Potentiometric Studies on Complexation Equilibria between Dimethyltin (IV) and Dioctyltin (IV) Cations with N-N Donor Ligands

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Abstract: *The interaction of dimethyltin [DMT] (IV) and dioctyltin [DOT] (IV) cations with* **2,2'-bipyridyl and 1,10-phenanthroline** *were performed potentiometrically for 1:1 systems in 10% alcohol medium at three ionic strengths (µ= 0.05, 0.10, 0.15M) and at three different temperatures 20°C, 30°C, 40°C. The experimental data are subjected to computational analysis in order to evaluate thermodynamic formation constants [ML, ML(OH) and ML(OH)$_2$] and other thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$). A stability constant of generalized species (SCOGS) computer program was employed for computation. The concentration distribution of the various complex species in solution has been evaluated as a function of pH and is presented in the form of speciation curves. The studies intimate that 2,2'-bipyridyl formed complexes of low stability than 1,10-phenanthroline. This is attributed to the difference in ring structure of two ligands.*

Keywords: DMT (IV), DOT (IV), Thermodynamic formation constants, SCOGS

1. Introduction

The importance of diorganotin complexes in the field of biology, medicine, environment and industry is of great concern. Literature survey reveals that considerable attempts have been made to understand the reactivity of diorganotin (IV) cations towards N, P and O donor ligands [1]-[5].

Many complexes of the type R_2SnX_2 (N-N) have been synthesized and tested [6], in which the N-N ligands are symmetric N,N-chelating agents such as bipyridine type ligands [7] or asymmetric ones such as 8-aminoquinoline [8]-[10]. Several research papers have been published by Pettinari et al. on tin (IV) and organotin (IV) complexes containing mono or bidentate N-donor ligands [11]-[16].

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'-tetraacetate are available in literature [17].

The biological activity of organotin complexes is believed to be independent on the structure of molecule and coordination number of metal are reported in recent past [18]. For compounds [$SnR_2X_2(LL)$], where LL is an N,N-bidentate ligand, antitumour activity depends on the Sn-N distances (>2.39 and <2.39 A°) for the active and inactive compounds, respectively [19]-[20], which suggests that dissociation of the ligand is a significant step in their mechanism of action.

In this paper we elaborate the subject and develop further understanding regarding the interaction of organotin (IV) cation with N-N donor ligands in order to calculate stability constants of the complexes and other thermodynamic parameters.

2. Experimental

2.1 Solution

All the reagents used were of analytical grade and prepared in deionised water. Solution of ligands viz. 2,2'-bipyridyl and 1,10-phenanthroline were prepared by dissolving accurately weighed amounts in double distilled water to get 0.01M solution of each. They were used as their diprotonated form by adding two equivalent of acid in the course of titration. Solutions of metal (0.01M) DMT(IV) dichloride and DOT(IV) dichloride (Aldrich) were prepared in distilled ethanol.

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 used for pH measurement. The pH meter was calibrated with aqueous buffers (pH 4.0 and 9.20) before and after titration.

2.3 Experimental Condition and Titrations

Three sets of titration mixtures (1, 2 and 3) were prepared at three different ionic strengths (µ=0.05M, 0.10M and 0.15M) maintained by $NaNO_3$, keeping the total volume 50ml. All the titration mixtures were maintained with the ratio of 10% alcohol and 90% water.The mixtures were titrared individually against 0.10M NaOH solution at three different temperatures (20±1ºC, 30±1ºC and 40±1ºC) and thus three titration curves are obtained.Temperature was maintained by Siskin Julabo, thermostat model V-12B. These titration mixtures are :
(i)   Acid titration: HNO_3 (2.0 $\times$ 10^{-3}M)
(ii)   Ligand titration: HNO_3 (2.0 $\times$ 10^{-3}M) + ligand (1.0 $\times$ 10^{-3}M)

(iii) Metal : Ligand (1:1) titration : HNO$_3$ (2.0 ✕ 10^{-3} M) + ligand (1.0 ✕ 10^{-3} M) + Metal (1.0 ✕ 10^{-3} M)

3. Results and Discussion

3.1 Titration Curves

For each set of experiments, pH was plotted against volume of titrant added and from these curves, moles of alkali required per mole of metal/ligand ('a') was determined. These titration curves were obtained by plotting pH vs. 'a'. Representative titration curves are given in figures 1 and 2.

