Journal of Molecular Liquids 195 (2014) 139–144

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Influence of the composition of water–organic mixtures and of organic solvents properties on solvation of glycyl-*L*-tyrosine at 298.15 K

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ARTICLE INFO

Article history:
Received 8 October 2013
Received in revised form 16 January 2014
Accepted 20 February 2014
Available online 6 March 2014

Keywords:
Peptides
Water
Organic solvents
Enthalpy of solution
Enthalpy of transfer
Mixed solvent

ABSTRACT

Enthalpies of dissolution of glycyl-*L*-tyrosine in the mixtures of water with methanol (MeOH), ethanol (EtOH), propanol (1-PrOH), 2-propanol (2-PrOH), acetonitrile (AN), 1,4-dioxane (DO),acetone (AN), dimethylsulfoxide (DMSO), formamide (FA), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) have been measured at 298.15 K. The standard enthalpies of the solution ($\Delta_{sol}H^{\circ}$) and transfer ($\Delta_{tr}H^{\circ}$) of glycol-*L*-tyrosine from water into aqueous solution of organic co-solvents as well as the enthalpy coefficients of pairwise interaction (h_{xy}) have been calculated. The interrelation between the enthalpy characteristics of dissolution (transfer) of glycyl-*L*-tyrosine and the composition of aqueous organic mixtures was established. Contributions of the organic co-solvent properties (molar volume, cohesion energy density, dipolarity/polarizability, acidity and basicity) to the energy of pairwise interactions were estimated quantitatively by means of a modified Kamlet–Taft equation. Some characteristics of intermolecular interactions of glycyl-*L*-tyrosine with the molecules of organic co-solvents with the analogous characteristics of glycylglycine and diglycylglycine were compared.

1. Introduction

In recent years, one observes a considerable increase of the interest in a study of the multicomponent model biological systems containing peptide (amino acid), organic solvent and, as the basic solvent, water [1–5]. This interest can be associated with the wide variety of the organic solvents, many of which, to one degree or another are constituents of the living organisms and are widely used in the synthesis of medicines, in the perfume industry. For the best understanding the interaction mechanism of organic co-solvents with various amino acids and peptides, and as a continuation of the thermochemical investigations of biological model molecular systems in our laboratory [6–10] we report in this paper on the interactions between glycyl-*L*-tyrosine and some organic co-solvents in the aqueous solution. Glycyl-*L*-tyrosine was chosen as object of research as its molecule contains an aromatic cycle ($-C_6H_5OH$). It allowed us to compare its thermodynamic characteristics of dissolution in aqueous organic mixtures with the similar dissolution characteristics of glycyl-peptides consisting of aliphatic amino acids. The organic solvents of different structures (alcohols, amides, ketone) and with various physico-chemical properties (electron-donor or acceptor ability, polarity and polarizability): MeOH, EtOH, 1-PrOH, 2-PrOH, AN, 1, 4-DO, AC, DMSO, FA, NMF, DMF and DMA were selected as the co-solvents. The experiment was carried out at 298.15 K and the mole fraction of organic solvent: $x_2 = 0$–0.35. The experimental data on the enthalpies of solution $\Delta_{sol}H^{m}$ were used to calculate the standard values of dissolution enthalpies, $\Delta_{sol}H^{\circ}$ and transfer, $\Delta_{tr}H^{\circ}$ of glycyl-*L*-tyrosine from H_2O to binary solvent and enthalpic coefficients of the pairwise interactions, h_{xy}, of glycyl-*L*-tyrosine with the molecules of organic solvent. The results were analyzed and interpreted from the point of view of the influence of acidity, basity, dipolarity/polarizability and cohesion energy density of the organic co-solvent on the interparticle interactions of organic co-solvent molecules with glycyl-*L*-tyrosine molecules. For this purpose, we used the Kamlet–Taft correlation equation [11]. Furthermore, we carried out comparative analysis of some of the thermochemical characteristics of glycyl-*L*-tyrosine with the similar characteristics of glycylglycine and glycylclycylclycine in the studied mixtures [7,8].

2. Experimental

Glycyl-*L*-tyrosine (CAS-No.658-79-7, Assay:99%, Sigma-Aldrich) was dried up in a vacuum box at 333 K within 48 h, was stored over P_2O_5 in a desiccator and was used without further purification. The molal concentration (m) of glycyl-*L*-tyrosine varied within the range of $5 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$ mol kg^{-1} of a mixed solvent. All alcohols are of Sigma-Aldrich brand: MeOH (CAS-No. 67-56-1, anhydrous, 99.8%), EtOH (CAS-No. 64-17-5, absolute, SPECTRANAL™, ≥99.8%, GC), 1-PrOH

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http://dx.doi.org/10.1016/j.molliq.2014.02.018
0167-7322/

