

Potentiometric Studies on Binary Complexes of Catecholic Compounds with Organotin (IV) Cations

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Abstract: Potentiometric studies are performed in aqueous solution in order to characterize the interaction of dimethyltin(IV) [DMT] and Trimethyltin(IV) [TMT] cation with catecholic ligands. Experiments are performed at three different temperatures (20°C, 30°C and 40°C) and at three ionic strengths ($\mu = 0.05, 0.10$ and 0.15 M). The analysis of stability constant ($\log \beta$) and stability order of investigated metal-ligand species [MHL, ML, ML(OH) and ML(OH)₂] are obtained by using computer programme SCOGS (stability constants of generalized species). The complex species formed are water soluble in the experimental pH range (3.0–10.5). Thermodynamic stability constants along with thermodynamic parameters i.e. standard free energy change (ΔG°) enthalpy change (ΔH°) and entropy change (ΔS°) are calculated for all the systems. The thermodynamic stabilities of DMT species are found to be more than TMT (IV) species. High stability of 4-methylcatechol complexes is attributed to greater basicity.

Keywords: Potentiometric studies, Organotin (IV), Catecholic compounds, SCOGS.

1. Introduction

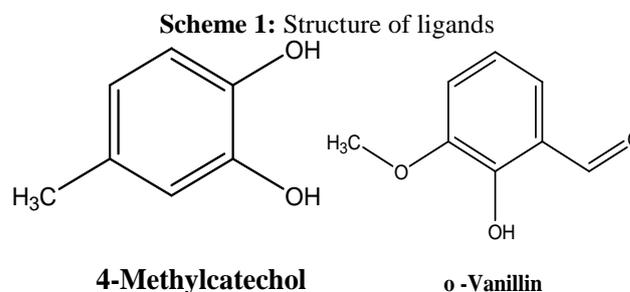
Most of the molecules behaving as ligands are protonated having dissociable protons in their structure. Hence, potentiometric technique is considered to be the most reliable for monitoring the dissociation of proton and association of metals with the ligands leading to the formation of metal-ligand complex formation.

In the present work potentiometric investigation of binary complexes involving catecholic compounds with Organotin(IV) cations is being reported.

Catechol is one of the common building block in organic synthesis and is produced on industrial scales as the precursor of pesticides, perfumes, and pharmaceuticals [1]. The catechol skeleton also occurs in a variety of natural products specially the antioxidants [2]. The well-known characteristic of the catechols is that they can be easily oxidized mainly due to their antioxidant activity and low oxidation potential [3].

4-Methylcatechol (4,MC), a potent stimulator of NGF (nerve growth factor) synthesis in vivo and in vitro, stimulates regeneration of the sciatic nerve and protects against or improves diabetes- and acrylamide-induced neuropathies [4]-[8]. O-Vanillin (4-hydroxy-3-methoxybenzaldehyde) the major component of natural vanilla which is one of the most widely used and important flavoring materials worldwide [9]-[12]. The chemistry of vanillin and its derivatives are important products of the chemical industry. Vanillin is used as an intermediate in pharmaceuticals and is the most important flavoring agent in confectionery, beverage foods, and perfumery [13]-[15].

In continuation to our work on equilibrium on equilibrium studies on Organotin(IV) cations and several biologically relevant ligands [16]-[18] here we report the result of investigation of equilibria involving catecholic ligands i.e. 4-methylcatechol and o-vanillin.



2. 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 CO₂-free water having pH \approx 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 ($\mu = 0.05$ M, 0.10 M and 0.15 M) maintained by adding different concentration of NaNO₃ solution to each titration mixture. These are:

1. HNO₃ (2.0×10^{-3} M)

2. $\text{HNO}_3 (2.0 \times 10^{-3}\text{M}) + \text{Ligand} (1.0 \times 10^{-3}\text{M})$
3. $\text{HNO}_3 (2.0 \times 10^{-3}\text{M}) + \text{Ligand} (1.0 \times 10^{-3}\text{M}) + \text{Metal ion} (1.0 \times 10^{-3}\text{M})$

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

3. Results and Discussion

3.1 Potentiometric Titration Curves

The pH titration curves for the binary metal-ligand complexes were drawn by plotting pH Vs volume of alkali. A representative pH titration curves for the studied binary system given in fig. 1 and 2 which shows the binary complexes of DMT(IV) and TMT(IV) by individual lines.