An examination of the ligand titration curves for 2,2'-bipyridyl (figure 1, curve 1) and 1,10-phenanthroline (figure 2, curve 1) show a buffer region in pH range 2.8 - 5.5 thereby indicting the liberation of two protons in overlapping steps. The values of dissociation constants obtained for the ligands are in good agreement with the literature values [21].
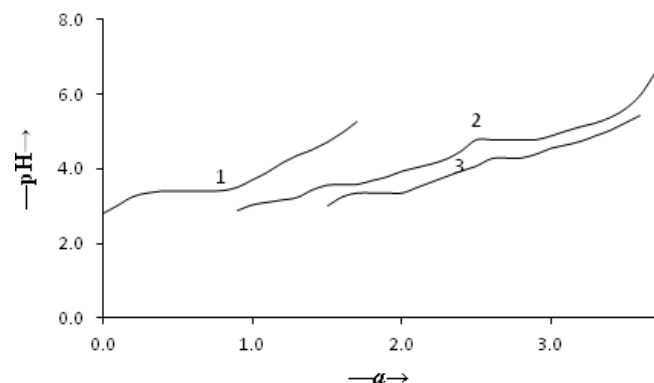

Figure 1: pH vs. '*a*' Curves for M(IV)-2,2'-Bipyridyl (1:1) System at 30±1°C[μ=0.10M(NaNO$_3$)]
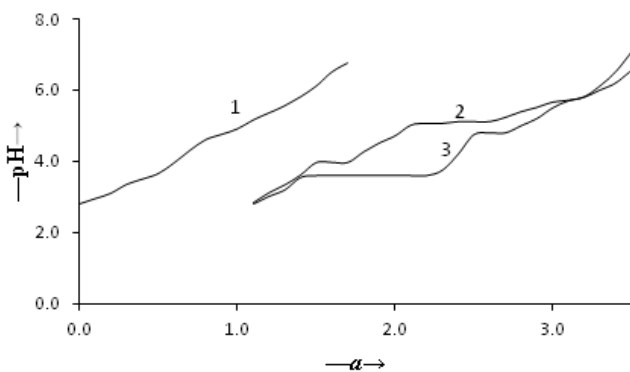
Figure 2: pH vs. '*a*' Curves for M(IV)-1,10-Phenanthroline (1:1) System at 30±1°C[μ=0.10M(NaNO$_3$)]
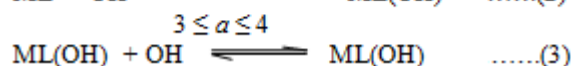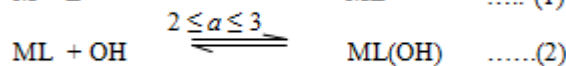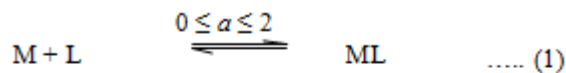
In figures 1and 2
Curve 1- represents Ligand titration curve
Curve 2- represents DMT (IV) Ligand titration curve
Curve 3- represents DOT(IV) Ligand titration curve

The metal-ligand titration curves (curves 2 and 3) in figures 1 and 2 suggest the formation of ML species in pH range 2.5 - 3.7 at *a* ≤ 2. The equilibria for various system can be represented as follows :

$0 \leq a \leq 2$

$$M + L \xrightleftharpoons{0 \leq a \leq 2} ML \qquad \ldots\ldots (1)$$

$$ML + OH \xrightleftharpoons{2 \leq a \leq 3} ML(OH) \qquad \ldots\ldots(2)$$

$$ML(OH) + OH \xrightleftharpoons{3 \leq a \leq 4} ML(OH) \qquad \ldots\ldots(3)$$

