

Study of the Interaction of Trimethyltin(IV) Chloride with N,N,N',N'-tetraethylethylenediamine in Reference to Marine Environmental Pollution

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Abstract

The interaction of trimethyltin(IV) with N,N,N',N'-tetraethylethylenediamine (Et₄en) was investigated potentiometrically. The hydrolysis constants of trimethyltin(IV) species and formation constants of the amine complexes are determined. The formation constant of the complex is high, which may suggest to use Et₄en as an antidote for triorganotin(IV) poisoning, the main source of marine environmental pollution. The effect of solvent dielectric constant of the medium and temperature on the complex formation equilibria was investigated.

Keywords: Complex formation equilibria, trimethyltin(IV), Stability constant, Antidote, Speciation

1. Introduction

In the last two decades coordination compounds of organotin(IV) exhibit interesting antitumoural activity against several human cancer cell lines (Zhu et al., 2004) and some of them are extremely toxic to animals and humans (Cardiano et al., 2008, Nolan et al., 2005). The deleterious effect of trialkyltin(IV) derivatives is due to the inhibition of mitochondrial oxidative phosphorylation (Aldridge, 1976) and the ability to bind certain proteins (Elliott et al., 1979). The toxicity of tetra-alkyltins also appears to be due to trialkyltin(IV) species which are produced as a result of dealkylation *in vivo*. For these reasons, significant attention is paid to environmental pollution by alkyltin compounds and to their presence in food. Consequently there is a need to study their complex formation equilibria with a hope to find an antidote for it. With this in mind and in conjunction with our previous studies (Shoukry, 2002; Shoukry et al., 1995; Shoukry et al., 2000; Shoukry et al., 1995; Shoukry et al., 1986), on metal complexes of biological significance, the present paper includes the results of the study of trimethyltin(IV) complexes with N,N,N',N'-tetraethylethylenediamine. The complex formation equilibria is investigated with the hope that such type of coordinating ligand might possess favorable properties, possibly as carries in body fluids.

2. Experimental details

2.1 Materials and reagents

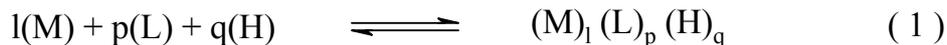
Trimethyltin(IV) chloride (TMA) were supplied by Merk Chem. Co. N,N,N',N'-tetraethylethylenediamine (Et₄en) was provided by Sigma Chem. Co. Sodium hydroxide stock solutions were prepared by diluting the content of BDH concentrated volumetric solution vials. These solutions were systematically checked by titration against potassium hydrogen phthalate. The amine solutions were prepared in the diprotonated form by dissolution in two equivalents of nitric acid solution.

2.2 Equipments and Measuring Techniques

Potentiometric titrations were performed with a Metrohm 686 titroprocessor. The titroprocessor and electrode were calibrated with standard buffer solutions (Bates, 1975), potassium hydrogen phthalate (pH 4.008) and a mixture of KH₂PO₄ and Na₂HPO₄ (pH 6.865) at 25°C.

The protonation constants of the amine and the hydrolysis constants of trimethyltin(IV) ion were determined by titrating 40ml of the protonated amines (1.25 mM) or the organotin(IV) (1.25 mM) solutions in 25% dioxane-water system. The stability constants of the organotin(IV) complexes were determined by titrating 40 ml of organotin(IV) (1.25 mM) and the amine with concentration of 1.25 mM. All solutions were adjusted to 0.1M strength by addition of NaNO₃, and were titrated against standard 0.05 M NaOH.

The equilibrium constants were evaluated from titration data, defined by Eqns. (1) and (2)



$$\beta_{lpqr} = \frac{[(M)_1 (L)_p (H)_q]}{[M]^1 [L]^p [H]^q} \quad (2)$$

Where, M, L, and H represent organotin(IV), amine and proton respectively. The calculations were performed using the computer program(Gans et.al, 1976) MINIQUA-75. The stoichiometries and stability constants of the complexes formed were determined by trying various possible composition models. The model selected gave the best statistical fit and was chemically constituent with the titration data without giving any systematic drift in the magnitude of various residuals, as described elsewhere (Gans et.al, 1976).

