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Equilibrium Studies on Interaction of Organotin(IV) Cations with Biologically Important Ligands

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ABSTRACT: Equilibrium studies of dimethyltin(IV) [DMT] and trimethyltin(IV) [TMT] cations with biologically important ligands i.e valine (val), serine (ser), leucine(leu) and phenylalanine(phe) are carried out potentiometrically. Experiments are performed in aqueous medium at three different temperatures (20ºC, 30ºC and 40ºC) and at three ionic strengths (μ = 0.05 ,0.10 and 0.15 M). The experimental data are subjected to computational analysis and thermodynamic parameters for ML, (MLOH) and $ML(OH)_2$ species are determined. SCOGS computer programme is used to obtain the speciation of various species formed in a particular equilibrium. The studies suggest that the formation of the complexes involving DMT are thermodynamically more stable than those involving TMT. This has been explained on the basis of cation charge and size .The stablity order with respect to different ligands for both DMT and TMT systems is found to follow the order :

Val > Ser > Phe > Leu

Keywords: Complex formation equilibria, organotin (IV), thermodynamic stability, speciation.

I. INTRODUCTION

Now a days, widespread use of organotin (IV) compounds in industrial, agriculture, and biological fields cause their release and accumulation into the environment and consequently in biological systems. Hence the knowledge of behaviour of organotin (IV) is of great importance. The toxicity scale (R_3Sn^+ > R_2Sn^{+2} > RSn^{+3} > Sn^{+4}) as documented in many reports , articles and reviews [1-15] in organotin (IV) compounds correlating to the number and kind of organic group bonded to the tin(IV) atom is well known.

Equilibrium studies of organotin (IV) in aqueous solution bear great significance because it can give information on the formation of complex with naturally occuring and anthropogenic component of the ionic medium (natural water or biological fluids) leading to the formation of other species whose stability can influence the solubility [16]. Therefore it becomes evident that speciation studies of this class of compounds in aqueous solution using equilibrium analysis need great attention.

Literature survey [17-22] reveals that a large part of investigations on the presence of organotin (IV) compounds in the environment refers to the speciation analysis. By speciation analysis it is possible to know the amount of organotin (IV) compound present in different matrices. However, it does not give any information on the chemical behaviour of single species in the presence of other components. These findings are reviewed by Sammartano and co-workers [17]. Sequestration of alkyltin (IV) cations by complexation with amino-polycarboxylic chelating ligands is also reported by Sammartano *et al.* [18]. Organotin complexes with Schiff bases derived from amino acids have been studied by Singh and Mukherjee [19]. Potentiometric determination of the stability of trimethyltin(IV) chloride complexes in water – dioxane mixture is reported recently [20-21]. Studies on antimicrobial activity of some triorganotin(IV) complexes have been reported very recently [22].

In this paper we report the thermodynamic formation constant together with other thermodynamic parameters and speciation of various species formed by the interaction of organotin(IV) cations with ligands of biological importance.

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'.

A. 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.

B. 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.

C. Experimental conditions

Three sets of titration mixtures were prepared and titrated against standard sodium hydroxide solution (0.10M) 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 at temperatures 20°C ± 1, 30ºC ± 1 and 40ºC ± 1. Temperature was maintained by Siskin Julabo, thermostat model V-12B.

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)

III. RESULTS AND DISCUSSION

Figs.1-4 represent the pH vs 'a' curves for DMT / TMT - amino acids systems. Curve 1 in each figure represents the ligand titration curve whereas curves 2 and 3 represent the DMT -ligand titration and TMT-ligand titration respectively, where DMT stands for dimethyltin(IV) dichloride and TMT stands for trimethyltin(IV) chloride.

