Study of intermolecular interactions in aqueous solutions by millimeter spectroscopy

6.* Negative hydration of the glycine zwitterion

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The absorption of millimeter electromagnetic radiation (ν = 1.4, 1.71, and 5 cm^{-1}) by aqueous solutions of glycine (pH 6.1—6.2) in the concentration range of 0.5—2.5 mol L^{-1} was measured. It was found that the absorbing ability of the water present in the solutions, is higher than that of pure water. This phenomenon is explained by the presence of a center of negative hydration in the structure of the glycine zwitterion, which results in an increase in the rotational mobility of water molecules immobilized in the hydrate shell of the glycine zwitterion.

Key words: glycine zwitterion, negative and positive hydration, aqueous solution, absorption of millimeter radiation.

The biological role of α-amino acids evokes great interest in the molecular mechanisms of their interaction with an aqueous medium. In an aqueous medium at neutral pH values, α-amino acids exist in the form of $NH_3^+CHRCOO^-$ zwitterions. Both charged groups can play the role of centers of the formation of H bonds with water molecules. The comparatively short distance between the withdrawing and donating centers is noticeably reflected in the acid-base and other physicochemical properties of α-amino acids. In particular, the IR spectra in the overtone region showed the formation of a stable 1 : 1 α-amino acid—water molecular complex.[2] The authors of this work assumed that in these complexes, a water molecule simultaneously forms two H bonds with the donor and acceptor groups of the α-amino acid, respectively. This mechanism of complex formation was not confirmed either in other experimental studies, or in a simulation of the hydration of glycine by the Monte-Carlo method.[3] *Ab initio* quantum-mechanical calculations of the glycine—water system showed, however, that this complex can exist.[4]

To obtain additional information on the character of intermolecular interactions of water molecules with the zwitterion of an α-amino acid, we used absorption millimeter spectroscopy (AMS). The AMS experiment and its interpretation are considered in detail in Ref. 5. In this review, in particular, some problems that appear in the study of the hydration of α-amino acids are discussed.

The absorption of millimeter (MM) radiation by aqueous systems is a smooth function of frequency. Nevertheless, the AMS method allows one to study the action of a dissolved substance on the aqueous component of the solution, detecting the number of water molecules that change their dynamic state in the hydrate shell of the dissolved substance.[5]

Experimental

The absorption coefficient* α (dB mm^{-1}) of the MM radiation (1.4—5 cm^{-1}) of aqueous solutions of glycine (pH 6.1—6.2; C_2 = 0.5—2.5/mol L^{-1}) was measured on quasi-optical and waveguide type setups in cells with variable thickness.[5] The absorption α_{exp} ($\sigma < 0.003$) was measured at a frequency of 5 cm^{-1} at 20 and 60 °C; measurements at frequencies of 1.71 and 1.40 cm^{-1} were performed only at 20 °C. Bidistilled water and twice recrystallized glycine (Reanal) were used for the preparation of solutions.

Results and Discussion

As can be seen from Fig. 1, the absorption of MM radiation by aqueous solutions of glycine at all frequen-

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* For Part 5, see Ref. 1.

† Deceased.

* $\alpha = \log(I/I_0)$ is the equivalent of the optical density in optical spectroscopy.

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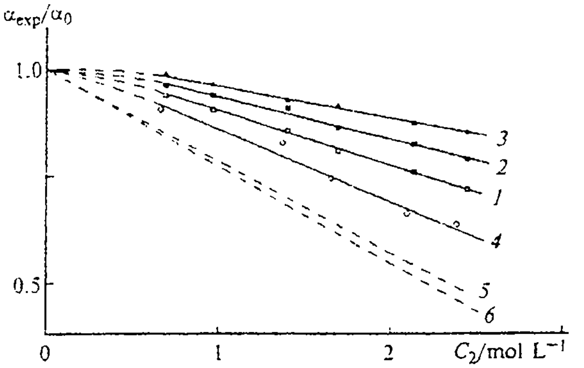


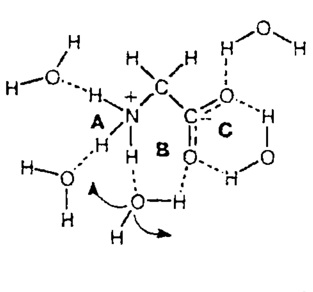
Fig. 1. Concentration dependence of the relative absorption of MM radiation (α_{exp}/α_0) in aqueous solutions of glycine at 20 °C (*1—3*) and 60 °C (*4*); ν/cm^{-1}: 5 (*1*, *4*), 1.71 (*2*), 1.40 (*3*). The calculated contributions of the water component to the absorption at 20 (*5*) and 60 °C (*6*).

cies used decreases as the concentration of glycine C_2 increases. The experimentally determined values of the absorption of the solutions α_{exp} (Fig. 1, curves *1—4*) at all frequencies at 20 and 60 °C are higher than the contribution of the water present in the solution to the absorption (α_1) (Fig. 1, curves *5* and *6*).