The fitted model was tested by comparing the experimental titration data points and the theoretical curve calculated from the values of acid dissociation constants of the amine and formation constants of the corresponding complexes. Tables (1 and 3) list the formation constants together with their standard deviations and sum of square of residuals as obtained from the program MINQUAD-75. The concentration distribution diagrams were obtained using the program SPECIES (Pettit).

3. Results and Discussion

The acid-dissociation constants of the amine in the protonated form were determined under the same experimental conditions of ionic strength (0.1M) and temperature (25 °C) used for the study of trimethyltin(IV) complex equilibria.

3.1 Hydrolysis of trimethyltin(IV)

The hydrolysis of trimethyltin(IV) (TMT) ion was previously investigated (Takahashi et.al.,1997, Hynes et. al., 1987) and the results were contradictory. The acid-base chemistry of trimethyltin(IV) has been investigated. The fitted model according to the aforementioned method of calculation was found to be consistent with the following acid-base equilibria, **Scheme (1)**.

The hydrolysed species 10-1, 10-2 and 20-1 were consistent with the model proposed by Takahashi et al. (Takahashi et. al., 1997). Considering the species 20-2 and 20-3, **Scheme (1)**, were found to improve the data fitting. The formation of the dimeric species through OH⁻ group was previously established by Extended X-ray Absorption Fine Structure (EXAFS) method (Takahashi et. al., 1997). The concentration distribution diagram for the hydrolysis of TMT is shown in **Fig. (1)**.

3.2 Organotin(IV) complexes with Et₄en:

The acid-base equilibria of the Et₄en, abbreviated as L, was investigated under the experimental conditions applied for the study of the stability constants of the organotin(IV) complexes. The titration data reveals the formation of simple L, HL⁺ and H₂L²⁺ complex species, where L represents Et₄en in the neutral form. The calculated overall protonation constants in aqueous solution at 25°C, in dioxane-water solution of various proportion and at different temperature are given in (**Tables 1,3**). The pK_a values of the protonated Et₄en in dioxane-water solutions are higher than those reported in water. This may be due the increased basicity of the ligand donor groups when one goes from water to dioxane solutions.

A comparison of the potentiometric titration curves of protonated Et₄en in the presence and absence of TMT shows that the complex titration curve is located at significantly lower pH value than that of the ligand. This corresponds to the formation of a complex species through release of a hydrogen ion. The formation equilibria were characterized by fitting their potentiometric data to various models; the best result were obtained for complexes with stoichiometric coefficients (110), (111) and (11-1). This model was tested by comparing the experimental titration data with theoretical curve calculated from the pK_a of the ligand and the stability constant of the formed complexes. A good agreement between the experimental and theoretical data, **Figs. (2)**, proved the validity of the model proposed.

The concentration distribution diagram of Et₄en complex with trimethyltin(IV) ion gives an interesting

information regarding the behavior of these organometallic compounds in biological systems. The distribution diagram is depicted in Fig. 3. It is interesting to note that in the physiological pH range the complex formation is quite feasible.

3.3 Effect of Temperature

The thermodynamic parameters ΔH° and ΔS° associated with the protonation of N,N,N',N'-tetraethylethylenediamine (Et₄en), hydrolysis of trimethyltin(IV) ion and its complex formation with Et₄en were calculated from the temperature dependence of the data in **Table (1)**. ΔH° and ΔS° were obtained by linear least square fit of $\ln K$ vs. $1/T$ ($\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R$) leading to an intercept $\Delta S^\circ/R$ and a slope $-\Delta H^\circ/R$, where K is the equilibrium constant and R is the universal gas constant. These data can be employed to extrapolate the equilibrium constants to other temperatures. The main conclusions from the data can be summarized as follows:

a) The formation constant for the hydroxyl complexes of trimethyltin(IV), β_{OH} can be calculated as:

$$\log(\beta_{OH})_{10-1} = \log K_w + \log \beta_{10-1}$$

The hydrolysis reactions (1-5) of TMT in **Table (2)** are exothermic, i. e. the hydrolysis are favored. The ΔH° values in **Table (2)** can be considered as the net summation of two opposing effects, namely the exothermic hydrolysis reaction and the endothermic liberation of ordered water of hydration. Reaction (3) leading to the formation of 20-1 species is endothermic. It has the largest change in entropy ($\Delta S^\circ = 242.3 \text{ J.K}^{-1}.\text{mol}^{-1}$) due to the release of two ordered water molecules of hydration. This makes more negative the free energy change ($\Delta G^\circ = -65.6 \text{ kJ.mol}^{-1}$). Also, the formation of species 20-1, can be considered as a summation of reaction (1), the formation of species 10-1 and the dimerization reaction (6). Although, the dimerization reaction (6) has a positive ΔH° , it has a large entropy change $114.0 \text{ J.K}^{-1}.\text{mol}^{-1}$ due to loss of ordered water of hydration, so the net contribution to ΔG° is negative ($\Delta G^\circ = -19.8 \text{ kJ. mol}^{-1}$). The formation of 10-1, reaction (1), and 20-2, reaction (4), both have similar ΔG° and large ΔS° . The formation of 10-2, reaction (2), and 20-3, reaction (5), both have comparable values of ΔH° , ΔS° and ΔG° . Although they have more negative ΔH° values, they are the least favored species $\Delta G^\circ \sim -20 \text{ kJ. mol}^{-1}$. This can be due to the longer bond length (Takahashi et. al., 1997) of the water molecules in the species 10-1 and 20-2. So, the loss of water molecules is not accompanied by a large disorder and the formation of species 10-2 and 20-3 have net negative ΔS° of -18.2 and $-13.5 \text{ J. K}^{-1}.\text{mol}^{-1}$, respectively.

b) The protonation reactions (7) and (8) of Et₄en are exothermic and of comparable ΔH° value. Three factors affects the protonation reactions: (i). The neutralization reaction, which an exothermic process. (ii). Desolvation of ions, which is an endothermic process. (iii). The change of the configuration and the arrangements of the hydrogen bonds around the free and the protonated ligands.

c) The complexation reaction (10,11) of TMT with Et₄en is exothermic, ΔH° values are negative -53.63 and $-30.25 \text{ kJ. mol}^{-1}$.

3.4 Effect of solvent

It is well established that the "effective" or "equivalent solution" dielectric constants in proteins (Kramer-Schnabel et. al., 1991; Rees, 1980) or active site cavities of enzymes (Rogers et. al., 1985) are smaller compared to that in bulk water. Estimates for the dielectric constants in such locations range from 30 to 70 (Kramer-Schnabel et. al., 1991; Rees, 1980; Rogers et.al., 1985; Sigel et. al., 1985). Hence by using aqueous solutions containing ≈ 10 -50% dioxane, one may expect to simulate to some degree the situation in active site cavities (Akerlof et.al., 1953), hence to extrapolate the data to physiological conditions. Careful examination of the medium effect on the equilibrium constants reveal the following features:

a) pK_a of the protonated Et₄en decreases linearly with increasing the percentage of organic solvent in the medium. This may be explained by better solvation of the neutral Et₄en by dioxane.

b) The hydrated trimethyltin(IV) is subjected to hydrolysis by deprotonation as shown in **Scheme (1)**. The deprotonation constants are increased with increasing dioxane proportion of the solvent. This may be correlated with the ability of a solvent of relatively low dielectric constant to increase the electrostatic attraction between the ionized proton and the hydrolysed species of trimethyltin(IV) ion.

c) The formation constants for trimethyltin(IV) complexes with Et₄en decrease upon addition of dioxane to an aqueous solution of the corresponding species. This can be explained by better solvation of virtually hydrophobic species $\text{CH}_3\text{Sn}^+/\text{CH}_3\text{SnCl}$ by dioxane resulting in lowering the complex stability. This behaviour is in agreement with that proposed for alkyltin(IV) complexes with D-glucosamine (Shoukry et. al., 1997).

4. Conclusion

The present report includes the results of the study of the interaction of trimethyltin(IV) compounds with Et₄en. The formation constants of the corresponding complexes were determined and the concentration distribution diagram was evaluated. The high stability constant of the complex may suggest to use Et₄en as an antidote for the triorganotin(IV) poisoning, which is one of the major contaminant in the marine environment

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Table 1. Formation Constants of trimethyltin(IV) (TMT) Complexes in Water at Different Temperature.

