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Interaction Of $Me_2Sn(IV)^{2+}$ And $Me_3Sn(IV)^{+}$ Cations With Catecholamines In Aqueous Media

Meena Devi[1], Renu Nair (Ahuja)[2], Jyotsna Gupta[3]and K.Dwivedi[4]
[1](School of Studies in Chemistry, Jiwaji University, Gwalior-474011 M.P. India)
[2](VijayaRaje Govt. Girls P.G. College, Morar, Gwalior -474001 M.P. India)

Abstract:*Solution studies of the interaction of $Me_2Sn(IV)^{2+}$ and $Me_3Sn(IV)^{+}$ with catecholamines (L- dopa and L-tyrosine) in aqueous medium (μ=0.05 ,0.10 and 0.15 M $NaNO_3$ and Temperature = 20±1°C, 30±1°C and 40±1°C) are performed. The concentrationdistribution of the various complex species in solution is evaluated as a function of pH.SCOGS computer programme is used for computational analysis. The complex species formed are water soluble in the pH range 2.8–10.5. In all of the studied systems, no polymeric species are detected in the experimental range. Thermodynamic stability constants along with thermodynamic parameters i.e. standard free energy change (ΔG^o) enthalpy change (ΔH^o) and entropy change(ΔS^o) are calculated for all the systems. It is observed that L-dopa interact more strongly than that of L- tyrosine with both $Me_2Sn(IV)^{2+}$ and $Me_3Sn(IV)^{+}$cations. Whereas, on the basis of metals it is concluded that complexes of $Me_2Sn(IV)^{2+}$are thermodynamically more stable than those of $Me_3Sn(IV)^{+}$ complexes. $Me_2Sn(IV)^{2+}$ and $Me_3Sn(IV)^{+}$stands for dimethyltin(IV) cation and trimethyltin(IV) cation.*

Keywords: *Catecholamines, organotin (IV) , SCOGS, Solution studies.*

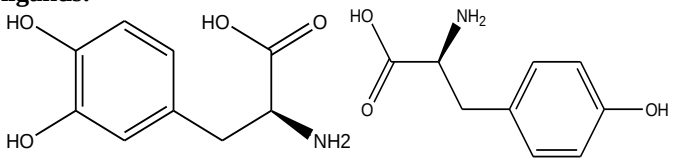
I. Introduction

Organotin compounds are widely used as PVC stabilizers, fungicides, wood and stone preservatives, surface disinfectants,antifouling agents in paints for ships and in glass coatingoperations, etc [1]-[7]. As a result of this, they may enter theenvironment directly/indirectly. In the natural environment,organotin compounds can also originate from chemical andbiological processes[8]-[9].Methyltin derivatives are the most encounteredorganotin compounds and are often present in the marineenvironment. Di- and trimethyltin compounds posses highmammalian toxicityand their solubility in water makesthem very dangerous for aquatic living organisms[10].Very few quantitative studies have been reported on the formation constants, stabilities and structures of organotin(IV) with catecholamines.In vitro speciation of organotin(IV) compoundsis highly desirable. Their solution equilibrium studiescould provide essential information on the biospeciation oforganotins and thus on their bioavailability.

Catecholamines are water-soluble and are 50%-bound to plasma proteins when they circulate in the bloodstream. In the human body, the most abundant catecholamines are epinephrine (adrenaline), norepinephrine (noradrenaline) and dopamine, all of which are produced from phenylalanine and tyrosine . Catecholamines cause general physiological changes that prepare the body for physical activity (fight-or-flight response). Some typical effects are increases in heart rate, blood pressure, blood glucose levels, and a general reaction of the sympathetic nervous system[11].

L-Dopa **(3,4dihydroxyphenylalanine)**is a precursor of dopamine and norepinephrine in the biosynthetic pathways for these neurotransmitters and these derivatives regulate a variety of physiological functions in the human body. L-dopa is a popular drug in the treatment of manganese poisoning and Parkinson's disease[12]-[18]. L-Tyrosine is synthesized in the body from phenylalanine and it is a direct precursor of adrenaline and thyroid hormones. Metabolic transformations of tyrosine require the presence of folic acid, niacin, vitamin C and copper. Its metabolic products include melanin, estrogen and encephalin. Tyrosine is used along with tryptophan to aid in the treatment of cocaine abuse and may also be useful in the control of anxiety or depression [19]-[22]. In the preset paper distribution of various species form in the equilibria involving interactions of organotin(IV) cations with catecholamines (L-dopa and L-tyrosine) are presented. Also the thermodynamic stability constants and other thermodynamic parameters such as standard free energy change (ΔG^o) standard enthalpy change (ΔH^o) and standard entropy change(ΔS^o) are discussed.