It is observed that in all the ligands the proton dissociates in higher pH range (pH≈8.2 -8.5) indicating their strong basic nature. The calculated values of protonation constants agree well with the literature values [23-26]. Curves 2 and 3 in Figs. 1-4 depicting the titration of DMT (IV)/TMT (IV) - amino acids respectively, show the right hand shift from the ligand titration curve 1, thereby suggesting the formation of ML complex in the pH ranging from 2.5 – 5.5 showing an inflection in between $0 \leq \underline{a \leq 1}$. Further appearance of inflections in the range $\underline{1 \leq a \leq 2}$ and $\underline{2 \leq a \leq 3}$ indicate the formation of monohydroxy ML(OH) and dihydroxy $[ML(OH)_2$ species respectively. These equilibria can be represented as follows :

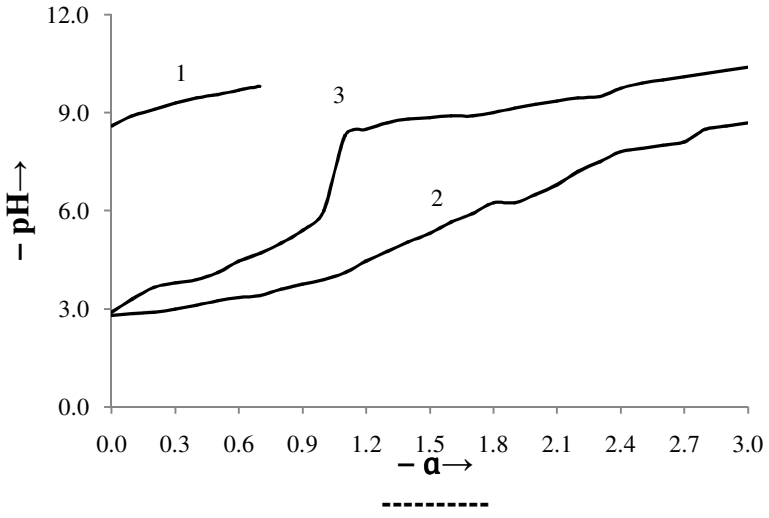

Fig. 1. pH vs 'a' curves for M(IV) – valine (1:1) system.

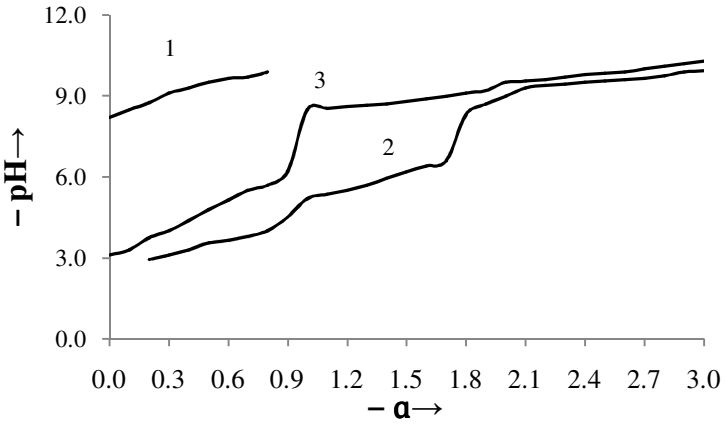

Fig. 2. pH vs 'a' curves for M(IV) – serine (1:1) system.

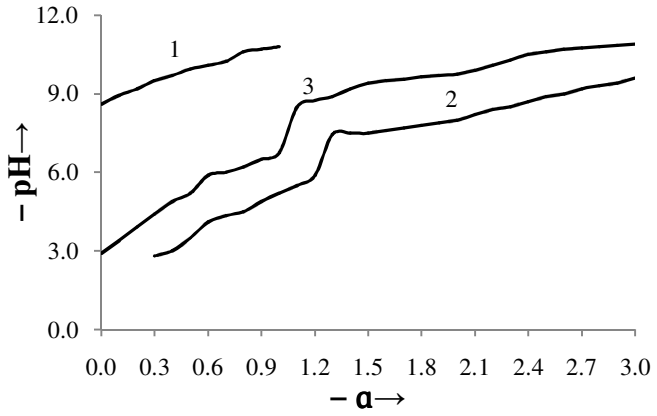

Fig. 3. pH vs 'a' curves for M(IV) – phenylalanine (1:1) system.

