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Speciation Studies of Dimethyltin (IV) and Trimethyltin (IV) - Carboxylates Systems

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Abstract: ***Speciation studies of the systems involving interaction of dimethyltin(IV) [DMT]and trimethyltin (IV)[TMT] cations with adipic acid, citric acid, tartaric acid and phthalic acid have been determined in aqueous solution in the pH range 2.7 to 10.5 at three different temperatures (20±1°C, 30±1°C and 40±1°C) and at three ionic strengths (μ=0.05 ,0.10 and 0.15 M), using potentiometric technique. The computational analysis is done using standard mathematical approaches and SCOGS (stability constant of generalized species)computer programme. The formation of protonated , nonprotonated and hydroxo species in various systems is presented in the form of distribution curves.The thermodynamic stabilities of DMT species are found to be more than TMT(IV) species. Based on coordination the stability trend for various ligands is found to be :Phthalic acid > Tartaric acid >Adipic acid > Citric acid.***

Keywords: Speciation, organotin(IV)-carboxylates, thermodynamic stability

1. Introduction

Organotin carboxylates have attracted considerable attention because of their wide application in many fields including biological activity as potential anti-tuberculosis agents, plastic stabilizers and polymer catalysts [1]-[9]. Moreover the structural diversity of organotin carboxylates is well recognized [10]. The stuctural diversity and wide range applications has made organotin carboxylates an interesting subject of research. Further, from the environmental and biological aspects,the speciation of organotin (IV) species in natural water and biological fluids is very important, if their reactivities are to be understood. Organotin(IV) derivatives are reported to show toxicity towards living organisms[11]-[13].

With the aim of defining the speciation of organotin(IV) compounds in environmental and biological systems , we have performed investigations in aqueous media containing ligands of biological and environmental interest. In this paper we are reporting the speciation analysis involving interaction of organotin(IV) with carboxylates ligands which are by far the most common binding sites in the molecular componrents of natural organic matter.

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 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

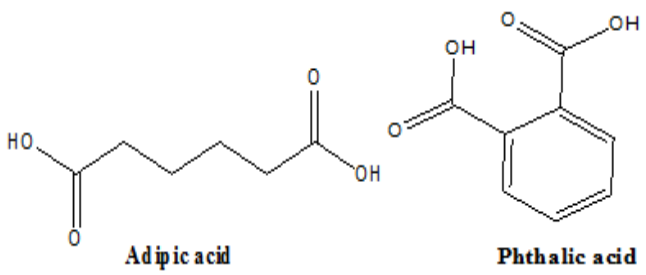
An Elico digital pH-meter model LI-127 with ATC probe and combined electrode type (CL-51B-Glass Body; range 0-14 pH unit; 0-100°C Automatic/Manual) with accuracy ±0.01 was employed for pH-measurement.

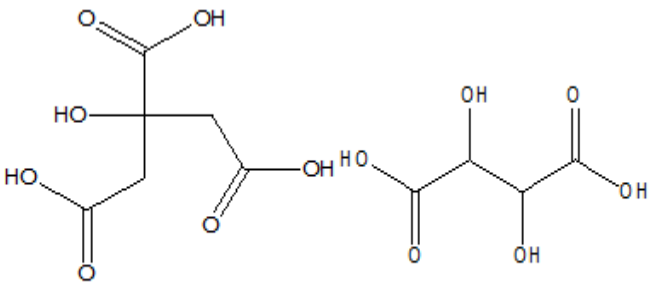
2.3 Experimental conditions

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 20±1°C, 30±1°C and 40±1°C .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)

Scheme 1.1 Structure of ligands :