Scheme 1. Structure of ligands:



L-DOPA **L-Tyrosine**

II. Experimental

All the binary systems were investigated under equimolar concentration ratio. For each set of titration moles of alkali required per mole of ligand / metal. 'a' was determined and curves were obtained by plotting pH vs 'a'.

2.1. Solution : All the reagents used were of highest purity Merck/Aldrich products. Solutions were prepared in doubly distilled CO_2-free water having pH ≈ 6.8. Solutions of metal and ligand (each 0.01M) were prepared by dissolving accurately weighed amounts in double distilled water.

2.2. Instrument: An Elico digital pH-meter model LI-127 with ATC probe and combined electrode type (CL-51B-Glass Body; range 0-14 pH unit; 0-100°C Automatic/Manual) with accuracy ±0.01 was employed for pH-measurement.

2.3. Experimental technique: Three sets of titration mixtures were prepared at three different ionic strengths (μ = 0.05M, 0.10M and 0.15M)maintained by adding different concentration of $NaNO_3$ solution to each titration mixture.

These are:

1. HNO_3 (2.0×10^{-3}M)
2. HNO_3 (2.0×10^{-3}M) + Ligand (1.0×10^{-3}M)
3. HNO_3 (2.0×10^{-3} M) +Ligand (1.0×10^{-3}M) + Metal ion (1.0×10^{-3}M)

Each set of mixture was titrated potentiometrically against standard sodium hydroxide solution (0.10M). Experiments were performed at three different temperatures 20±1°C, 30±1°C and 40±1°C.Temperature was maintained by Siskin Julabo, thermostat model V-12B.

III. Results and discussion

Titration curves for DMT(IV) and TMT(IV) – L-dopa and L-tyrosine in the form of pH vs 'a'are given in figs. 1-4.

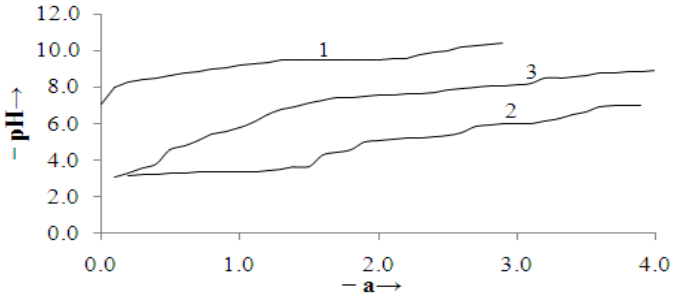


Fig.1. pH vs 'a' curves for M(IV)- L-dopa (1:1) system

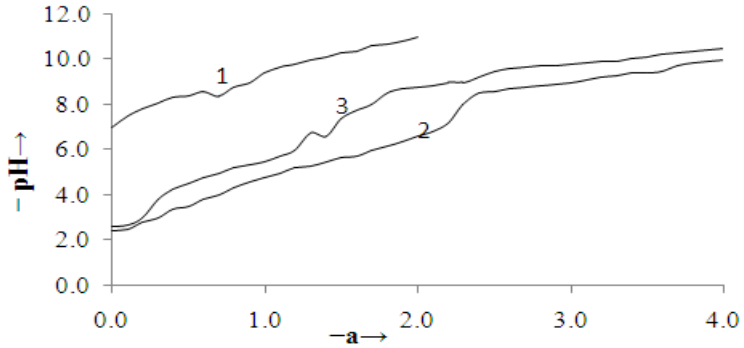


Fig.2. pH vs 'a' curves for M (IV)- L-tyrosine (1:1) system

In figs. 1and 2.
Temperature = 30±1ºC, μ = 0.10M maintained by $NaNO_3$.
Curve 1.represents ligand titration curve .
Curve 2.represents DMT- ligand titration curve.
Curve 3.represents TMT - ligand titration curve.

