

Thermodynamics of interactions between zwitterions of several L- α -amino acids and ethanol in aqueous solution

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Abstract

Dissolution enthalpies of L- α -alanine, L- α -valine and L- α -leucine in aqueous ethanol solutions have been measured by calorimetry at 298.15 K. The results obtained were used to calculate the enthalpic heterogeneous pair interaction coefficients between zwitterions of amino acids and a molecule of ethanol in water.

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1. Introduction

Studies on natural amino acids in water and in aqueous solutions of electrolytes [1–3] or non-electrolytes [4,5] have been carried out in many research centres, including ours [6–9]. These contribute to a better understanding of the mechanisms of reactions in which amino acids take part. Therefore, it is of interest to investigate the interactions in aqueous solutions between amino acids and organic substances that occur in the biological environment. Such organic compounds include ethanol as a by-product of glycolysis. Moreover, ethanol is a solvent and a component of numerous pharmaceuticals and cosmetics.

Thermodynamic parameters that describe the interactions of zwitterions of amino acids with a molecule of ethanol in water solutions include enthalpic heterogeneous pair interaction coefficients derived from McMillan–Mayer theory [10] as modified by Friedman and Krishnan [11], Franks et al. [12] and Desnoyers et al. [13]. These coefficients

describe the sum of interactions between ethanol and the amino acids with the competitive participation of water molecules.

To determine these parameters, dissolution enthalpies of several L- α -amino acids in aqueous solutions of ethanol were measured by calorimetry at 298.15 K.

2. Experimental

L- α -Alanine, L- α -valine and L- α -leucine (all 99.5% Fluka) were dried in vacuum at 320 K; ethanol (99.8% POCh Poland) was purified by standard methods [14]. The water used in the experiments was deionised, distilled and degassed. Water–ethanol mixtures 0.5–5.0 mol(EtOH) kg⁻¹(H₂O) were prepared by weight. The enthalpies of dissolution were measured with an isoperibol calorimeter [15]. The accuracy was $\pm 0.5\%$.

The standard enthalpies of solution were determined by linear extrapolation to zero amino acids concentration of the values of 8–10 independent measurements of amino acids dissolution enthalpies in the concentration range 0.001–0.01 mol(A) kg⁻¹(solvent). The ampoules containing

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Table 1
Standard enthalpies of solution of L- α -amino acids in aqueous ethanol solutions at 298.15 K

$m_{(\text{EtOH})}$ (mol(EtOH) kg ⁻¹ (H ₂ O))	$\Delta H_{\text{S(W+EtOH)}}^0$ (kJ mol ⁻¹)		
	L- α -Alanine	L- α -Valine	L- α -Leucine
0	7.67 ± 0.04	3.12 ± 0.03	3.42 ± 0.03
0.5	8.35 ± 0.05		
1.0	8.84 ± 0.05	4.93 ± 0.03	5.29 ± 0.03
1.5	9.60 ± 0.05		
2.0	10.11 ± 0.05	6.63 ± 0.03	7.37 ± 0.04
2.5	10.78 ± 0.05		
3.0	11.32 ± 0.06	8.51 ± 0.05	9.24 ± 0.05
4.0	12.50 ± 0.06	10.11 ± 0.05	11.05 ± 0.05
5.0	13.36 ± 0.06	11.72 ± 0.05	12.86 ± 0.06

the amino acids were filled in a dry box and weighed with a Mettler AE 240 balance.

3. Results and discussion

The standard enthalpies of solution of amino acids in water ($\Delta H_{\text{S(W)}}^0$) and aqueous ethanol solutions ($\Delta H_{\text{S(W+EtOH)}}^0$) are presented in Table 1. The dissolution enthalpies were used to determine enthalpic pair interaction coefficients by the equation proposed by Desnoyers [13]:

$$\Delta H_{\text{S(W+EtOH)}}^0 = \Delta H_{\text{S(W)}}^0 + 2h_{(\text{A,EtOH})}m_{(\text{EtOH})} + 3h_{(\text{A,EtOH,EtOH})}m_{(\text{EtOH})}^2 + \dots \quad (1)$$

where $m_{(\text{EtOH})}$ is molal concentration of ethanol in water mol(EtOH) kg⁻¹(H₂O), $h_{(\text{A,EtOH})}$ the enthalpic pair interaction coefficient and $h_{(\text{A,EtOH,EtOH})}$ denotes the enthalpic triplet interaction coefficient. The enthalpic pair and triplet interaction coefficients are listed in Table 2. The interpretation of the triplet interaction coefficients is obscured by the fact that they also contain pairwise interaction terms [16] and for that reason are not discussed in this paper.

