A Study of the Structure of the Complexes of Glycine and Glycyl-glycine with Cu(II) in Solution, Based on Viscosity Measurements

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In the relation \( \eta_r = 1 + Bm + Dm^2 \) the B values of the complexes bis(glycinato)Cu(II) and (glycylglycinato)Cu(II) between 10 and 40 °C indicate that these complexes are hydrated by two molecules of water at their carboxyl oxygens. Large values of D indicate solute-solute interactions via the axial positions of the cupric square microsymmetry, as the molecules are moving in the liquid streamlines. For both complexes dB/dT was found to be positive in the examined temperature range. This presumably indicates that the examined complexes have a structure breaking effect on the water structure.

1. Introduction

Dipolar ions behave as non-electrolytes and a linear relationship exists between partial molal quantities and concentration, when dilute solutions are investigated. For interpreting viscosity data of aqueous solutions of several dipolar ions Tsangaris and Martin\(^1\) used the Eqn. (1):

\[
\eta_r = 1 + Bm + Dm^2 \tag{1}
\]

where \( \eta_r \) is the relative viscosity, and m the molal concentration. The coefficient B is related with the solvent-solute interaction and is always positive, whereas D measures the solute-solute interaction.

It has also been proposed\(^2\) that the plus or minus sign of dB/dT in Eqn (1) indicates the structure breaking or structure making ability of the dipolar ions on the water structure, respectively. Sofar, based on this criterion, seven dipolar ions, \( i.e. \) sulfamic acid, taurine, glycine, betaine, serine, glycyl-glycine and triglycine, have been shown to be structure breakers (dB/dT > 0)\(^3\) and five dipolar ions, \( i.e. \) sarcosine, hydroxyproline, proline, \( \varepsilon \)-aminocaproic acid and glutathione, to be structure makers (dB/dT < 0)\(^4\).

The dipolar character of the amino acids and peptides disappears when these compounds are chelated with transition metal ions.

The aim of the present research is to investigate the action of the chelated amino acids on the pseudocrystalline structure of water, as it is manifested by viscosity measurements. It is interesting to clarify if the chelated amino acids continue to have the same kind of action on the water structure as before chelation. Glycine and glycyl-glycine chelates of Cu(II) were selected for this task, because glycine is without any ambiguity a structure breaker\(^1\) and the solid structures of both complexes bis (glycinato)Cu(II) and (glycyl-glycinato)Cu(II) are very well established\(^4\) which may help the interpretation of the obtained results.

Viscosity measurements of aqueous solutions of chelated compounds are rare. Charles\(^5\) studied the viscosities of aqueous solutions of several metal chelates derived from the EDTA as ligand. It was found that a relationship exists between viscosity B coefficient of the metal chelates and the radius of metal cation as well as the cation electronegativity and the second ionisation potential. Temperature variations of the B coefficient were not examined.

2. Experimental

All materials used were from Fluka Co, in puriss grade. Cis-bis(glycinato)Cu(II) monohydrate and (Glycyl-glycinato)Cu(II) trihydrate were prepared according to Abderhalden and Schnitzler\(^6\) and were recrystallized twice from a mixture of alcohol, water and ether. Solutions were prepared by weighing the appropriate amounts of the prepared complexes in filtered distilled water of conductivity...
Table I. B and D coefficients of the Eqn \( \eta_r = f(m) \) for the complexes (Cu(gly)_2 and Cu(glygly)); \( a \) radius of their hydrodynamic sphere.

<table>
<thead>
<tr>
<th>Complex</th>
<th>10 °C B</th>
<th>10 °C D</th>
<th>25 °C B</th>
<th>25 °C D</th>
<th>30 °C B</th>
<th>30 °C D</th>
<th>40 °C B</th>
<th>40 °C D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(gly)_2</td>
<td>2.20</td>
<td>7.0</td>
<td>53.12</td>
<td>2.30</td>
<td>7.1</td>
<td>53.00</td>
<td>2.75</td>
<td>7.5</td>
</tr>
<tr>
<td>Cu(glygly)</td>
<td>2.62</td>
<td>7.4</td>
<td>36.30</td>
<td>2.75</td>
<td>7.5</td>
<td>43.33</td>
<td>2.85</td>
<td>7.6</td>
</tr>
</tbody>
</table>

less than 10^{-6} \( \Omega^{-1} \text{ cm}^{-1} \). The prepared solutions were measured within two days after their preparation.

Densities were measured in different temperatures in 25 ml pycometers with a capillary neck and a sintered stopper.

Viscosities and densities were measured in a constant temperature bath at 10, 25, 30 and 40 °C with a variation of temperature within the range ± 0.01 to ± 0.03 °C as repeatedly was checked by a Beckman thermometer.

Low concentrations were used, ranging from 0.002 to 0.02 M because the complexes have limited solubility in water and in addition low concentrations are important in evaluating the results.

Two calibrated Ostwald viscometers were used.

Before each measurement the viscometers were carefully and repeatedly cleaned with a number of filtered solvents. The viscometers were fitted into the glass-baths in vertical reproducible position. Verticality was checked by a cathetometer and the observation of the dropping liquid surface in the capillary of the viscometer was effected by the cathetometer telescope. Viscometers were filled with the same volume of liquid for each experiment.

The number of measurements of the efflux times were twenty for each temperature and each concentration and the mean deviations were ± 0.05 to ± 0.09 sec. If the mean deviations were greater than 0.1%, the run was discarded. Small kinetic energy corrections were made for each run.

The calibration of viscometers was made by water at the temperatures 10, 25, 30 and 40 °C. The absolute viscosities and densities of water of these temperatures were taken as follows.

