EQUILIBRIUM STUDIES OF DIBUTYLTIN(IV) COMPLEXES WITH AMINO ACIDS AND PEPTIDES

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Summary

Complex formation equilibria of dibutyltin(IV) with amino acids and peptides have been investigated. Stoichiometry and stability constants for the complexes formed were determined at 25°C and ionic strength 0.1 M $NaNO_3$. The results showed the formation of 1:1 and 1:2 (organotin : ligand) complexes with amino acids. The effect of the pK_a value of the amino acid on the stability constant of its complex species was elucidated. Peptides form both 1:1 complexes and the corresponding deprotonated amide species. In the latter species the binding with dibutyltin(IV) occurs through the terminal amino group, carboxylate oxygen and the amide nitrogen atoms. The concentration distribution of the complexes in solution was evaluated.

Keywords

Equilibrium studies; Dibutyltin(IV) complexes; Amino acid; Peptide.

Introduction

Organotin compounds R_nSnX_{4-n} exhibit a variety of biological effects depending on the number n, the type of organic groups R bound to tin and the ligand X^-. Following the discovery of the antimour activity of platinum complexes[1], cis-platin found extensive clinical application in a large number of tumours, being particularly potent in the treatment of testicular tumours, ovarian carcinomas and lung cancers[2-4], but has the major disadvantage of exhibiting severe side effects which includes nephrotoxicity, nausea and vomiting, myelosuppression[5], ototoxicity, and decrease in serum electrolytes. These side effects have encouraged the search for organotin compounds as possible candidates for antitumour agents and to identify compounds containing active antitumour organotin moieties $R_nSn^{(4-n)+}$ (with respect to n and R) by antileukemia screaning tests.

Among organotin, the dialkyl derivatives exhibit a greater antitumour activity than the corresponding mono-, tri- and tetraalkyl derivatives[6-9]. In vitro the relative activity of dialkyltins increases from dimethyls to dibutyls and then decreases to the higher dialkyls. In conjunction with our research program directed to study the organotin(IV) complexes[10-13], the present paper aims to study the dibutyltin(IV) complex formation equilibria with amino acids and peptides with the hope that such types of coordinating ligands might possess favorable properties, possibly as carriers in body fluids.

Experimental

Materials and Reagents:

Dibutyltin(IV) chloride was received from Merck Chem. Co. The ligands (L) used were glycine, alanine, proline, valine, β-phenylalanine, S-methylcysteine, hydroxyproline, iso-leucine, threonine, methionine, methylamine, imidazole, 2-amino-n-butyric acid, glutamic acid, histidine, histamine.2HCl, lysine.HCl, ornithine.HCl, aspartic acid, penicillamine, mercaptoethylamine.HCl, mercaptopropionic acid, cysteine, glutathione, glycinamide.HCl, glycylglycine, glycylalanine, glycylvaline, glycylleucine and leucylalanine. These materials were supplied by Fluka Chem. Co. Solutions of methylamine, imidazole and histidine were prepared in the protonated form by dissolving in equimolar HNO_3 solutions. Carbonate-free sodium hydroxide stock solutions were prepared by diluting the contents of BDH concentrated volumetric solution vials. These solutions were systematically checked by titration against potassium hydrogen phthalate. Dibutyltin(IV) chloride (DBT) solutions were prepared in dioxane. The other solutions were prepared in deionized water.

Procedure and Measuring Techniques:

Potentiometric titrations were carried out using a Metrohm 686 titroprocessor equipped with a 665 dosimat (Switzerland-Herisaue). The NBS buffer solutions[14] were used for calibration. The protonation constants of the ligands were determined by titrating 40 ml of ligand solution (2.5×10^{-3} M). The hydrolysis constants of dibutyltin(IV) were determined by titrating 40 ml of dibutyltin solution with concentrations 2.5×10^{-3} M and 1.25×10^{-3} M. The formation constants of dibutyltin(IV) complexes were determined by titrating 40 ml of solution containing the ligand (2.5×10^{-3} M) and dibutyltin(IV) with concentrations 1.25×10^{-3} M and 6.25×10^{-4} M. The ionic strength was adjusted to 0.1 M by $NaNO_3$. The titrations were performed in a special vessel described previously[15] at 25°C in a purified N_2 atmosphere. pK_w in dioxane-water solutions was determined as described previously[16]. For this purpose various amounts of standard NaOH solution were added to a solution containing 0.10 M $NaNO_3$. The [H] was calculated from the amount of base added. The product of [OH] and [H] was taken. The mean values obtained in this way for the log concentration product are $\log K_w$ = 16.21and 16.90 for 75% and 85% dioxane-water solutions. These values are in fair agreement with that previously determined[16] in 70% dioxane, as amounting to $\log K_w$ = 16.0.