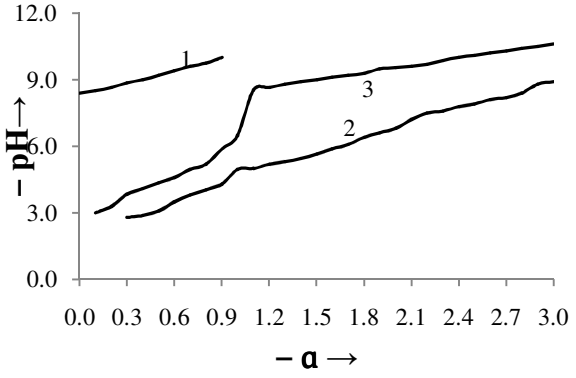

Fig. 4. pH vs 'a' curves for M(IV) – leucine (1:1) system.

Figs. 1 – 4: 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.

$$M + L \overset{0 \le a \le 1}{\rightleftharpoons} ML \quad \ldots(i)$$

$$ML + OH \overset{1 \le a \le 2}{\rightleftharpoons} ML(OH \quad \ldots(ii)$$

$$ML(OH) + OH \overset{2 \le a \le 3}{\rightleftharpoons} ML(OH)_2 \quad \ldots(iii)$$

(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 [27-29]. Method developed by Chandra is used for the calculation of stability constants of hydroxy species [30]. The data so obtained are subjected to computational analysis using SCOGS computer programme [31-33]. This provided the detailed information of the various species present in a particular equilibrium and the percentage of each species. This has been presented in the form of speciation curves (Figs. 5–12). Values of thermodynamic protonation constants for all the ligands are given in Table 1. The thermodynamic formation constants and thermodynamic parameters so evaluated are presented in Table 2.

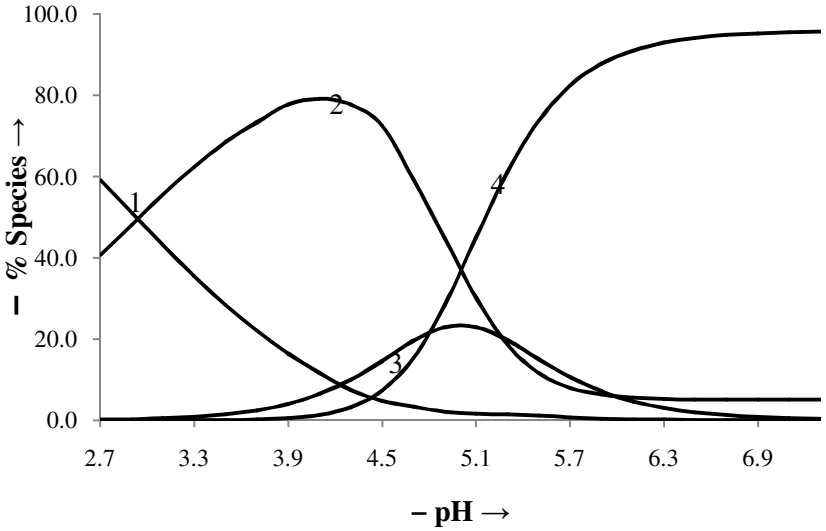

Fig. 5. Speciation curves for DMT(IV) – valine (1:1) system.