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

Algebraic method of Martell and Chaberek as modified by Dey et al. has been used to obtain the values of proton and metal equilibrium constants [22]-[26]. The calculation of stability constants of metal ligand hydroxy species is done by applying method developed by M. Chandra [27]. The values of protonation constants for various ligands and the formation constants of metal-ligand complexes are tabulated in tables 1 -3. Values of formation constants were plotted against $\sqrt{\mu}$ and extrapolated to zero ionic strength, to calculate thermodynamic stability constants. 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 logarithmic values of equilibrium constants for various proton-ligand and metal-ligand systems were refined by using the SCOGS computer programme [28]-[30]. These data was used to obtain the speciation curves . Analysis of these curves is discussed here under:

Distribution curves of DMT (IV)- 2,2'-bipyridyl and DOT (IV)- 2,2'-bipyridyl system show a very low percentage of free metal ion (curve 1) in the initial stage followed by the continuous decrease. The formation of ML species is observed from initial pH and the percentage is significantly high. The percentage of ML species in DMT (IV)-2,2'-bipyridyl system is about 58 % which is low as compared to that observed in case of DOT (IV) - 2,2'-bipyridyl system (i.e. 85%). With the increasing pH the percentage of ML species decreases continuously and attains the minima at pH ≈ 4.8. The speciation of hydroxo species is presented by curves 3 and 4 in figures 3 and 4. The monohydroxy species is formed in negligible amount and the dihydroxy species ML(OH)$_2$ is observed to be the major species in the distribution profile.

Curve 1 shows the concentration of free metal ion to be nearly 42% in initial stage in case of DMT(IV)- 1,10-phenanthroline system whereas it is quite low in DOT(IV)-1,10-phenanthroline system. The formation of ML species (curve 2) occurs from the initial pH and the reaches the maximum percentage (≈ 60%) at about pH 3.0 in the former system whereas the concentration of ML species is about 75% in case of latter system. In the higher pH range formation of monohydroxy complex and dihydroxy complex is observed, depicted by curve 3 and 4. It is evident from figure 5 that the dihydroxy species is predominant. However in figure 6, demonstrating the distribution curve for DOT (IV) – 1,10-phenanthroline system, monohydroxy species is also significant but the dihydroxy species is highest in percentage (90%).
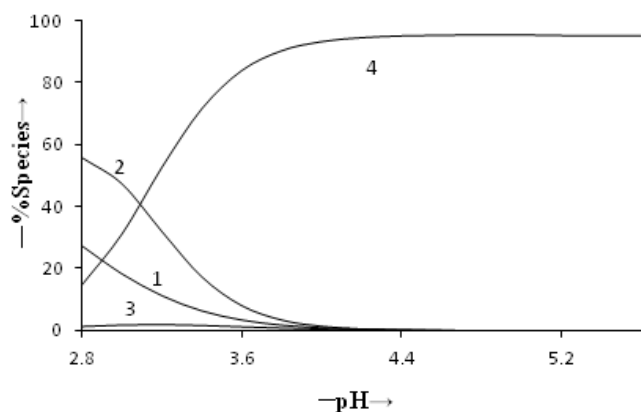
Figure 3: Speciation Curves for DMT(IV)-2,2'-Bipyridyl (1:1) System at 30±1°C[μ=0.10M(NaNO₃)]
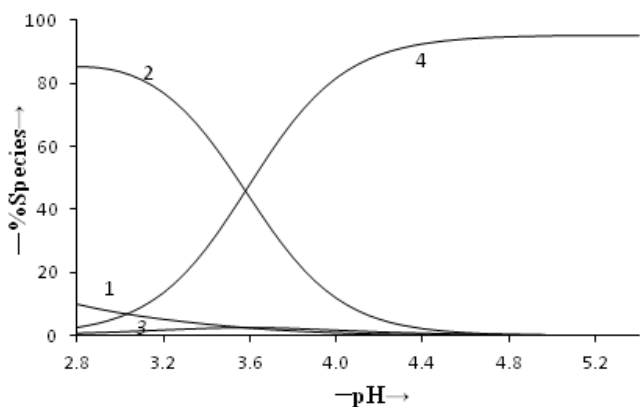

