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POTENTIOMETRIC STUDIES ON THE TERNARY COMPLEX SYSTEMS: M (II) - SALICYLIC ACID - AMINO ACIDS

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ABSTRACT

Ternary complex systems M(II): salicylic acid derivatives (as primary ligands): acidic and basic amino acids (as secondary ligands) have been investigated by the potentiometric technique. Formation constant values of the various binary and ternary complexes liable to exist in such systems have been determined at 25 °C and $\mu = 0.2$ mol dm^{-3} KCl. The order of stability of the binary or ternary complexes in terms of nature of metal ion, salicylic acid derivative and amino acid as well as the stability of the ternary complex compared to that of the binary amino acid complex are examined and discussed.

INTRODUCTION

Due to the biological importance of both salicylic acid derivatives and amino acids, considerable interest has been shown in the literature concerning transition metal ion ternary complexes containing each of these two ligands with numerous N or N, N or N, O or O, O donor ligands. However, little information was available concerning the formation constant values of the ternary systems containing the two competing ligands, amino acids and salicylic acids[1-3]. Martin and Paris[1] analysed the data from pH-titration of the aqueous mixture of 1: 1: 1 Cu(II): glycinate: 5-sulphosalicylate. Gerbeleu, et al.[2] studied the mixed ligand complexes of the system Fe(III)-salicylate ion- α-amino acid spectrophotometrically. Migal and Coworkers[3] investigated the effect of substitutent of α-aminobutyric acids on the stabilitiy of the mixed ligand Cu(II) complexes of the salicylate and sulphosalicylate series in aqueous solutions. It was proved that the stability of the complex decreases with the introduction of OH and S substitutents into α-aminobutryric acid.

Accordingly in this paper a systematic study on the complex formation between some divalent transition metal ions (Co(II), Ni(II), Cu(II), salicylic acid derivatives H_2SAD (3, 5-dinitro, 5-sulpho-and

thio-salicylic acid, 3,5-DNSA, 5-SSA, TSA respectively) as primary ligands and acidic and basic amino acids a.a. (L-serine, L-proline, L-threonine, L-aspartic and L-asparagine, L-glutamine and L-lysine respectively) as secondary ligands in aqueous media has been carried out using the potentiometric technique. The formation constants of the binary and ternary metal complexes have determined adopting the Irving and Rossotti technique[4]. The aim of this work is to determine the formation constant values of the different binary and ternary complexes that are liable to form in such systems. The stability of the formed ternary complexes has been examined and discussed in relation to that of the corresponding binary complexes as well as in terms of nature of metal ion, salicylic acid derivative and amino acid moities.

EXPERIMENTAL

Materials and Solutions:

All the chemicals used were of analytical grade products. Metal ion solutions were estimated using the conventional standard method[5]. Carbonate free NaOH solution was prepared and standardized by potassium hydrogen phthalate. $HClO_4$ solution was prepared and used after standardization. Standard solutions of the various amino acids and substituted salicylic acid derivatives were prepared. Stock solution of KCl was also prepared. It is worthy to note that due to the weak solubility of TSA in water, the required amount of TSA was dissolved in absolute ethanol.

Potentiometric Titrations:

Numerous titrations with a relatively high concentrated standard carbonate free sodium hydroxide solution of different M(II)-3,5-DNSA, 5-SSA, TSA and/or amino acid in 1:1:1 molar ratio (1×10^{-3} mol dm^{-3} for each) were performed at 25 ± 0.1°C. A constant ionic strength was obtained with 0.2 mol dm^{-3} KCl and total volume was kept constant at 50 ml. pH's were measured with Orion model 701 A digital pH-meter with a glass calomel electrode assembly at 25 ± 0.1°C. The solutions titrated can be represented according to the following scheme:

$HClO_4$ (a); $HClO_4$ + salicylic acid derivative (b);

$HClO_4$ + salicylic acid derivative + M (II) (c);

$HClO_4$ + a.a. (d); $HClO_4$ + a.a. + M (II) (e);

$HClO_4$ + salicylic acid derivative + a.a. + M (II) (f).

In the case of the primary ligand TSA, 50 % v/v ethanolwater mixture was used. Accordingly the pH values of such media were corrected by making use of the procedure described by Douheret[6]: pH* = pH (R)–δ where pH* and pH(R) are the corrected and meter readings, respectively, δ for 50 % (v/v) water–ethanol mixture is 0.128[6].