System ^a	Temp.(°C)	l	p	q ^b	Logβ ^c	S ^d
TMT	15	1	0	-1	-6.14(0.01)	3.3E-8
		1	0	-2	-16.84(0.04)	
		2	0	-1	-2.74(0.02)	
		2	0	-2	-9.07(0.01)	
		2	0	-3	-19.40(0.04)	
TMT-Et ₄ en	15	0	1	1	9.94(0.01)	1.5E-8
		0	1	2	16.80(0.01)	
		1	1	0	6.81(0.00)	
		1	1	1	13.26(0.01)	
		1	1	-1	-3.20(0.02)	
TMT	20	1	0	-1	-6.01(0.01)	3.2E-8
		1	0	-2	-16.61(0.04)	
		2	0	-1	-2.62(0.02)	
		2	0	-2	-8.83(0.01)	
		2	0	-3	-19.04(0.04)	
TMT-Et ₄ en	20	0	1	1	9.81(0.01)	1.4E-8
		0	1	2	16.54(0.01)	
		1	1	0	6.68(0.00)	
		1	1	1	13.08(0.01)	
		1	1	-1	-3.48(0.04)	
TMT	25	1	0	-1	-5.90(0.02)	3.8E-8
		1	0	-2	-16.40(0.03)	
		2	0	-1	-2.44(0.02)	
		2	0	-2	-8.56(0.04)	
		2	0	-3	-18.70(0.05)	
TMT-Et ₄ en	25	0	1	1	9.65 (0.01)	3.4E-8
		0	1	2	16.22 (0.02)	
		1	1	0	6.52(0.00)	
		1	1	1	12.80(0.01)	
		1	1	-1	-3.21(0.05)	
TMT	30	1	0	-1	-5.78(0.02)	7.7E-8
		1	0	-2	-16.22(0.04)	
		2	0	-1	-2.27(0.03)	
		2	0	-2	-8.28(0.02)	
		2	0	-3	-18.37(0.08)	
TMT-Et ₄ en	30	0	1	1	9.51(0.01)	9.3E-9
		0	1	2	15.94(0.01)	
		1	1	0	6.36(0.01)	
		1	1	1	12.53(0.02)	
		1	1	-1	-2.81(0.03)	
TMT-Et ₄ en	30	1	1	0	6.18(0.00)	1.3E-10
		1	1	1	12.30(0.01)	
		1	1	1	12.30(0.01)	
		1	1	1	12.30(0.01)	
		1	1	-1	-2.58(0.04)	

^a l, p and q are the stoichiometric coefficient corresponding to organotin(IV), Et₄en and H⁺, respectively; ^c Standard deviations are given in parentheses; ^d Sum of square of residuals.

Table 2. Thermodynamic parameters for the equilibria of trimethyltin(IV) complexes.^a

Equilibrium ^b	ΔH° kJmol ⁻¹	ΔS° JK ⁻¹ mol ⁻¹	ΔG° kJmol ⁻¹
TMT			
1) $M(H_2O)_2^+ + OH^- \rightleftharpoons M(H_2O)(OH) + H_2O$	-7.63(0.12)	128.3(1.1)	-45.9(1.2)
2) $M(H_2O)(OH) + OH^- \rightleftharpoons M(OH)_2^- + H_2O$			
3) $2M(H_2O)_2^+ + OH^- \rightleftharpoons M_2(H_2O)_2(OH)^+ + 2H_2O$	-24.8(0.3)	-18.2(0.4)	-19.4(0.5)
4) $M_2(H_2O)_2(OH)^+ + OH^- \rightleftharpoons M_2(H_2O)(OH)_2 + H_2O$	6.60(0.13)	242.3(1.2)	-65.6(1.4)
5) $M_2(H_2O)(OH)_2 + OH^- \rightleftharpoons M_2(OH)_3^- + H_2O$	-14.7(0.2)	100.2(1.0)	-44.6(0.9)
6) $M(H_2O)_2^+ + M(H_2O)(OH) \rightleftharpoons M_2(H_2O)_2(OH)^+ + H_2O$	-25.5(0.4)	-13.5(0.5)	-21.5(0.7)
	14.2(0.2)	114.0(1.2)	-19.8(0.4)
Et₄en			
7) $L + H^+ \rightleftharpoons LH^+$	-49.60	-40.76	-37.44
8) $LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	-45.78	31.98	-55.31
9) $L + 2H^+ \rightleftharpoons LH_2^{2+}$	-95.38	-8.74	-92.75
TMT-Et₄en			
10) $M(Cl) + L \rightleftharpoons ML(Cl)$	-53.63	-55.39	-37.12
11) $M(Cl) + LH^+ \rightleftharpoons MLH(Cl)^+$	-30.25	18.76	-35.84
12) $MLCl \rightleftharpoons MCl(LH_1) + H^+$	-153.80	-331.08	-555.09

