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Short Communication

Influence of the composition of aqueous-alcohol solvents on enthalpic characteristics of L-glutamine dissolution at $T = 298.15$

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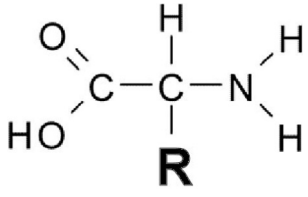
ABSTRACT

The enthalpies of the solution of L glutamine in aqueous solution of ethanol (EtOH), 1 propanol (1-PrOH) and 2 propanol (2-PrOH) with alcohol content up to 0.25 mol fractions, have been determined calorimetrically at $T = 298.15$ K. The standard enthalpies of the solution ($\Delta_{sol}H^{\infty}$) and transfer ($\Delta_{tr}H^{\infty}$) of L glutamine from water to aqueous alcohol have been calculated. The enthalpic coefficients of pairwise interactions (h_{xy}) between L glutamine and alcohol molecules have been computed by the McMillan–Mayer formalism. It has been found that these coefficients become increasingly positive in EtOH, 1-PrOH, and 2-PrOH sequence. A linear relationship between the enthalpic coefficients of pairwise interactions of L glutamine-alcohol and those of alcohol-H_2O is also established. A comparative analysis of the thermochemical characteristics of L glutamine dissolution and some amino acids in the mixtures studied has been made.

1. Introduction

The studies on the thermodynamic properties of various amino acids and simple peptides in aqueous solutions of organic substances are of current interest due to their importance for a better insight into the nature and mechanisms taking place in biological systems. The research [1–6] of the interactions of amino acids and peptides with the components of various aqueous-organic mixtures is still under way in our laboratory. Highlighted in this article are the results of our investigation of thermochemical characteristics of L glutamine dissolution in aqueous solutions of alcohols. L glutamine (I) is amino acid with a side chain $R = -(CH_2)_2CONH_2$. It is conditionally essential amino acid obtained by an enzyme glutamine synthesis from glutamate and ammonia. L glutamine is an important contributor to a variety of biochemical processes (as a nitrogen donor for the biosynthesis of many compounds, including other amino acids, purines and pyrimidines) [7–10]. Here the major objectives of the authors of this work were: a) to study the way the changes in the structures of alcohols (EtOH, 1-PrOH, 2-PrOH) and their concentrations exert an influence on the thermochemical characteristics of L glutamine dissolution in the aqueous solution of alcohols (up to 0.30 mol fractions of alcohol and at $T = 298.15$ K); b) to compare the resulting data with those obtained earlier for some amino acids with various side-chains: DL alanine [11], L valine [12], L threonine [13] and L methionine [14] in similar mixtures; c) to evaluate the contribution of the side chains of various amino acids to the energy of their interparticle interactions with the molecules of alcohols in aqueous solutions. The experimental data for L glutamine presented by the authors are original.



(I)

2. Experimental

The substances used in the experiments, their molecular mass, formula, provenance, purity, and H_2O content are presented in Table 1. Molality (m) of L glutamine in a mixed solvent varied in the range from (0.5 to 1.5)·10^{-2} mol·kg^{-1}. Alcohols were used without further purification, their concentration varying from 0 to 0.25 mol fractions. H_2O has been purified by double distillation followed by degassing (electrical conductivity $p \approx 1 \cdot 10^{-6}$ S cm^{-1}). All the solutions were prepared immediately before the experiment. Mixtures and samples of L glutamine have been weighed by means of VLR-200 balances

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Table 1
The list of chemicals, their provenance and purity values.

