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Short Communication

Influence of *N*-methyl substitution in the glycine molecule on its enthalpic dissolution characteristics in mixed aqueous-amide solvents at $T = 298.15$ K

Valeriy I. Smirnov *, Valentin G. Badelin

Laboratory of Thermodynamics of Non-electrolyte Solutions and Biologically Active Substances, G.A.Krestov Institute of Solution Chemistry, Russian Academy of Sciences, 1 Akademicheskaya Street, 153045 Ivanovo, Russia

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ABSTRACT

The dissolution enthalpies of *N*-methylglycine were obtained in aqueous solutions of formamide (FA), *N*-methylformamide (MFA), *N,N*-dimethylformamide (DMF), acetamide (AM) and *N*, *N*-dimethylacetamide (DMA) with amide mole fraction (x_2) from 0 to 0.25 at $T = 298.15$ K. The results obtained have been used to calculate the standard values of dissolution enthalpies ($\Delta_{sol}H^{\circ}$) and transfer enthalpies ($\Delta_{tr}H^{\circ}$) of *N*-methylglycine from water into (water + amide) mixtures as well as the coefficients of pairwise interaction (h_{xy}) of *N*-methylglycine with the amide molecules in aqueous solutions. The interdependence between enthalpy characteristics of *N*-methylglycine dissolution (transfer) and the concentration of amide in aqueous solutions has been established. Comparison of the resulting data with those obtained earlier for glycine (Gly) and (*L*-)*DL*-α-alanine (Ala) in the same mixed solvents at $T = 298.15$ K has been made.

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1. Introduction

As the continuation of previous thermochemical research of the processes of dissolution and solvation of various amino acids in the aqueous organic mixtures [1–7], in the current paper reports on the impact of *N*-methyl substitution in the glycine molecule on its enthalpic dissolution characteristics in mixed aqueous-amide solvents at $T = 298.15$ K. As the object of the study, we selected *N*-methylglycine (I). It is a natural amino acid playing a significant role in metabolic processes of living cells as a source of serine, creatine, and purine. It is of interest to various chemical and biological processes that find its niche in beauty product industry and medicine [8–11]. The investigation of the processes of dissolution of glycine [1,12,13] and alanine [2,14] in the water + amide mixtures we carried out earlier, enables us to evaluate the effect of *N*-methyl substitution in the amino acid molecule on its energy of interaction with the molecules of various amides in aqueous solution. Since *N*-methylglycine (sarcosine) is practically an “isomer” of alanine, new data obtained will show how the substitution of one proton in the amino acid molecule in both the NH_2-group (*N*-methylglycine) and CH_2-group (alanine) for CH_3-group can affect the thermochemical characteristics of glycine dissolution in similar mixtures. Use was made of aqueous solutions of some amides (FA, MFA, DMF, AM and DMA) as a mixed solvent. Liquid amides form an attractive class of solvents, as a small change in the chemical structure of the amide molecule results in a dramatic change of its solvent properties. Amide co-solutes are of particular interest because they bear structural resemblance with proteins (they contain a functional (-CONH) group, which is a fragment of protein systems). Aqueous solutions of amides are widely used in industry, biochemistry, pharmacology, as well as in the research of molecular interactions between the molecules of biologically active substances. The purpose of this study was to get new experimental data for estimating the effect of methyl substitution in NH_2- group of the glycine molecule on its thermochemical characteristics of dissolution in mixed (water + amide) solvents. With that end in view, the dissolution enthalpies of *N*-methylglycine in the aqueous solutions of amides: FA, MFA, DMF, AM and DMA at $T = 298.15$C and the concentrations of amide $x_2 = 0 \div 0.25$ mol fraction were measured. Their standard values, as well as the enthalpies of the transfer from H_2O into (H_2O + amide) mixtures and the enthalpic coefficients of pairwise interactions (h_{xy}) between *N*-methylglycine molecules and the amide molecules, were calculated. The results of this work and those given in [13,14] as well as the data obtained earlier for glycine [1]

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* Corresponding author.
E-mail address: vis@isc-ras.ru (V.I. Smirnov).

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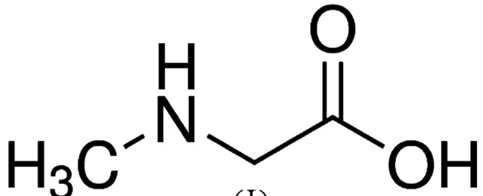
and alanine [2] in similar water-amide mixtures were compared and discussed.



(I)

2. Experimental

The substances used in the experiments, their molecular mass, formula, provenance, purity, and contents of H_2O are presented in Table 1. Molality (m) of *N*-methylglycine in a mixed solvent varied in the range from $(0.5 \text{ to } 1.5) \cdot 10^{-2}$ mol·kg^{-1}. Amides 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 *N*-methylglycine have been weighed by means of VLR-200 balances ("Gosmetr", Sankt-Peterburg, Russia), the accuracy of measurements being $5 \cdot 10^{-5}$ g. Calorimetric measurements of the dissolution enthalpies of *N*-methylglycine have been carried out in a calorimeter with an isothermal shell at $T = (298.15 \pm 0.01)$ K and $P = (100.5 \pm 0.7)$ kPa. A scheme of the experimental set-up and the description of the experimental procedure have been presented 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] → [14], [17] → [18] and [19] → [20].