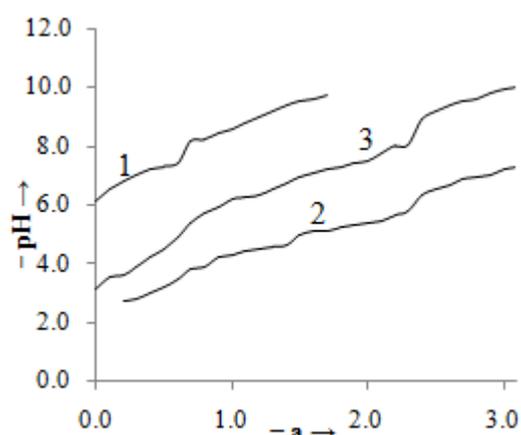


Figure 1: pH vs 'a' curves for M (IV) -o- vanillin (1:1) system.

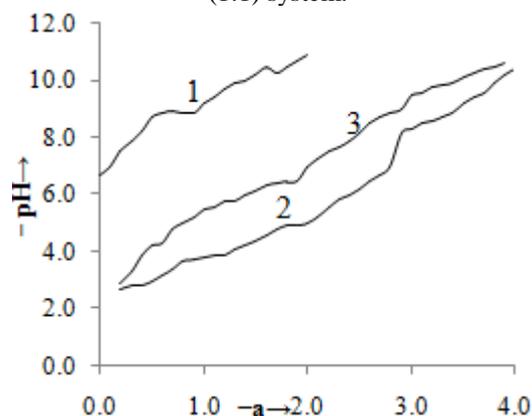


Figure 2: pH vs 'a' curves for M (IV) -4-methylcatechol (1:1) system.

In figs. 1 and 2.

Temperature = $30 \pm 1^\circ\text{C}$, $\mu = 0.10\text{M}$ maintained by NaNO_3 .

Curve 1. represents ligand titration curve .

Curve 2. represents DMT- ligand titration curve.

Curve 3. represents TMT - ligand titration curve.

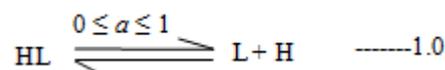
4. Analysis of Titration Curves

Analysis of titration curves in fig.1 curve 1 (representing ligand titration for o-vanillin) shows a inflection at $0 \leq a \leq 1$

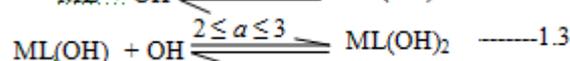
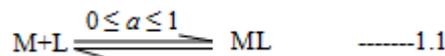
at $\text{pH} \approx 7.5$, thereby indicating the release of one proton from the ligand. The metal – ligand titration curves (curve 2 and 3) extends from $\text{pH} \approx 2.5 - 4.0$ at $0 \leq a \leq 1$, suggesting the formation of ML complex. Further, between $\text{pH} \approx 4.0- 9.5$ formation of hydroxo species occur leading to the formation of $\text{ML}(\text{OH})$ and $\text{ML}(\text{OH})_2$ species in two distinct steps. Formation of hydroxo complexes is further supported by the colour change observed during the titration. It is observed that the solution which is initially colourless changes to light green coloured soluble complex between $1 \leq a \leq 2$ and deep green coloured soluble complex between $2 \leq a \leq 3$.

