

Formation constants of binary and ternary complexes of Cu(II) with ninhydrin and some O, O; N, O and N, N donor ligands in aqueous medium

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The formation constants of 1:1 and 1:2 binary chelates of Cu(II) with ninhydrin (1,2,3-triketohydrindene hydrate or 2,2-dihydroxy-1,3-indanedione) and the corresponding 1:1:1 ternary chelates involving oxalic acid, catechol, α -alanine, valine, ethylenediamine and 2,2-bipyridyl as primary ligands have been determined pH metrically at 20°, 30°, 40° and 50°C at 0.1 M (KNO₃) ionic strength. The effect of change in ionic strength has also been studied at 30°C. The order of stabilities of ternary complexes has been discussed in terms of $\Delta \log K$, basicity of the ligands, nature of donor sites and thermodynamic parameters.

The synthesis, characterisation and biological activities of Co(II), Ni(II) and Zn(II) complexes of schiff base of ninhydrin and glycine have been reported earlier¹. The present work was undertaken to study the nature of Cu(II) complexes formed in solution by ninhydrin (nin) in the presence of other donors like alanine (ala), valine (val), oxalic acid (oxa), catechol (cat), ethylenediamine (en) and 2,2-bipyridyl (bipy) under different conditions.

Experimental

All the chemicals used were of AR grade. The following sets of solutions (volume 50 ml) were prepared in doubly distilled water and titrated potentiometrically against 0.1 M carbonate free standard KOH under N₂ atmosphere.

1. HNO₃ (4×10^{-3} M); 2. HNO₃ (4×10^{-3} M) + A (primary ligand) (2×10^{-3} M); 3. HNO₃ (4×10^{-3} M) + L (secondary ligand) (2×10^{-3} M); 4. HNO₃ (4×10^{-3} M) + A (2×10^{-3} M) + Cu(II) (2×10^{-3} M); 5. HNO₃ (4×10^{-3} M) + L (2×10^{-3} M) + Cu(II) (2×10^{-3} M); 6. HNO₃ (4×10^{-3} M) + A (2×10^{-3} M) + L (2×10^{-3} M) + Cu(II) (2×10^{-3} M).

For the [Cu(II)-A-L] ternary system, where A = catechol, the concentrations used were [Cu(II)] = [A] = [L] = 1×10^{-3} M in all the sets. An ionic strength of 0.1 M (KNO₃) was maintained in all the sets, while

studying temperature effect and a temperature of 30°C was maintained while studying the effect of ionic strength. For the binary systems, a metal-ligand ratio of 1:5 was maintained.

The proton-ligand dissociation constant (pK_a) of ninhydrin (secondary ligand) and the formation constants of metal-ninhydrin binary systems have been evaluated by analysing the titration curves using the methods of Irving and Rossotti². The formation constants of ternary chelates were determined using the method of Santhappa and Ramamoorthy³. The results have been presented in Table 1. The thermodynamic parameters ΔH (enthalpy), ΔS (entropy) and ΔG (free energy) have been calculated using the standard equations.

Results and discussion

The \bar{n} values (0.1 to 1.9) for the binary systems indicate the formation of 1:1 (Cu-L) and 1:2 (Cu-L₂) complexes. The ligand (nin) starts coordinating to Cu(II) at \approx pH 5.6. The standard deviations for proton-ligand and metal-ligand and ternary formation constants are within ± 0.06 log units.

In all the ternary systems studied, the mixed ligand curves closely follow the 1:1 [Cu(II)-A] where A = oxa, cat, ala, val, en and bipy binary curves in the lower pH region until the protons of primary ligands are neutralised, indicating the formation of binary [Cu(II)-A] complexes in this region. The divergence of the ternary curves from those of the binary [Cu(II)-A] system, above this pH region confirms the formation of ternary complexes of the type [Cu(II)-A-L] in two step equilibria.