Citric acid **Tartaric acid**

3. Results and Discussion

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

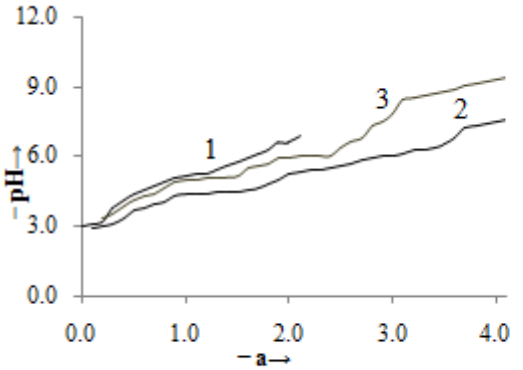


Figure 1: pH vs 'a' curves for M(IV)- adipic acid (1:1) system

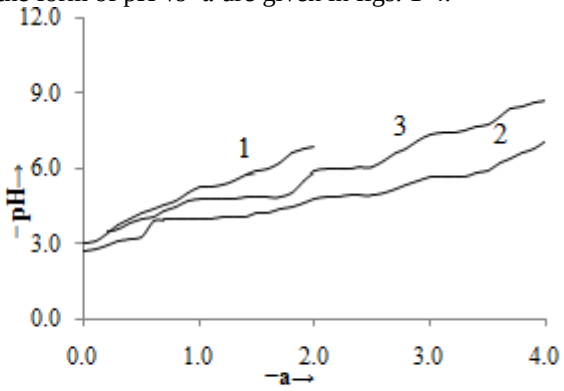


Figure 2: pH vs 'a' curves for M(IV)- citric acid (1:1) system

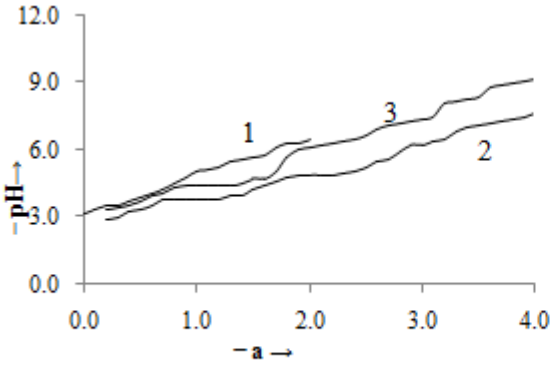


Figure 3: pH vs 'a' curves for M(IV)- tartaric acid (1:1) system

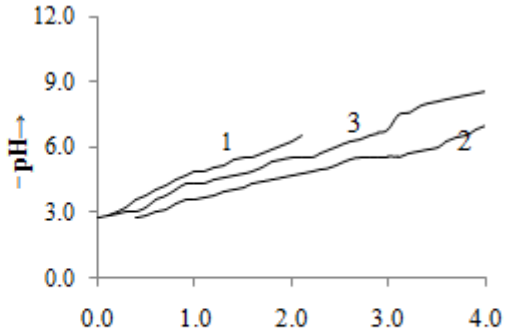


Figure 4: pH vs 'a' curves for M(IV)- phthalic acid (1:1) system

In 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.

The titration curves for adipic acid /citric acid /tartaric acid / phthalic acid systems follow the same trend. Examination of the above referred (figs.1-4) show that the reactions proceed by successive release of two protons. An inflection in metal - ligand curves at $0 \leq a \leq 1$ indicates the formation of MHL species. The release of proton from MHL and formation of ML species is evidenced between $1 \leq a \leq 2$. Above pH~5.0 formation of monohydroxo ML(OH) and dihydroxo $ML(OH)_2$ species could be understood by observing the inflections at a≈3 and a ≈4.

Various equilibria can be represented as follows:
Proton-ligand:

$$H_2L \underset{}{\overset{0 \leq a \leq 1}{\rightleftharpoons}} HL + H \quad \text{-------1.1}$$

$$HL \underset{}{\overset{1 \leq a \leq 2}{\rightleftharpoons}} L + H \quad \text{-------1.2}$$

Metal-ligand:

$$M + HL \overset{0 \le a \le 1}{\rightleftharpoons} MHL \quad \text{------1.3}$$

$$MHL \overset{1 \le a \le 2}{\rightleftharpoons} ML + H \quad \text{------1.4}$$

$$M + L \overset{1 \le a \le 2}{\rightleftharpoons} ML \quad \text{------1.5}$$

$$ML + OH \overset{2 \le a \le 3}{\rightleftharpoons} ML(OH) \quad \text{------1.6}$$

$$ML(OH) + OH \overset{3 \le a \le 4}{\rightleftharpoons} ML(OH)_2 \quad \text{---1.7}$$

(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) [14]-[16]. Method developed by M.Chandra is used for the calculation of stability constants of metal hydroxy species[17]. 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 [18]-[20]. The complex formation equilibria were elucidated with the help of speciation curves (represented in figs.5-12).