Various equilibria for o-vanillin can be represented as follows:

Proton-ligand:



Metal-ligand:

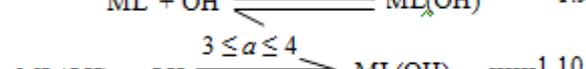
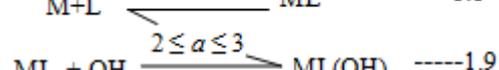
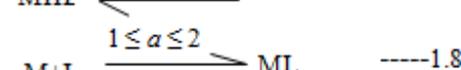
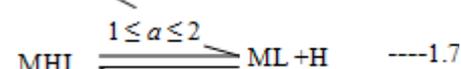
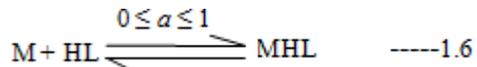


On examining fig.2 which represent the titration curve for organotin (IV) – 4-methylcatechol system, it is seen that ligand titration curve shows two inflections at $a \approx 1$ and $a \approx 2$, thereby suggesting the release of two protons in two distinct steps. The nature of metal – ligand titration curve clearly manifests the formation of MHL species in the pH range $\approx 2.5 - 5.0$ at $0 \leq a \leq 1$. Further the deprotonation of MHL species releases the proton. Above $\text{pH} \approx 6.0$ between $2 \leq a \leq 3$ formation of $\text{ML}(\text{OH})$ and between $3 \leq a \leq 4$. This is further supported by colour changes observed during the titration above $\text{pH} \approx 7.0$, 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 for 4-methylcatechol can be represented as follows:

Proton-ligand:



Metal-ligand:



(Charges have been omitted for the sake of simplicity)

Table 1: Protonation constant of ligands at different temperatures and 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
o - Vanillin									
log β _{HL}	8.78	8.70	8.64	8.58	8.50	8.45	8.43	8.35	8.28
4 -Methylcatechol									
log β _{HL}	9.50	9.42	9.30	9.45	9.20	9.12	9.00	8.95	8.80
log β _{H2L}	16.35	16.28	16.19	16.26	16.18	16.10	16.20	16.12	15.95

Table 2: Thermodynamic parameters of M(IV)- o-Vanillin System

DMT(IV) – o-Vanillin								
Parameters	20±1°C		30±1°C		40±1°C		-ΔH° kJmol ⁻¹	ΔS° JK ⁻¹ mol ⁻¹
	logK ₀ ^{μ→}	-ΔG° kJmol ⁻¹	logK ₀ ^{μ→}	-ΔG° kJmol ⁻¹	logK ^{μ→0}	-ΔG° kJmol ⁻¹		
logK _{ML} ^M	8.00	44.88	7.80	45.25	7.70	46.14	17.77	91.90
logK _{ML(OH)}} ^{ML}	10.50	58.90	10.40	60.33	10.35	62.02	8.88	170.40
logK _{ML(OH)2}} ^{ML(OH)}	16.50	92.56	16.35	94.85	16.25	97.38	15.04	264.33
TMT(IV) – o-Vanillin								
logK _{ML} ^M	6.00	33.66	5.95	34.51	5.90	35.35	8.15	93.82
logK _{ML(OH)}} ^{ML}	9.00	50.49	8.95	51.92	8.88	53.33	6.15	151.26
logK _{ML(OH)2}} ^{ML(OH)}	13.20	74.05	13.10	76.00	13.00	77.90	12.30	210.61