The ligand titration curve for L-dopa in fig.1 is seen to extend between $0 \leq a \leq 3$ with feeble inflections followed by a buffer region indicating that the ligand is triprotonated (H_3L) and results in the release of three protons. The examination of metal-ligand titration curves between $0 \leq a \leq 3$ reveals the formation of MH_2L, MHL and ML species respectively. With the increase of pH, the formation of ML(OH) species is evident between $3 \leq a \leq 4$. Formation of the yellow coloured soluble complex in this range further confirms the existence of ML(OH) species in the solution.

Values of equilibrium constants can be presented by following equation:
Proton-ligand:

$$H_3L \overset{0 \leq a \leq 1}{\rightleftharpoons} H_2L + H \qquad \text{-------1.1}$$

$$H_2L \overset{1 \leq a \leq 2}{\rightleftharpoons} HL + H \qquad \text{-------1.2}$$

$$HL \overset{2 \leq a \leq 3}{\rightleftharpoons} L + H \qquad \text{-------1.3}$$

Metal-ligand:

$$M + H_2L \overset{0 \leq a \leq 1}{\rightleftharpoons} MH_2L \qquad \text{--------1.4}$$

$$MH_2L \overset{1 \leq a \leq 2}{\rightleftharpoons} MHL + H \qquad \text{--------1.5}$$

$$MHL \overset{2 \leq a \leq 3}{\rightleftharpoons} ML + H \qquad \text{--------1.6}$$

$$M + L \overset{2 \leq a \leq 3}{\rightleftharpoons} ML \qquad \text{--------1.7}$$

$$ML + OH \overset{3 \leq a \leq 4}{\rightleftharpoons} ML(OH) \qquad \text{--------1.8}$$

(Charges have been omitted for the sake of simplicity).

On examining the fig. 2 which represent the titration curve for organotin (IV) - L- tyrosine systems , it is seen that ligand titration curve shows two inflections at a≈1 and a ≈2, thereby suggesting the release of two protons in two distinct steps. The nature of metal – ligand titration curves clearly manifests the formation of MHL species at $0 \leq a \leq 1$. Further the deprotonation of MHL species between $1 \leq a \leq 2$ leads to the formation of ML complexes. Above this between $2 \leq a \leq 3$ formation of ML(OH) and between $3 \leq a \leq 4$ formation of $ML(OH)_2$ is evident.This is further spported by colour changes observed during the titration above pH ≈7.0, leading the formation of light brown coloured soluble complex between $2 \leq a \leq 3$ and dark brown coloured soluble complex between $3 \leq a \leq 4$.

Various equilibria can be represented as follows:

Proton-ligand:

$$H_2L \overset{0 \leq a \leq 1}{\rightleftharpoons} HL + H \qquad \text{-------1.9}$$

$$HL \overset{1 \leq a \leq 2}{\rightleftharpoons} L + H \qquad \text{-------1.10}$$

Metal-ligand:

$$M + HL \overset{0 \leq a \leq 1}{\rightleftharpoons} MHL \qquad \text{--------1.11}$$

$$MHL \overset{1 \leq a \leq 2}{\rightleftharpoons} ML + H \qquad \text{--------1.12}$$

$$M + L \overset{1 \leq a \leq 2}{\rightleftharpoons} ML \qquad \text{--------1.13}$$

$$ML + OH \overset{2 \leq a \leq 3}{\rightleftharpoons} ML(OH) \qquad \text{--------1.14}$$

$$ML(OH) + OH \overset{3 \leq a \leq 4}{\rightleftharpoons} ML(OH)_2 \qquad \text{-------1.15}$$

Charges have been omitted for the sake of simplicity).

Algebraic method of Martell and Chaberek as modified by Dey et al. has been applied to calculate the values of proton and metal –ligand equilibrium constants (which are given in tables 1-3) [23]-[25]. Method developed by M.Chandra is used for the calculation of stability constants of metal hydroxy species[26]. Calculation of equilibrium constants is done by using experimental data obtained by potentiometric technique. Computation of data was done by using **SCOGS (**stability constants of generalized species) computer program[27-29].

The complex formation equilibria were elucidated with the help of speciation curves (represented in figs.3-6).