^a TMT or M denote trimethyltin(IV), Et₄en denote tetraethylethylenediamine; Standard deviations are given in parentheses. ^b Stepwise formation constants.

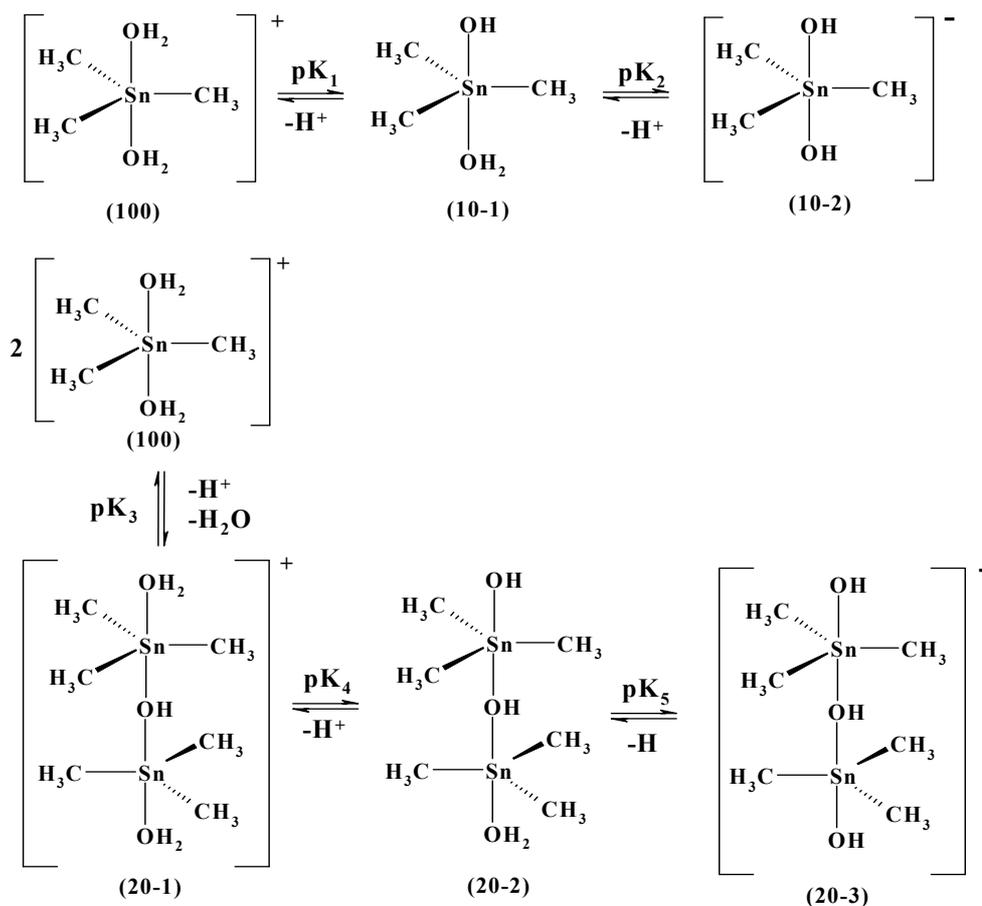
Table 3. Formation Constants of Trimethyltin(IV) Complexes with Et₄en in Dioxane-Water Solutions of Different Compositions.