RESULTS AND DISCUSSION

Identical bunches of titration curves are obtained for the different ternary systems under investigation according to the sequence described in the experimental section. Representative curves are displayed in Figs 1–3. Examination of the obtained curves for the 1:1 binary M (II)–SAD complex solutions reveals that these complexes are formed at lower pH's (5.1–6.3, 4.1–6.0 and 2.6–4.5 for Co (II), Ni (II) and Cu (II) complexes respectively). This is attained from the appeared divergence of each of the titration curve of the binary complex solution (curve c) from that of the corresponding free SAD one (curve b). It is worthy to indicate that the binary complex solutions of Cu (II) with 3,5–DNSA or TSA show precipitates at pH $\sim$ 10. This can be likely ascribed to the behaviour that these complexes undergo hydrolysis reaction where hydroxo complex species are probably formed. Accordingly in such cases a further study was not possible beyond the precipitation point in each case. On the other hand, the titration curves of the different M (II)–amino acid binary complex solutions reveal that these complexes begin to form in the pH ranges 5.6–7.5, 3.5–6.0 and 3.2–4.5 for Co (II), Ni (II) and Cu (II) respectively.

With respect to the titration curves of the 1:1:1 ternary complexes, one deduces that these titration curves strongly overlap with the titration curves of the 1:1 binary M (II)–SAD at lower pH's (curves f and c). This suggests that in the lower pH's where M (II)–SAD complex takes place, the amino acid does not combine with M (II). Generally, at higher pH's one observes a divergence of the ternary titration curve from that of the corresponding binary M(II)–SAD one. The pH value at which divergence occurred is largely dependent on the nature of both the metal ion and the two ligands. This behaviour reveals that the coordination of amino acid with the binary M (II)–SAD takes place in stepwidse manner as represented below:

$$M(II) + H_2SAD \rightleftarrows [M(SAD)] + 2H^+$$

$$M(SAD) + a.a. \rightleftarrows [M(SAD\ (a.a.)]^{-x}$$

$x = -1$, for monocarboxylic amino acids

$x = -2$, for dicarboxylic aspartic acid

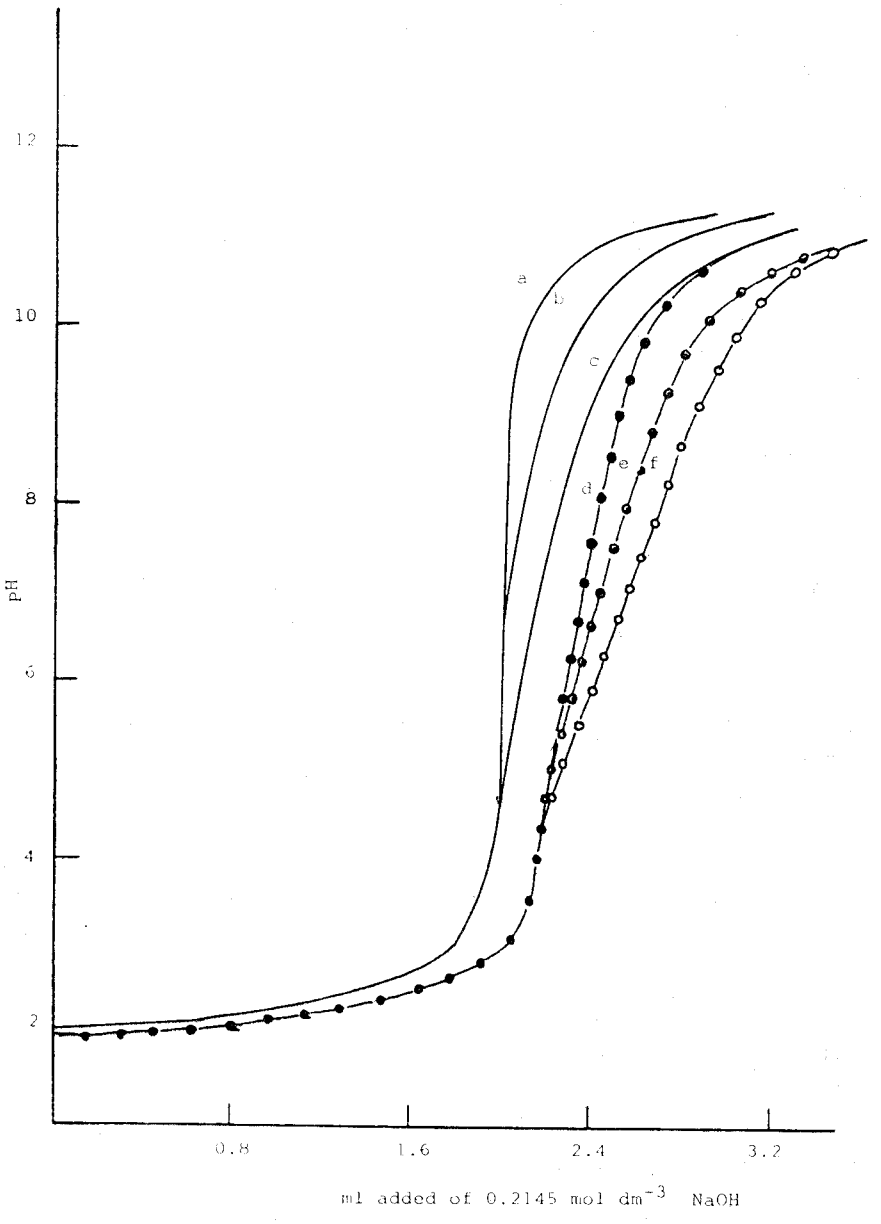

Fig. 1. Titration curves for [Ni (II)–3,5–DNSA–threonine] system at 25 °C and at $\mu = 0.2$ mol. dm^{-3} with 0.2145 mol. dm^{-3} NaOH.