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
	Adipic acid								
log β_{HL}	6.47	6.32	6.20	6.30	6.16	6.10	6.25	6.12	6.09
log β_{H2L}	10.00	9.95	9.81	9.90	9.70	9.50	9.75	9.55	9.42
	Citric acid								
log β_{HL}	6.15	6.08	6.00	5.98	5.92	5.80	5.90	5.81	5.69
log β_{H2L}	9.78	9.70	9.63	9.65	9.40	9.27	9.50	9.43	9.35
	Tartaric acid								
log β_{HL}	5.56	5.33	5.18	5.40	5.20	4.90	5.10	4.96	4.72
log β_{H2L}	9.45	9.20	9.02	9.01	8.94	8.88	8.97	8.90	8.87
	Phthalic acid								
log β_{HL}	5.98	5.88	5.75	5.91	5.80	5.66	5.81	5.68	5.55
log β_{H2L}	9.65	9.48	9.30	9.40	9.28	9.17	9.25	9.13	9.00

Table 2: Thermodynamic parameters of DMT(IV)- carboxylic acid systems DMT(IV) - Adipic acid System

Parameter	**20±1°C**		**30±1°C**		**40±1°C**		**$-\Delta H^o$ kJmol^{-1}**	**ΔS^o JK^{-1}mol^{-1}**
	$\log K^{\mu \to 0}$	**$-\Delta G^o$ kJmol^{-1}**	**$\log K^{\mu \to 0}$**	**$-\Delta G^o$ kJmol^{-1}**	**$\log K^{\mu \to 0}$**	**$-\Delta G^o$ kJmol^{-1}**		
$\log K^{M}_{MLH}$	4.15	23.28	4.05	23.49	4.00	23.97	8.88	48.82
$\log K^{MLH}_{ML}$	6.35	35.62	6.30	36.65	6.20	37.15	9.57	89.03
$\log K^{ML}_{ML(OH)}$	8.90	49.93	8.80	51.05	8.65	51.83	15.72	116.79
$\log K^{ML(OH)}_{ML(OH)2}$	12.00	67.32	11.95	69.32	11.85	71.01	9.57	197.2

DMT(IV) - Citric acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	3.90	21.87	3.80	22.04	3.65	22.87	15.72	21.06
$\log K^{MLH}_{ML}$	5.70	31.97	5.55	32.19	5.30	32.73	25.30	22.97
$\log K^{ML}_{ML(OH)}$	8.80	49.36	8.75	50.76	8.50	50.94	19.83	101.47
$\log K^{ML(OH)}_{ML(OH)2}$	11.70	66.73	11.60	68.45	11.55	69.21	22.56	151.26

DMT(IV) -Tartaric acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	4.20	23.56	4.10	23.78	4.00	23.97	12.30	38.29
$\log K^{MLH}_{ML}$	6.45	35.62	6.35	36.84	6.30	37.75	8.88	92.86
$\log K^{ML}_{ML(OH)}$	9.90	55.54	9.70	56.27	9.65	57.83	14.36	139.77
$\log K^{ML(OH)}_{ML(OH)2}$	12.10	67.88	12.00	69.61	11.85	71.01	15.72	178.06

Table 2: Thermodynamic parameters of DMT(IV)- carboxylic acid systems DMT(IV) - Phthalic acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	8.80	49.36	8.55	49.60	8.90	50.94	17.09	109.13
$\log K^{MLH}_{ML}$	10.75	60.30	10.55	61.20	10.50	62.92	14.36	156.04
$\log K^{ML}_{ML(OH)}$	13.00	72.93	12.90	74.84	12.85	77.01	8.88	218.27
$\log K^{ML(OH)}_{ML(OH)2}$	16.10	90.32	16.00	92.82	15.90	95.28	12.30	266.14

Table 3: Thermodynamic parameters of TMT(IV)- carboxylic acid systems TMT(IV) - Adipic acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	2.90	16.29	2.80	16.34	2.75	16.48	8.88	24.89
$\log K^{MLH}_{ML}$	4.65	26.08	4.50	26.10	4.45	26.66	11.62	48.82
$\log K^{ML}_{ML(OH)}$	7.90	44.31	7.85	45.53	7.80	46.74	6.15	130.20
$\log K^{ML(OH)}_{ML(OH)2}$	9.90	55.54	9.80	56.85	9.75	58.43	8.88	158.92