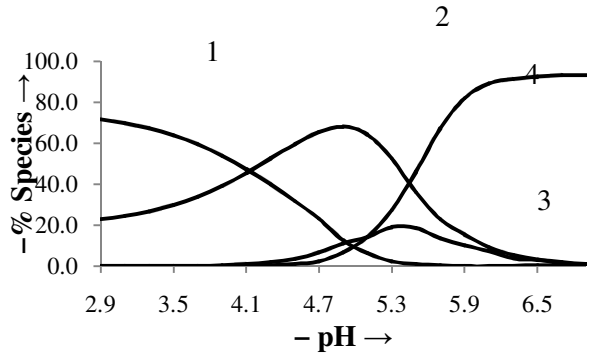

Fig. 6. Speciation curves for TMT(IV) – valine (1:1) system.

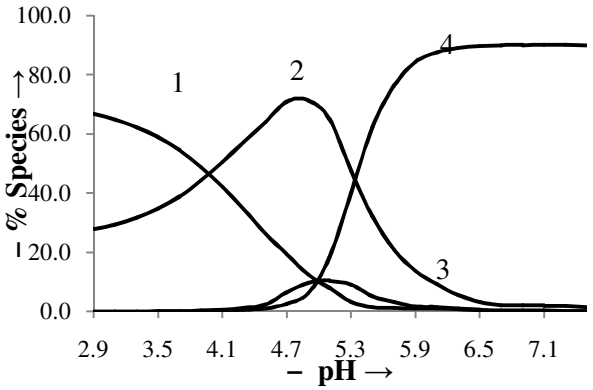

Fig. 7. Speciation curves for DMT(IV) – serine (1:1) system.

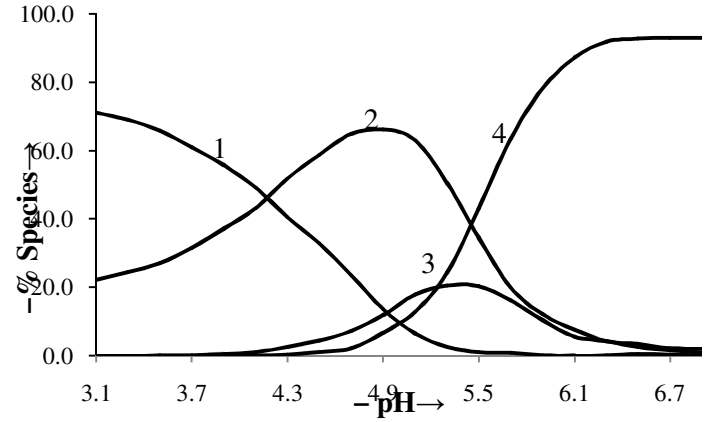

Fig. 8. Speciation curves for TMT(IV) – serine (1:1) system.

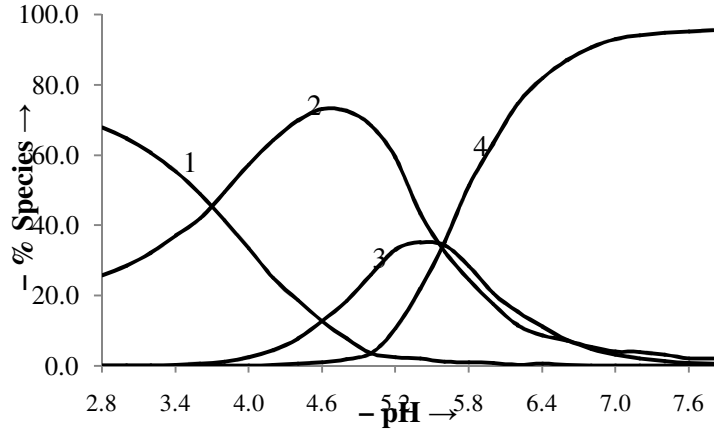

Fig. 9. Speciation curves for DMT(IV) – phenylalanine (1:1) system.