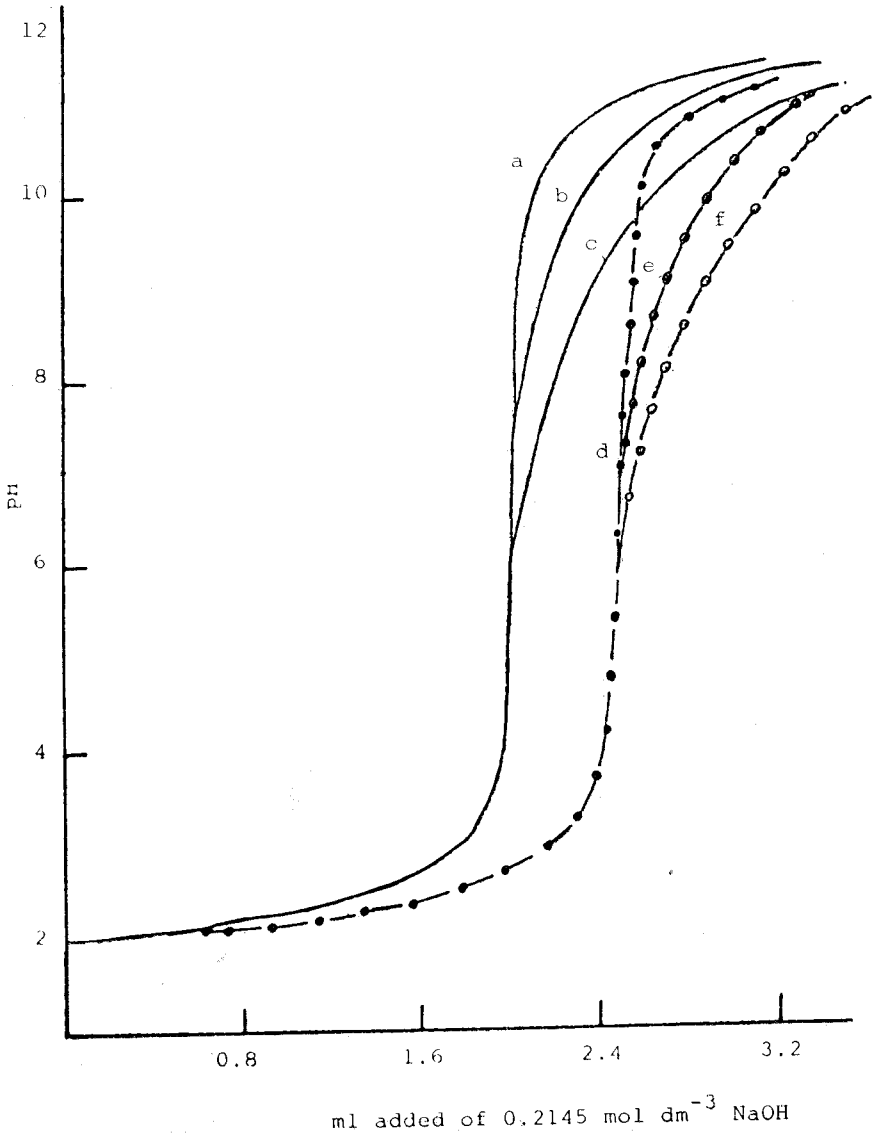

Fig. 2. Titration curves for [Co(II)–5–SSA–glutamine] system at 25 °C and at $\mu = 0.2$ mol. dm^{-3} with 0.2145 mol. dm^{-3} NaOH.

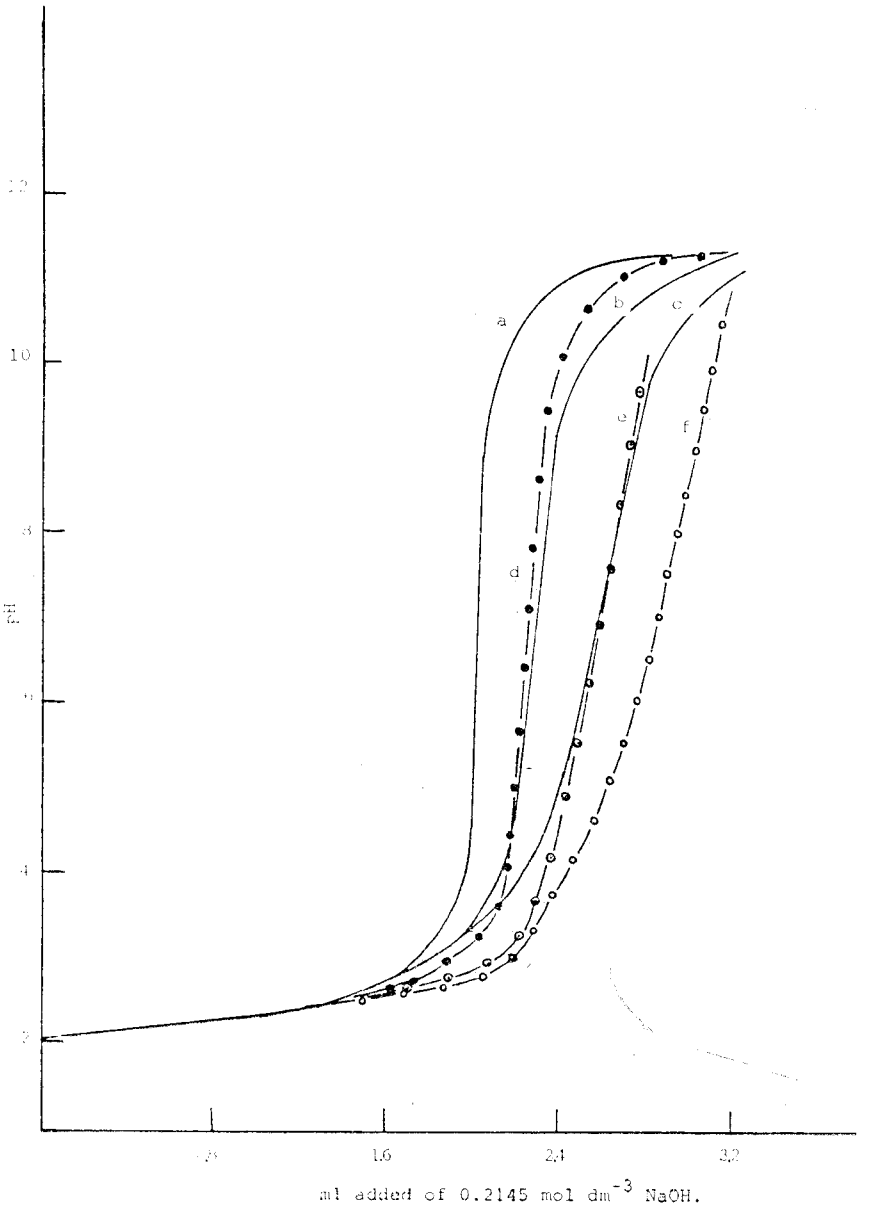

Fig. 3. Titration curves for [Cu(II)–TSA–Aspartic] system at 25°C and at $\mu = 0.2$ mol. dm^{-3} with 0.2145 mol. dm^{-3} NaOH.