TMT(IV) - Citric acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	3.25	17.23	3.10	17.75	3.00	17.98	15.04	10.53
$\log K^{MLH}_{ML}$	3.50	19.63	3.40	19.72	3.35	20.07	8.88	36.37
$\log K^{ML}_{ML(OH)}$	7.05	39.55	7.00	40.61	6.90	41.35	9.57	102.43
$\log K^{ML(OH)}_{ML(OH)2}$	9.90	55.54	9.75	56.56	9.65	57.83	15.04	137.85

TMT(IV) - Tartaric acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	2.95	16.54	2.90	17.11	2.85	17.37	6.15	35.42
$\log K^{MLH}_{ML}$	5.45	30.57	5.35	31.61	5.30	32.06	8.88	73.71
$\log K^{ML}_{ML(OH)}$	8.15	45.72	8.10	47.28	8.05	48.54	6.15	134.98
$\log K^{ML(OH)}_{ML(OH)2}$	10.85	60.86	10.75	62.74	10.70	64.42	8.88	177.11

Table 3: Thermodynamic parameters of TMT(IV)- carboxylic acid systems TMT(IV) - Phthalic acid System

Parameter	20±1°C		30±1°C		40±1°C		-ΔH° kJmol^{-1}	ΔS° JK^{-1}mol^{-1}
	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}	logK$^{\mu\to 0}$	-ΔG° kJmol^{-1}		
$\log K^{M}_{MLH}$	8.05	45.16	8.00	46.41	7.80	46.74	16.41	98.60
$\log K^{MLH}_{ML}$	9.25	51.89	9.15	53.08	9.05	54.23	12.30	134.98
$\log K^{ML}_{ML(OH)}$	11.75	66.19	11.80	68.16	11.70	70.11	6.15	204.87
$\log K^{ML(OH)}_{ML(OH)2}$	14.15	79.38	14.10	81.80	14.00	83.90	9.57	238.38

Speciation profiles for various species are represented in figs. 5-12.

