Dielectric Behaviour in the MHz range of cis-bis (glycynato)Cu(II) monohydrate and (glycylglycinato)Cu(II) trihydrate in Water

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The dielectric properties of Cu(gly)$_2$ and Cu(glygly) in diluted aqueous solution were examined in the MHz range at 273 to 313 K. The complexes exhibit dielectric absorption in the ranges 5.09×10^7 to 9.34×10^7 Hz and 4.63×10^7 to 8.01×10^7 Hz, respectively, depending on concentration and temperature. This absorption was attributed to rotational relaxation of the unhydrated and monohydrated complexes. The following data for the two complexes in solution at 293 K have been obtained, respectively: dipole moment 19.3 D and 34.0 D, charge separation 2.01 Å and 3.54 Å, relaxation time 2.3×10^{-9} sec and 2.6×10^{-9} sec, molecular radius 6.36 Å and 6.47 Å, activation energy for the relaxation process 5.6 kcal mole^{-1} for both complexes.

1. Introduction

The dielectric behaviour of amino acid chelates with transition metal ions has not been investigated so far. The purpose of the present study is the examination of the dielectric behaviour of the chelates of glycine and glycylglycine with Cu(II) in aqueous solutions. In a previous paper [1] the dielectric relaxation of glycine and glycylglycine was investigated in the MHz range and conclusions were drawn about the relaxation time of both dipolar ions. The dielectric behaviour of these chelates in aqueous solutions can be correlated with their hydration. The present study may be useful for the clarification of the interactions of water with copper proteins [2, 3].

Solvent – solute interactions of aqueous solutions of metal chelates were studied by viscosity measurements [4] and mainly by p.m.r. techniques [5]. The p.m.r. technique was found useful for the detection of a second coordination sphere in the complex tris(alaninato)Co(III) in D_2SO_4-D_2O solutions [5].

Dielectric properties can be evaluated in the MHz range by dielectric absorption measurements, at low concentrations and this is an advantage over the other methods used.

2. Experimental

For the measurements and calculations the same methods were used as in [1]. The frequency was varied from 7.5×10^5 to 1×10^7 Hz, the concentration of the chelates from 2×10^{-3} to 1×10^{-2} M (M = molarity) and the temperature from 273 to 313 K. The examined concentrations were low because of the limited solubility of the chelates. This is not a disadvantage because these concentrations prevail in biological systems [6].

All materials were purchased in puriss grade (Fluka Co.). Cis-bis(glycinato)Cu(II) monohydrate and (glycylglycinato)Cu(II) trihydrate were prepared according to Abderhalden and Schnitzler [7] and recrystallized from a mixture of alcohol, water and ether. The solutions were prepared with distilled water of conductivity less than $10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and the measurements were carried out within two days of preparation.

The cell for the dielectric measurements was calibrated with a number of liquids of known dielectric constant. To ensure the reproducibility of the obtained results each measurement was repeated several times. The temperature variation was controlled to ±0.1 °C.

3. Results

From the dielectric constant ε' and the dielectric loss ε'' the relaxation time τ, the dielectric increment δ, the dipole moment μ, the charge separation r and the molecular radius a of the complexes have been calculated (cf. Tables 1 – 3). The calculation of all these quantities was made according to equations cited in [1]. The mean free activation energy ΔF^* of the dielectric relaxation is found to be 5.6 kcal mole^{-1} for both complexes and while the mean enthalpy of activation ΔH^* for the same range of temperature and concentration is found to be 1.6 kcal mole^{-1} for the complex Cu(gly)$_2$ and 1.5 kcal mole^{-1} for the complex Cu(glygly). Consequently the mean activation entropy ΔS^* is -13.4 e.u mole^{-1} for the complex Cu(gly)$_2$, and -14.0 e.u mole^{-1} for the complex Cu(glygly).

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Table 1. Dielectric loss and relaxation time for the complex Cu(gly)$_2$.

