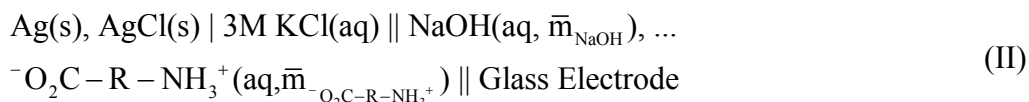
Amino acids dissociate in aqueous solutions according to:



The equilibrium constant can be determined by electromotive force (EMF) measurements using a combined glass pH electrode by measuring the change in activity between two solutions of different composition. [5] Two electrolyte cells are used:



and



As the activity of a pure solid is set to unity, the Nernst equation for cell I results in:

$$E_{\text{I}} = E^{\circ}(\text{T}) - \frac{\text{RT}}{\text{F}} \ln(a_{\text{H}_3\text{O}^{+}} a_{\text{Cl}^{-}, 3\text{M}})_{\text{I}} \quad (2)$$

and for cell II:

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

As both cells are at the same temperature, they have the same standard potential, E[°]:

$$\ln(a_{\text{H}_3\text{O}^{+}} a_{\text{Cl}^{-}, 3\text{M}})_{\text{II}} = \frac{\text{F}}{\text{RT}} (E_{\text{I}} - E_{\text{II}}) + \ln(a_{\text{H}_3\text{O}^{+}} a_{\text{Cl}^{-}, 3\text{M}})_{\text{I}} \quad (4)$$

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

$$\bar{n}_{-\text{O}_2\text{C-R-NH}_3^+} = n_{-\text{O}_2\text{C-R-NH}_3^+} + n_{-\text{O}_2\text{C-R-NH}_2} \quad (5)$$

$$\bar{n}_{\text{NaOH}} = n_{\text{Na}^+} \quad (6)$$

$$\bar{n}_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} + n_{\text{H}_3\text{O}^+} + n_{\text{OH}^-} \quad (7)$$

Electroneutrality results in:

$$n_{\text{Na}^+} + n_{\text{H}_3\text{O}^+} = n_{-\text{O}_2\text{C-R-NH}_2} + n_{\text{OH}^-} \quad (8)$$

The chemical equilibrium conditions for both reactions present are:

$$K_w(T) = \frac{a_{\text{H}_3\text{O}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}^2} \quad (9)$$

$$K(T) = \frac{a_{-\text{O}_2\text{C-R-NH}_2} a_{\text{H}_3\text{O}^+}}{a_{-\text{O}_2\text{C-R-NH}_3^+} a_{\text{H}_2\text{O}}} \quad (10)$$

For a given temperature and composition, the electromotive forces E_I and E_{II} are measured. Activities of HCl and KCl are estimated using the excess energy model of Pitzer from Holmes [6] and Pabalan [7], and the activity of water follows from the Gibbs-Duhem equation. 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. The changes in the compositions of the electrolyte cells due to the outflow of KCl electrolyte from the electrode were neglected. The water dissociation constant, K_w , was taken from Fisher [8]. With this information equation (4) to equation (10) 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 acids, and the 'true' equilibrium constants of the dissociation of the amino acids are determined in a two-step extrapolation procedure:

$$\lim_{\substack{\bar{m}_{\text{NaOH,II}} = \text{const} \\ \bar{m}_{-\text{O}_2\text{C-R-NH}_3^+} \rightarrow 0}} [K_{2,\text{exp}}(T, \bar{m}_{-\text{O}_2\text{C-R-NH}_3^+}, \bar{m}_{\text{NaOH,II}})] = K_{2,\text{exp}}(T, \bar{m}_{\text{NaOH,II}}) \quad (11)$$

$$\lim_{\bar{m}_{\text{NaOH,II}} \rightarrow 0} K_{2,\text{exp}}(T, \bar{m}_{\text{NaOH,II}}) = K_2(T) \quad (12)$$

However, if $\bar{m}_{\text{NaOH,II}}$ is small enough (e.g. $\bar{m}_{\text{NaOH,II}} \leq \sim 0.01$ mol/kg), the second extrapolation is not necessary. Measurements of the dissociation constant of protonated methyldiethanolamine (MDEA) were performed in a similar manner to validate the experimental technique. However, HCl was used in cell II instead of NaOH, and consequently equation (5) to equation (12) had to be adapted to describe the composition of the cells.

