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Solution Equilibria of Cobalt(II)- and Nickel(II)-2,2′,2″-Terpyridine-Amino Acids Ternary Systems

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Solution equilibria of the ternary systems Co^{II}-, Ni^{II}-2,2′,2″-terpyridine-mono- or dicarboxylic amino acids are investigated potentiometrically. The stability constants of the binary and ternary complexes are determined at 20° and ionic strength of 0.2 mol dm^{-3} ($NaClO_4$). It is duduced that the stability of the ternary complex containing the secondary ligand monocarboxylic amino acid is lower than that of the corresponding binary amino acid-metal complex. On the other hand, a reverse behaviour is observed for the secondary ligand dicarboxylic amino acid. Stability of different complexes is examined and discussed in terms of the molecular structure of the amino acid moiety.

Terpyridine is capable of reacting as planar tridentate ligand forming five- or six-coordinate complexes with divalent transition metal ion[1]. Although metal complexes of terpyridine are considered as important compounds from both the analytical and structural points of view[2], the literature reveals very scarce data concerning potentiometric studies on binary and ternary metal complexes of this ligand[3]. In view of these findings, the present communication is devoted to a potentiometric investigation of the ternary systems, M(II)-terpy-aa, where M(II) is Co^{II} or N^{II} and aa is the biologically important amino acids glycine, alanine, valine, isoleucine, aspartic acid and glutamic acid. The study involves the potentiometric determination of the formation constants of the different binary and ternary complexes formed in these systems adopting the Irving and Rossotti technique[4], in an aqueous medium containing 50% (v/v) ethanol at 20° and an ionic strength of 0.2 mol dm^{-3} ($NaClO_4$). The stability of the ternary complexes formed is examined and discussed in relation to that of the binary M(II)-amino acid complex as well as the nature of the amino acid moiety. Aqueous ethanol medium is used due to the low solubility of both terpyridine and its M(II) complexes in pure aqueous medium.

Results and Discussion

Representative typical titration curves are shown in Figs. 1 and 2. Two acid dissociation constants (3.17 and 4.37) were calculated for terpyridine considering the two titration curves (a) and (b) making use of the Rossotti and Irving formulation[4]. These values can be considered to be in a good agreement with those determined before (3.28 and 4.66)[5] using spectrophotometric measurements at 25° and μ = 0.01 mol dm^{-3} ($NaClO_4$) in pure aqueous medium. Moreover, the amino acid dissociation constants were determined under identical conditions from the titration curves (a) and (d). The values obtained are in consistency with the literature values[6]. It is to be noted that the first dissociation constant values for all the amino acids used are low ($\simeq$ 2.0), i.e. occur in strongly acidic media, therefore these values are not used in the calculations.

Calculation of $\bar{n}$ for the M(II)-terpy complexes from the titration curves (b) and (c) reveals a nearly complete complex formation at low

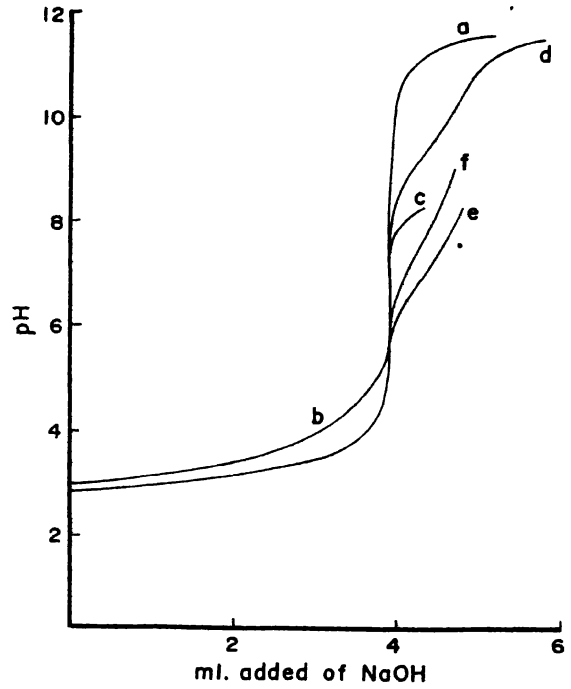

Fig. 1. Titration curves for Co^{II}-terpy-gly system (2.5×10^{-3} mol dm^{-3} of each) at 25° and μ = 0.2 mol dm^{-3} ($NaClO_4$) in the presence of 50% (v/v) ethanol with 0.1562 mol dm^{-3} NaOH (total volume = 50 ml) : (a) 1.22×10^{-2} mol dm^{-3} $HClO_4$; (b) soln. (a) + terpy; (c) soln. (b) + Co^{II}; (d) soln. (a) + gly; (e) soln. (d) + Co^{II}; (f) soln. (e) + terpy.