Table 3: Thermodynamic parameters of M(IV)- 4-Methylcatechol System

DMT(IV) –4-Methylcatechol System								
Parameters	20±1°C		30±1°C		40±1°C		-ΔH° kJmol ⁻¹	ΔS° JK ⁻¹ mol ⁻¹
	logK ₀ ^{μ→}	-ΔG° kJmol ⁻¹	logK ₀ ^{μ→}	-ΔG° kJmol ⁻¹	logK ^{μ→0}	-ΔG° kJmol ⁻¹		
logK _{MLH}} ^M	8.90	49.93	8.70	50.47	8.65	51.83	14.36	120.62
logK _{ML}} ^{MLH}	15.10	84.71	15.00	87.05	14.90	89.29	12.30	246.99
logK _{ML(OH)}} ^{ML}	17.30	97.05	17.20	99.78	17.05	102.18	15.72	277.63
logK _{ML(OH)2}} ^{ML(OH)}	20.15	113.04	19.90	115.45	19.80	118.96	17.09	326.45
TMT(IV) –4-Methylcatechol System								
logK _{MLH}} ^M	7.90	44.31	7.75	44.96	7.60	45.54	18.46	88.07
logK _{ML}} ^{MLH}	11.00	61.71	10.95	63.52	10.85	65.02	9.57	178.06
logK _{ML(OH)}} ^{ML}	13.90	77.98	13.60	78.90	13.50	80.90	2325	185.72
logK _{ML(OH)2}} ^{ML(OH)}	16.50	92.56	16.40	95.14	16.30	97.68	12.30	273.80

Speciation Curves: The speciation curves were obtained by plotting percent (%) concentration of the species against pH obtained through SCOGS computer programmed. 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) [19]-[21]. Method developed by M.Chandra is used for the calculation of stability constants of metal hydroxy species [22]. Calculation of equilibrium constants is done by using experimental data obtained by potentiometric technique.

Computation of data was done by using **SCOGS** computer program [23]-[25]. The complex formation equilibria were elucidated with the help of speciation curves (represented in figs.3-6).