The enthalpic interaction coefficients $h_{(\text{A,EtOH})}$ describe the effects connected with:

- the direct interaction between the zwitterionic “head” (–CHCO₂[–]NH₃⁺) of the amino acid and the hydroxyl group of ethanol (exothermic process),
- partial dehydration of the zwitterionic “head” of amino acid and the polar hydroxyl group of ethanol (endothermic processes),

Table 2
Heterogeneous enthalpic pair and triplet interaction coefficients for L- α -amino acids with ethanol in water at 298.15 K

L- α -Amino acids	$h_{(\text{A,EtOH})}$ (J kg mol ⁻²)	$h_{(\text{A,EtOH,EtOH})}$ (J kg ² mol ⁻³)
Glycine [11]	551	–11.9
Alanine	658 ± 26	–11.1 ± 3.4
Valine	920 ± 27	–7.8 ± 3.5
Leucine	1000 ± 28	–7.3 ± 3.4

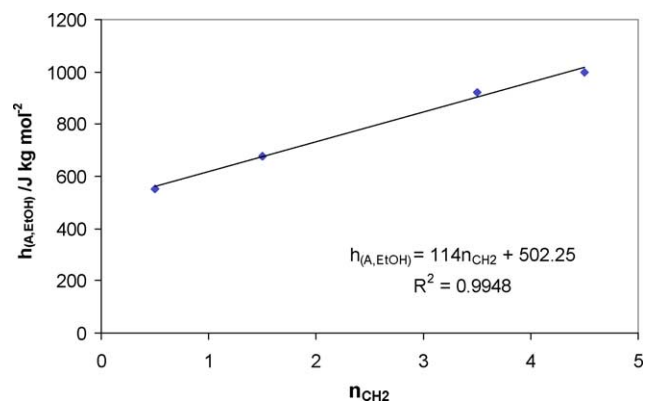


Fig. 1. The dependence of the enthalpic pair interaction coefficients between zwitterions of amino acids and ethanol on the number of CH₂ groups in the side chain of the amino acid. The number of CH₂ groups in the amino acid were determined with Savage and Wood's convention [21], in which one CH₃ group corresponds to 1.5 CH₂ and a CH group is equal to 0.5 CH₂.

(c) hydrophobic hydration phenomena that intensify the endothermic dehydration processes, i.e. hydrogen bonds between water molecules in the vicinity of hydrophobic groups are stronger [17–20]. Removal of some water molecules from the hydration sheath, which hinder direct approach of the interacting groups, is endothermic and dominates the exothermic effect of the direct interactions between the polar groups. The values of the enthalpic pair interaction coefficients, thus, become positive.

The enthalpic interaction coefficient of ethanol with glycine (Gly) has a positive value [7].

The replacement of hydrogen at C^α in the amino acid with an alkyl substituent in the case of L- α -alanine (Ala), L- α -valine (Val) or L- α -leucine (Leu) brings about an increase in the value of the enthalpic pair interaction coefficient (Table 2). The values increase in the sequence: Gly < Ala < Val < Leu (Table 2; Fig. 1). The increase in the length of alkyl side substituent linked to the zwitterionic “head” causes the interaction between ethanol and amino acid to become more endothermic.

This relationship is described by the equation:

$$h_{(\text{A,EtOH})} = 502.25 + 114n_{\text{CH}_2} \quad (R^2 = 0.9948)$$

The first term in the equation describes the interaction between the zwitterion “head” of the amino acid and ethanol. The endothermic dehydration effects dominate the exothermic effects of the direct interactions between polar groups. The positive value of the slope describes the endothermic contribution made by consecutive non-polar, hydrophobic CH₂ groups in the side chain of the amino acids.

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