A Study of Complex Equilibria of Phenylglycine with Nickel(II), Copper(II) and Zinc(II) in Water and in Water—Methanol Solution

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The complex equilibria of the systems phenylglycine—nickel(II), copper(II) and zinc(II) in water and in water—methanol solution have been studied by computer analysis of potentiometric data. The mode of coordination has been established by $^{13}$C-NMR and IR studies.

[Keywords: Complexes; Copper(II); Nickel(II); Phenylglycine; Zinc(II)]

It was found earlier$^{1-3}$ that the substitution of methyl or phenyl groups in the glycine molecule changes considerably the acid-base nature of both functional groups, i.e. the amino and carboxyl group. Consequently (also considering the modified spatial conditions) the complex-forming properties of its derivatives are altered when compared with the glycine molecule. This is particularly manifested in the lower stability of N-phenylglycine complexes$^{2}$. A similar effect of the phenyl group is observed in phenylglycine (the benzene ring substituted at the $\alpha$-carbon); however, the resulting changes are much less conspicuous. Table 1 presents the dissociation constants of phenylglycine ($PHEN$) and, for comparison, those of glycine and N-
Table 1. Dissociation constants of phenylglycine and, for comparison, of glycine and N-methylglycine in water and in water-methanol solution

<table>
<thead>
<tr>
<th>Mole Fraction of Methanol</th>
<th>Phenylglycine</th>
<th>Glycine</th>
<th>N-Methylglycine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$pK_1$</td>
<td>$pK_2$</td>
<td>$pK_1$</td>
</tr>
<tr>
<td>0</td>
<td>1.61</td>
<td>9.14</td>
<td>2.40</td>
</tr>
<tr>
<td>0.10</td>
<td>1.81</td>
<td>9.10</td>
<td>2.70</td>
</tr>
<tr>
<td>0.16</td>
<td>1.99</td>
<td>9.07</td>
<td>2.81</td>
</tr>
<tr>
<td>0.23</td>
<td>2.18</td>
<td>9.06</td>
<td>2.99</td>
</tr>
<tr>
<td>0.31</td>
<td>2.44</td>
<td>9.05</td>
<td>3.17</td>
</tr>
<tr>
<td>0.41</td>
<td>2.72</td>
<td>9.01</td>
<td>3.40</td>
</tr>
</tbody>
</table>

methylglycine in water and water—methanol solution. As in the case of N-phenylglycine (N-PHEN), the $pK_1$ values increase along with the increase of the mole fraction of methanol, whereas the $pK_2$ values decrease. A change in the dielectric constant of the solvent has a less pronounced effect on N—H bonds of a covalent character than on O—H bonds, where the contribution of electrostatic interaction is higher. The presented results indicate that a change in the $pK_1$ value is linearly correlated with the reciprocal of the dielectric constant of a solvent. This dependence is also approximately true for $pK_2$ values; an exact analysis, however, is hindered by the relatively small differences in $pK_2$ (Table 1). Considering the similar chemical nature of water and methanol molecules the above dependence suggests that the dielectric constant of the solvent, determining its “ionizing power”, is a major factor influencing $pK$ values.

A comparison of molecular models indicates that the presence of the phenyl group at the α-carbon has a smaller effect on the conditions for complex bond formation than the presence of two methyl groups in N,N-dimethylglycine (DMG). On the other hand, however, the basicity of both functional groups is lower (e.g. in water $pK_1 = 1.61, pK_2 = 9.14$ for PHEN and $pK_1 = 1.90, pK_2 = 9.77$ for DMG). It was found that the stabilities of phenylglycine complexes are similar to those of DMG complexes, lower than those of N-methylglycine compounds but distinctly higher than those of N-PHEN compounds.

The complexes formed in the analyzed systems as well as their stability constants are presented in Table 2. Nickel, both in water and water—methanol solvent (50%/50% v/v), forms only the complexes NiL and NiL₂. In systems with copper, apart from CuL and CuL₂, the occurrence of CuL₂OH in water and CuLOH and CuL₂OH in mixed solvent has been detected. Zinc, apart from ZnL and ZnL₂ compounds, forms in water non-stable ZnHL. In the investigated concentration