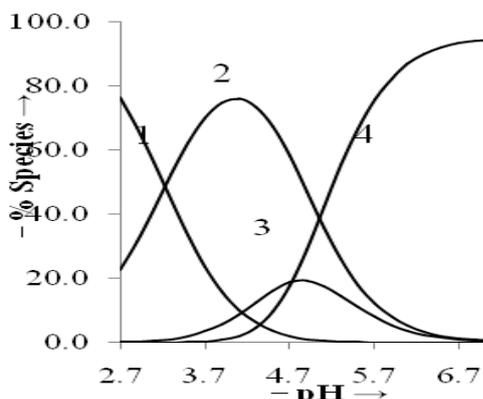


Figure 3: Speciation curves for DMT(IV)- o-vanillin

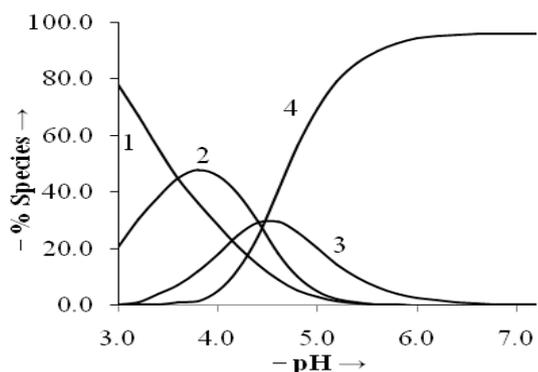


Figure 4: Speciation curves for TMT(IV)-o-vanillin (1:1) system (1:1) system

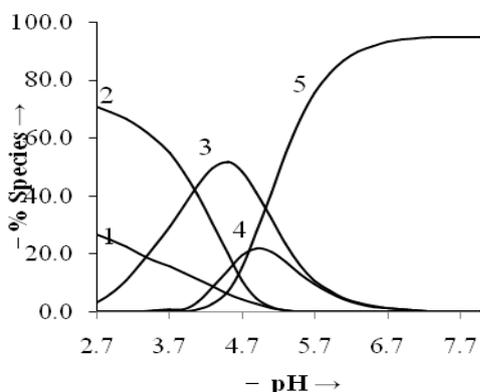


Figure 5: Speciation curves for DMT(IV)- 4-methylcatechol (1:1) system

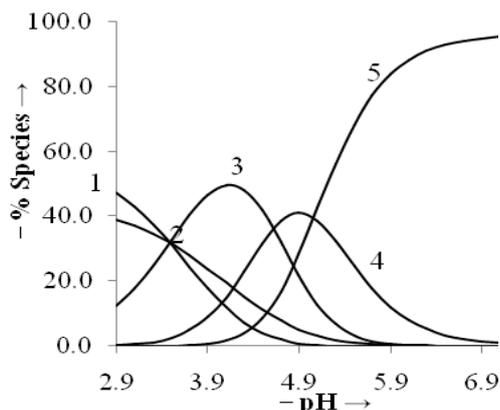


Figure 6: Speciation curves for TMT(IV)-4-methylcatechol (1:1) system

In figs.3- 6
 Temperature = $30 \pm 1^\circ\text{C}$, $\mu = 0.10\text{M}$ maintained by NaNO_3 In figs.3 and 4. Curve 1 : [M]; 2 : [ML]; 3 : [ML(OH)]; 4 [ML(OH)₂].

In figs. 5 and 6. Curve 1: [M]; 2 : [MHL]; 3 : [ML]; 4 : [ML(OH)]; 5 : [ML(OH)₂]

The observation of above referred fig.3 reveals that free metal concentration is initially very high which decreases continuously. Simultaneously the formation of ML complex is seen to commence at $\text{pH} \approx 2.9$ and continuously increases upto $\text{pH} \approx 4.7$ attaining maximum value of about 50-77%. After this its concentration decreases and the formation of ML(OH) species becomes evident and attains a maximum value of 20 -30%. With the increase of pH i.e. $\text{pH} > 5.0$, a sharp rising graph provides the evidence of formation of ML(OH)₂ species with a value of $\approx 95\%$.

In case of methylcatechol (figs. 4) the ligand (H₂L) 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 (20-30%) and significantly higher percentage of MHL species (50-60%) 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 attaining a maxima $\approx 55\%$ at $\text{pH} \approx 4.5$. Above this pH the formation of ML(OH) in low concentration and ML(OH)₂ in higher range $\approx 95\%$ is obvious from the curves 4 and 5 in the above referred fig.5. The trends for R₃Sn(IV) – o-vanillin and 4-methylcatechol systems (figs. 4 and 6) are same as for R₂Sn(IV) – o-vanillin and 4-methylcatechol systems.

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 $K^{\mu \rightarrow 0}$ is used to determine the ligational standard free energy change (ΔG°) for the complexation reaction from Van't Hoff isotherm :

$$\Delta G^\circ = -2.303RT \log K^{\mu \rightarrow 0} \quad \text{----- (1.11)}$$

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

$$\log K^{\mu \rightarrow 0} = \frac{-\Delta H^\circ}{2.303R} \frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \quad \text{----- (1.12)}$$

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 $\log K^{\mu \rightarrow 0}$ [26] . In equation (1.12)

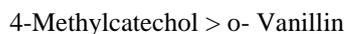
$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R}$$

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

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

5. Conclusion

The protonation constants of the ligands chosen are found to show the following trend:



The stability constant of metal complexes are found to be in accordance with basicity of the ligands. Hence metal complexes of 4-methylcatechol is higher than o-vanillin. The reason for the observed trend can be explained on the basis that in case of 4-methylcatechol, the coordination sites become available by the liberation of two protons from the hydroxyl groups, thereby leading to the chelate formation by O-O donor sites.

On comparing the stabilities of $\text{Me}_2\text{Sn (IV)}^{2+}$ and $\text{Me}_3\text{Sn (IV)}^+$ 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 [27]-[28]. 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 variation in the equilibrium constants as with respect to ionic strength and temperature show the expected trend i.e. stability constant values decrease with increase in ionic strength and temperature. The negative value of both free energy (ΔG°) and enthalpy change (ΔH°) and positive value of entropy change (ΔS°) confirms the favourable conditions for complex formation.

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