When a dissolved substance exerts no effect on the absorption of water, the absorption of the solution is determined by the concentration of water: $\alpha_1 = \alpha_0 \cdot C_1/C_0$, where α_0 is the absorption of pure water, and C_1 and C_0 are the concentrations of water (mol L^{-1}) in the solution and in the pure solvent (Fig. 1, curves *5* and *6*). However, the experimental data show that in aqueous solutions of glycine, as in the majority of cases, $\alpha_{exp}/\alpha_0 \neq C_1/C_0$,*.[5] The fact that the absorption is nonadditive ($\delta\alpha/\alpha_0 = C_1/C_0 - \alpha_{exp}/\alpha_0$) is related to a change in the fraction of water molecules that absorb MM radiation[5] in the solution. The sign of the absorption deficiency[5] $\delta\alpha$ indicates whether the contributions of positive ($\delta\alpha > 0$) or negative ($\delta\alpha < 0$) hydration to the experimentally determined hydration number $N_\theta = (\delta\alpha/\alpha_0) \cdot (C_0/C_2)$ (1 mole of H_2O per mole of glycine) predominate. The negative $\delta\alpha/\alpha_0$ values for glycine indicate that effects breaking the water structure predominate in aqueous solutions of glycine (see Fig. 1), which confirms the assumption[7] that glycine breaks the water structure.

It has been previously established[8] that a similar effect ($\alpha_{exp}/\alpha_0 > C_1/C_0$) for aqueous solutions of urea is caused by structural features of this substance. The shape of the potential energy profile of the urea—water system (according to the *ab initio* quantum-chemical data[9]) is such that only one water molecule, which can freely move from one H atom to another while retaining its rotational mobility, can be arranged near two closely located *cis*-H atoms. This water molecule can be a secondary center of hydration, resulting in the decomposition of the water structure in the "second" hydrate layer of the dissolved substance (negative hydration).

We assume that the negative deficiency of absorption[3,8] ($\delta\alpha < 0$) in aqueous solutions of urea and glycine is caused by the same mechanism of hydration of these compounds, *i.e.*, by the existence of a center of negative hydration (rather closely arranged atoms, capable of forming hydrogen bonds with water molecules) in the glycine zwitterion. Three centers of hydrophilic hydration[4] **A**, **B**, and **C** can exist in the glycine zwitterion.



The question is which of these centers is a site of localization of positive hydration and which is a center of negative hydration. The AMS studies of alkaline forms of α-amino acids and some salts of carboxylic acids showed that positive hydration of the COO$^-$ group is preferable (center **C**). Three water molecules can be arranged in the hydrate shell of a COO$^-$ group, and one of them forms strong H bonds simultaneously with both oxygen atoms.[4] The NH_3^+ group is capable of forming hydrogen bonds with three water molecules, but one of them simultaneously forms an H bond with an oxygen atom of the COO$^-$ group.[4] Thus, the space between the NH and CO groups (center **B**) is the most probable center of negative hydration in the glycine zwitterion. The "bound" water molecule present in this space can likely migrate freely from the H atom to the O atom while retaining its rotational mobility as in the case of urea. The published data[2—4] do not contradict this viewpoint. Four water molecules that form hydrogen bonds with two H atoms of the ammonium group (center **A**) and with oxygen atoms of the carboxyl group

Table 1. Hydration numbers of glycine (N_θ) at different wavelengths (ν = 5, 1.71 and 1.40 cm^{-1}) and temperatures

T/°C	C_2 /mol L^{-1}	N_θ 5	1.71	1.40
20	0.68	−1.3	−1.7	−2.2
	0.96	−1.3	−1.7	−1.9
	1.39	−1.3	−1.7	−1.9
	1.68	−1.2	−1.5	−1.9
	2.13	−1.2	−1.5	−1.8
	2.43	−1.2	−1.5	−1.8
60	0.67	−0.8		
	1.37	−1.1		
	1.65	−0.8		
	2.09	−0.7		
	2.39	−0.7		

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* Dispersion of glycine lies outside the millimeter range.[6]

(center C) lose rotational mobility and contribute to positive hydration. The hydration number of glycine $N_{\theta,\mathrm{exp}}$ calculated from the experimental data, is equal to −1.2—−2.0 (see Table 1). Taking into account the algebraic character of hydration numbers determined from AMS data ($N_{\theta,\mathrm{exp}} = N_\theta^+ + N_\theta^-$),[5] it should be assumed that the glycine zwitterion can retain five to six mobile water molecules. Then the total number of water molecules in the hydrate shell of the glycine zwitterion $N = |N_\theta^+| + |N_\theta^-|$ can be 9 to 10. This value agrees well with the results of simulation of the hydration process of the glycine zwitterion by the Monte-Carlo method.[3]

The fact that the negative hydration of the glycine zwitterion is somewhat smaller at 60 °C (see Table 1) can be explained by an increase in the thermal motion of water molecules in solution, which results in weakening of the role of the "bound" water molecule as the secondary center of negative hydration.

It is noteworthy that at $\nu < 2$ cm^{-1}, the negative N_θ values increase (see Table 1). This can be explained by the manifestation of relaxation processes in the bulk water as the wavelength increases, whereas the corresponding effects almost do not appear in the 3—10 cm^{-1} region.[10]

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