Chemical	Formula	M[a]	CAS No.[b]	Provenance	Purity[c]	Water[d] content	Evapn. residue
L Glutamine	$C_5H_{10}N_2O_3$	146.14	56-85-9	Sigma-Aldrich	≥0.990 (HPLC)	–	–
Ethanol	C_2H_5OH	46.07	64-17-5	Sigma-Aldrich	≥0.998, (anhydrous)	<0.005%	<0.0005%
1 Propanol	C_3H_7OH	60.10	71-23-8	Sigma-Aldrich	≥0.997, (anhydrous)	<0.005%	<0.0003%
2 Propanol	C_3H_7OH	60.10	67-63-0	Sigma-Aldrich	≥0.995, (HPLS)	<0.05%	<0.0003%
Water	H_2O	18.02	7732-18-5	–	([e])	–	–

[a] Molecular mass, ($g \cdot mol^{-1}$).
[b] Chemical Abstract Service registry number.
[c] Mass fraction (as stated by the supplier).
[d] Karl Fisher titration (mass %).
[e] H_2O – bidistillate, electrical conductivity $p \approx 1 \cdot 10^{-6}$ $S \cdot cm^{-1}$, refractive index $n^{20}/D = 1.34$.

("Gosmetr", Sankt-Peterburg, Russia), the accuracy of measurements being $5 \cdot 10^{-5}$ g. The calorimetric measurements were performed at $T = 298.15 \pm 0.01$ K and $P = (100.5 \pm 0.7)$ kPa by using an isoperibolic calorimeter described in detail earlier [15]. The calibration data of the calorimeter and the calculation of measurement errors are presented in [16]. The reliability of the resulting data of the dissolution of some amino acids and peptides in water is confirmed by comparing them with similar results of other authors [17–21].

3. Results

The standard dissolution enthalpies, $\Delta_{sol}H^{\circ}(\equiv\Delta_{sol}H^{\infty})$, of L glutamine are calculated by averaging the results of the five independent measurements of $\Delta_{sol}H^{m}$ for each alcohol composition. No dependence between $\Delta_{sol}H^{m}$ and m is observed in the concentration range of L glutamine under study. The data on $\Delta_{sol}H^{\circ}$ obtained for L glutamine in the aqueous solution of alcohols under study are collected in Table 2. The transfer enthalpies of L glutamine $\Delta_{tr}H^{\circ}$ are calculated from the Eq. (1).

$$\Delta_{tr}H^{\circ} = \Delta_{sol}H^{\circ}(w+y) - \Delta_{sol}H^{\circ}(w), \quad (1)$$

where $\Delta_{sol}H^{\circ}(w+y)$ is the dissolution enthalpy of L glutamine in each aqueous solution of the alcohol, $\Delta_{sol}H^{\circ}(w)$ – is the dissolution enthalpy of L glutamine in pure H_2O. The dissolution enthalpy of L glutamine in H_2O we obtained is $\Delta_{sol}H^{\circ}(w) = (20.52 \pm 0.05)$ kJ mol^{-1} at infinite dilution. The changes in $\Delta_{tr}H^{\circ}$ for L glutamine relative to alcohol content are shown in Fig.1.

Table 2
The standard dissolution enthalpies of L glutamine ($\Delta_{sol}H^{\circ}$, kJ mol^{-1}) with the standard uncertainty ($u(\Delta_{sol}H^{\circ}$, kJ mol^{-1})) at different mole fraction (x_2) of alcohols in aqueous solution at $T = 298.15$ K and $p = 100.5$ kPa.

EtOH			1-PrOH			2-PrOH		
x_2	$\Delta_{sol}H^{\circ}$	$u(\Delta_{sol}H^{\circ})$	x_2	$\Delta_{sol}H^{\circ}$	$u(\Delta_{sol}H^{\circ})$	x_2	$\Delta_{sol}H^{\circ}$	$u(\Delta_{sol}H^{\circ})$
0.015	21.18	0.04	0.013	21.42	0.04	0.011	22.13	0.04
0.028	21.62	0.04	0.022	21.89	0.05	0.022	23.34	0.05
0.043	22.14	0.05	0.035	22.64	0.05	0.032	24.68	0.06
0.058	22.73	0.05	0.047	23.35	0.05	0.045	25.73	0.05
0.075	23.34	0.04	0.057	23.82	0.05	0.058	26.93	0.05
0.091	23.88	0.04	0.068	24.29	0.05	0.069	27.66	0.05
0.107	24.46	0.04	0.079	24.79	0.05	0.084	28.31	0.06
0.127	24.96	0.04	0.098	25.37	0.06	0.097	28.63	0.06
0.146	25.34	0.05	0.138	25.96	0.06	0.113	28.86	0.06
0.167	25.84	0.05	0.195	25.28	0.06	0.128	28.79	0.06
0.209	26.04	0.05	0.252	22.29	0.05	0.163	27.77	0.05
0.234	25.96	0.06		–	–	0.194	26.51	0.06

