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RESEARCH ARTICLE

Thermodynamic Studies Of Binary Complexes of Organotin (IV) Cations With Nitrogen Donor Ligands

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Abstract

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Thermodynamic studies of dimethyltin (IV) and dioctyltin (IV) cations with nitrogen donor ligands were performed potentiometrically for 1:1 systems in 10% ethanol medium at three ionic strengths (μ = 0.05, 0.10, 0.15M) and at three different temperatures 20°C, 30°C, 40°C. Thermodynamic formation constants of various complexes have been calculated. Stability constants of generalized species (SCOGS) computer program was employed for computation. The strength of interaction is discussed in terms of stability constants of various complexes and other thermodynamic parameters i.e. $\Delta G^{\circ} \Delta H^{\circ}$ and ΔS° . The concentration distribution of the various complex species in solution has been evaluated as a function of pH.

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INTRODUCTION

Diorganotin complexes containing nitrogen donor ligands have attracted considerable attention in recent years due to their potential antitumour activity against P388 leukemia (Crowe et al., 1980, 1984). The studies on complexation equilibria and structures of dimethyltin (IV) with N-methyliminodiacetate, pyridine-2,6-dicarboxylate, ethylenediamine-N,N'-diacetate and ethylenediamine-N,N',N',N'-tetraacetate are available in literature (Sen-ichi Aizawa et al., 1996). Diorganotin dihalide complexes of N-bidentate ligands have been studied and their crystal structures are reported (Casas et al., 1999). Shoukry (2011) reported the study of trimethyltin (IV) chloride with N,N,N',N'-tetraaethylenediamine in reference to marine environmental pollution. Synthesis, characterization and thermodynamic studies of complexes of dimethyl, diethyl and diphenyltin (IV) dichlorides with (2H)-1,4-benzothiazine-2,3-(4H)-dione dioxime are investigated (Momeni et al., 2012).

The significant findings described in literature, prompted us to investigate several new equilibria involving dimethyltin (IV) and dioctyltin (IV) cations with N-N bidentate ligands. Here we report the further studies for understanding the behaviour of organotin (IV) cation with nitrogen donor ligands.

Material and Methods

All the chemicals used were of analytical grade and the solutions of ligands were prepared in doubly distilled CO_2 free water. Imidazole was used as it diprotonated form by adding two equivalent acid. Dimethyltin (IV) and Dioctyltin (IV) metal were prepared by dissolving their accurate weighed amounts in ethanol. 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 used for pH measurement. The pH meter was calibrated with aqueous buffers (pH 4.0 and 9.20) before and after titration. Temperature was maintained by Siskin Julabo, thermostat model V-12B. The electrode correction in mixed solvent (Uitert et al., 1953) for the calculation of the protonation constants has not been necessary in the work , because the practical value of the protonation constants may be employed without correction for obtaining the stability constants of the metal complexes.

Three titration mixtures were prepared with the ratio of 10% alcohol and 90% water by keeping total volume 50mL and titrated against 0.10M NaOH solution, ionic strengths (μ =0.05, 0.10, 0.15M) is maintained by adding different concentration of NaNO₃ solution to each titration mixture at temperature 20±1°C, 30±1°C and 40±1°C. These are:

Mixture 1 :- $HNO_3(2.0 \times 10^{-3} M)$ (Acid titration)

Mixture 2 :- HNO₃ $(2.0 \times 10^{-3} \text{M})$ + ligand $(1.0 \times 10^{-3} \text{M})$ (Ligand titration)

Mixture 3:- HNO₃ (2.0 x 10^{-3} M) + ligand (1.0 x 10^{-3} M) + Metal (1.0 x 10^{-3} M) (Metal : Ligand (1:1) titration)

Results and Discussion

Algebraic method of Martell and Chaberek (1952, 1955) as modified by Dey et al., (1974, 1976) has been used to obtain the values of equilibrium constants. Method suggested by Chandra (1983) is being used for calculating the concentration of hydroxyl species. The ligand titration curves for imidazole and ethylenediamine show a sharp inflection at a=1 followed by weak inflection at a=2 thereby suggesting the liberation of two protons in distinct steps. The pattern of metal-ligand curves are suggested the formation of protonated species (MLH) at $a \le 1$. Further an inflection at a = 1 indicates the formation of non-protonated species by deprotonation of MLH complex. However in case of dioctyltin (IV) – imidazole the formation of MLH is not clearly evidenced. The formation of hydroxo complex at a > 2 is observed in each system. The observation and dissociation constant of the ligands are in accordance with the reported value in chemical literature.(Legette, 1985)

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	$0 \le a \le 1$		
M + HL		MLH	1.0

	$1 \le a \le 2$	
MLH	\longrightarrow ML + H	1
	$2 \le a \le 3$	
MILOH	\longrightarrow MI (OH)	1

$$ML + OH \xrightarrow{\qquad } ML(OH) \qquad ----1.2$$
$$ML(OH) + OH \xrightarrow{\qquad } ML(OH)_2 \qquad ----1.3$$