		0.002 M		0.005 M		0.01 M	
T K	f, 10^6 Hz	ε'' 10^{-2}	τ 10^{-9} sec	ε'' 10^{-2}	τ 10^{-9} sec	ε'' 10^{-2}	τ 10^{-9} sec
273	0.75	—	3.0	—	3.1	—	3.1
	2	0.26		0.67		1.26	
	4	0.53		1.39		2.59	
	7	0.93		2.44		4.96	
	10	1.33		3.49		7.28	
283	0.75	—	2.6	—	2.6	—	2.7
	2	0.22		0.55		1.06	
	4	0.45		1.10		2.14	
	7	0.79		1.95		4.23	
	10	1.13		2.95		6.19	
293	0.75	—	2.3	—	2.3	—	2.3
	2	0.17		0.48		0.89	
	4	0.40		0.93		1.92	
	7	0.60		1.72		3.73	
	10	0.86		2.46		5.35	
303	0.75	—	2.0	—	2.0	—	2.1
	2	0.16		0.43		0.82	
	4	0.30		0.83		1.71	
	7	0.52		1.49		3.21	
	10	0.75		2.00		4.55	
313	0.75	—	1.7	—	1.8	—	1.9
	2	0.15		0.35		0.75	
	4	0.25		0.68		1.53	
	7	0.45		1.27		2.73	
	10	0.66		1.94		4.00	

Table 2. Dielectric loss and relaxation time for the complex Cu(glygly).

		0.002 M		0.005 M		0.01 M	
T K	f, 10^6 Hz	ε'' 10^{-2}	τ 10^{-9} sec	ε'' 10^{-2}	τ 10^{-9} sec	ε'' 10^{-2}	τ 10^{-9} sec
273	0.75	—	3.3	—	3.4	—	3.4
	2	0.93		2.35		4.73	
	4	1.85		4.63		9.31	
	7	3.08		7.92		16.22	
	10	4.43		11.30		22.15	
283	0.75	—	2.8	—	2.9	—	2.9
	2	0.77		1.99		4.04	
	4	1.49		3.80		7.79	
	7	2.58		6.57		13.44	
	10	3.71		9.35		19.07	
293	0.75	—	2.5	—	2.6	—	2.6
	2	0.66		1.74		3.60	
	4	1.32		3.41		7.00	
	7	2.33		5.90		12.06	
	10	3.33		8.39		17.16	
303	0.75	—	2.2	—	2.3	—	2.3
	2	0.58		1.55		3.06	
	4	1.19		3.00		6.12	
	7	2.04		5.09		10.52	
	10	2.94		7.30		14.86	
313	0.75	—	2.0	—	2.0	—	2.1
	2	0.52		1.36		2.83	
	4	1.05		2.62		5.52	
	7	1.83		4.64		9.41	
	10	2.50		6.56		13.34	

The measured values of the dielectric loss ε'' were corrected for the conductivity contribution of the solute, so that the remaining values of the dielectric loss are only due to dielectric polarization. Both complexes were found to exhibit dielectric absorption in the frequency region used, and the maximum was calculated, by extrapolation, to be, for the complex Cu(gly)$_2$ from 5.09×10^7 to 9.34×10^7 Hz and for the complex Cu(glygly) from 4.63×10^7 to 8.01×10^7 Hz, depending on concentration and temperature. The relaxation time (Tables 1, 2) for both complexes does not vary markedly with concentration, keeping the temperature constant, and consequently can be considered constant. By increasing the temperature, keeping the concentration constant, the relaxation time decreases as it is expected.

To provide the errors for the measured quantities the estimation theory[8] with a confidence level 99% was used, and subsequently, an error analysis for all calculated values was performed. The mean errors of the measured and calculated values are as follows: $\varepsilon'' \pm 3\%$, $\tau \pm 9.5\%$, $\delta \pm 4\%$, $\mu \pm 2.5\%$, $r \pm 2.5\%$, $\Delta F^* \pm 0.06$ (kcal mole^{-1}), $\Delta H^* \pm 0.4$ (kcal mole^{-1}).

4. Discussion

The critical relaxation times, 7×10^{-11} sec and 1.46×10^{-10} sec, and the dipole moments, 15.9 D and 27.7 D, at 293 K of glycine and glycylglycine[1, 9, 10] increase on chelating with Cu(II), giving 2.3×10^{-9} sec and 19.3 D for Cu(gly)$_2$ and 2.6×10^{-9} sec and 34.0 D for Cu(glygly). The increase in relaxation time, as well as the shift of the dielectric absorption towards lower frequencies, can be attributed to the increase in mass of the relaxing species and possibly to hydration.