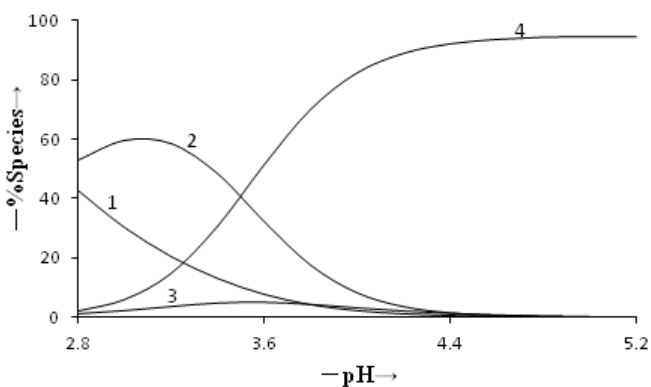**Figure 4:** Speciation Curves for DOT(IV)-2,2'-Bipyridyl (1:1) System at 30±1°C[μ=0.10M(NaNO₃)]

Figure 5: Speciation Curves for DMT(IV)-1,10 Phenanthroline (1:1) System at 30±1°C[μ=0.10M(NaNO₃)]
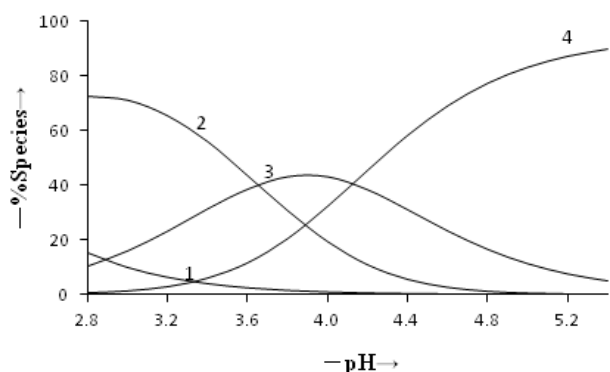

Figure 6: Speciation Curves for DOT(IV)-1,10 Phenanthroline (1:1) System at 30±1°C[μ=0.10M(NaNO₃)]

Where 1. [M] 2. [ML] 3. [ML(OH)] 4.[ML(OH)₂] (fig.3-6)
The values of thermodynamic stability constant $\log K_{\mu \to 0}$, are used to determine the ligational standard free energy change ($\Delta G°$) for the complexation reaction from Van't Hoff isotherm ($\Delta G° = -2.303RT \ln K_{\mu \to 0}$). By putting this in Gibb's Helmholtz equation ($\Delta G° = \Delta H° - T\Delta S°$) and this can be written as:

$$\log K_{\mu \to 0} = \frac{-\Delta H°}{2.303\,R}\frac{1}{T} + \frac{\Delta S°}{2.303\,R} \text{ ----- (4)}$$

The standard enthalpy change ($\Delta H°$) and entropy change($\Delta S°$) have been determined by linear least square fit method between $\log K_{\mu \to 0}$ and $\frac{1}{T}$. In equation (4) Slope= $\frac{-\Delta H°}{2.303\,R}$ and intercept = $\frac{\Delta S°}{2.303\,R}$

5. Conclusion

It is concluded from the observed facts that complexes formed with 2,2'-bipyridyl show lower stability than those formed with 1,10-phenanthroline. This may be attributed to the difference in ring structure of two ligands. In 2,2'-bipyridyl ring is separated by single bond which decrease its aromaticity and conjugation whereas in case of 1, 10-phenanthroline three fused rings increases its aromaticity and conjugation.

On observing the values recorded in tables 1-3 it is observed that complex formation decreases with increasing ionic strength and increasing temperature. Thermodynamic parameters for various systems are recorded in tables 2 and 3. The negative values of $\Delta G°$ show that complex formations are energetically favourable. This is further supported by negative enthalpy and positive entropy values.