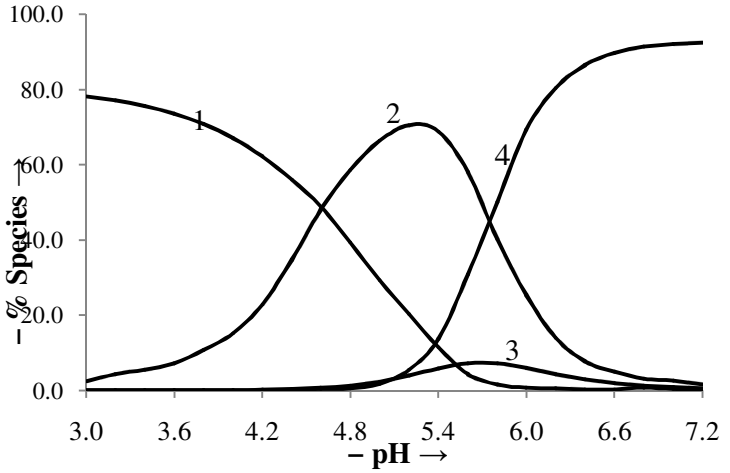

Fig. 10. Speciation curves for TMT(IV) – phenylalanine (1:1) system.

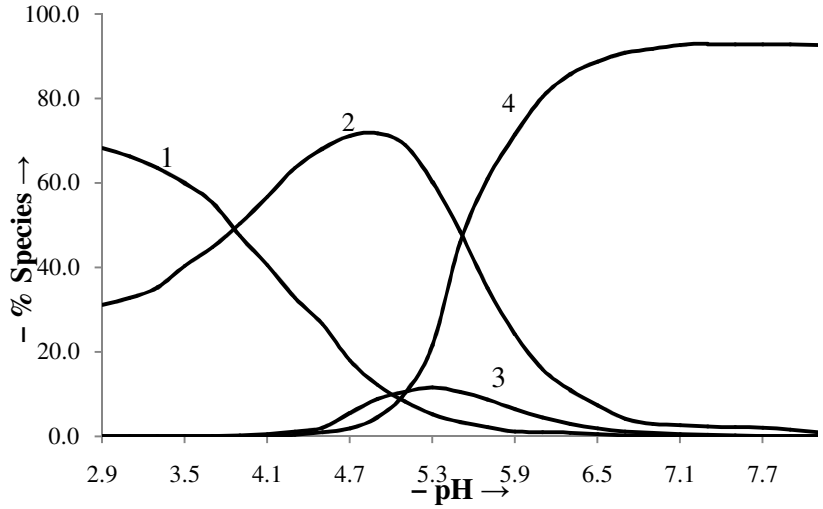

Fig. 11. Speciation curves for DMT(IV) – leucine (1:1) system.

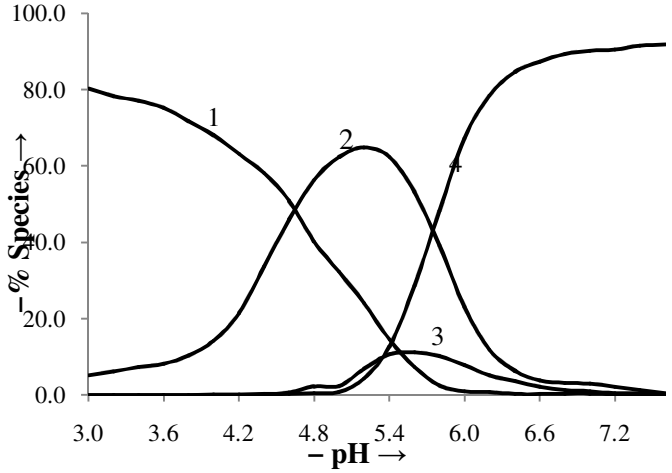

Fig. 12. Speciation curves for TMT(IV) – leucine (1:1) system.

