

# Thermodynamics of proton dissociations from aqueous alanine at temperatures from (278.15 to 393.15) K, molalities from (0.0075 to 1.0) mol · kg<sup>-1</sup>, and at the pressure 0.35 MPa: Apparent molar heat capacities and apparent molar volumes of alanine, alaninium chloride, and sodium alaninate

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## Abstract

We have measured the densities of aqueous solutions of alanine, alanine plus equimolar HCl, and alanine plus equimolar NaOH at temperatures  $278.15 \leq T/K \leq 368.15$ , at molalities  $0.0075 \leq m/\text{mol} \cdot \text{kg}^{-1} \leq 1.0$ , and at the pressure  $p = 0.35$  MPa using a vibrating tube densimeter. We have also measured the heat capacities of these solutions at  $278.15 \leq T/K \leq 393.15$  and at the same  $m$  and  $p$  using a twin fixed-cell differential temperature-scanning calorimeter. We used the densities to calculate apparent molar volumes  $V_\phi$  and the heat capacities to calculate apparent molar heat capacities  $C_{p,\phi}$  for these solutions. We used our results and values from the literature for  $V_\phi(T, m)$  and  $C_{p,\phi}(T, m)$  for HCl(aq), NaOH(aq), and NaCl(aq) and the molar heat capacity change  $\Delta_r C_{p,m}(T, m)$  for ionization of water to calculate parameters for  $\Delta_r C_{p,m}(T, m)$  for the two proton dissociations from protonated aqueous cationic alanine. We integrated these results in an iterative algorithm using Young's Rule to account for the effects of speciation and chemical relaxation on  $V_\phi(T, m)$  and  $C_{p,\phi}(T, m)$ . This procedure yielded parameters for  $V_\phi(T, m)$  and  $C_{p,\phi}(T, m)$  for alaninium chloride {H<sub>2</sub>Ala<sup>+</sup>Cl<sup>-</sup>(aq)} and for sodium alaninate {Na<sup>+</sup>Ala<sup>-</sup>(aq)} which successfully modeled our observed results. Values are given for  $\Delta_r C_{p,m}$ ,  $\Delta_r H_m$ ,  $pQ_a$ ,  $\Delta_r S_m$ , and  $\Delta_r V_m$  for the first and second proton dissociations from protonated aqueous alanine as functions of  $T$  and  $m$ .

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## 1. Introduction

In our continuing efforts to enlarge the database of thermodynamic properties of aqueous solutions of L-2-amino acids in their protonated, zwitterionic, and deprotonated forms, we have studied aqueous alanine. Alanine is a major component of silks, and it is the simplest amino acid following glycine. It is a non-essential amino acid, which plays

a role in human metabolism as a transamination product of pyruvate.

We have reported recently analogous results for the apparent molar volumes  $V_\phi$  and apparent molar heat capacities  $C_{p,\phi}$  of aqueous histidine [1,2], proline [3], valine [4], L-2-aminobutanoic acid [4], glycine [5], and serine [6]. In this paper, we report our measured densities and heat capacities of aqueous solutions of zwitterionic alanine {HAla<sup>±</sup>(aq)}, alanine plus equimolar HCl {HAla<sup>±</sup>(aq) + HCl(aq)}, and alanine plus equimolar NaOH {HAla<sup>±</sup>(aq) + NaOH(aq)}. Our analysis applies Young's Rule and a relaxation heat capacity term to account for the equilibrium molalities of

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the species  $\{\text{H}_2\text{Ala}^+\text{Cl}^-(\text{aq})\}$ ,  $\text{HAla}^\pm(\text{aq})$ , and  $\{\text{Na}^+\text{Ala}^-(\text{aq})\}$  present in the solutions containing  $\text{HCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$ . Our resulting values of  $V_\phi$  and  $C_{p,\phi}$  for  $\{\text{H}_2\text{Ala}^+\text{Cl}^-(\text{aq})\}$  and for  $\{\text{Na}^+\text{Ala}^-(\text{aq})\}$  allow calculation of the thermodynamic quantities  $\Delta_r C_{p,m}$ ,  $\Delta_r H_m$ ,  $pQ_a$ ,  $\Delta_r S_m$ , and  $\Delta_r V_m$  for the first and second proton dissociations from protonated aqueous alanine.

## 2. Experimental

Crystalline L-alanine ( $\text{HAla}^\pm$ , 2-aminopropanoic acid,  $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ , molar mass  $M_2 = 89.0935 \text{ g} \cdot \text{mol}^{-1}$ ; Fluka, lot 397418/1, 0.998 mass fraction) was used as received. Purity of the solute was verified by elemental analysis to be 0.998 mass fraction alanine. We prepared aqueous stock solutions of L-alanine by mass using distilled, deionized, autoclaved, degassed water. We prepared stock solutions of  $\{\text{HAla}^\pm(\text{aq}) + \text{HCl}(\text{aq})\}$  and  $\{\text{HAla}^\pm(\text{aq}) + \text{NaOH}(\text{aq})\}$  in a similar fashion, combining mass dilutions of the  $\text{HAla}^\pm(\text{aq})$  solution with previously standardized stock solutions of  $\text{HCl}(\text{aq})$  [7] and carbonate-free  $\text{NaOH}(\text{aq})$  [8] to achieve nearly 1:1 equimolar ratios of L-alanine +  $\text{HCl}$   $\{m(\text{HAla}^\pm)/m(\text{HCl}) = 0.998\}$

and L-alanine +  $\text{NaOH}$   $\{m(\text{HAla}^\pm)/m(\text{NaOH}) = 1.01_0\}$ . Subsequent solutions were prepared by mass dilution of these stock solutions. Air buoyancy corrections were applied to all weighings.