There are two geometric parameters that can be deduced from the dielectric data, the charge separation and the molecular radius. We define the charge separation in the case of Cu(gly)$_2$, as the vector sum of the position vectors of the carboxyl oxygens with respect to the cupric ion as origin, and in the case of Cu(glygly) as the vector sum of the position vectors of the carboxyl oxygen and peptide nitrogen around the cupric ion. There is also a mesomeric form of Cu(glygly) which bears negative charge on the carboxyl oxygen of the peptide bond[11], and consequently an additional charge separation value can be considered which is the vector sum of the position vectors of the carboxyl oxygen and the carbonyl oxygen. All the above position vectors can be calculated from the published crystallographic data[12, 13].

From the value of the dipole moment the charge separation of Cu(gly)$_2$ is found to be 2.01 Å for the 1×10^{-2} M solution at 293 K. This value is lower than the value 2.70 Å calculated from the crystallographic data. There are two possible reasons for this small difference: To some extent the cis complex may be converted in solution to the trans complex which does not exhibit a dipole moment; also the angle OCuO of the molecule is possibly more obtuse in solution than in the crystal.

For the complex Cu(glygly) the charge separation in the 1×10^{-2} M aqueous solutions at 293 K was found from the dipole moment to be 3.54 Å. This value is larger than those calculated from the crystallographic data 2.87 Å and 2.95 Å for the two mesomeric forms of Cu(glygly)[11]. Possibly the puckering of the rings is more pronounced in solu-

Table 3. Dielectric increment, dipole moment, charge separation and molecular radius for the complexes Cu(gly)$_2$ and Cu(glygly).

	0.002 M					0.005 M				0.01 M			
Complex	T [K]	δ	μ [D]	r [Å]	a [Å]	δ	μ [D]	r [Å]	a [Å]	δ	μ [D]	r [Å]	a [Å]
Cu(gly)$_2$	273	36.0	19.8	2.06		35.6	19.7	2.05		35.6	19.7	2.05	
	283	35.0	19.5	2.03		34.8	19.4	2.02		34.8	19.4	2.02	
	293	34.0	19.2	2.00	6.39	34.0	19.2	2.00	6.36	34.2	19.3	2.01	6.36
	303	33.0	18.9	1.97		33.6	19.1	1.99		33.6	19.1	1.99	
	313	33.0	18.9	1.97		32.8	18.9	1.96		32.8	18.9	1.96	
Cu(glygly)	273	108.0	34.3	3.57		108.0	34.3	3.57		108.2	34.3	3.57	
	283	107.0	34.1	3.55		106.8	34.1	3.55		107.0	34.1	3.55	
	293	106.0	33.9	3.54	6.48	106.0	33.9	3.54	6.47	106.2	34.0	3.54	6.47
	303	105.0	33.8	3.52		105.2	33.8	3.52		105.2	33.8	3.52	
	313	104.0	33.6	3.50		104.0	33.6	3.50		104.2	33.7	3.51	

tion than in the crystal, causing serious deviations from the planarity of the molecule. In this case the angle NCuO or OCuO should be more acute in solution than in the crystal.

As the molecular radius of a complex we define the radius of the relaxing species if approximated as a sphere. Several approximations are involved in this definition[1] and for this reason the discussion of this parameter is not very rigorous. The value found for the molecular radius of Cu(gly)$_2$ in aqueous solutions is 6.36 Å while the value calculated from the crystallographic data[12] for the same molecule with a hydrogen bonded water molecule connected to the oxygen of the carboxyl group is 6.95 Å. The corresponding molecular radius of Cu(gly)$_2$ without the attached water molecule is 4.01 Å.

This seems to indicate that the complex in solution during relaxation in the alternating electric field is bonded most of the time with one water molecule. The same situation is met with Cu(glygly).

The hydration can be correlated with thermodynamic data considering the relaxation as a rate process. The energy required for breaking one hydrogen bond is 5 kcal mole^{-1}. Considering the activation energies of both complexes during relaxation, one hydrogen bond is broken in the process. The measured relaxation time in both complexes corresponds to monohydrates and unhydrates. An increase in temperature results in an increase in the number of unhydrates with corresponding shortening of the relaxation time.

Viscosity measurements[4] have shown that the chelates of glycine and glycylglycine are moving in the fluid as dihydrates. When an alternating electrical field is applied, one water molecule breaks off during relaxation, resulting in monohydrates as conjectured in the present study.

The negative values of the activation entropy of the relaxation process for both complexes indicate that more order is produced in the vicinity of the relaxing species.

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