Table 1. Thermodynamic protonation constant of ligands (log $K_{HL}^{\mu \to 0}$)

Parameters	Valine		
	20°C	30°C	40°C
$K_{HL}^{\mu \to 0}$	9.70	9.60	9.50
	Serine		
$K_{HL}^{\mu \to 0}$	9.33	9.25	9.20
	Phenylalnine		
$K_{HL}^{\mu \to 0}$	9.40	9.30	9.25
	Leucine		
$K_{HL}^{\mu \to 0}$	9.80	9.75	9.70

In Figs. 5–12 Temp. = 30±1ºC, μ = 0.10M maintained by $NaNO_3$. Curve 1: [M]; 2: [ML]; 3: [ML(OH)]; 4: [$ML(OH)_2$.

It is observed from the speciation curves (Figs. 5-12) that the concentration of free metal (curve1) decreases continuously with increase of pH, thereby indicating the formation of ML complex (curve2) which reaches to maximum extent at pH ≈5.0. Above this pH ML species undergo hydrolysis leading to the formation of ML(OH) species (curve 3), which subsequently leads to the formation of dihydroxy species $ML(OH)_2$ (curve 4) at pH ≈7.5. Same trends are observed in the speciation curves for all the systems investigated.

The values of the thermodynamic stability constant $\log K^{\mu \to 0}$ are used to determine the standard free energy change (ΔG°) for the complexation reaction from Van't Hoff isotherm :

$$\Delta G^\circ = -2.303RT \log K^{\mu \to 0}$$

The Gibb's Helmholtz equation ($\underline{\Delta}G^\circ = \Delta H^\circ - T\Delta S^\circ$) and Van't Hoff isotherm ($\underline{\Delta}G^\circ = -2.303RT \log K^{\mu \to 0}$) can be put in the following form:

$$\log K^{\mu \to 0} = \frac{-\Delta H^\circ}{2.303R} \frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \quad \ldots(iv)$$

The standard enthalpy change ($\underline{\Delta}H^\circ$) and entropy change ($\underline{\Delta}S^\circ$) have been determined by linear least square fit method by plotting a graph between $\frac{1}{T}$ vs $\log K^{\mu \to 0}$ using equation (iv). In this equation:

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

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

The values of $\underline{\Delta}G^\circ$, $\underline{\Delta}H^\circ$ and $\underline{\Delta}S^\circ$ are presented in Table 2. The negative values of $\underline{\Delta}G^\circ$ in each case indicate that the complexation is spontaneous. The enthalpy changes ($\underline{\Delta}H^\circ$) are exothermic. The positive values for $\underline{\Delta}S^\circ$ indicate that the change in the reactions under experimental conditions are favourable.

IV. CONCLUSION

It is observed from the table 2 that DMT complexes are more stable than TMT complexes, this can be explained on the basis of cation charge and size. The small size and high charge of $(CH_3)_2Sn(IV)^{+2}$ [DMT] as compared to $(CH_3)_3Sn(IV)^+$ [TMT] therefore suggest the greater stability in former system . Earlier publications [34-38] suggests trigonal bipyramidal geometry for $(CH_3)_3Sn(IV)^+$ cation whereas octahedral geometry for $(CH_3)_2Sn(IV)^{+2}$ cation. Hence the higher stability of $(CH_3)_2Sn(IV)^{+2}$ complexes as compared to $(CH_3)_3Sn(IV)^+$ complexes as observed in the present studies can also be justified on the basis of coordination geometry of these two ions. Further the formation of ML(OH) and $ML(OH)_2$ species with both the cations and their comparative stabilities (Table 2) suggest that probably in both the systems the coordination geometry around tin in $ML(OH)_2$ species is octahedral. However, further spectroscopic are needed for structural elucidation. The stability order with respect to different ligands for both systems DMT and TMT is found to be:

Val > Ser > Phe > Leu

Table 2. Thermodynamic formation constants and thermodynamic parameters of M (IV) – amino acid binary Systems along with ($\log K^{\mu\to 0}$).