We measured solution densities  $\rho_s$  at regular temperature intervals in the range  $278.15 \leq T/\text{K} \leq 368.15$  with an Anton PAAR (Graz, Austria) Model 512 vibrating-tube densimeter and calculated  $V_\phi(T, m)$  with the following equation:

$$V_\phi = M_2/\rho_s - (\rho_s - \rho_w)/(\rho_s \cdot \rho_w \cdot m), \quad (1)$$

where  $\rho_w$  [3] is the density of water. Detailed discussions of the procedures used to obtain  $\rho_s$  from our experiments have been published previously [3–5,9].

Heat capacities of solutions  $c_{p,s}$  were determined with a Calorimetry Sciences Corp. (Lindon, UT, USA) Model 6100 Nano-DSC twin fixed-cell, differential-output, power-compensation, temperature-scanning calorimeter at  $278.15 \leq T/\text{K} \leq 393.15$  as described recently [3–5,9]. We used values of the heat capacity of water  $c_{p,w}$  [3] and our  $c_{p,s}$  with the following equation to calculate  $C_{p,\phi}$ :

$$C_{p,\phi} = M_2 \cdot c_{p,s} + (c_{p,s} - c_{p,w})/m. \quad (2)$$

TABLE 1  
Observed apparent molar volumes  $V_\phi$  for aqueous zwitterionic alanine at  $p = 0.35 \text{ MPa}^a$

$m/(\text{mol} \cdot \text{kg}^{-1})$	$V_\phi/(\text{cm}^3 \cdot \text{mol}^{-1})$			
	$T = 278.15 \text{ K}$	$T = 283.15 \text{ K}$	$T = 288.15 \text{ K}$	$T = 298.15 \text{ K}$
0.0152	$44.3 \pm 7.7$	$46.3 \pm 6.3$	$48.8 \pm 5.2$	$51.0 \pm 4.0$
0.0299	$63.5 \pm 3.9$	$64.2 \pm 3.2$	$66.2 \pm 2.6$	$65.4 \pm 2.0$
0.0500	$62.94 \pm 0.22$	$62.47 \pm 0.19$	$62.46 \pm 0.39$	$62.70 \pm 0.43$
0.0800	$56.34 \pm 0.15$	$57.27 \pm 0.13$	$57.93 \pm 0.24$	$58.79 \pm 0.27$
0.1247	$60.08 \pm 0.67$	$60.34 \pm 0.68$	$60.66 \pm 0.52$	$61.11 \pm 0.45$
0.2493	$60.25 \pm 0.34$	$60.58 \pm 0.34$	$60.87 \pm 0.26$	$61.39 \pm 0.23$
0.5149	$59.76 \pm 0.17$	$60.31 \pm 0.17$	$60.71 \pm 0.13$	$61.38 \pm 0.12$
1.0019	$59.59 \pm 0.10$	$60.03 \pm 0.10$	$60.40 \pm 0.07$	$61.01 \pm 0.07$
	$T = 308.15 \text{ K}$	$T = 318.15 \text{ K}$	$T = 328.15 \text{ K}$	$T = 338.15 \text{ K}$
0.0152	$53.2 \pm 3.4$	$53.0 \pm 2.3$	$55.9 \pm 2.8$	$62.4 \pm 4.1$
0.0299	$65.6 \pm 1.7$	$66.7 \pm 1.2$	$67.0 \pm 1.4$	$67.2 \pm 2.1$
0.0500	$63.23 \pm 0.35$	$63.19 \pm 0.25$	$59.35 \pm 0.27$	$63.5 \pm 1.1$
0.0800	$59.22 \pm 0.22$	$59.92 \pm 0.16$	$60.73 \pm 0.17$	$61.00 \pm 0.67$
0.1247	$61.68 \pm 0.28$	$62.18 \pm 0.34$	$62.39 \pm 0.23$	$61.87 \pm 0.60$
0.2493	$61.76 \pm 0.15$	$62.08 \pm 0.17$	$62.26 \pm 0.12$	$62.10 \pm 0.30$
0.5149	$61.91 \pm 0.08$	$62.39 \pm 0.09$	$62.61 \pm 0.06$	$62.88 \pm 0.15$
1.0019	$61.52 \pm 0.05$	$61.92 \pm 0.05$	$62.18 \pm 0.04$	$62.29 \pm 0.08$
	$T = 348.15 \text{ K}$	$T = 358.15 \text{ K}$	$T = 368.15 \text{ K}$	
0.0152	$59.60 \pm 0.74$	$59.27 \pm 0.08$	$58.95 \pm 0.41$	
0.0299	$68.95 \pm 0.38$	$69.01 \pm 0.04$	$71.06 \pm 0.21$	
0.0500	$63.21 \pm 0.38$	$62.87 \pm 0.75$	$62.83 \pm 0.61$	
0.0800	$61.23 \pm 0.24$	$61.33 \pm 0.47$	$61.47 \pm 0.38$	
0.1247	$62.44 \pm 0.12$	$62.47 \pm 0.09$	$62.53 \pm 0.03$	
0.2493	$62.49 \pm 0.06$	$62.52 \pm 0.05$	$62.71 \pm 0.03$	
0.5149	$63.02 \pm 0.04$	$63.14 \pm 0.03$	$63.21 \pm 0.03$	
1.0019	$62.57 \pm 0.03$	$62.67 \pm 0.03$	$62.69 \pm 0.03$	

The  $\pm$  values are from propagation of uncertainties as described in reference [9].

<sup>a</sup> Experimental values of  $\rho_s$  can be obtained by equation (1) with  $m$ ,  $\rho_w$  from reference [3], and  $M_2 = 75.0672 \text{ g} \cdot \text{mol}^{-1}$ .

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