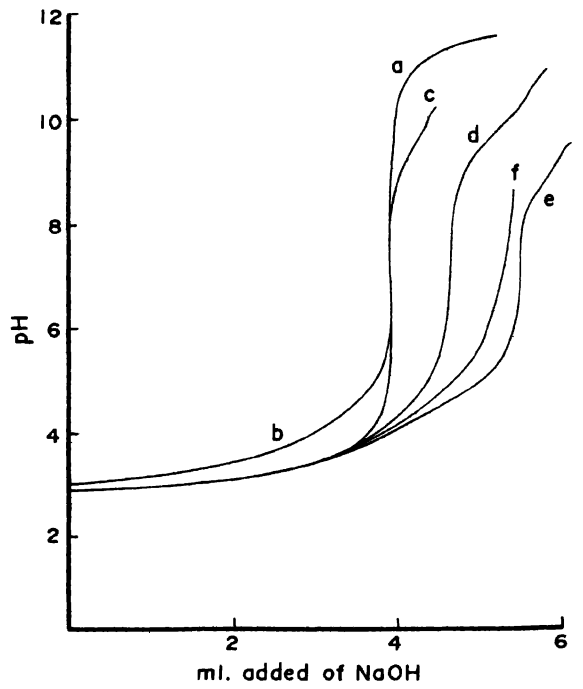

Fig. 2. Titration curves for Ni^{II}-terpy-asp system (2.5×10^{-3} mol dm^{-3} of each) at 25° and μ = 0.2 mol dm^{-3} ($NaClO_4$) in the presence of 50% (v/v) ethanol with 0.1562 mol dm^{-3} NaOH (total volume = 50 ml) : (a) 1.22×10^{-2} mol dm^{-3} $HClO_4$; (b) soln. (a) + terpy; (c) soln. (b) + Ni^{II}; (d) soln. (a) + asp; (e) soln. (d) + Ni^{II}; (f) soln. (e) + terpy.

pH's ($\bar{n} \simeq 1$ at pH 3.05). Thus determination of the formation constant values of the binary two complexes, under these experimental conditions, could not be possible. In this respect it is worthy to note that Co^{II}, Ni^{II}-terpy complexes are stable up to pH 7.7 and 8.5 respectively, where at high pH's hydrolysis reaction of such complexes occurred leading to the formation of hydroxo complex species. With respect to the titration curves of the Co^{II} and Ni^{II}-amino acids binary complex solutions studied, one deduces that the complexes of the monocarboxylic amino acids begin to form at pH $\simeq$ 5.0. On the other hand, the complexes of the dicarboxylic amino acids, aspartic and glutamic, begin to form at relatively lower pH's ($\simeq$ 3.0). Generally the titrated solutions of all the binary M(II)-aa complexes do not show precipitation in the pH range of complex formation, denoting that hydrolysis reactions of the metal ions Co^{II} and Ni^{II}, do nto interfere in the determination of the formation constants of these binary complexes.

The determined formation constant values of the different 1 : 1 binary Co^{II} and Ni^{II}-amino acid complexes are reported in Table 1. In general, these values agree well with the corresponding literature ones, taking into consideration the effect of the organic cosolvent (ethanol) as well as the differences in ionic strength[7]. This can be viewed as a measure for the suitability of the technique we used for such a study.