system	20ºC		30ºC		40ºC			
	$\log k^{\mu\to 0}$	$-\Delta G^{o}$ kJmol^{-1}	$\log k^{\mu\to 0}$			$-\Delta G^{o}$ kJmol^{-1}	$-\Delta H^{o}$ kJmol^{-1}	ΔS^{o} Jk^{-1}mol^{-1}
DMT(IV)-valine								
$\log K^{M}_{ML}$	10.20	57.22	10.10	58.59	10.00	59.93	12.30	153.17
$\log K^{ML}_{ML(OH)}$	13.05	73.21	13.00	75.42	12.95	77.61	6.15	228.80
$\log K^{ML(OH)}_{ML(OH)2}$	21.50	120.61	21.40	124.15	21.30	127.65	12.30	369.53
TMT(IV)-Valine								
$\log K^{M}_{ML}$	9.05	50.77	9.00	52.21	8.85	53.03	12.9	129.24
$\log K^{ML}_{ML(OH)}$	11.40	63.95	11.55	65.84	11.30	67.72	9.15	197.21
$\log K^{ML(OH)}_{ML(OH)2}$	19.10	107.15	19.00	110.23	18.95	113.56	8.88	335.07
DMT(IV)-Serine								
$\log K^{M}_{ML}$	9.75	54.69	9.70	56.27	9.65	57.83	6.15	165.62
$\log K^{ML}_{ML(OH)}$	12.85	72.08	12.80	74.26	12.75	76.41	6.16	224.97
$\log K^{ML(OH)}_{ML(OH)2}$	21.15	118.65	21.10	122.41	21.05	126.15	6.15	383.90
TMT(IV)-Serine								
$\log K^{M}_{ML}$	8.25	46.28	8.20	47.57	8.15	48.84	6.15	136.90
$\log K^{ML}_{ML(OH)}$	11.15	62.55	11.10	64.39	11.05	66.22	6.15	192.42
$\log K^{ML(OH)}_{ML(OH)2}$	18.45	103.50	18.35	106.45	18.25	109.37	12.30	311.14
DMT(IV) – Phenylalanine								
$\log K^{M}_{ML}$	9.65	53.29	9.60	55.69	9.58	57.41	4.10	170.60
$\log K^{ML}_{ML(OH)}$	12.75	71.52	12.68	73.56	12.60	75.51	9.30	212.34
$\log K^{ML(OH)}_{ML(OH)2}$	21.25	119.21	21.20	122.99	21.10	126.45	9.57	374.32

TMT(IV) – Phenylalanine								
$\log K^{M}_{ML}$	8.20	46.00	8.15	47.28	8.09	48.48	6.83	133.64
$\log K^{ML}_{ML(OH)}$	11.10	62.27	11.05	64.10	11.00	65.92	6.15	191.47
$\log K^{ML(OH)}_{ML(OH)2}$	19.15	107.43	18.40	108.74	18.30	109.67	7.86	200.08
DMT(IV)-Leucine								
$\log K^{M}_{ML}$	9.70	54.41	9.65	55.98	9.55	57.23	9.57	153.17
$\log K^{ML}_{ML(OH)}$	12.45	69.84	12.36	71.70	12.30	73.71	9.02	207.36
$\log K^{ML(OH)}_{ML(OH)2}$	20.60	115.56	20.55	119.22	20.50	122.85	6.17	373.36
TMT(IV)- Leucine								
$\log K^{M}_{ML}$	8.25	46.28	8.15	47.28	8.05	48.24	12.30	115.84
$\log K^{ML}_{ML(OH)}$	10.80	60.58	10.65	61.78	10.60	63.52	11.62	166.58
$\log K^{ML(OH)}_{ML(OH)2}$	17.20	96.49	17.15	99.49	17.05	102.18	9.57	296.78

However, the variation lies in the range of less than one log unit (Table 2). This suggests that nature of the ligand (aromatic or aliphatic) and the presence of bulky side groups (phenylalanine versus valine) does not play any significant role in deciding the stability of the system. This makes one think that solvophobic forces are insignificant [39].

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