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

$$\Delta_r G_m = -RT \ln K \quad (13)$$

$$\Delta_r H_m = -R \frac{d \ln K}{d(1/T)} \quad (14)$$

$$\Delta_r S_m = \frac{(\Delta_r H_m - \Delta_r G_m)}{T} \quad (15)$$

$$\Delta_r C_{p,m} = \frac{d\Delta_r H_m}{dT} \quad (16)$$

and the change of standard state properties ($T = T^\circ = 298.15 \text{ K}$) for the dissociation of an amino acid in water are calculated from equation (13) to equation (16).

Experimental section

For the EMF measurements a pH voltmeter (Metrohm, type 780) with a resolution of 0.1 mV and 0.1 K was used, together with a combined pH glass electrode (Metrohm, type 6.0258.010) with 3 M KCl (Metrohm, type 6.2308.020) reference electrolyte and an integrated Pt1000 temperature sensor. When not in use, the electrode was stored in a storage solution (Metrohm, type 6.2323.000). Before the measurements, the electrode was carefully rinsed with distilled water and dried with paper tissue. The cells were completely filled with the electrolyte solutions and 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.

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 NaOH in cell II were held constant in all solutions ($\bar{m}_{\text{HCl,I}} \approx \bar{m}_{\text{NaOH,II}} \approx 0.01 \text{ mol/kg}$), and the overall molality of the amino acids were between 0.038 mol/kg and 0.7 mol/kg. The overall molality of HCl in cell I and cell II was held constant ($\bar{m}_{\text{HCl,I}} \approx \bar{m}_{\text{HCl,II}} \approx 0.01 \text{ mol/kg}$) during measurements of the dissociation constant of protonated MDEA. The overall molality of MDEA was between 0.046 mol/kg and 0.8 mol/kg. Measurements where the temperature in cell I and cell II deviated by more than $\pm 0.1 \text{ K}$ were not considered in further described calculations.

Chemicals

β -Alanine, taurine, sarcosine, 6-aminohexanoic acid, and MDEA (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 $\sim 0.01 \text{ M}$ and checked by means of titration. Water was demineralised and further purified by vacuum distillation.

Results and discussion

Figure 1 shows the dissociation constant of protonated MDEA from this work in comparison with literature values [9] [10] [11] [12] [13], and the results are in good agreement with the results by Kamps [9] and Oscarson [10]. In Figure 2, $\ln(K_{2,\text{exp}})$ is plotted against the dimensionless overall molality of β -alanine. The extrapolations to zero amino acid molality were done by linear regression for all amino acids. Figure 3 to 6 show the second dissociation constants of β -alanine, taurine, sarcosine, and 6-aminohexanoic acid, respectively. For β -alanine, values are reported by several investigators [14] [15] [16] [17] [18]. Results obtained in this work are in good agreement with the results by Boyd [18]. For taurine and sarcosine, the results obtained in this work are in good agreement with the results reported by King [19] and Datta [20], respectively. The results reported in literature for 6-aminohexanoic acid [15] [21] [22] are always larger than those obtained in this work.