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

The considerably high values of formation constants for ML species observed from these tables support that the complex formed is thermodynamically stable. At higher pH range hydroxo complex appear to be the major species. The value of ligational standard free energy change (ΔG°) is determined using Van't Hoff equation. The other thermodynamic parameters such as standard enthalpy change (ΔH°) and standard entropy change (ΔS°) have been obtained by least square fit method (Skoog et al., 2005). A linear plot of graph is obtained between logK vs. 1/T. In this linear plot slope is equal to $-\Delta H^{\circ}/2.303R$ and intercept is equal to $\Delta S^{\circ}/2.303R$. The logarithmic values of equilibrium constants for various proton-ligand and metal-ligand systems were refined by using the SCOGS computer programme (Sayce, 1968, 1971, 1972). These data was used to obtain the speciation curves . Analysis of these curves is discussed here under:

Organotin (IV) - Imidazole System

Speciation curves for DMT (IV)- imidazole system show the existence of free metal to be approximately 90% in the initial stage followed by the sharp decrease. The speciation profile indicates the formation of dihydroxy complex as the most significant one, other species being formed in negligible amount. In DOT (IV) – imidazole system the concentration of free metal is high in initial stage as shown by curve 1. The formation of ML species occurs from the initial pH and reaches the maximum at pH ≈ 3.6 (58%) after which a continuous decrease is observed. Simultaneously an increasing percentage of hydroxo complex is evident from curve 4, which is supporting the existence of dihydroxo complex as the most prominent species in the higher pH range.

Organotin (IV) – Ethylenediamine System

It is observed that the interaction of metal ion with ligand leads to continuous decrease in the concentration of free metal ion thereby indicating its association with the ligand. Formation of protonated species (MLH) is indicated by curve 2. Its initial percentage is about 36% and decreases regularly with the increase of pH. The formation of non protonated ML species is shown by curve 3. It is clearly seen that the formation of ML species reaches its maximum (35% approx.) at pH 4.3. With the further increase of pH, formation of monohydroxy complex and dihydroxy complex is noticed. It is seen that dihydroxy complex attains the value as high as about 95%, thereby supporting the formation of ML(OH)₂ complex as the major species. However in the distribution curves for DOT(IV)-ethylenediamine system, monohydroxy species is also significant, but the dihydroxy species ML(OH)₂ is observed to be the major species (95%).







Figure : 2 pH vs. 'a' Curves for M(IV)- Ethylenediamine (1:1) System at 30±1°C[μ=0.10M(NaNO₃)] Where curve 1:Respective ligand titration curve; curve 2:DMT(IV)-ligand titration curve; curve 3:DOT(IV)-ligand titration curve in figure 1 and 2.



Figure: 3 Speciation Curves for DMT(IV)-Imidazole (1:1) System at 30±1°C[µ=0.10M(NaNO₃)]



Figure:4 Speciation Curves for DOT(IV)-Imidazole(1:1) System at 30±1°C[µ=0.10M(NaNO₃)]



Figure:5 Speciation Curves for DMT(IV)-Ethylenediamine (1:1) System at 30±1°C[µ=0.10M(NaNO₃)]



Figure:6 Speciation Curves for DOT(IV)-Ethylenediamine (1:1) System at 30±1°C[µ=0.10M(NaNO₃)

Table: 1 Protonatio	n Constant of	Ligands at	different 7	Femperatures &	& Ionic Strengths
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Panamatana	20°C				30°C				40°C			
1 arameters	0.05 M	0.10M	0.15M	µ→0	0.05 M	0.10M	0.15M	µ→0	0.05 M	0.10M	0.15M	µ→0

Imidazole												
$\log\beta_{HL}$	7.38	7.33	7.16	7.48	7.11	7.10	7.00	7.50	6.11	5.91	5.62	6.68
$log \; \beta_{\rm H2L}$	11.68	11.62	11.33	11.80	10.43	10.29	10.01	11.00	9.83	9.49	9.41	10.25
Ethylenediam	ine											
$\log\beta_{HL}$	9.32	9.24	9.00	9.30	8.83	8.68	8.62	9.10	8.53	8.25	8.00	9.28
$\log\beta_{\rm H2L}$	14.95	14.80	14.70	15.28	13.76	13.40	13.30	14.32	12.96	12.73	12.72	13.25

 Table : 2 Thermodynamic Parameters of M (IV)- Imidazole Systems

 DMT(IV)- Imidazole System

	20°C		30°C		40°C		A T T O	ΔS^{o}
Parameter	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	-AH kJmol ⁻¹	JK ⁻ ¹ mol ⁻¹
	4.40	42.08	4.35	43.39	4.15	43.00	12.44	3.35
	7.50	54.98	7.48	56.56	7.10	56.00	38.29	14.55
	9.80	73.21	9.75	75.42	9.30	74.00	47.87	26.17
logK ^{ML(OH)} _{ML(OH)2}	13.05	24.68	13.00	25.24	12.30	24.87	71.80	7.82
DOT(IV)- Imida	azole System							
	20°C		30°C		40°C		A T T 0	ΔS^{o}
Parameter	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	-An kJmol ⁻¹	JK ⁻ ¹ mol ⁻¹
	8.60	48.25	8.58	49.78	8.55	51.24	4.79	148.42
	11.82	66.31	11.50	66.72	11.81	70.78	0.96	221.05
logK ^{ML(OH)} _{ML(OH)2}	14.30	80.22	13.90	80.64	13.89	83.24	39.25	139.10