The mixed ligand titration curve (f) and that of the binary complex, M(II)-terpy, curve (c) are overlapped at relatively low pH's indicating that the amino acid does not bind with the metal ion in this pH range. At high pH's,

a divergence of such two curves occurred indicating the coordination of the amino acid moiety to the M(II)-terpy binary complex. This reaction can be represented as

$$M(II) + terpy \rightleftharpoons [M(terpy)]^{2+}$$

$$[M(terpy)]^{2+} + aa \rightleftharpoons [M(terpy)aa]^{n+}$$

where M(II) = Co^{II} or Ni^{II}, n = 1 and zero for mono- and dicarboxylic amino acids respectively. The observed divergence of curve (f) from curve (c) at lower pH's on using the dicarboxylic amino acids, asp and glut as secondary ligands relative to that on using the monocarboxylic amino acids under investigation, could be ascribed to the available additional coordination site that can be exerted by the two dicarboxylic amino acids. Such an additional coordination tends to promote the binding of these acids to the binary M(II)-terpy complex even at lower pH values. In this respect it is noteworthy that the binary M(II)-terpy complex is stable up to the pH where the attachment of the amino acid takes place. Thus one can deduce that the diferent ternary complexes under investigation are formed below the pH of the hydrolysis of the corresponding binary metal-terpy complexes.

The titrated solutions of the different ternary complexes under investigation, except for those of Co^{II}-terpy-valine, isoleuc, do not show precipitation up to the pH value corresponding to complete complex formation. However, for Co^{II}-terpy-val, -isoleuc, precipitation occurred at pH 7.3 and 7.5 respectively. This could be ascribed to the possible hydrolysis of these complexes leading to the formation of hydroxo complexes. Thus for these two complexes a further study beyond the precipitation point could not be possible.

From the horizontal distance between curves (c) and (f) in the pH range of ternary complex formation, $\bar{n}_{mix}$ (average number of amino acid molecules associated to binary M(II)-terpy complex) can be evaluated using the equation,

$$\bar{n}_{mix} = \frac{(v_f - v_c)\,[N^o + E^o + T^o_L\,(y - \bar{n}_H)]}{(v_o + v_c)\bar{n}_H\,T^o_M}$$

where T^o_M is the concentration of [M(II)-terpy] which equals that of M(II), y the number of dissociable protons of the amino acid (y = 1 and y = 2 for mono- and dicarboxylic amino acid respectively), v_o the original volume (50 ml), v_c and v_f are the volumes of alkali consumed to reach the same pH value in curves (c) and (f) and all other symbols have their usual meaning[4]. In general, the obtained $\bar{n}_{mix}$ values were always below unity indicating that only one amino acid molecule combines with the complex $[M(terpy)]^{2+}$.

Using the values of $\bar{n}_{mix}$, the free ligand exponent, PL_{max}, was calculated from the equation

$$PL_{mix} = \log\left[\frac{\sum_{y=0}^{y=1\text{ or }2} \beta^H_y \left(\frac{1}{10^B}\right)^y}{T^o_L - \bar{n}_{mix}\,T^o_M} \cdot \frac{v_o + v_c}{v_o}\right]$$

where β^H_y is the formation constant values of the applying amino acid and B the pH-meter reading.

The formation constant values of the different 1 : 1 : 1 ternary complexes under investigation obtained from the corresponding experimental formation curves are depicted in Table 1. Examination of the data reveals the following important features. (i) The stability constants of the same metal ion binary or ternary complex decreases as the length of the amino acid side chain (R) is increased, according to the sequence : gly (R = H) > ala (R = CH_3) > val (R = $-CH(CH_3)_2$) > isoleuc (R = $-CH(CH_3)CH_2CH_3$); and for the dicarboxylic amino acid asp (R = $-CH_2COOH$) > glut (R = $-CH_2CH_2COOH$). This behaviour is in accordance with the fact that steric effects play a major role in determining the stability of the amino acid complexes[8]. Thus, increasing the length of the amino acid chain (R) would result in more strain on its bending leading to a lower stability of its complexes. (ii) The stability constants of the complexes containing the dicarboxylic amino acids are higher than those containing the monocarboxylic amino acids.