(CAS-No. 71-23-8, biotech. grade, 99.7%), 2-PrOH (CAS-No. 67-63-0, anhydrous, 99.5%), AN (CAS-No. 75-05-8, anhydrous, purity 0.998, Sigma-Aldrich), 1,4-DO (CAS-No. 123-91-1, anhydrous, purity 0.998, Sigma-Aldrich), AC (CAS-No. 67-64-1, capillary GC grade, purity ≥0.999, Fluka), DMSO (CAS-No. 67-68-5, GC, purity ≥0.995, Sigma), FA (CAS-No. 75-12-7, purum, purity ≥0.980, Fluka), MFA (CAS-No. 123-39-7, purity 0.99, Aldrich), DMF (CAS-No. 68-12-2, anhydrous, purity 0.998, Sigma-Aldrich) and DMA (CAS-No. 127-19-5, anhydrous, purity 0.998, Sigma-Aldrich) were used without further purification. H_2O content in the organic co-solvent, defined by titration by Karl Fisher's method [12], did not exceed 0.04% of mass. The H_2O was purified by distillation (a specific conductivity of *ca.* $1.0 \cdot 10^{-5}$ S m^{-1}). All weightings were done on an analytic balance VLR-200 ("Gosmetr", Sankt-Petersburg, Russia) within the accuracy from $\pm 5 \cdot 10^{-5}$ g. Calorimetric measurements have been performed in an "isoperibol" hermetic calorimeter. The calorimeter was tested by measuring (10 experiments) the enthalpy of solution of potassium chloride (KCl) in water at 298.15 K according to [13–15]. Our values of ($\Delta_{sol}H^m$ (m = 0.111 mol kg^{-1}) = 17.60 ± 0.04 kJ mol^{-1} and $\Delta_{sol}H^\circ$ = 17.23 ± 0.07 kJ mol^{-1}) agree with the recommended literature values 17.58 ± 0.02 kJ mol^{-1} [15] and 17.22 ± 0.04 kJ mol^{-1} [13,14], respectively). The relative random error of measurements did not exceed 0.5%. All measurements were made at (298.15 ± 0.01) K.

3. Results

The dependence of the dissolution enthalpy of glycyl-*L*-tyrosine on the concentration within the studied concentration range of glycyl-*L*-tyrosine in the mixtures is not detected. For that reason the values of the standard enthalpy of solution ($\Delta_{sol}H^\circ$) in all investigated systems were calculated as a mean value of five measurements of $\Delta_{sol}H^m$ for each composition of H_2O + organic solvent. The confidence interval half with ($\pm\xi_n$) of the $\Delta_{sol}H^\circ$ value was determined by the Peters formula [16] for the root-mean-square error, $\xi_n = t_{0.95}\frac{4}{5}\sum_{i=1}^{n}|x_i - \widetilde{x}_i|/\left[n(n-1)^{1/2}\right]$ with correction for a Student criterion of $t_{0.95}$ = 2.78. Here (n = 5) is the number of runs, $x_i = \Delta_{sol}H^m$ and $\widetilde{x}_i = |\Delta_{sol}H^m|_{av}$. The obtained values of $\Delta_{sol}H^\circ$ for glycyl-*L*-tyrosine in the investigated systems and their standard deviations are presented in Table 1. The transfer enthalpy $\Delta_{tr}H^\circ$ was calculated from 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 enthalpy of glycyl-*L*-tyrosine dissolution in the aqueous organic solvent; $\Delta_{sol}H^\circ(w)$—is the enthalpy of glycyl-*L*-tyrosine dissolution in pure water. The enthalpy of glycyl-*L*-tyrosine dissolution in pure H_2O measured by us is $\Delta_{sol}H^\circ(w)$ = 23.63 ± 0.04 kJ/mol. The dependences of $\Delta_{tr}H^\circ$ for glycyl-*L*-tyrosine against the organic solvent mole-fraction content are shown in Figs. 1–3.

4. Discussion

One can see from Figs. 1, 2 and 3 that a change in enthalpy of the transfer of glycyl-*L*-tyrosine from the H_2O into the H_2O + organic solvent mixtures depends both on the nature of organic solvent (alcohols, amides and aprotic organic solvents) and on its content in the mixture. The values of the glycyl-*L*-tyrosine transfer enthalpies can be only endothermic (in the H_2O + AN, H_2O + MeOH, H_2O + EtOH and H_2O + 2-PrOH mixtures) or only exothermic (in the H_2O + FA, H_2O + MFA mixtures) in all studied mole-fraction range of organic co-solvent.