The species formed in the systems studied were characterized by the general equilibrium processes (1) while the formation constants for these generalized species are given by Eq. (2).

$$p(M) + q(L) + r(H) \rightleftharpoons (M)_p(L)_q(H)_r \qquad (1)$$

$$\beta_{pqr} = \frac{[(M)_p(L)_q(H)_r]}{[M]^p[L]^q[H]^r} \quad (2)$$

(Charges are omitted for simplicity; M and L denote Bu_2Sn^{2+} and fully deprotonated ligand form respectively)

The calculations were performed using the computer program[17] MINIQUAD-75 loaded on an IBM-486 computer. The stoichiometries and stability constants of the complexes formed were determined by trying various possible composition models for the system studied. The model selected gave the best statistical fit and was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals, as described elsewhere[17]. The fitted model was tested by comparing the experimental titration data points and the theoretical curve calculated from the values of acid dissociation constant of the ligand and formation constants of the corresponding complexes. Table 1, lists the stability constants together with their standard deviations and the sum of the square of residuals as obtained from the program MINIQUAD-75. The Concentration distribution diagrams were obtained using the program SPECIES[18].

Table 1. Formation constants of $Bu_2Sn(IV)$ Comlexes Involving Amino Acids and Peptides.

System	l	p	q[a]	logβ[b]	S[c]
$Bu_2Sn(IV)$	1	0	-1	-3.41(0.01)	1.2E-7
	1	0	-2	-7.84(0.01)	
	1	0	-3	-16.19(0.02)	
$Bu_2Sn(IV)$[d]	1	0	-1	-3.24(0.02)	6.1E-9
	1	0	-2	-7.17(0.01)	
	1	0	-3	-14.34(0.03)	
Glycine	0	1	1	9.82(0.01)	2.2E-7
	1	1	0	11.11(0.07)	1.1E-7
	1	2	0	18.23(0.07)	
Alanine	0	1	1	10.06(0.01)	1.3E-7
	1	1	0	10.65(0.05)	5.9E-8
	1	2	0	17.74(0.07)	
Proline	0	1	1	10.69(0.01)	2.0E-7
	1	1	0	11.72(0.06)	4.2E-8
	1	2	0	19.72(0.08)	
Valine	0	1	1	9.83(0.00)	2.1E-7
	1	1	0	10.96(0.04)	1.2E-8
	1	2	0	18.10(0.05)	

Table 1. continued

β-Phenylalamine	0	1	1	9.21(0.00)	6.3E-8
	1	1	0	10.92(0.07)	1.4E-7
	1	2	0	17.27(0.06)	
S-Methylcysteine	0	1	1	9.08(0.00)	2.0E-7
	1	1	0	9.94(0.06)	2.7E-8
	1	2	0	16.64(0.07)	
iso-Leucine	0	1	1	9.79(0.00)	1.7E-8
	1	1	0	11.71(0.05)	1.8E-7
	1	2	0	18.45(0.06)	
2-Amino-n-butric acid	0	1	1	9.86(0.00)	3.5E-8
	1	1	0	11.82(0.08)	1.9E-7
	1	2	0	18.87(0.06)	
Threonine	0	1	1	9.39(0.00)	3.9E-8
	1	1	0	10.65(0.06)	1.1E-7
	1	2	0	17.33(0.05)	
Methionine	0	1	1	9.34(0.00)	1.9E-8
	1	1	0	11.00(0.05)	2.5E-8
	1	2	0	17.82(0.04)	
Serine	0	1	1	9.38(0.00)	2.8E-8
	1	1	0	10.82(0.06)	1.3E-7
	1	2	0	17.60(0.05)	
Hydroxyproline	0	1	1	9.89(0.01)	5.3E-8
	1	1	0	11.36(0.08)	1.7E-7
	1	2	0	18.81(0.06)	
Mathylamine	0	1	1	10.08(0.01)	1.0E-7
	1	1	0	10.98(0.10)	9.2E-8
	1	2	0	18.31(0.14)	
Histidine	0	1	1	9.66(0.01)	2.1E-7
	0	1	2	15.29(0.02)	
	1	1	0	10.61(0.06)	2.4E-8
	1	1	1	16.22(0.03)	
Histamine	0	1	1	9.50(0.00)	8.3E-9
	0	1	2	14.90(0.01)	
	1	1	0	10.44(0.09)	5.6E-8
	1	1	1	16.19(0.04)	
Ornithine	0	1	1	10.68(0.00)	7.3E-8
	0	1	2	19.47(0.01)	
	1	1	0	15.690.04)	1.3E-7
	1	1	1	21.18(0.11)	
Lysine	0	1	1	10.42(0.00)	2.5E-9
	0	1	2	19.60(0.00)	
	1	1	0	16.16(0.04)	7.5E-8
	1	1	1	21.56(0.11)	