Thus, it may be assumed that amino acid would combine with M (II)–SAD binary complex species in ternary systems similarly as it does with $[M(H_2O)n]^{z+}$ binary system. In this respect it is worthy to indicate that except in the case of Cu (II)–TSA binary complex the other binary [M (SAD)] complexes are quite stable up to the pH range where the attachement of amino acid takes place forming the ternary complex. Thus one can easily deduce that the different metal ternary complexes under investigation are formed before hydrolysing pH's of the corresponding binary [M (SAD)] complexes. However for all ternary metal complex solutions studied, precipitation is occurred in the case of the systems Ni (II): 5–SSA: proline, Cu (II): 5–SSA: threonine, Co (II), Ni (II): 3,5–DNSA: proline, Ni (II): 3,5–DNSA: asparagine, glutamine and Cu (II): 3,5–DNSA: monocarboxylic amino acids. Thus beyond the precipitation point for each of these ternary systems, further study was not possible, hence the hydroxo species likely to be formed after this stage could not be studied. The observed very weak tendency of Cu (II)–TSA binary complex to undergo reaction with each of the amino acids under investigation can be ascribed to the tendency of this complex to undergo hydrolysis reaction [i.e. formation of hydroxo species at pH lower than that suitable for the coordination of the amino acid].

The acid dissociation constants for all SAD and amino acids were determined under identical conditions from the titration curves a, b and a, d respectively, making use of the Irving and Rossotti formulate[4]. The values obtained for 5–SSA, 3,5–DNSA, TSA and a.a. are in good agreement with the corresponding ones reported in the literature[7–11]. It is worth mentioning that pKa_1 value for all amino acids studied are too low (≤ 2.01 and exist only in strongly acid solutions). Accordingly these values are not used in the calculation of the binary or ternary complex formation constants.

Formation constants values:

The horizontal distance between curves c and f can be measured and used for the calculation of $\bar{n}_{mix.}$ (average number of secondary ligand amino acid molecules associated with one [M(SAD)]. The equation used for the calculation of $\bar{n}_{mix.}$ will be the same as the original paper[4].

$$\bar{n}_{mix.} = \frac{(V_f - V_c)\ [N^\circ + E^\circ + T_L^\circ\ (Y - \bar{n}_H)]}{(V_0 + V_c)\ \bar{n}_H\ T^\circ_M} \qquad (1)$$

where T°_M is the concentration of M (II) used; Y = no. of dissociable protons of amino acid; V_0 = original volume (50 ml); V_c and V_f are the volumes of alkali consumed to reach the same pH values in curves c and f. All other symbols have their usual meaning[4]. $\bar{n}_H$ for the secondary ligand, amino acid, at different pH values were available from determination of the amino acids formation constants values as described above. from the values of $\bar{n}_{mi^x}$. so obtained, free secondary ligand exponent, PL'_{mix}. was calculated using the equation:

$$pL_{mix.} = \text{Log} \left(\sum_{y=0}^{Y=1 \text{ or } 2} \frac{\beta^H_y \cdot 10^{\left(\frac{1}{\beta}\right)^Y}}{T^{\circ}_L - \bar{n}_{mix.} \cdot T^{\circ}_M} \cdot \frac{V_0 + V_f}{V_0} \right) \quad (2)$$

β^H_y = second and third formation constant values for the applying amino acids.

β = the pH – meter reading.

Formation curves corresponding to the various mixed ligand M (II)–SAD–a.a. systems were obtained by plotting $\bar{n}_{mix.}$ vs $PL'_{mix.}$ (respresentative results are shown in Fig. 4. The corresponding formation constants

$$\text{Log } K^{M\,(SAD)}$$

M (SAD) (a.a.) obtained by the average value method are reported in Table 1. For comparison of the stability of the M (II)–SAD–a.a. ternary complex with that of the binary M (II)–SAD or M (II)–a.a., the formation costants of the different binary complexes were determined. This as made by applying the original equations of Irving and Rossotti[4] to the binary complex solutions systems (curves b, c and h, e for M (II)–SAD and a.a. respectively). The various

$\text{Log } K^{M}_{M\,(SAD)}$ and $\text{Log } K^{M}_{M\,(a.a.)}$ values obtained from the experimental formation curves of the binary complex systems by the average value method are reported in Table 1. Some of these values are in good agreement with those found in the literature[7]. Examination of the obtained formation constant values for the complexes studied in terms of nature of each of the three constitutents reveals the following important conclusions:

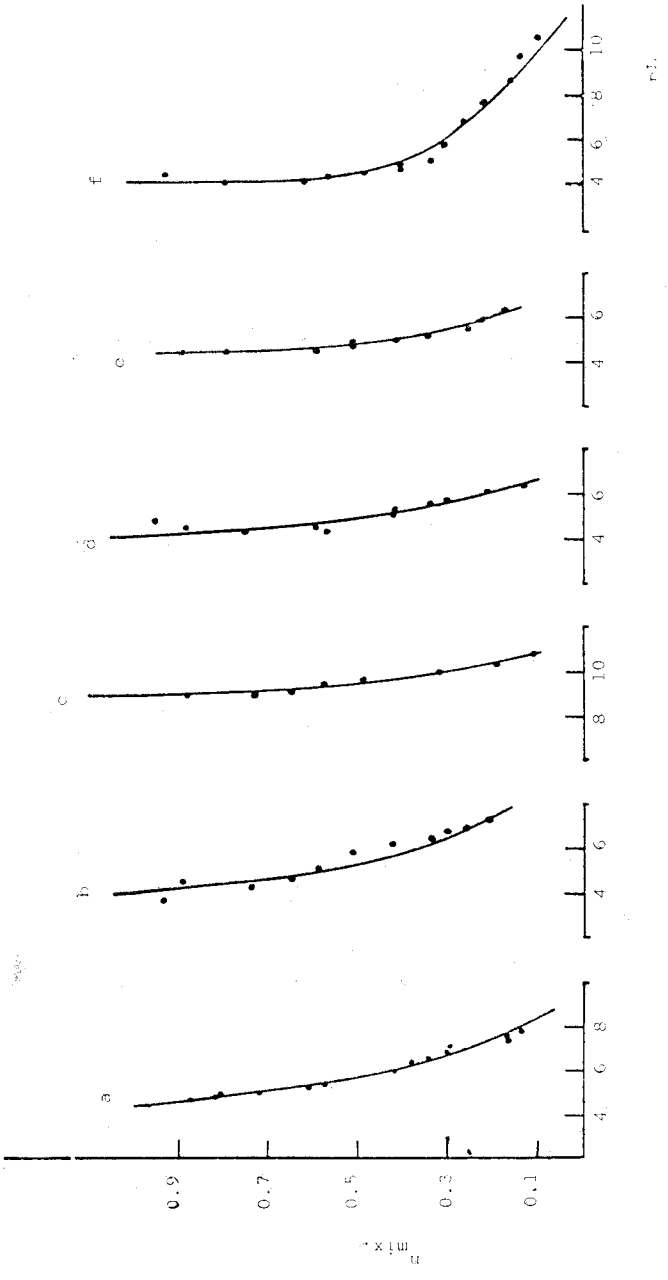

Fig. 4. Experimental formation curves for the ternary 1: 1: 1 Ni(II)–5–SSA–amino acids complexes ($\bar{n}_{mix}$ –pL) at 25°C and at $\mu = 0.2$ mol. dm^{-3} KCl.
a) Serine; b) Threonine; c) Aspartic; d) Asparagine; e) Glutamine and f) Lysine.

Table 1. Formation Constant Values of the Binary and Ternary Complexes.

Ligand	Log K^{M}_{SAD} or Log $K^{M}_{M(a.a.)}$			Log $K^{M(SAD)}_{M(SAD)(a.a.)}$								
	CO (II)	Ni (II)	Cu (II)	Co (II)			Ni (II)			Cu (II)		
				3,5-DNSA	5-SSA	TSA	3,5-DNSA	5-SSA	TSA	3,5-DNSA	5-SSA	TSA
3,5-DNSA	3.40	3.60	6.00									
5-SSA	6.20	7.18	8.75									
TSA	6.20	7.75	13.20						—		—	
Serine	4.40	5.80	8.10	4.30	4.00	4.10	5.20	5.60	5.20		7.80	—
Threonine	5.00	5.70	7.40	4.20	3.70	4.00	5.60	5.10	4.50	—	—	—
Prol=Wu	5.40	6.25	9.00	—	4.20	3.50	—	—	4.40	—	8.60	—
Aspartic	5.45	7.00	8.80	8.60	9.35	8.90	9.30	9.40	9.80	9.40	9.60	—
Asparagine	4.70	5.10	8.00	4.50	4.20	3.80	—	4.80	4.90	—	7.80	—
Glutamine	4.40	5.20	7.90	4.30	4.10	3.80	—	4.60	4.70	—	7.80	—
Lysine	5.00	5.80	10.00	4.70	4.40	4.90	4.53	4.60	5.70		4.20	—