Table 1
Standard enthalpies of glycyl-*L*-tyrosine dissolution ($\Delta_{sol}H^\circ$, kJ mol^{-1}) in different molal concentrations (m_2, mol kg^{-1}) of organic solvents in an aqueous solution at 298.15 K.

m_2	MeOH	m_2	EtOH	m_2	1-PrOH	m_2	2-PrOH
1.115	25.69 ± 0.03	0.830	26.51 ± 0.03	0.588	25.84 ± 0.03	0.567	26.14 ± 0.03
2.229	27.68 ± 0.03	1.608	28.46 ± 0.03	1.169	27.21 ± 0.03	1.175	28.26 ± 0.03
3.480	28.84 ± 0.03	2.496	30.62 ± 0.03	1.831	28.58 ± 0.03	1.828	29.44 ± 0.03
4.704	29.72 ± 0.02	3.402	31.11 ± 0.02	2.574	29.64 ± 0.02	2.501	31.35 ± 0.03
6.129	31.41 ± 0.02	4.472	33.35 ± 0.02	3.327	30.43 ± 0.02	3.244	32.82 ± 0.02
7.729	32.04 ± 0.02	5.528	33.95 ± 0.02	4.185	30.83 ± 0.02	4.069	33.95 ± 0.02
9.234	31.29 ± 0.02	6.655	33.87 ± 0.02	5.040	30.55 ± 0.02	4.928	34.67 ± 0.02
11.156	29.94 ± 0.02	8.055	33.51 ± 0.02	6.081	29.95 ± 0.02	5.886	34.57 ± 0.02
13.185	29.35 ± 0.02	9.518	32.66 ± 0.02	7.086	28.28 ± 0.02	6.923	33.77 ± 0.02
17.861	27.31 ± 0.03	11.090	31.92 ± 0.02	8.301	26.39 ± 0.02	8.005	32.76 ± 0.02
23.672	24.41 ± 0.03	14.693	30.55 ± 0.03	11.054	22.12 ± 0.03	10.653	29.55 ± 0.03
m_2	FA	m_2	MFA	m_2	DMF	m_2	DMA
1.005	22.71 ± 0.03	0.677	23.42 ± 0.03	0.579	24.23 ± 0.03	0.474	24.06 ± 0.03
2.326	21.88 ± 0.03	1.539	23.19 ± 0.03	1.192	24.59 ± 0.03	1.009	24.85 ± 0.03
3.644	20.82 ± 0.03	2.352	23.05 ± 0.03	1.833	24.67 ± 0.03	1.523	25.18 ± 0.03
5.146	19.92 ± 0.03	3.365	22.81 ± 0.03	2.560	24.84 ± 0.02	2.129	25.38 ± 0.02
6.845	18.89 ± 0.02	4.450	22.44 ± 0.02	3.303	24.95 ± 0.02	2.810	25.59 ± 0.02
8.944	18.47 ± 0.02	5.632	22.05 ± 0.02	4.202	24.63 ± 0.02	3.581	25.22 ± 0.02
11.067	17.46 ± 0.02	6.875	21.72 ± 0.02	5.158	23.96 ± 0.02	4.303	25.19 ± 0.02
13.540	17.37 ± 0.02	8.451	21.70 ± 0.02	6.233	23.23 ± 0.02	5.237	24.78 ± 0.02
16.794	17.16 ± 0.03	10.200	21.42 ± 0.02	7.590	22.19 ± 0.03	6.135	24.16 ± 0.02
19.168	17.58 ± 0.03	12.267	21.34 ± 0.03	9.044	21.15 ± 0.03	7.256	22.79 ± 0.03
m_2	AN	m_2	1,4-DO	m_2	AC	m_2	DMSO
0.787	23.46 ± 0.03	0.518	24.45 ± 0.03	0.569	24.32 ± 0.03	0.591	23.95 ± 0.03
1.810	23.29 ± 0.03	1.111	24.84 ± 0.03	1.219	24.79 ± 0.03	1.255	24.18 ± 0.03
2.661	23.14 ± 0.03	1.698	25.22 ± 0.03	1.828	25.08 ± 0.03	2.034	24.43 ± 0.03
3.634	23.93 ± 0.03	2.352	25.41 ± 0.03	2.572	25.73 ± 0.02	2.854	24.82 ± 0.02
4.737	22.77 ± 0.02	3.074	25.49 ± 0.02	3.324	25.86 ± 0.02	3.812	25.22 ± 0.02
5.856	22.54 ± 0.02	3.970	25.11 ± 0.02	4.113	26.14 ± 0.02	4.830	25.49 ± 0.02
7.112	22.27 ± 0.02	4.817	24.33 ± 0.02	4.927	26.29 ± 0.02	6.023	25.67 ± 0.02
8.499	22.11 ± 0.02	5.938	23.28 ± 0.02	6.028	25.98 ± 0.02	7.367	25.83 ± 0.02
9.941	21.75 ± 0.03	7.109	21.67 ± 0.02	7.072	25.57 ± 0.03	8.888	25.86 ± 0.02
11.210	21.61 ± 0.03	8.579	20.43 ± 0.03	8.283	24.52 ± 0.03	10.764	25.49 ± 0.03
15.519	20.71 ± 0.03	11.995	18.23 ± 0.03	11.023	21.85 ± 0.03	15.496	22.72 ± 0.03