Standard uncertainties (u) are $u(x_2) = 0.001$ mol fraction, $u(T) = 0.01$ K and $u(p) = 0.7$ kPa.

4. Discussion

From Fig. 1 it is seen that the transfer enthalpies of L glutamine are endothermic in character in all aqueous solutions of alcohols and depend both on the composition of a mixed solvent and the structure of an alcohol molecule. The $\Delta_{tr}H^{\circ}$ value increases monotonically with the growth in alcohol concentration up to $x_2 \approx 0.20$ in (H_2O + EtOH), $x_2 \approx 0.15$ in (H_2O + 1-PrOH) and $x_2 \approx 0.12$ in (H_2O + 2-PrOH) mixtures. The slope of a curve depends on the structure of alcohol and increases in series EtOH < 1-PrOH < 2-PrOH, which is can be associated with the enhancement of the hydrophobic properties of alcohols in the same order. In the range of these alcohol concentrations, the effects of partial dehydration of L glutamine and alcohol molecules predominate over effects of the direct interactions between them. Besides, the positive values of $\Delta_{tr}H^{\circ}$ of L glutamine may be associated with the destruction of the structure of water and the formation of a mixed solvent in which L glutamine can be involved in spatial configuration due to the formation of H-bonds with the components of the mixture. In the range of alcohol concentrations $x_2 = 0.11 \div 0.22$, endothermic maxima are observed on the curves $\Delta_{tr}H^{\circ} = f(x_2)$. This is typical for solutions of non-electrolytes [22–24]. An endothermic maximum of $\Delta_{tr}H^{\circ} = f(x_2)$ dependence corresponds to an exothermic maximum of the excess molar enthalpies of binary systems (H_2O + alcohol) at virtually the same mixed solvent composition [25–27]. With the increase in the concentration of alcohols above maximums, the exothermic contribution from the direct interaction of

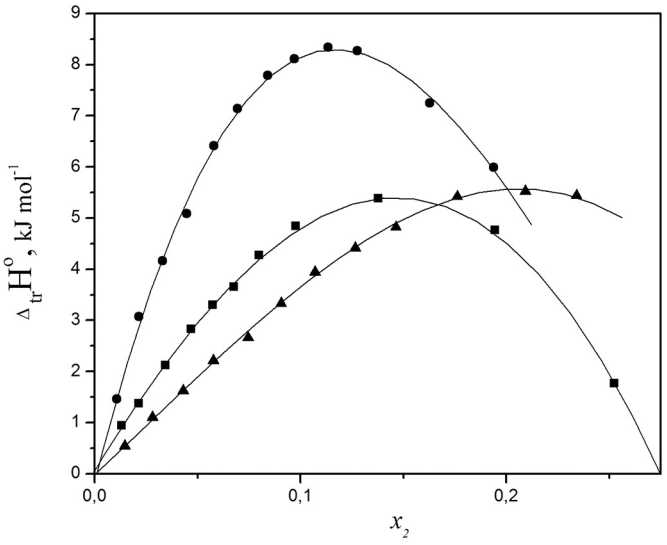

Fig. 1. The transfer enthalpies, $\Delta_{tr}H^{\circ}$, of L-glutamine from H_2O into H_2O + EtOH (-▲-), H_2O + 1-PrOH (-■-) and H_2O + 2-PrOH (-●-) mixed solvents as a function of the alcohol mole fraction (x_2) at $T = 298.15$ K.