i- The stability of the different 1:1 binary M (II)–SAD complexes increases according to the order:

$$3,5\text{–DNSA} < 5\text{–SSA} < \text{TSA}$$

This can be interpreted in terms of the effect of basicity of these compounds since the pKa_1 and pKa_2 values of 3,5–DNSA are low relative to the corresponding ones of 3,5–DNSA are low relative to the corresponding ones of 5–SSA and TSA (pK_{COOH} and pK_{OH} for 3,5–DNSA and 5–SSA are 1.31, 7.07 and 2.49, 12[8] respectively and pK_{COOH} and pK_{SH} for TSA are 5.44 and 9.52[9,10]. Furthermore the presence of high electron withdrawing groups (two NO_2 in 3,5–DNSA and SO_3H in 5–SSA) reflect their self in low stabiliy of the complexes containing these ligands. On the other hand, te possibility of M $\rightarrow$S π interaction in the case of M (TSA) complex is expected to play a significant role in increasing stability of such a complex.

ii- The stability of the binary and ternary complex containing amino acid is largely dependent on the nature of the amino acid used. Generally the complexes containing the α, β– dicarboxylic aspartic acid (O, O, N ligand) where two chelated rings are formed (Five and Six membered) is characterized by higher stability relative to the corresponding ones containing α– monocarboxylic amino acids. However the dependence of the complex stability on the nature of the α–monocarboxylic amino acid is found to follow the order:

$$\text{Proline}\ \left(\begin{matrix}pKa_2 = 10.64,\\ R = -CH_2\,CH_2\,CH_2\end{matrix}\right) > \left(\begin{matrix}pKa_2 = 09.21,\\ \text{Serine}\\ R = OH\,CH_2\end{matrix}\right) > \text{Threonine}$$

(For acidic amino acids, O, N–ligands) $\left(\begin{matrix}pKa_2 = 9.1,\\ R = CH\ (OH)\ CH_3\end{matrix}\right)$

and

$$\text{Lysine}\left(\begin{matrix}pKa_2 = 10.63,\\ R = CH_2CH_2CH_2CH_2\text{–}NH_2\end{matrix}\right) > \text{Asparagine}\left(\begin{matrix}pKa_2 = 8.8,\\ R = CH_2\,CO\,NH_2\end{matrix}\right) \geq$$

$$\text{Glutamine}\quad \left(\begin{matrix}pKa_2 = 9.28,\\ R = CH_2CH_2CO\,NH_2\end{matrix}\right)$$

(For basic amino acids, N, N, O–ligands).

This behaviour can be explained on the principle of the effective basicity of the free conjugate bases of these amino acids[11] (i.e. their

tendencies to act asσ-donor) as well as the steric effect results from the side chain R.

iii- Except in the case of applying the α, β-dicarboxylic aspartic acid, the stability of the ternary complex is lower than that of the corresponding binary [M (a.a.)] complex, i.e. Δ log K values are negative, Table 1. This behaviour is expected and can be explained on the basis that there are fewer number of sites available for bonding on the [M (SAD)] binary complex than that on the aquated M(II) ions. Thus the secondary ligand amino acid is expected to bind the [M(SAD)] complex with a smaller formation constant than that with the aquated metal ion. However, the observed high stability of the ternary complexes containing aspartic acid relative to that of the corresponding binary [M (SAD)] ($\triangle$ log K values are positive) can be ascribed to the behaviour that aspartic acid is much more prone in complex formation since it coordinates to the metal ion as tridentate O, O, N ligand leading to the formation of two metal chelated rings (Five and Six membered).

iv- The dependence of the stability of the binary and ternary complexes studied on nature of metal ion is found to follow the trend: Co (II) $<$ Ni (II) $<<$ Cu (II). This is in confirmity with the Irving-Williams order. The additional high stability of the Cu (II) complex is attributed to the unique electronic configuration ($3d^9$) of Cu (II) ion which is capable of additional stabilization due Jahn-Teller distortion.

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