Table : 1Protonation constant of ligands at different temperaturesand ionic strengths

Parameters	20±1°C			30±1°C			40±1°C		
	0.05 M	0.10M	0.15M	0.05 M	0.10M	0.1 M	0.05 M	0.10M	0.15M
			L-DOPA						
$\log \beta_{HL}$	12.10	12.05	12.00	12.08	12.00	11.94	11.95	11.88	11.80
$\log \beta_{H2L}$	19.50	19.42	19.35	19.43	19.38	19.31	19.34	19.29	9.18
$\log \beta_{H3L}$	29.40	29.34	29.29	29.38	29.28	29.24	29.27	29.18	29.10
	L-Tyrosine								
$\log \beta_{HL}$	9.30	9.17	9.08	9.22	9.14	9.05	9.15	9.02	9.95
$\log \beta_{H2L}$	15.90	15.82	15.74	15.80	15.73	15.65	15.77	15.72	15.68

Table: 2Thermodynamic formations constants ($\log K^{\mu\rightarrow 0}$) along with thermodynamic parameters of M(IV)- L-Dopa systems

system	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	$\log K^{\mu\rightarrow 0}$	-ΔG° kJmol^{-1}	$\log K^{\mu\rightarrow 0}$	-ΔG° kJmol^{-1}	$\log K^{\mu\rightarrow 0}$	-ΔG° kJmol^{-1}		
$Me_2(Sn)^{2+}$-L-Dopa								
$\log K^{M}_{MH2L}$	9.10	51.05	8.90	51.63	8.70	52.13	24.61	89.99
$\log K^{MH2L}_{MHL}$	19.95	111.90	19.70	114.29	19.50	116.86	27.35	288.16
$\log K^{MHL}_{ML}$	13.35	74.89	13.00	75.52	12.90	77.31	25.98	165.62
$\log K^{ML}_{ML(OH)}$	36.10	202.52	35.00	203.05	34.00	203.76	128.55	250.82
$Me_3(Sn)^{+}$-L-Dopa								
$\log K^{M}_{MH2L}$	7.90	44.31	7.50	43.51	7.35	44.09	25.02	62.61
$\log K^{MH2L}_{MHL}$	16.80	94.24	15.90	92.24	14.95	89.59	54.02	134.03
$\log K^{MHL}_{ML}$	12.70	71.24	11.95	69.32	11.40	68.32	35.55	120.62
$\log K^{ML}_{ML(OH)}$	40.20	225.52	38.00	220.46	36.00	215.75	42.39	624.19

Table: 3Thermodynamic formations constants ($\log K^{\mu\rightarrow 0}$) along with thermodynamic parameters for M(IV)- L-Tyrosine systems

System	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	$\log K^{\mu\rightarrow 0}$	-ΔG° kJmol^{-1}	$\log K^{\mu\rightarrow 0}$	-ΔG° kJmol^{-1}	$\log K^{\mu\rightarrow 0}$	-ΔG° kJmol^{-1}		
$Me_2(Sn)^{2+}$-L-Tyrosine								
$\log K^{M}_{MLH}$	8.65	48.52	8.55	49.60	8.50	49.68	8.88	134.98
$\log K^{MLH}_{ML}$	13.00	72.93	12.90	74.84	12.75	75.75	15.72	195.30
$\log K^{ML}_{ML(OH)}$	15.05	84.43	15.00	87.02	14.90	88.39	9.57	255.61
$\log K^{ML(OH)}_{ML(OH)2}$	18.35	102.94	18.10	105.00	18.00	106.79	20.51	280.50
$Me_3(Sn)^{+}$-L-Tyrosine								
$\log K^{M}_{MLH}$	7.80	43.75	7.70	44.67	7.60	45.54	12.30	107.22
$\log K^{MLH}_{ML}$	10.50	58.90	10.35	60.04	10.25	61.42	15.04	149.34
$\log K^{ML}_{ML(OH)}$	13.50	75.73	13.40	77.74	13.35	80.00	8.88	227.85
$\log K^{ML(OH)}_{ML(OH)2}$	16.50	92.56	16.40	95.14	16.30	97.68	12.30	273.80

Speciation profiles for various species are represented in figs. 3-6.

