Dielectric Behaviour of Glycine and Glycylglycine in Water in the Range of MHz

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The dielectric behaviour of glycine and glycylglycine in aqueous solution was examined for low concentrations and in the range of MHz, at 273 to 313 K. Only the solutions of glycylglycine exhibit dielectric absorption in the range 7.05×10^8 to 1.6×10^9 Hz. The dielectric absorption was attributed to the relaxation of glycylglycine molecules rotating with one or two molecules of water. The charge separation of the dipolar ion in solution was found to be 5.7 Å, the molecular radius 3 Å and the activation energy for the relaxation process 4 kcal/mole.

1. Introduction

The dielectric behaviour of aqueous solutions of glycine and glycylglycine was examined by Sandus and Lubitz [1] in the region of 9.37×10^9 Hz and by Aaron and Grant [2] in the region of 4.5×10^8 Hz to 9×10^8 Hz and at high concentrations. At these frequencies the dielectric absorption of the solutions is mainly due to the water, hence the contribution of the solutes to the dielectric absorption of the whole solution is very low [3].

In the present work the dielectric behaviour of the aqueous solutions of glycine and glycylglycine is studied in the region of 7.5×10^5 Hz to 1×10^7 Hz which is considerably lower compared to the frequency region used by the previous workers. No dielectric absorption was detected in aqueous solutions of glycine in the region examined in this research, while the solutions of glycylglycine exhibit dielectric absorption with a maximum at 7.05×10^8 to 1.6×10^9 Hz, depending on concentration and temperature.

In the region of frequencies used in the present work water has no dielectric absorption, therefore the contribution to the dielectric absorption of the solution of glycylglycine is due to the dielectric absorption of the solute. Low concentrations were used ranging from 2×10^{-3} to 1×10^{-2} M (M = molarity). The Debye [4] theory was applied for the evaluation of the results. Low concentrations are involved in biological systems for which the present work may be useful [5]. Conclusions regarding the activation energies of dielectric relaxation were also drawn by carrying out dielectric absorption measurements at five temperatures from 273 to 313 K.

2. Experimental

The dielectric measurements were performed using an apparatus [6] provided by Ferisol Co. (France). The measurements are based on the method of a series resonance of an oscillating (L, C) circuit. The apparatus covers the frequency region 1×10^3 to 7×10^7 Hz. The calculations of the dielectric constant ε' and the dielectric loss ε'' values were performed in the frequency region 7.5×10^5 to 1×10^7 Hz using the relations

$$\varepsilon' = 1 + \Delta C / C_a \,, \qquad (1)$$

$$\varepsilon'' = \frac{C_0}{C_a} \frac{\Delta Q}{Q\, Q_0} \qquad (2)$$

where $\Delta C = C - C_0$ and C_0, C are the cell capacitances without and with dielectric respectively, C_a is the active capacitance of the measuring cell, $\Delta Q = Q_0 - Q$, Q_0 is the Q factor for the empty cell and Q is the Q factor for the cell filled with the dielectric.

The cell was calibrated by using liquids of known dielectric constant. Each of the measurements was repeated several times to ensure the reproducibility of the results. A temperature control was achieved to ± 0.1 K as checked by a Beckman thermometer.

Glycine and glycylclycine purchased from Schuchardt Co were of purity greater than 99.5%. The compounds were recrystallized once from alcohol and water. The water used for the preparation of the solutions had a specific conductivity lower than $10^{-6}\, \Omega^{-1}\, \mathrm{cm}^{-1}$. The prepared solutions were used within two days of preparation.

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3. Results

Since the present work was concerned with the dielectric behaviour of glycine and glycylglycine, in aqueous solutions, it was necessary to find the incremental values of ε' and ε'' by deducing, from the total solution values, the contribution due to free water. This was done by defining at each measuring frequency a dielectric increment $\Delta\varepsilon'$ and a loss increment $\Delta\varepsilon''$ with the following relations:

$$\Delta\varepsilon' = \varepsilon' - \varepsilon_w' , \qquad (3)$$

$$\Delta\varepsilon'' = \varepsilon'' - \varepsilon_w'' \qquad (4)$$

where ε_w' and ε_w'' are the dielectric constant and loss of pure water.

The ionic conductivity of all solutions used was measured at 1 kHz, both before and after each measurement. The values of the measured dielectric loss ε_δ'' were corrected for conductivity contribution acording to the equation

$$\varepsilon'' = \varepsilon_\delta'' - (\sigma/f)\, 1.8 \times 10^{12} \qquad (5)$$

where σ is the specific conductivity (in $\Omega^{-1}\,\mathrm{cm}^{-1}$) and f the frequency.

The relaxation time τ of the dissolved species was calculated by the equation

$$\tau = \frac{\lambda}{2\pi c_0} \frac{\Delta\varepsilon''}{\Delta\varepsilon'} \qquad (6)$$

where λ is the free-space wavelength and c_0 is the velocity of light. This Eqn is deduced from the Debye[4] Eqs. (7) and (8) according to the relations (3) and (4).