<table>
<thead>
<tr>
<th>( t ) [°C]</th>
<th>( \eta_w ) [mp]</th>
<th>( d_w ) [g.cm^{-3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>13.097</td>
<td>0.99973</td>
</tr>
<tr>
<td>25</td>
<td>8.949</td>
<td>0.99707</td>
</tr>
<tr>
<td>30</td>
<td>8.004</td>
<td>0.99567</td>
</tr>
<tr>
<td>40</td>
<td>6.536</td>
<td>0.99224</td>
</tr>
</tbody>
</table>

For the measurement of efflux times an electric timer was used giving an accuracy ± 0.01 sec.

3. Results

Eqn (1) was used in evaluating B and D coefficients. For each complex and temperature a plot of \( \eta_r - 1/m \) vs molality \( m \) was constructed. Straight lines were obtained using four concentrations. B coefficient was calculated from the intercept and D coefficient from the slope of obtained lines.

In Table I B and D coefficients are reported for each complex and temperature. B coefficients can be correlated with the radius \( a \) in Å of the hydrodynamic sphere of the species in solution, by the relation (2) provided that spherical shape predominates.

\[
a = 5.417 B^{1/3}
\]  
Values of \( a \) are reported for each complex and temperature in Table I.

For both complexes, \( \text{dB/dT} \) was found positive for all temperature intervals examined, as it is shown in Table II.

Table II. \( \text{dB/dT} \) Coefficients of the complexes Cu(gly)_2 and Cu(glygly) in aqueous solutions and in different temperature intervals.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Cu(gly)_2</td>
<td>+ 0.0067</td>
<td>+ 0.02</td>
<td>+ 0.03</td>
</tr>
<tr>
<td>Cu(glygly)</td>
<td>+ 0.0087</td>
<td>+ 0.02</td>
<td>+ 0.023</td>
</tr>
</tbody>
</table>

4. Discussion

Supposing spherical shape for the molecule of cis-bis(glycinato)Cu(II), a value \( a = 7.1 \) Å at 25 °C for its hydrodynamic sphere was found. This value is large enough compared with the value 4.1 Å of the distance between copper and the more distant atom of the complex, in the solid state, which is the carboxyl oxygen. The value 4.1 Å was calculated from the data of Freeman et al. The excess radius...
of 3 Å of the hydrodynamic sphere is certainly due to the hydration.

Relative viscosities can be related with the relative volume concentration of solutes $\varphi$ by Eqn 3:

$$\eta = 1 + a_1 \varphi + a_2 \varphi^2 + a_3 \varphi^3 + \ldots$$  \hspace{1cm} (3)

The first virial coefficient of the Eqn (3) is associated with the shape of the dissolved particles and is independent of its size. Comparing Eqn (3) with (1) the relation (4) is obtained:

$$a_1 = \frac{1000 B}{V_{\text{eff}} N}$$  \hspace{1cm} (4)

where $V_{\text{eff}}$ is the effective volume of the dissolved particles in Å$^3$ and $N$ is the Loschmidt's number.

Assuming that one molecule of water is attached by hydrogen bond to the carboxyl oxygen of the Cu(gly)$_2$ molecule in solution, the complex may be represented by an ellipsoid of revolution with semi-axis 6.96 Å and 1.98 Å is the distance between the Cu atom and the hydrogens of the molecule of water which is attached to the carboxyl oxygen of the complex and 1.98 Å is the distance between Cu and the nitrogen of the glycine molecule in the complex. The volume of this ellipsoid was calculated $V_{\text{eff}} = 401$ Å$^3$, therefore from (4) $a_1 = 9.45$ was obtained. Simha\textsuperscript{9} derived a relation (5) of $a_1$ with the axial ratio ($J$) of the dissolved particles having the shape of ellipsoids.

$$a_1 = \frac{14}{15(\ln 2J - \frac{3}{2})} + \frac{14}{15}$$  \hspace{1cm} (5)

The axial ratio of the considered ellipsoid is $J = 3.57$. This value upon substitution to the Eqn (5) gives $a_1 = 4.49$. The obtained values of $a_1$ by two different ways are in disagreement because the B coefficient of the complex is subjected to greater shape factor influence.

Furthermore, assuming that instead of one, two molecules of water are attached by hydrogen bond to the carboxyl oxygen of the complex, an ellipsoid of revolution with semi-axis 9.72 Å and 1.98 Å is considered. This ellipsoid has a volume $V_{\text{eff}} = 799$ Å$^3$ giving $a_1 = 4.75$. Using Simha's Eqn (5) $a_1 = 5.70$ was obtained. Analogous results were obtained considering the complex Cu(glygly).

From the above discussion it is possible to consider the molecules of both complexes moving in the fluid streamlines hydrated mainly by two molecules of water attached to the carboxyl groups of the complexes of hydrogen bonds.

The small positive $dB/dT$ values for both complexes in the range of temperatures examined give some evidence that these compounds exhibit an almost structure breaking effect to the water structure. This effect is more remarkable between 25 and 30 °C.

The high values of D coefficients in both examined complexes, even though low concentrations were considered, indicate strong solute-solute interactions which may be arisen from the cupric-cupric interactions of the dissolved complexes via axial positions.

The carboxyl oxygen atom in both complexes is the most distant from the copper atom. Since it is considered that the hydration takes place in this particular atom, it is impossible considering the B coefficient to detect any other hydration site in the complexes which is closer to the copper atom. Therefore the possible hydration in the axial positions around the square microsymmetry of copper cannot be detected. The large value of D coefficient, which lead to the assumption of strong solute-solute interactions, indicate presumably that the axial positions of the copper atom are not occupied by water molecules. In contrary if these positions were occupied copper-copper interactions would be much weaker and consequently small values of D coefficient would be obtained.

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