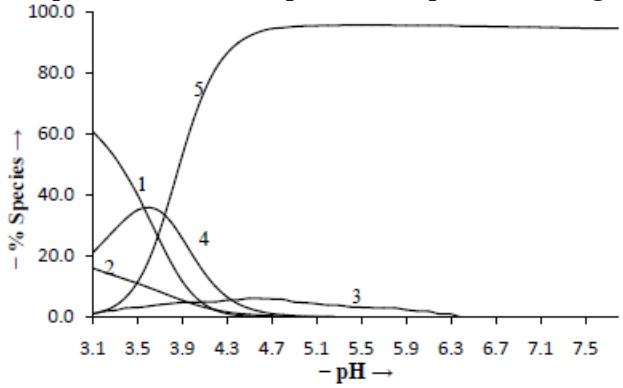


Fig.3. Speciation curves for $Me_2(Sn)^{2+}$- L-Dopa

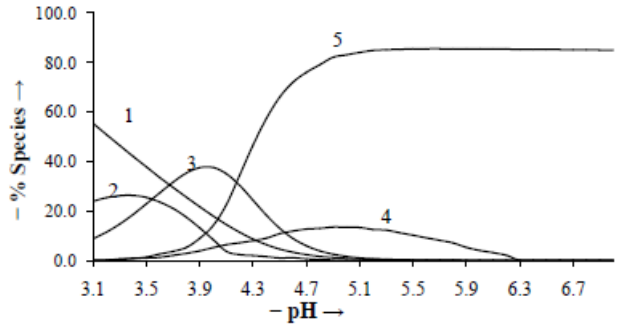


Fig.4. Speciation curves for $Me_3(Sn)^{+}$- L-Dopa

In figs.3 and 4Curve 1 : [M]; 2 : [MH_2L]; 3 : [MHL]; 4: [ML]; 5: [ML(OH)]

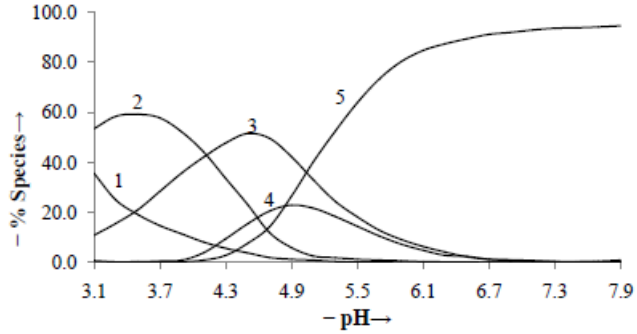


Fig.5. Speciation curves for $Me_2(Sn)^{2+}$-L-Tyrosine

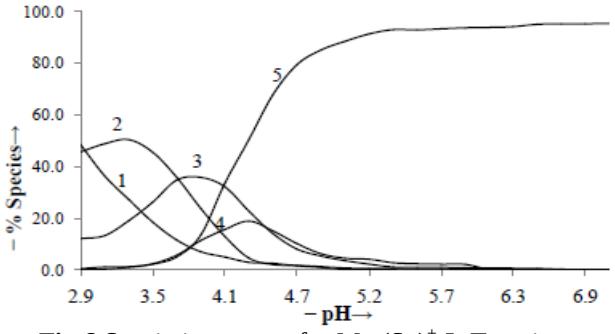


Fig.6. Speciation curves for $Me_3(Sn)^{+}$-L-Tyrosine

In figs. 5 and 6Curve 1 : [M]; 2 : [MHL]; 3 : [ML]; 4 : [ML(OH)]; 5 : [$ML(OH)_2$]
In figs. 3- 6.
Temperature = 30±1ºC, μ = 0.10M maintained by $NaNO_3$.

$Me_2(Sn)^{2+}$ / $Me_3(Sn)^{+}$- L-Dopasystems :

From the observation of speciation curves(figs.3 and 4) it becomes obivious that formation of various species i.e. MH_2L, MHL and ML is confined in a minimum pH range pH ≈3.1- 4.5. The percentage concentration of MH_2L and MHL is less than 15% and that of ML is about 36% .Above pH ≈4.5 the formation of ML(OH) commences and a sharp rising curve (curve 5) clearly provides the evidence of formation of hydroxo complex which attain the maxima at about 95%.

In case of**Me_3**Sn(IV)$^{+}$- L-Dopa system it is observed that free metal concentration is ≈56% at pH ≈3.1and simultaneously MH_2L species is formed in low concentration ≈26%.With the increase in pH, concentration of MH_2L decreases and MHL increases and attains maximum concentration of about 39%. Dissociation of MHL species and the formation of (1:1) ML species goes on hand in hand. However, the formation percentage of ML species is quite low in concentration (≈15%). Above pH 5.0 formation of monohydroxo species is observed which attains maximum concentration of ≈85%.