6. Acknowledgement

Table 1 : Protonation Constant of Ligands at different Temperatures & Ionic Strengths

Parameters	20°C				30°C				40°C			
	0.05 M	0.10M	0.15M	$\mu\rightarrow0$	0.05 M	0.10M	0.15M	$\mu\rightarrow0$	0.05 M	0.10M	0.15M	$\mu\rightarrow0$
2,2'-Bipyridyl												
$\log\beta_{HL}$	4.32	4.22	4.20	4.58	4.16	4.14	4.02	4.30	4.00	3.84	3.70	4.20
$\log\beta_{H2L}$	7.55	7.53	7.31	7.60	7.06	7.05	7.00	7.20	5.90	5.21	5.11	5.82
1,10-Phenanthroline												
$\log\beta_{HL}$	5.10	5.01	5.00	5.30	4.98	4.78	4.73	5.32	4.86	4.61	4.60	5.20
$\log\beta_{H2L}$	8.79	8.56	8.30	9.50	7.54	7.25	6.00	8.37	5.74	5.55	5.40	6.22

Table 2 : Thermodynamic Parameters of M (IV)- 2,2'-Bipyridyl Systems

DMT(IV)- 2,2'-Bipyridyl System							
Parameter	20ºC		30ºC		40ºC		$-\Delta H^\circ$ kJmol^{-1}	ΔS° JK^{-1} mol^{-1}
	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}		
$\log K_{ML}^{M}$	5.15	28.89	5.00	29.00	4.90	29.37	23.93	17.10
$\log K_{ML(OH)}^{ML}$	7.72	43.31	7.70	44.67	7.40	44.35	30.64	44.55
$\log K_{ML(OH)2}^{ML(OH)}$	11.07	62.10	11.00	63.81	10.68	64.00	37.34	85.81

DOT(IV)- 2,2'-Bipyridyl System							
Parameter	20ºC		30ºC		40ºC		$-\Delta H^\circ$ kJmol^{-1}	ΔS° JK^{-1} mol^{-1}
	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}		
$\log K_{ML}^{M}$	6.90	38.71	6.60	38.29	6.55	39.25	33.51	17.39
$\log K_{ML(OH)}^{ML}$	9.15	51.33	9.10	52.79	9.09	54.48	5.74	155.54
$\log K_{ML(OH)2}^{ML(OH)}$	12.35	69.28	12.30	71.36	11.80	70.72	52.65	58.88

Table 3 : Thermodynamic Parameters of M (IV)-1,10-Phenanthroline Systems

DMT(IV)-1,10-Phenanthroline System							
Parameter	20ºC		30ºC		40ºC		$-\Delta H^\circ$ kJmol^{-1}	ΔS° JK^{-1} mol^{-1}
	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}		
$\log K_{ML}^{M}$	6.58	36.91	6.50	29.00	6.48	29.37	9.57	93.25
$\log K_{ML(OH)}^{ML}$	8.80	49.37	8.78	44.67	8.72	44.35	7.66	142.58
$\log K_{ML(OH)2}^{ML(OH)}$	12.10	67.88	11.95	63.81	11.93	64.00	16.28	175.93

DOT(IV)- 1,10-Phenanthroline System							
Parameter	20ºC		30ºC		40ºC		$-\Delta H^\circ$ kJmol^{-1}	ΔS° JK^{-1} mol^{-1}
	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}	$\log K_{\mu\rightarrow0}$	$-\Delta G^\circ$ kJmol^{-1}		
$\log K_{ML}^{M}$	6.50	36.47	6.48	37.59	6.45	38.66	4.79	108.21
$\log K_{ML(OH)}^{ML}$	10.10	56.66	9.98	57.44	10.02	60.05	7.66	166.84
$\log K_{ML(OH)2}^{ML(OH)}$	12.60	70.69	12.59	73.04	12.50	74.91	9.57	208.96

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