The proton-ligand dissociation constant (pK_a) of ninhydrin, formation constants of binary complexes (1:1 and 1:2 binary) as well as those of mixed ligand complexes (1:1:1) were found to decrease with increase in ionic strength of the medium. To find out whether the ligands coordinate in dissociated or undissociated form and also to know the mechanism of complexation equilibria, the stability constants ($\log K$) obtained at different ionic strengths were plotted against $\sqrt{\mu}$. The plots gave straight line. The slope values ranging from -0.45 to -0.78 obtained in all the cases were far less than the expected values^{4,5}. The shapes of the formation curves were also similar at different ionic strengths indicating similar type of interaction. From these observations, it was evident that the ninhydrin reacts with [CuA] primary complex both in dissociated and undissociated forms.

Table 1—Stability constants and thermodynamic parameters of Cu(II) binary and ternary complexes in aqueous medium
[Temp. = 30°C; $\mu = 0.1 M$ (KNO₃)]

System	$\log K_{CuAL}^{Cu}$	$\Delta \log K$	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Cu(II)-nin			16.1	32.7	54.8
Cu(II)-oxa-nin	5.01	-0.63	9.9	29.1	63.3
Cu(II)-cat-nin	5.21	-0.43	10.4	30.2	65.4
Cu(II)-en-nin	5.26	-0.38	10.6	30.5	65.8
Cu(II)-bipy-nin	5.32	-0.32	10.7	30.9	66.6
Cu(II)-ala-nin	5.24	-0.40	10.5	30.4	65.6
Cu(II)-val-nin	5.22	-0.42	10.5	30.3	65.4

$$\log K_{CuL}^{Cu} = 5.64 \text{ (1:1)}$$

$$\log K_{CuL}^{Cu} = 5.15 \text{ (1:2)}$$

$$pK_a \text{ of ninhydrin} = 8.81$$

$$-\Delta H \text{ and } -\Delta G \text{ are accurate within } \pm 0.5\text{--}1.5 \text{ kJ mol}^{-1}$$

$$\Delta S \text{ accurate within } \pm 1.5 \text{ J mol}^{-1}\text{K}^{-1}$$

It can be seen that the binary complexes are more stable than the ternary complexes, resulting in negative $\Delta \log K$ values for all the ternary systems. Such a lowering of stabilities in the case of ternary complexes compared to those of binary chelates may be due to the availability of lesser number of coordination sites for ninhydrin on the metal in the primary complex [CuA] as compared to the free metal ion.

The order of overall stabilities of the [CuAL] ternary systems is bipy > en > ala > val \geq cat > oxa. This sequence of stabilities is in accordance with the basicities, nature of donor atoms and $\Delta \log K$ values of the ligands. From these studies it is observed that, though schiff base formation is established in the synthesis of metal complexes of ninhydrin and amino acids, no such condensation takes place between ninhydrin and amino acids in aqueous medium in the presence of metal ions and instead ternary complex formation takes place.

The decrease in $\log K$ values with increase in temperature and negative ΔG values shows that all the reactions are exothermic and spontaneous. The negative ΔH (enthalpy) and positive ΔS (entropy) values (Table 1) are the major driving forces for the

spontaneity of binary and ternary complex formation. The higher $\log K$ value for [Cu(II)-nin] binary complex may be due to its greater ΔH value compared to that of ternary complexes. The ΔS values for the formation of [CuAL] ternary complexes are higher than those for [Cu(II)-nin] binary system. Thus the entropy factor appears to be responsible for the observed trend in $\log K_{CuL}^{Cu}$ and $\log K_{CuAL}^{Cu}$ values. This could be due to the greater destabilisation of ternary chelates caused by enthalpy changes as compared to the stabilisation induced by the entropy changes. Hence, it can be concluded that a number of factors such as $\Delta \log K$ [$\log K_{CuAL}^{Cu} - \log K_{CuL}^{Cu}$], basicity, nature of donor atoms, enthalpy, entropy etc affect the stabilities of these chelates.

References

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