$Me_2(Sn)^{2+}$ / $Me_3(Sn)^{+}$-L-tyrosine systems :

From the speciation profiles of $Me_2Sn\ (IV)^{2+}$ - L- tyrosine systems(figs.5 and 6)it is observed that the ligand (H_2L) dissociates at very low pH to give (HL) species and its association with metal, leading to the formation of MHL species which is evident by low concentration of free metal 26-35% and significantly higher percentage of MHL species 60-70% in the initial stage. With the progress of pH the dissociation of MHL and formation of ML species is clearly depicted by the decreasing concentration of MHL and increasing concentration of ML attaing a maxima ≈52% at pH ≈4.5. Above this pH the formation of ML(OH) in low concentration and $ML(OH)_2$ in higher range≈95% .

The trend for $Me_3Sn(IV)^{+}$–L-tyrosine systems is same as for $Me_2Sn\ (IV)^{2+}$–L-tyrosine system. But the concentration of various species varies. It is seen that the formation of MHL and ML species is less and formation of ML(OH) and $ML(OH)_2$ are little greater in concentration.

The thermodynamic values of the stability constant have been obtained by extrapolation of log K values to zero ionic strength. The values of the thermodynamic stability constant $K^{\mu\to0}$ is used to determine the ligational standard free energy change (ΔG°) for the complexation reaction from Van't Hoff isotherm :

$$\Delta G^\circ = -2.303RT \log K^{\mu\to0} \quad \text{------- (1.16)}$$

The Gibb's Helmholtz equation ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$) andVan't Hoff isotherm ($\Delta G^\circ = -2.303RT \log K^{\mu\to0}$) can be put in the following form:

$$\log K^{\mu\to0} = \frac{-\Delta H^\circ}{2.303R}\frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \text{-----(1.17)}$$

The standard enthalpy change (ΔH°) and entropy change (ΔS°) have been determined by linear least square fit method by plotting a graph between $\frac{1}{T}$ vs $\log K^{\mu\to0}$[30] . In equation (1.17)

$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R}$$

and $$\text{Intercept} = \frac{\Delta S^\circ}{2.303R}$$

The values of ΔG°, ΔH° and ΔS° are tabulated in tables 2 and 3.

IV. Conclusion

The trend for stability constant of complex species is :L-dopa > L-tyrosine

The reason for the observed trend can be explained on the basis that L-dopa coordinates with metal ion in glycine like mode at lower pH range. This is in conformation with earlier reports which states that L-dopa behaves as ambidentate ligand changing its coordination mode depending on pH [31]-[33]. It is established that at higher pH range L-dopa coordinates in pyrocatechol mode consequently leading to polymeric species[34]. In the present investigation no polymeric species are observed,the formation of ML species is established in lower pH range. L-Tyrosine bears structural similarity with L- dopa only with the difference of having anextra –OH group which makes it more basic than L-tyrosine. The stability constant values of the metal-ligand complexes are nearly same. This indicates that both the ligands coordinate with the metal in glycine like mode. However, the slightly lower values of constants obtained in case of L-tyrosine as compared to L-dopa can be attributed due to their basicity difference.

On comparing the stabilities of $Me_2Sn\ (IV)^{2+}$ and $Me_3Sn\ (IV)^{+}$ complexes, the stability constants for former systems are higher than in the latter systems. The reason for the observed trend is as expected on the basis of cation charge and size [35]-[36]. Finally it can be concluded that the differences in the values of stability constants are most probably caused by the overall charge of the formed complexes and the deprotonation reaction of ligands. The most prominent species in case of L-dopa is ML(OH).Whereas, in case of

L-tyrosine it is $ML(OH)_2$ This is due to the fact that monohydroxo species involving L-dopa and dihydroxo species involving L-tyrosine both assume octahedral geometry. Hence justifying their highest stability.
The values of equilibrium constants as regards to ionic strength and temperature decrease with increase in ionic strength and temperature.The negative value of both free energy ($\Delta G°$) and enthalpy change ($\Delta H°$) and positive value of entropy change ($\Delta S°$) confirms the favourable conditions for complex formation.

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