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\lambda_c/\lambda)^2} , \qquad (7)$$

$$\varepsilon'' = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (\lambda_c/\lambda)} \frac{\lambda_c}{\lambda} . \qquad (8)$$

In the Eqs. (7), (8) ε_0 ad ε_∞ are the dielectric constants at very low and high frequencies respectively and λ_c is the critical wavelength. The dielectric increment δ was calculated from the expression $\delta = \Delta\varepsilon'/c$, where c is the molar concentration.

Using Smyth's approximations of Kirkwood's dielectric mixture theory[7], the dipole moment μ of the glycine and glycylglycine molecules was calculated from the equation

$$\mu = 3.30\, \delta^{1/2} . \qquad (9)$$

The charge separation $r = \mu/e$ is easily deduced. The radius a was calculated from the relation

$$\tau = 4\pi a^3 \eta / k T \qquad (10)$$

where η is the viscosity and a the radius of the dissolved molecule.

Using data on the variation of relaxation time with temperature the thermodynamic quantities ΔF^*, ΔH^* and ΔS^* (free energy, enthalpy and entropy of activation for dipole relaxation) have been calculated. The calculation[8] is based on the consideration that the dipole orientation is a rate process involving the existance of a potential energy barrier, having a certain probability for the dipole to jump from one orientation to another. ΔF^* was calculated from the equation

$$\tau = (h/k T) \exp(\Delta F^*/R T) \qquad (11)$$

where h is Planck's constant. From the Eq. (11), the Eq. (12) is obtained:

$$\tau = (h/k T) \exp(\Delta F^*/R T) \exp(-\Delta S^*/R) . \quad (12)$$

ΔH^* was calculated from the slope of the curve $\ln\tau = f(1/T)$. The plot $\ln\tau$ versus $1/T$ has been experimentally established to be approximately linear[9]. Finally, the values of all the above calculated quantities were tabulated for each concentration, frequency and temperature in the Tables 1, 2.

Error theory[10] with a confidence level 99% for the measured quantities was used to provide the errors in ε' and ε''. Subsequently, an error analysis of all calculated values was performed. The mean errors of the measured and calculated values are as follows: ε' $\pm 1\%$, $\Delta\varepsilon'$ $\pm 4\%$, ε'' $\pm 3\%$, τ $\pm 9.5\%$ (sec), δ $\pm$ 4%, μ $\pm 2.5\%$ (Debye units), r $\pm 2.5\%$ (Å), ΔF^* ± 0.06 (kcal mole^{-1}), ΔH^* ± 0.4 (kcal mole^{-1}).

4. Discussion

For the aqueous solutions of glycine no dielectric absorption was found in the frequency region studied in this paper. The values found for the magnitudes of δ, μ and r are in agreement with those found by Kirkwood[6], Sandus and Lubitz[1], Aaron and Grant[2]. From the obtained values of μ (16.1 to 15.5 D) and r (3.37 to 3.22 Å) it is concluded that the molecule of glycine in solution is not subjected to conformational changes but essentially remains in solution as in the crystal[11, 12]. Glycylglycine was found to exhibit dielectric absorption in

Tab. 1. Dielectric parameters and relaxation time for glycylglycine.

T K	f, 10^6 Hz	0.002 M				0.005 M				0.01 M			
		ε'	$\Delta\varepsilon'$	ε'' 10^{-2}	τ, 10^{-10} sec	ε'	$\Delta\varepsilon'$	ε'' 10^{-2}	τ, 10^{-10} sec	ε'	$\Delta\varepsilon'$	ε'' 10^{-2}	τ, 10^{-10} sec
273	0.75	88.17	0.14	—	2.21	88.39	0.36	—	2.26	88.75	0.72	—	2.26
	2	88.09	0.15	—		88.31	0.37	—		88.66	0.72	—	
	4	88.03	0.15	0.07		88.25	0.37	0.20		88.61	0.73	0.43	
	7	87.94	0.14	0.14		88.16	0.36	0.37		88.53	0.73	0.72	
	10	87.84	0.14	0.19		88.05	0.35	0.48		88.42	0.72	1.03	
283	0.75	84.26	0.15	—	1.80	84.46	0.35	—	1.85	84.81	0.70	—	1.87
	2	84.17	0.14	—		84.39	0.36	—		84.75	0.72	—	
	4	84.12	0.14	0.05		84.35	0.37	0.20		84.70	0.72	0.32	
	7	84.05	0.14	0.11		84.27	0.36	0.30		84.63	0.72	0.58	
	10	83.96	0.14	0.16		84.17	0.35	0.40		84.53	0.71	0.85	
293	0.75	80.45	0.15	—	1.38	80.66	0.36	—	1.43	81.00	0.70	—	1.46
	2	80.35	0.14	—		80.56	0.35	—		80.92	0.71	—	
	4	80.29	0.14	0.04		80.50	0.35	0.11		80.86	0.71	0.25	
	7	80.22	0.14	0.08		80.43	0.35	0.21		80.78	0.70	0.45	
	10	80.13	0.13	0.12		80.34	0.35	0.32		80.70	0.70	0.64	
303	0.75	76.87	0.14	—	1.04	77.07	0.34	—	1.14	77.41	0.68	—	1.17
	2	76.79	0.14	—		77.00	0.35	—		77.35	0.70	—	
	4	76.74	0.14	0.04		76.95	0.35	0.10		77.30	0.70	0.21	
	7	76.67	0.14	0.06		76.88	0.35	0.17		77.23	0.70	0.38	
	10	76.58	0.13	0.09		76.79	0.34	0.25		77.14	0.69	0.48	
313	0.75	73.45	0.13	—	1.00	73.68	0.36	—	1.06	74.01	0.69	—	1.04
	2	73.38	0.14	—		73.58	0.34	—		73.92	0.68	—	
	4	73.34	0.14	0.03		73.54	0.34	0.09		73.89	0.69	0.21	
	7	73.28	0.14	0.06		73.48	0.34	0.16		73.82	0.68	0.35	
	10	73.20	0.14	0.09		73.39	0.33	0.22		73.74	0.68	0.39	