The results for β -alanine, taurine, sarcosine, and 6-aminohexanoic acid are correlated [23] by:

$$\ln K_2 = \frac{A}{T} + B + C \ln(T) \quad (17)$$

and the results for protonated MDEA are correlated [23] by:

$$\ln K = \frac{A}{T} + B + C \ln(T) \quad (18)$$

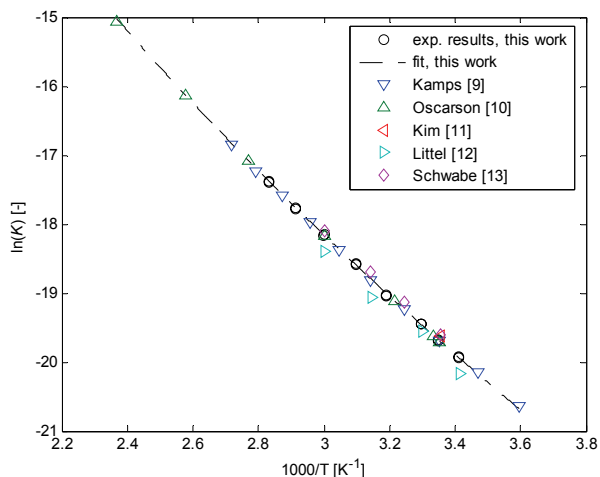


Figure 1: Dissociation constant of protonated MDEA

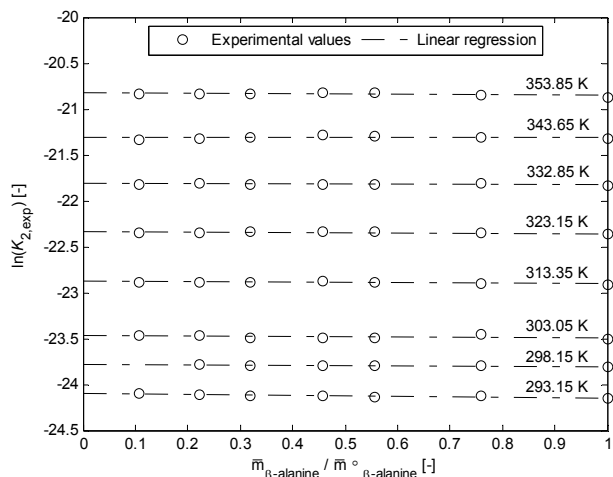


Figure 2: Influence of the dimensionless overall molality of β -alanine on $\ln(K_{2,\text{exp}})$