This can be interpreted on the principle of the high effective basicity of the conjugated bases of the former acids, i.e. good σ-donors, relative to those of the latter ones. This reflects itself in the behaviour that the dicarboxylic amino acids can probably act as tridentate ligands (NOO donors) whereas the monocarboxylic amino acids act only as bidentate ligands (NO donors). (iii) The stability of the ternary metal ion complex containing the monocarboxylic amino acid as a secondary ligand is lower than that of the corresponding $[M\text{-}aa]^+$ binary complex. This can be explained on the basis that there is fewer number of sites avialable for bonding on $[M(terpy)]^{2+}$ complex than that on the aquated M(II) ions. On the other hand, the stability of the ternary metal complexes containing the dicarboxylic amino acid moieties, asp or glut, is higher than that of the corresponding [M-aa] binary complex. This behaviour could be likely ascribed to the tendency of the dicarboxylic amino acids to act as NOO tridentate ligands leading to the formation of two chelate rings (five-, six-membered chelate rings in case of aspartic acid and five-, seven-membered rings in case of glutamic acid). This reflects itself in high stability of the ternary complexes containing these two acids. The observed high stability of the ternary complex containing asparate moiety relative to that containing the glutamate moiety (Table 1) can be considered as convincing evidence for such an explanation. (iv) Generally, for all the binary and mixed ligand complexes studied, the stability of the Ni^{II} complex is higher than that of the corresponding Co^{II} complex which is in confirmity with the Irving-Williams order.

Experimental

2,2′,2″-Terpyridine and the amino acids (Sigma, A.R.) were used as such. All other chemicals ($NaClO_4$, $HClO_4$, NaOH, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$) were of A.R. grade. A 10^{-2} *M* terpy solution was prepared in CO_2-free distilled water. The molarity of $HClO_4$ was checked by titration against standard carbonate-free NaOH solution.

TABLE 1–FORMATION CONSTANT VALUES FOR THE BINARY M(II)-TERPY, M(II)-AMINO ACIDS AND TERNARY M(II)-TERPY-AMINO ACIDS COMPLEXES

Temp 25°, μ = 0 2 mol dm^{-3} ($NaClO_4$) in 50% (v/v) aqueous ethanol mixture

Ligand	$\log K^{M(II)}_{M(II)\text{-terpy}}$		$\log K^{M(II)}_{M(II)\text{-aa}}$		$\log K^{M(II)\text{-terpy}}_{M(II)\text{-terpy-aa}}$	
	Co^{II}	Ni^{II}	Co^{II}	Ni^{II}	Co^{II}	Ni^{II}
terpy	4 38	5.14				
gly			5 33	6 09	5 15	5 71
ala			4 78	5 93	4 64	5 29
val			4 67	5 68	–	5 03
isoleuc			4 59	5 44	–	4 71
asp			6 47	7 63	7 69	7.95
glut			4.96	5 99	6 85	6 97

Potentiometric titrations : Titrations of 1 : 1 M(II)-aa as well as of 1 : 1 : 1 M(II)-terpy-aa (2.5×10^{-3} mol dm^{-3} of each) in aqueous-ethanol mixtures (50%, v/v) with a relatively highly concentrated NaOH solution (0.1562 mol dm^{-3}) were performed at 20 ± 1°. Constant ionic strength was maintained with 0.2 *M* $NaClO_4$ and the total volume was kept constant at 50 ml. pH-measurements were carried out with an Orion-501 digital ionalyzer (± 0.01 pH unit). The accuracy of the pH-meter was checked by 0.05 mol dm^{-3} KH-phthalate solution (pH 4.008 at 20°) and 0.01 mol dm^{-3} borax solution (pH 9.180 at 20°). The following solutions were titrated : (a) $HClO_4$; (b) $HClO_4$+ terpy; (c) $HClO_4$ + terpy + M^{2+}; (d) $HClO_4$ + aa; (e) $HClO_4$ + aa + M^{2+}; (f) $HClO_4$ + terpy + aa + M^{2+}.

In order to account for the difference in acidity, basicity, dielectric constant and ion activities in partially aqueous solutions relative to the pure aqueous ones, the pH values of the former solutions were corrected making use of the reported procedure[9,10]

$$pH^* = pH(R)-\delta$$

where pH^* is the corrected reading, pH(R) the pH-meter reading obtained in partially aqueous solutions, where the pH-meter was standardised using aqueous buffers, and the value of δ for 50% (v/v) water-ethanol mixture is 0.13[10].

The potentiometric titration curves were constructed by a Calom plotter connected to a

Mainframe computer IBM-370 VM-machine. Various calculations were made on the same computer.

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