the frequency region used and its maximum was calculated by extrapolation to be at 7.05×10^8 to 1.6×10^9 Hz, depending on concentration and temperature. This maximum does not significantly differ from the one obtained by Aaron and Grant [2] for the concentration of 0.25 M. In the frequency region used by these authors the water has significant dielectric absorption, therefore corrections are anavoidable. In the frequency region used in this paper, water has no dielectric absorption and consequently the observed value is only due to the solute. For these reasons the investigation of the dielectric behaviour of peptides in the frequency region used in this paper may by promising. Low concentrations can be used in the proposed method without any appreciable error in the obtained and calculated results. For glycylglycine the observed decrease of ε'' and of the relaxation time τ, by increasing the temperature, is obvious, regarding only the kinetic energy aspect of the process, since the dipolar ion moves faster in an applied field as the temperature increases.

The charge separation value of glycylglycine in solution was found to be 5.85 to 5.68 Å, which is significantly lower than calculated value (6.7 Å) using crystallographic data [13]. The difference suggests a rather curved conformation of the glycylglycine molecule in solution.

Since the radius of glycylglycine was found (3.04 Å) to be approximately equal to half of the charge separation value it is tentatively concluded that the glycylglycine molecule is relaxing in solution in a curvilinear conformation along an axis which passes through the middle of the distance separating the charges of the dipolar ion. This result is not very rigorous since many hydrodynamic approximations are involved in the calculation of the r value which usually is found to be shorter.

A glycylglycine molecule can presumably form up to a maximum of six bonds with the neighbouring water molecules, four being of the N – H . . . O and two being of the O – H . . . O type. It seems reasonable to suppose that at any instant there will be a statistical assembly of 0, 1, 2, . . . , 6

Tab. 2. Dielectric increment, dipole moment, charge separation and molecular radius for glycylglycine.

T K	0.002 M				0.005 M				0.01 M			
	$\bar{\delta}$	μ D	r Å	a Å	$\bar{\delta}$	μ D	r Å	a Å	$\bar{\delta}$	μ D	r Å	a Å
273	72.0	28.0	5.83	3.04	72.4	28.1	5.85	3.04	72.4	28.1	5.85	3.03
283	71.0	27.8	5.79		71.6	27.9	5.81		71.4	27.9	5.81	
293	70.0	27.6	5.75		70.0	27.6	5.75		70.4	27.7	5.77	
303	69.0	27.4	5.71		69.2	27.4	5.72		69.4	27.5	5.72	
313	69.0	27.4	5.71		68.4	27.3	5.68		68.4	27.3	5.68	

bonded with water glycylglycine molecules, of which only zero-bonded and one-bonded molecules are free to rotate. The value found for the activation energy ΔF^* 3.87 to 4.07 kcal/mole, in the temperature region 273 to 313 K, is equivalent to the energy required to break one hydrogen bond type $N-H\ldots O$ [14]. Consequently, the observed relaxation time is due to the rotations of the glycylglycine molecules bonded with one or perhaps two water molecules the applied field breaking one hydrogen bond in the relaxation process. The increase of the temperature may also have as a result an increase of the number of the one or two bonded glycylglycine molecules with water. This possibly explains why the relaxation time became shorter with increasing temperature. Entropy changes during the relaxation process are negligible if the concentration and the temperature are increased. The value for ΔH^* was found to be 3.4 to 3.5 kcal/mole.

Any effect on the solvent-solute interaction as the temperature increases cannot be concluded from the dielectric relaxation.

This, perhaps, can be achieved regarding the variations of the dielectric increament δ with temperature. The values of δ found for glycine and glycylglycine remain essentially constant as the temperature and the concentration varies. It has been proposed that these molecules act as typical breakers of the water structure [15]. On the contrary, molecules such as L-prolin, ε-aminocaproic acid exhibit significant variation of δ as the temperature increases according to Shepherd and Crant [16]. It is also known that L-prolin and ε-aminocaproic acid exhibit a structure making effect on water [15]. The validity of this observation for amino acids and peptides, is under investigation.

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