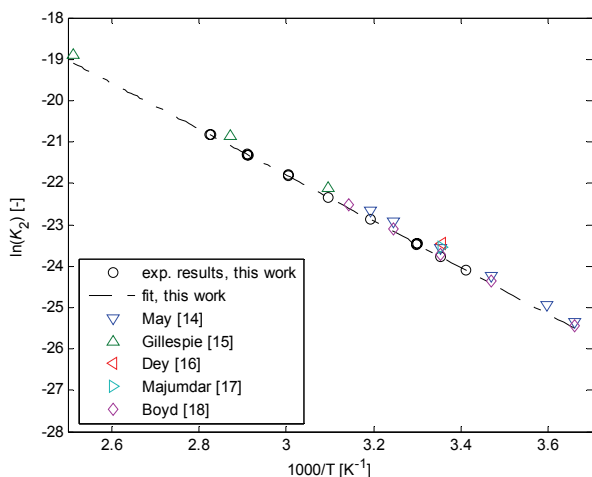


Figure 3: Dissociation constant of β -alanine

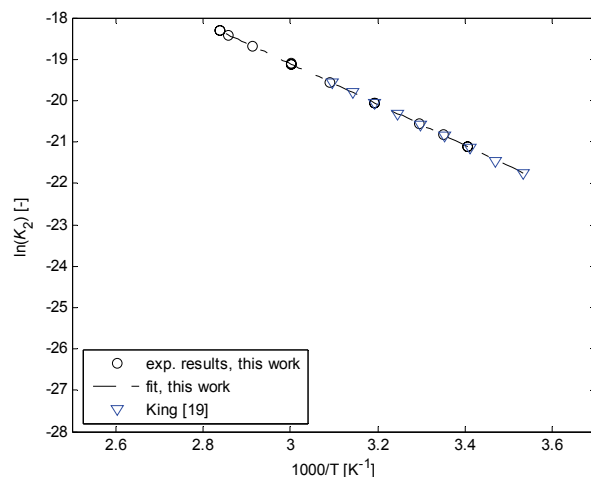


Figure 4: Dissociation constant of taurine

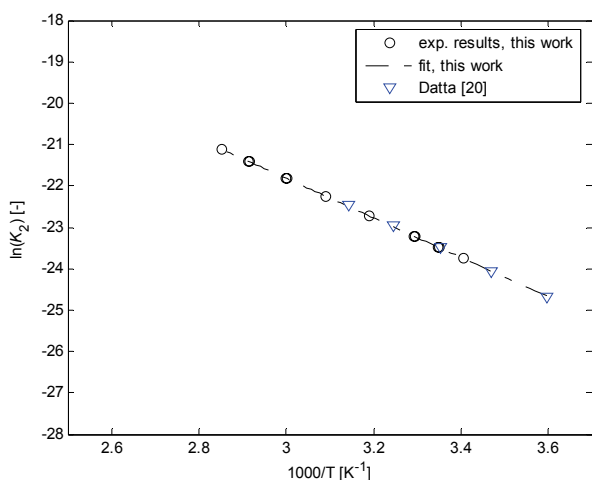


Figure 5: Dissociation constant of sarcosine

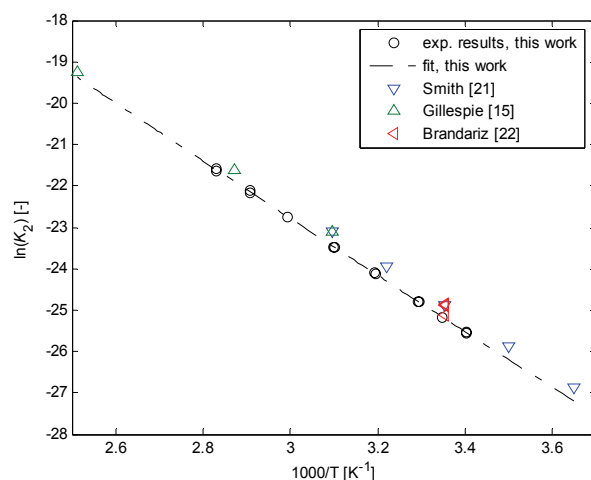


Figure 6: Dissociation constant of 6-aminohexanoic acid

The coefficients A, B, and C are given in Table 1. The change of standard state properties for β -alanine, taurine, sarcosine, 6-aminohexanoic acid, and protonated MDEA are calculated from equation (13) to equation (16) and given in Table 2.

Table 1: Coefficients in equation (17) and equation (18)

	β -alanine	taurine	sarcosine	6-aminohexanoic acid	MDEA
A [-]	-5987.5	-5801.9	-4840.7	-5871.3	-1077.3
B [-]	3.2126	14.185	-6.1228	-23.198	-75.247
C [-]	-1.2133	-2.7344	-0.20162	3.1031	10.383

Table 2: Reaction standard state properties

	$\Delta_r G_m^\circ$ [kJ/mol]	$\Delta_r H_m^\circ$ [kJ/mol]	$\Delta_r S_m^\circ$ [J/ (mol K)]	$\Delta_r C_p^\circ$ [J/ (mol K)]
β -alanine	58.95	46.8	-40.9	-10.1
taurine	51.69	41.5	-34.3	-22.7
sarcosine	58.27	39.7	-62.1	-1.7
6-aminohexanoic acid	62.49	56.5	-20.1	25.8
MDEA	48.84	34.7	-47.4	86.3

Conclusion

The second dissociation constants of β -alanine, taurine, sarcosine, 6-aminohexanoic, and the dissociation constant of protonated MDEA were determined from EMF measurements from 293 K to 353 K. The results agree well with literature values.

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