 Table : 3 Thermodynamic Parameters of M (IV)-Ethylenediamine Systems

 DMT(IV)- Ethylenediamine System

	20°C	•	30°C		40°C		A TT0	A C'0
Parameter	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	$\log K_{\mu \to 0}$	-∆G° kJmol ⁻¹	-∆H [*] kJmol ⁻¹	∆S [°] JK ⁻¹ mol ⁻¹
	4.20	23.56	4.18	24.25	4.17	24.99	12.44	70.62
	8.92	50.04	8.91	51.69	8.90	53.31	1.91	164.28
	11.55	64.79	11.44	66.37	11.40	68.32	14.36	172.10
logK ^{ML(OH)} _{ML(OH)2}	14.10	79.10	14.08	81.74	14.09	84.38	0.96	266.62
DOT(IV) Ethy	lonodiomino	System						
DOI(IV)- Elliy	leneulainne	System						
	20°C	System	30°C		40°C		A T T 9	4 5 9
Parameter	$\frac{20^{\circ}\text{C}}{\log \text{K}_{\mu \to 0}}$	- ΔG°	$\frac{30^{\circ}\text{C}}{\log\text{K}_{\mu\to0}}$	-\Delta G ^o k Imol ⁻¹	$\frac{40^{\circ}\text{C}}{\log\text{K}_{\mu\to0}}$	-\Delta Go	-∆H° kJmol ⁻¹	∆S° JK ⁻¹ mol ⁻¹
Parameter	$\frac{20^{\circ}\text{C}}{\log \text{K}_{\mu \to 0}}$	-\(\Delta G^\) kJmol ⁻¹	$\frac{30^{\circ}\text{C}}{\log K_{\mu \to 0}}$	-ΔG° kJmol ⁻¹	$\frac{40^{\circ}\text{C}}{\log \text{K}_{\mu \to 0}}$	-∆G° kJmol ⁻¹	-ΔH° kJmol ⁻¹	ΔS° $JK^{-1}mol^{-1}$
Parameter	$\frac{20^{\circ}\text{C}}{\log \text{K}_{\mu \to 0}}$	-Δ G° kJmol⁻¹ 23.84	30°C log K _{µ→0} 4.23	-Δ G° kJmol⁻¹ 24.54	40°C log K_{μ→0} 4.20	-Δ G° kJmol ⁻¹ 25.17	-ΔH° kJmol ⁻¹	Δ S° J K ⁻¹ mol ⁻¹ 65.13
Parameter logK ^M _{MLH} logK ^{MLH}	$20^{\circ}C$ $\log K_{\mu \to 0}$ 4.25 9.70	-Δ G° kJmol⁻¹ 23.84 54.42	30°C log K_{μ→0} 4.23 9.55	-Δ G° kJmol⁻¹ 24.54 55.41	40°C log K_{μ→0} 4.20 9.52	-Δ G° kJmol⁻¹ 25.17 57.05	-Δ H° kJmol⁻¹ 12.45 17.23	Δ S° J K⁻¹mol⁻¹ 65.13 126.75
Parameter logK ^M _{MLH} logK ^{ML} _{ML} logK ^{ML} _{ML} (OH)	20°C $\log K_{\mu \to 0}$ 4.25 9.70	-Δ G° kJmol⁻¹ 23.84 54.42	30°C log K_{μ→0} 4.23 9.55	-Δ G° kJmol⁻¹ 24.54 55.41	40°C log K_{μ→0} 4.20 9.52	-Δ G° kJmol⁻¹ 25.17 57.05	-Δ H° kJmol⁻¹ 12.45 17.23	Δ S° JK ⁻¹ mol ⁻¹ 65.13 126.75
Parameter logK ^M _{MLH} logK ^{ML} _{ML} logK ^{ML} _{ML} logK ^{ML} _(OH)	20°C $\log K_{\mu \to 0}$ 4.25 9.70 12.50	-Δ G° kJmol⁻¹ 23.84 54.42 70.13	30°C log K_{μ→0} 4.23 9.55 12.45	-Δ G° kJmol⁻¹ 24.54 55.41 72.23	40°C log K_{μ→0} 4.20 9.52 12.10	-Δ G° kJmol⁻¹ 25.17 57.05 72.52	-Δ H° kJmol⁻¹ 12.45 17.23 38.29	Δ S° JK ⁻¹ mol ⁻¹ 65.13 126.75 110.09

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