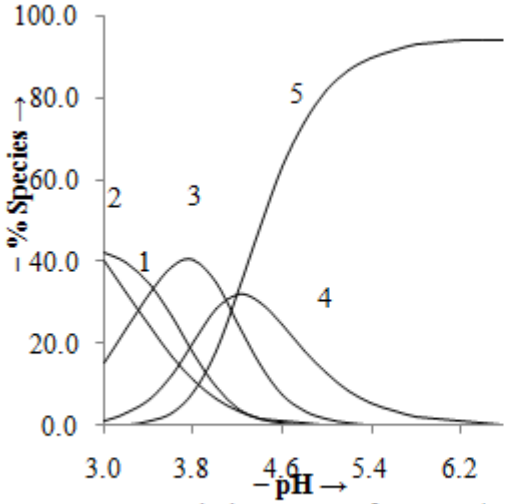


Figure 5: Speciation curves for DMT(IV)-adipic acid acid (1:1) system

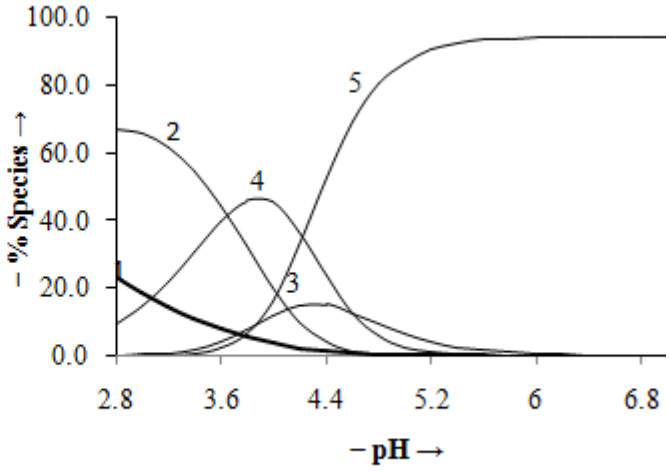


Figure 6: Speciation curves for DMT(IV)- citric (1:1) system

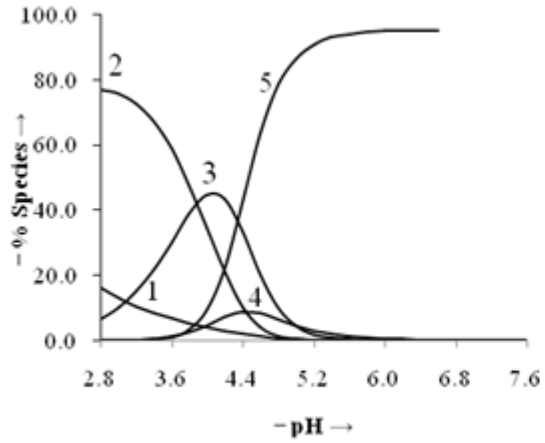


Figure 7: Speciation curves for DMT (IV)- tartaric acid (1:1) system

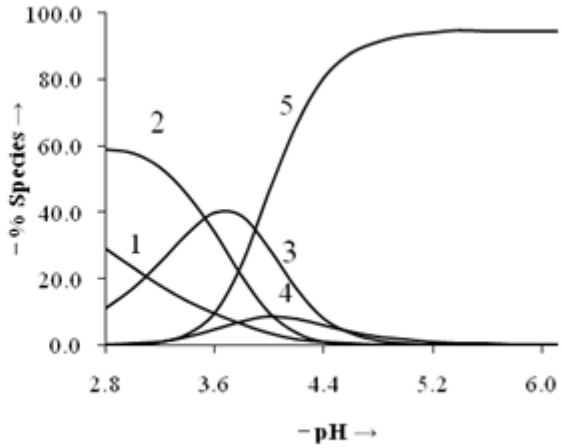


Figure 8: Speciation curves for DMT(IV)-phthalic acid (1:1) system

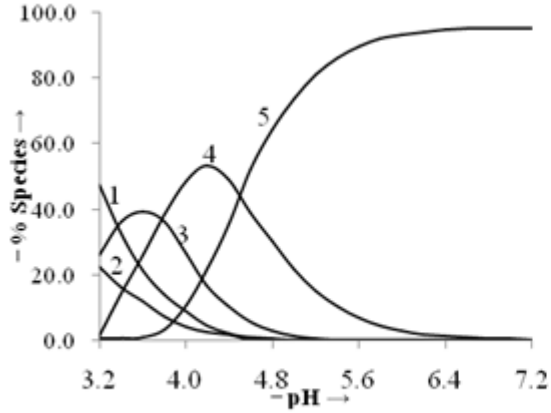


Figure 9: Speciation curves for TMT(IV)- adipic acid (1:1) system

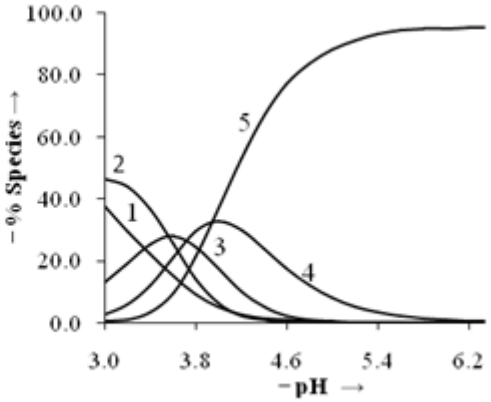


Figure 10: Speciation curves for TMT(IV)- citric acid (1:1) system

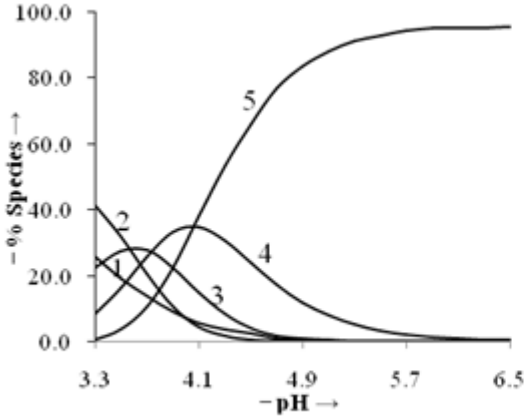


Figure 11: Speciation curves for TMT (IV)- tartaric acid system (1:1)