System	Dioxane %	l	P	q ^a	Logβ ^b	S ^c
TMT	12.5	1	0	-1	-6.16(0.03)	1.6E-7
		1	0	-2	-16.67(0.07)	
		2	0	-1	-2.45(0.08)	5.1E-8
		2	0	-2	-9.12(0.06)	
		2	0	-3	-19.54(0.07)	
TMT-Et ₄ en	12.5	0	1	1	9.75(0.01)	1.8E-8
		0	1	2	16.40(0.02)	
		1	1	0	6.33(0.00)	5.3E-10
		1	1	1	11.89(0.06)	
		1	1	-1	-2.52(0.07)	
TMT	25	1	0	-1	-6.21(0.02)	4.4E-8
		1	0	-2	-16.96(0.05)	
		2	0	-1	-2.73(0.02)	2.8E-9
		2	0	-2	-9.29(0.01)	
		2	0	-3	-19.94(0.03)	
TMT-Et ₄ en	25	0	1	1	9.57(0.01)	2.8E-9
		0	1	2	16.02(0.01)	
		1	1	0	6.11(0.00)	1.83E-9
		1	1	1	11.79(0.03)	
		1	1	-1	-2.49(0.04)	
TMT	37.5	1	0	-1	-6.39(0.02)	6.1E-8
		1	0	-2	-17.29(0.06)	
		2	0	-1	-2.86(0.03)	1.1E-8
		2	0	-2	-9.62(0.02)	
		2	0	-3	-20.39(0.08)	
TMT-Et ₄ en	37.5	0	1	1	9.38(0.01)	1.1E-8
		0	1	2	15.72(0.01)	
		1	1	0	5.82(0.01)	1.4E-8
		1	1	1	11.71(0.09)	
		1	1	-1	-2.52(0.06)	
TMT	50	1	0	-1	-6.54(0.03)	3.8E-8
		1	0	-2	-17.60(0.05)	
		2	0	-1	-2.98(0.02)	1.5E-8
		2	0	-2	-9.90(0.01)	
		2	0	-3	-20.83(0.05)	
		0	1	1	9.17(0.01)	1.5E-8
		0	1	2	15.30(0.01)	
		1	1	0	5.50(0.01)	3.7E-9
		1	1	1	11.54(0.05)	
		1	1	-1	-2.51(0.03)	

TMT	62.5	1	0	-1	-6.70(0.02)	1.7E-7
		1	0	-2	-17.87(0.07)	
		2	0	-1	-3.11(0.05)	
		2	0	-2	-10.15(0.04)	
		2	0	-3	-21.28(0.09)	
TMT-Et ₄ en		0	1	1	9.04(0.01)	1.1E-8
		0	1	2	15.11(0.01)	
		1	1	0	5.20(0.01)	1.5E-8
		1	1	1	11.37(0.08)	
		1	1	-1	-2.51(0.03)	

^al, p and q are the stoichiometric coefficient corresponding to organotin(IV), Et₄en and H⁺ respectively;

^bStandard deviations are given in parentheses; ^cSum of square of residuals.



