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Enthalpies of solution of L-threonine in aqueous alcohol solutions

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Abstract

Enthalpies of solution of L-threonine in aqueous solutions of isopropanol, 1,2-propanediol and propanetriol were measured and enthalpies of transfer of L-threonine from water to these solutions calculated. Endothermic interactions, partial dehydrations and the interaction between alkyl groups, dominate exothermic interaction between polar groups.

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Keywords: L-Threonine; Alcohol; Enthalpy of solution; Structure interaction

1. Introduction

Biochemical interest in aqueous alcohol solution centers on the denaturing effects on proteins [1–6]. Amino acids and simple peptides are useful as models of proteins in aqueous solutions. A more detailed understanding of these effects might be acquired from the dissolution enthalpies of amino acids in aqueous alcohol solutions. This paper reports the dissolution enthalpies of Lthreonine and calculated the enthalpies of transfer of L-threonine from pure water to aqueous solutions of isopropanol (i-PrOH), 1,2-propanediol (1,2-PrD) and propanetriol (G-ol).

2. Experimental

L-Threonine (Sino-American Biotechnology Company) was used without further purification. Potassium chloride (KCl), used as the primary standard reagent for chemical calibration, was ground in an agate mortar, sieved and dried to a constant weight in an infrared drier. I-PrOH (>99.5%), 1,2-PrD (>99%) and G-ol (>99.0%) were purified as previously described [7–9]. Water was deionized and distilled with a quartz subboiling purifier. Aqueous alcohol solutions were prepared by weight.

0040-6031/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2005.08.031 Calorimetric measurements were carried out with a twin heatflux calorimeter RD496-III. The sensitivity obtained from the chemical calibration is 64.27 mV W^{-1} at 298.15 K. All experiments were performed at least twice and were reproducible within 1%.

3. Results and discussion

Dissolution enthalpies of L-threonine are listed in Table 1. Enthalpy of solution of L-threonine in pure water (10.35 kJ mol⁻¹) agrees well with the referenced value (10.33 kJ mol⁻¹) [10]. The enthalpy of transfer of L-threonine from pure water to aqueous alcohol solutions ΔH_{trs} are illustrated in Fig. 1.

The ΔH_{trs} is a probe of the interactions between L-threonine and alcohol molecule in aqueous solutions. The overall effect is the superposition of primary processes. The positive values of ΔH_{trs} show that endothermic effects dominate.

The ΔH_{trs} value in i-PrOH solution is the highest and that in G-ol solution is the lowest. Investigations of the structure of water in solutions of various cosolvents indicate that hydrogenbonds between water molecules in the hydration shells surrounding alkyl groups are stronger than those in bulk water [11,12]. This effect tightens the interaction between the water molecule and the –OH group. Since the removal of water molecules from the hydration shells of interacting molecules becomes more difficult and requires a higher energy supply, the endothermic effect of partial dehydration is more obvious. Accordingly, the larger

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Table 1 Enthalpies of solution	of L-threonine in aqueous i-Pr	OH, 1,2-PrD and G-ol solution	ons	
i-PrOH		1,2-PrOH		
$\overline{m_{\rm v}~({\rm mol}{\rm kg}^{-1})^{\rm a}}$	$\Delta H_{\rm s} ({\rm J} {\rm mol}^{-1})$	$\overline{m_{\rm v}} ({\rm mol}{\rm kg}^{-1})$	$\Delta H_{\rm s} ({\rm J}{\rm mol}^{-1})$	

i-PrOH		1,2-PrOH		G-ol	
$\overline{m_{\rm y}~({\rm mol}{\rm kg}^{-1})^{\rm a}}$	$\Delta H_{\rm s} ({\rm J} {\rm mol}^{-1})$	$\overline{m_{\rm y}~({\rm mol}{\rm kg}^{-1})}$	$\Delta H_{\rm s} ({\rm J}{\rm mol}^{-1})$	$m_{\rm y} ({\rm mol}{\rm kg}^{-1})$	$\Delta H_{\rm s} ({\rm J} {\rm mol}^{-1})$
0.0000	10347	0.0000	10347	0.0000	10347
0.2998	11042	0.3000	10748	0.2999	10453
0.6000	11502	0.6000	11027	0.6000	10559
0.9999	12070	0.9999	11552	0.9982	10705
1.4999	12903	1.5000	12083	1.5000	10962
2.5000	13521	1.9995	12551	2.0000	11148
2.9999	13673	2.4998	12929	3.0000	11363
4.0001	13847	2.9995	13066	3.9996	11721
		4.0000	13237		

^a m_y is the concentration of cosolvent.

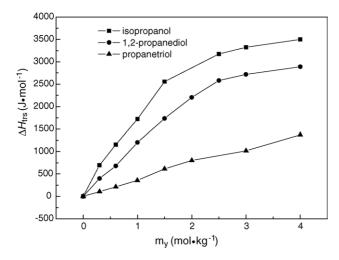


Fig. 1. Enthalpies of transfer of L-threonine from water to aqueous i-PrOH, 1,2-PrD and G-ol solutions.

alkyl group in i-PrOH molecule will lead to more endothermic effect (partial dehydrations and the interaction between alkyl groups) and less exothermic effect (the interaction between polar groups) resulting in positive contribution to the ΔH_{trs} values.

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