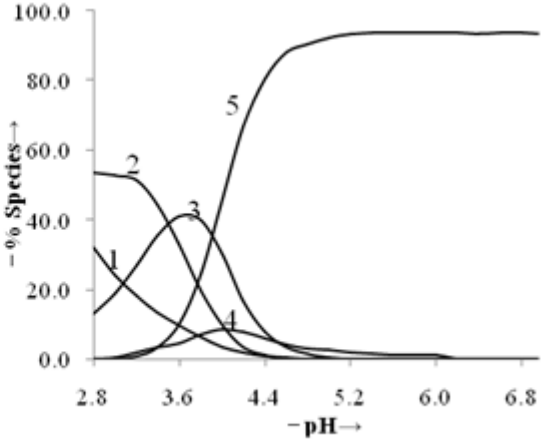


Figure 12: Speciation curves for TMT(IV)-phthalic acid (1:1) system

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

It is observed from the speciation curves (figs.5-12) 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, in the initial pH range ≈2.8, hence leading to the formation of protonated species (MHL).This is probably due to the fact that H_2L ligand is deprotonated at very low pH leading to the formation of HL which in turns gets associated with metal to form MHL complex species. The percentage of MHL species ranges from 42-77% between a≈0 and a≈1 in different systems, which continuously decreases upto pH≈3.6. The formation of non protonated ML species commences simultaneously with the deprotonation of MHL and the maximum percentage of ML species reaches nearly 45% in all the systems between a≈1 and a≈2 in the pH range 3.6-4.0. Above pH ≈ 4.5 the monohydroxo species ML(OH) is formed in low concentration i.e. about 32% between a≈2

and $a \approx 3$, whereas dihydroxo species is formed between $a \approx 3$ and $a \approx 4$. The percentage concentration of $ML(OH)_2$ is quite high ≈95% .

For R_3Sn (IV) - adipic acid /citric acid / tartaric acid / phthalic acid systems the concentration of free metal is 25-48% at low pH and that of MHL complex is between 22-53% for different systems. With the increase in pH, deprotonation of MHL species leads to the formation of ML complex which varies between 28-41% for various systems. In the higher pH range formation of monohydroxo ML(OH) and the dihydroxyo species $ML(OH)_2$ is observed. The monohydroxo complexes are low in percentage whereas dihydroxo complexes attain maximum concentration i.e.95%.

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

$\Delta G° = -2.303RT \log K^{\mu \to 0}$ ------- (1.8)

The Gibb's Helmholtz equation is :

$\Delta G° = \Delta H° - T\Delta S°$ ------- (1.9)

This can be written as equation (1.10) by putting $\Delta G° = -2.303RT \log K^{\mu \to 0}$

$$\log K^{\mu \to 0} = \frac{-\Delta H°}{2.303R}\frac{1}{T} + \frac{\Delta S°}{2.303R} \quad \text{-----(1.10)}$$

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 $\log K^{\mu \to 0}$ [21] . In equation (1.10)

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

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

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

4. Conclusion

The stability trend is dimethyltin (IV) > trimethyltin (IV) and monocarboxylic < dicarboxylic for the organotin moieties and carboxylate ligands respectively. The reason for the observed trend is as expected in terms of size and charge of cation and anion [22]-[23]. Precisely the stability constant of ML species with respect to different carboxylic ligands is found to be:

Phthalic acid > Tartaric acid >Adipic acid > Citric acid

Higher stability with phthalic acid can be attributed to formation of stable chelate structure. Tartaric acid, citric acid and adipic acid have open chain structures. The former two ligands have additional – OH group for coordination. But low stability as compared to phthalic acid suggests that –OH groups are not involved in the coordination. However, further studies are needed for deciding the exact coordination behaviour of the ligands.

The high percentage of dihydroxo species as compared to monohydroxo species perhaps is due to the formation of octahedral geometry in the former case which leads to the formation of stable complexes, as compared to monohydroxo species where the coordination number is five which may lead to either square planar or trigonal bipyramidal, which are often less stable than octahedral geometry .

The proton-ligand and metal-ligand equilibrium constants decrease with increase of temperature and ionic strength of the medium.value of ΔG° decrease with increase in temperature. This supports that reaction proceeds from left to right. The change in ΔG° with respect to temperature is seen to bear inverse relation. Negative value of ΔH° and positive value of ΔS° support the favorable conditions for complex formation.

5. Acknowledgement

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