Scheme (1) The acid - base equilibria of trimethyltin(IV) species

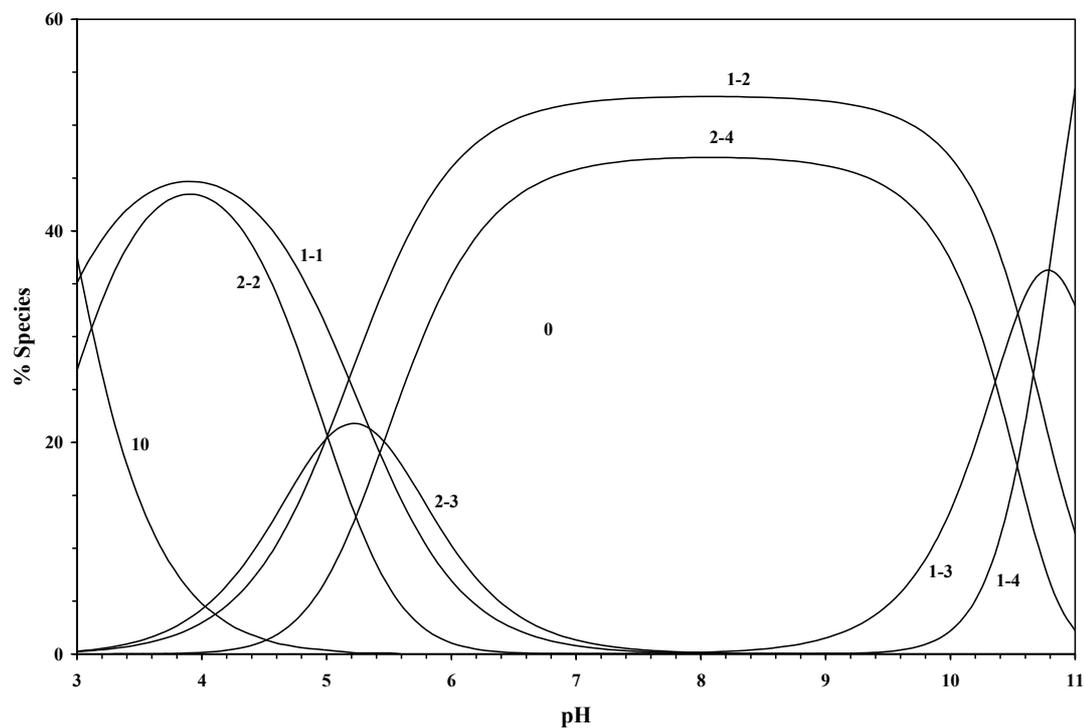


Figure 1. Concentration distribution of various species as a function of pH in the $\text{Sn}(\text{CH}_3)_3\text{-OH}$ system. (at concentrations of 1.25 mmol/liter for $(\text{CH}_3)_3\text{Sn}(\text{IV})$)