3. Results

The standard dissolution enthalpies, $\Delta_{sol}H^{\circ}(\equiv\Delta_{sol}H^{\infty})$, of *N*-methylglycine are calculated by averaging the results of the five independent measurements of $\Delta_{sol}H^{m}$ for each amide composition. No dependence between $\Delta_{sol}H^{m}$ and m is observed in the concentration range of *N*-methylglycine under study. The data on $\Delta_{sol}H^{\circ}$ obtained for *N*-methylglycine in the aqueous solution of amides under study are given in Table 2. The transfer enthalpies of *N*-methylglycine $\Delta_{tr}H^{\circ}$ are calculated from the following equation:

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

where $\Delta_{sol}H^{\circ}\ (w+y)$ is the dissolution enthalpy of *N*-methylglycine in each aqueous solution of the amide,$\Delta_{sol}H^{\circ}\ (w)$ – is the dissolution enthalpy of *N*-methylglycine in pure H_2O. The dissolution enthalpy of *N*-methylglycine in H_2O we obtained is $\Delta_{sol}H^{\circ}\ (w) = (3.97 \pm 0.03)$ kJ·mol^{-1} at infinite dilution. The changes in $\Delta_{tr}H^{\circ}$ for *N*-methylglycine relative to amides content are shown in Fig.1.

4. Discussion

From the experimental results presented in Table 2 and Fig. 1, it becomes evident that the dissolution and transfer enthalpies of *N*-methylglycine depend on both the structure and the concentration of amides in the aqueous solution. The values of $\Delta_{tr}H^{\circ}$ of *N*-methylglycine are endothermic over all the amide concentration ranges studied (MFA, DMF, AM and DMA). In these mixtures the molecules of *N*-methylglycine and amides undergo strong hydration, and a contribution of the energy of this dehydration and hydrophobic/hydrophobic interactions to the total energy effect of interactions dominates over the contribution of the direct interactions. The increase in the concentration of amides increases contribution of the dehydration energy of their molecules to $\Delta_{tr}H^{\circ}$. Fig. 1 shows that the endothermicity of *N*-methylglycine transfer from water into $H_2O + FA$, $H_2O + AM$, $H_2O + MFA$, $H_2O + DMF$ and $H_2O + DMA$ mixtures grows in size in the order of increasing of hydrophobic properties of amides: FA < AM < MFA < DMF < DMA [21]. That is, the enhancement of the hydrophobic properties of amides promotes the growth of endothermicity of *N*-methylglycine transfer enthalpies due to the gain in hydrophobic-hydrophobic interactions between amide and *N*-methylglycine molecules. The exothermic values of $\Delta_{tr}H^{\circ}$ for *N*-methylglycine in (H_2O + FA) mixture are attributed to the formation of the weak H-bonds between FA and H_2O molecules. The enthalpies of (H_2O + FA) mixing have low positive values [21,22]. Therefore, the energy consumption for the dehydration of FA molecules is not great. Increasing FA concentration in the aqueous solution results in but only slight increase in the exothermicity of dissolution and transfer of *N*-methylglycine. Since the transfer enthalpies of glycine and alanine in mixed solvents were calculated in [1,2], we compared the values of $\Delta_{tr}H^{\circ}$ for glycine, alanine, and *N*-methylglycine (as an example) in (H_2O + FA) mixture by changing the amide concentration. Fig. 2 demonstrates that the endothermicity of $\Delta_{tr}H^{\circ}$ grows in magnitude in the order: Gly < MGly < Ala. This can be explained as follows: a) replacement of the proton in NH_2-group of glycine by CH_3-group weakens its proton-donor properties (the ability to form H– bonds) and enhances hydrophobic properties (hydrophobic-hydrophobic interactions with amide molecules); b) the transition from glycine to alanine results in further increase of the endothermicity of alanine transfer due to the hydrophobic effect of the alkyl group on the COOH-group. In addition, an increase in the FA concentration in the aqueous solution changes the form of $\Delta_{tr}H^{\circ} = f(x_2)$ dependence. Characteristic for the glycine and *N*-methylglycine are the exothermic peaks at $x_2 \approx 0.2$. In case with glycine, it is twice as large as that for *N*-methylglycine. This suggests a stronger intermolecular interaction between glycine and FA molecules as compared with *N*-methylglycine (this is the case for the

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
N-methylglycine	$C_3H_7NO_2$	89.09	107-97-1	Fluka	≥0.990	–	–
L-alanine	$C_3H_7NO_2$	89.09	56-41-7	Aldrich	≥0.990 (GLC)	–	–
Formamide	CH_3NO	45.04	75-12-7	Sigma-Aldrich	≥0.998	<0.030%	<0.02% (free acid)
N-methyl-formamide	C_2H_6NO	59.07	123-39-7	Aldrich	≥0.990	<0.030%	–
N,N-dimethyl-acetamide	C_4H_9NO	87.12	127-19-5	Sigma-Aldrich	≥0.998, (anhydrous)	<0.005%	<0.0010%
N,N-dimethyl-formamide	C_3H_7NO	73.09	68-12-2	Sigma-Aldrich	≥0.990, (anhydrous)	<0.005%	<0.0005%
Water	H_2O	18.02	7732-18-5	–	(e)	–	–

[a] Molecular mass, (g·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·cm^{-1}, refractive index n^{20}/D = 1.34.

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