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Thermodynamics of proton dissociations from aqueous threonine and isoleucine at temperatures from (278.15 to 393.15) K, molalities from (0.01 to 1.0) mol · kg^{-1}, and at the pressure 0.35 MPa: Apparent molar heat capacities and apparent molar volumes of zwitterionic, protonated cationic, and deprotonated anionic forms

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Abstract

We have measured the densities of aqueous solutions of isoleucine, threonine, and equimolal solutions of these two amino acids with HCl and with NaOH at temperatures $278.15 \leqslant T/\mathrm{K} \leqslant 368.15$, at molalities $0.01 \leqslant m/\mathrm{mol \cdot kg^{-1}} \leqslant 1.0$, and at the pressure 0.35 MPa using a vibrating tube densimeter. We have also measured the heat capacities of these solutions at $278.15 \leqslant T/\mathrm{K} \leqslant 393.15$ 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_ϕ 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 each of the protonated aqueous cationic amino acids. We used Young's Rule and integrated these results iteratively to account for the effects of equilibrium speciation and chemical relaxation on $V_\phi(T,m)$ and $C_{p,\phi}(T,m)$. This procedure gave parameters for $V_\phi(T,m)$ and $C_{p,\phi}(T,m)$ for threoninium and isoleucinium chloride and for sodium threoninate and isoleucinate which modeled our observed results within experimental uncertainties. We report values 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 threonine and isoleucine as functions of T and m.

Keywords: Apparent molar volume; Apparent molar heat capacity; Threonine; 2-Amino-3-hydroxybutanoic acid; Isoleucine; 2-Amino-3-methylpentanoic acid; Zwitterion; Threoninium chloride; Isoleucininium chloride; Sodium threoninate; Sodium isoleucinate; Proton dissociations; Acidity; Young's Rule

1. Introduction

Although there is an abundance of work reported in the literature on the properties of aqueous amino acids, the great majority of this work focuses on the unionized zwitterionic forms of the amino acids. The works that include information for the charged species often neglect or approximate the effects of incomplete ionization and equilibrium concentrations, introducing significant uncertainties in the values of their thermodynamic properties. In our continuing efforts to enlarge the database of accurate thermodynamic properties of aqueous solutions of L-2-amino acids in their protonated, zwitterionic, and deprotonated forms, taking into account the actual species concentrations, we have studied aqueous threonine and isoleucine. Both are essential amino acids, meaning that they are not produced by humans and must be included in the diet. Threonine is required for the formation of collagen and elastin and is concentrated in the central nervous

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system. Isoleucine is found particularly in muscle tissue and is necessary for formation of hemoglobin. It contributes significantly to the tertiary structure of proteins.

We recently reported our results for the apparent molar volumes V_ϕ and apparent molar heat capacities $C_{p,\phi}$ of aqueous proline [1], valine [2], L-2-aminobutanoic acid [2], serine [3], alanine [4], and others. In this paper we report our measured densities and heat capacities of aqueous solutions of threonine and isoleucine in their zwitterionic forms $HThr^{\pm}(aq)$ and $HIle^{\pm}(aq)$ and with the addition of equimolal HCl $\{HThr^{\pm}(aq) + HCl(aq)\}$ and $\{HIle^{\pm}(aq) + HCl(aq)\}$, and equimolal NaOH $\{HThr^{\pm}(aq) + NaOH(aq)\}$ and $\{HIle^{\pm}(aq) + NaOH(aq)\}$. Our analysis applies Young's Rule and a relaxation heat capacity term to account for the equilibrium molalities of the species $H_2Thr^+Cl^-(aq)$, $H_2Ile^+Cl^-(aq)$, $HThr^{\pm}(aq)$, $HIle^{\pm}(aq)$, $Na^+Thr^-(aq)$, and $Na^+Ile^-(aq)$ present in the solutions containing HCl(aq) and NaOH(aq). Our resulting values of $V_\phi(T,m)$ and $C_{p,\phi}(T,m)$ for $H_2Thr^+Cl^-(aq)$, $H_2Ile^+Cl^-(aq)$, $Na^+Thr^-(aq)$, and $Na^+Ile^-(aq)$ 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 threonine and isoleucine. We have compared all of our results to those found in the literature [5–45].