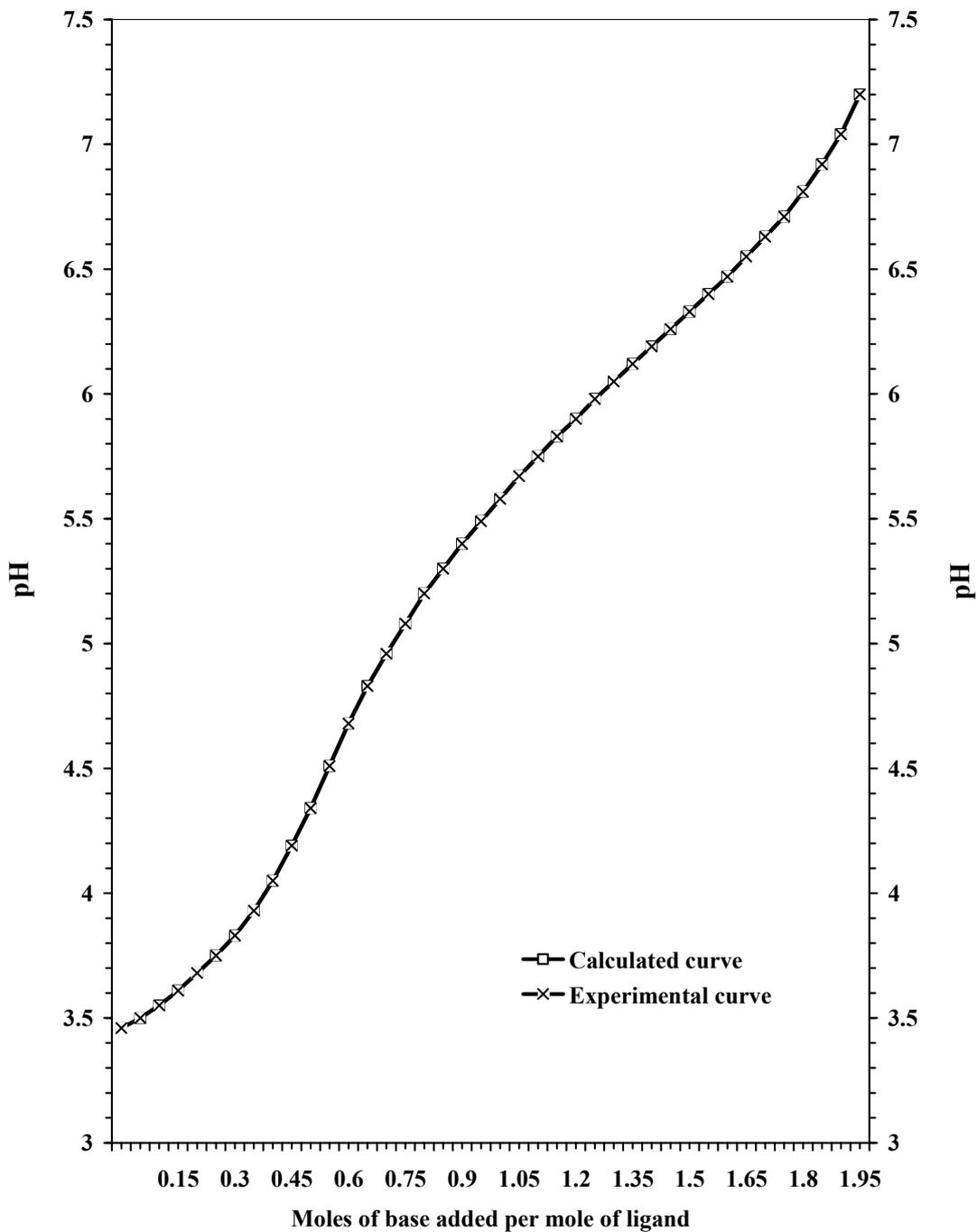


Figure 2. Potentiometric titration curve of the TMT-Et4en system

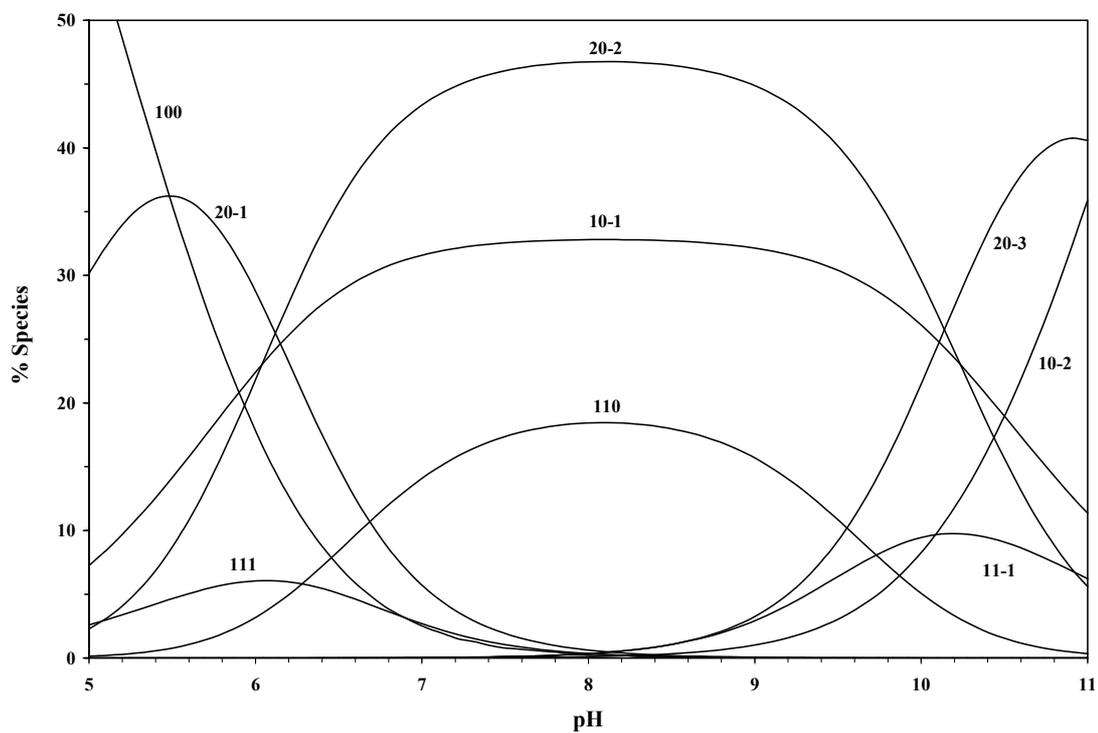


Figure 3. Concentration distribution of various species as a function of pH in the TMT-Et₄en system