2. Experimental

Crystalline L-threonine {$HThr^{\pm}$(c), 2-amino-3-hydroxybutanoic acid, $CH_3CH(OH)CH(NH_2)COOH$, molar mass $M_2 = 119.1197\ g \cdot mol^{-1}$, density $\rho_c = 1.5\ g \cdot cm^3$; Fluka 89179, lot 1132757, 0.995+ mass fraction} and L-isoleucine {$HIle^{\pm}$(c), 2-amino-3-methylpentanoic acid, $C_2H_5CH(CH_3)CH(NH_2)COOH$, $M_2 = 131.1736\ g \cdot mol^{-1}$, $\rho_c = 1.2\ g \cdot cm^3$; Fluka 58879, lot 413187/1, 0.995+ mass fraction} were used as received. The purity of each solute was confirmed by elemental analysis by MHW Laboratories. We prepared aqueous stock solutions of L-threonine and L-isoleucine by mass using distilled, deionized, autoclaved, degassed water. We prepared stock solutions of $\{HThr^{\pm}(aq) + HCl(aq)\}$, $\{HThr^{\pm}(aq) + NaOH(aq)\}$, $\{HIle^{\pm}(aq) + HCl(aq)\}$, and $\{HIle^{\pm}(aq) + NaOH(aq)\}$ in a similar fashion, using previously standardized stock solutions of HCl(aq) [46] and carbonate-free NaOH(aq) [47] to achieve the nearly equimolal ratios of amino acid + HCl or + NaOH as follows: $\{m(HThr^{\pm})/m(HCl)\} = 0.999_7$, $\{m(HThr^{\pm})/m(NaOH)\} = 0.999_7$, $\{m(HIle^{\pm})/m(HCl)\} = 0.997$ and $\{m(HIle^{\pm})/m(NaOH)\} = 0.998$. All other solutions were prepared by mass dilution of these stock solutions with water. Air buoyancy corrections ($\rho_{air} = 0.0010\ g \cdot cm^3$) were applied to all weighings.

TABLE 1A
Observed densities ρ_s and apparent molar volumes V_ϕ for aqueous zwitterionic threonine at $p = 0.35$ MPa

m	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ	ρ_s	V_ϕ
$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^3$	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$
	$T = 278.15$ K		$T = 283.15$ K		$T = 288.15$ K		$T = 298.15$ K	
0.0157	1.00036	102 ± 13	1.00006	104 ± 13	0.99945	105 ± 12	0.99739	105 ± 13
0.0301	1.00146	73.7 ± 1.1	1.00118	74.0 ± 1.4	1.00055	74.81 ± 0.91	0.99848	75.0 ± 1.8
0.0501	1.00202	80.6 ± 4.3	1.00170	81.5 ± 4.0	1.00105	82.4 ± 3.7	0.99887	84.8 ± 4.0
0.1011	1.00454	74.80 ± 0.52	1.00421	75.43 ± 0.58	1.00355	76.02 ± 0.47	1.00139	77.00 ± 0.66
0.1993	1.00862	75.7 ± 1.1	1.00825	76.2 ± 1.1	1.00754	76.7 ± 1.0	1.00530	77.7 ± 1.1
0.3956	1.01693	75.29 ± 0.42	1.01645	75.85 ± 0.42	1.01561	76.45 ± 0.41	1.01325	77.29 ± 0.42
0.6542	1.02745	75.24 ± 0.48	1.02687	75.73 ± 0.47	1.02598	76.20 ± 0.46	1.02339	77.09 ± 0.46
	$T = 308.15$ K		$T = 318.15$ K		$T = 328.15$ K		$T = 338.15$ K	
0.0157	0.99438	104 ± 13	0.99056	104 ± 12	0.98606	103 ± 10	0.98092	104 ± 10
0.0301	0.99541	76.9 ± 1.2	0.99149	80.29 ± 0.64	0.98695	81.22 ± 0.64	0.98188	79.2 ± 0.6
0.0501	0.99580	86.0 ± 4.1	0.99198	86.3 ± 3.9	0.98747	86.3 ± 3.2	0.98235	86.1 ± 3.2
0.1011	0.99829	77.86 ± 0.52	0.99445	78.22 ± 0.42	0.98992	78.55 ± 0.43	0.98475	79.06 ± 0.42
0.1993	1.00215	78.5 ± 1.1	0.99825	79.0 ± 1.1	0.99370	79.40 ± 0.90	0.98854	79.71 ± 0.90
0.3956	1.01005	77.88 ± 0.41	1.00610	78.34 ± 0.40	1.00149	78.75 ± 0.41	0.99628	79.15 ± 0.41
0.6542	1.01998	77.82 ± 0.47	1.01589	78.39 ± 0.47	1.01123	78.80 ± 0.46	1.00598	79.18 ± 0.46
	$T = 348.15$ K		$T = 358.15$ K		$T = 368.15$ K			
0.0157	0.97523	103.8 ± 9.7	0.96907	100.3 ± 8.0	0.96239	98.4 ± 5.7		
0.0301	0.97617	79.82 ± 0.76	0.96995	79.71 ± 0.54	0.96324	79.90 ± 0.50		
0.0501	0.97666	86.3 ± 3.1	0.97043	86.6 ± 2.5	0.96373	86.7 ± 1.8		
0.1011	0.97904	79.42 ± 0.44	0.97280	79.79 ± 0.42	0.96609	79.99 ± 0.42		
0.1993	0.98279	80.21 ± 0.87	0.97658	80.36 ± 0.76	0.96988	80.51 ± 0.62		
0.3956	0.99053	79.50 ± 0.40	0.98429	79.78 ± 0.41	0.97759	79.98 ± 0.41		
0.6542	1.00021	79.51 ± 0.47	0.99398	79.75 ± 0.46	0.98723	80.09 ± 0.47		

The ± values are from propagation of uncertainties as described in reference [48].