Table 1. continued

Aspartic acid	0	1	1	10.26(0.01)	3.8E-8
	0	1	2	15.43(0.01)	
	1	1	0	11.06(0.09)	5.2E-8
	1	1	1	16.23(0.06)	
Glutamic acid	0	1	1	10.14(0.01)	5.7E-8
	0	1	2	15.85(0.01)	
	1	1	0	11.03(0.09)	3.8E-8
	1	1	1	16.64(0.04)	
Mercaptoethylamine[d]	0	1	1	12.46(0.01)	2.1E-7
	0	1	2	20.82(0.01)	
	1	1	0	24.88(0.05)	1.6E-7
	1	2	0	31.45(0.06)	
	1	1	1	29.12(0.06)	
Mercaptopropionic acid[d]	0	1	1	12.37(0.01)	7.8E-8
	0	1	2	19.07(0.01)	
	1	1	0	24.27(0.04)	1.4E-7
	1	2	0	30.71(0.05)	
Penicillamine[d]	0	1	1	12.41(0.01)	1.2E-7
	0	1	2	20.73(0.02)	
	1	1	0	23.32(0.06)	9.8E-8
	1	2	0	29.78(0.06)	
	1	1	1	29.30(0.06)	
Glutathione[d]	0	1	1	10.89(0.02)	4.8E-7
	0	1	2	20.13(0.02)	
	0	1	3	25.27(0.05)	
	1	1	0	20.31(0.07)	1.4E-7
	1	2	0	25.13(0.08)	
	1	1	1	25.82(0.09)	
Cysteine[d]	0	1	1	12.24(0.01)	3.8E-7
	0	1	2	21.22(0.03)	
	1	1	0	16.89(0.22)	1.3E-7
	1	2	0	25.13(0.19)	
	1	1	1	22.40(0.15)	
Glycinamide	0	1	1	7.85(0.00)	3.6E-9
	1	1	0	8.84(0.07)	8.8E-8
	1	1	-1	3.53(0.08)	
Glycylglycine	0	1	1	7.81(0.01)	3.3E-9
	1	1	0	10.19(0.07)	1.9E-7
	1	1	-1	4.19(0.07)	
Glycylalanine	0	1	1	8.04(0.00)	2.2E-9
	1	1	0	9.96(0.05)	8.7E-8
	1	1	-1	3.74(0.06)	
Glycylvaline	0	1	1	8.35(0.01)	2.1E-8
	1	1	0	10.52(0.06)	5.0E-8
	1	1	-1	4.21(0.07)	

Table 1. continued

Glycylleucine	0	1	1	8.29(0.01)	1.4E-8
	1	1	0	11.84(0.07)	1.2E-7
	1	1	-1	5.69(0.05)	
Leucylalanine	0	1	1	8.08(0.00)	2.8E-9
	1	1	0	13.04(0.10)	3.2E-7
	1	1	-1	5.89(0.07)	

[a]l, p and q are the stoichiometric coefficient corresponding to $Bu_2Sn(IV)$, amino acid or peptide and H^+ respectively [b]Standard deviations are given in parentheses [c]Sum of square of residuals and [d]in 75% (V/V) dioxane-water solution; and 85% for other systems.

Results and Discussion

The effective dielectric constants in proteins[19,20] or active-site cavities of enzymes[21] are reduced compared to that in pure water. Estimates for the dielectric constants in such locations may reach the value ≈25[19-21]. Hence by studing the dibutyltin(IV) complex formation equilibria in 75% dioxane-water solutions one may expect to simulate to some degree the situation in the active-site cavities[22].

The acid-base equilibria of the ligands and those of their complex formation were investigated in 85% dioxane-water solutions, except those of sulphur ligands as penicillamine, mercaptoethylamine, mercaptopropionic acid cysteine and glutathione where 75% dioxane-water solution was used as a solvent. The pK_a values obtained, Table 1, are higher than those reported in water[23]. This may be due to the increased basicity of the ligand donor groups when one goes from pure water to dioxane water-solutions.

The hydrolysis of the dimethyl- and diethyltin(IV) ions were investigated by Arena et al[24] and Buzas et al[25]. The hydrolysis of the dibutyltin(IV) was characterized by fitting the potentiometric data to various acid-base models. The fitted model was found to be consistent with the formation of $M(OH)$, $M(OH)_2$ and $M(OH)_3$ species. This model resembels that obtained in the diethyltin(IV) system[24]. The polymeric species as $[M(OH)]_2$ and $M_2(OH)_3$ reported by Arena et al[24] were rejected. This may be explained on the premise that the concentration range of dibutyltin(IV) used is low to allow the formation of polymeric species. The concentration distribution diagram for Bu_2Sn-OH system is shown in Figure 1. The concentration of the mono- hydroxo species increases with increasing pH attaining a maximum of 62.0% at pH = 3.90. Further increase in pH is accompanied by a decrease in the mono-hydroxo species and an increase in the dihydroxo species reaching the maximum concentration of 97.8% at pH = 6.40. The tri-hydroxo species starts to form at pH = 6.10 and attains a maximum concentration of 100% at pH = 10.60.

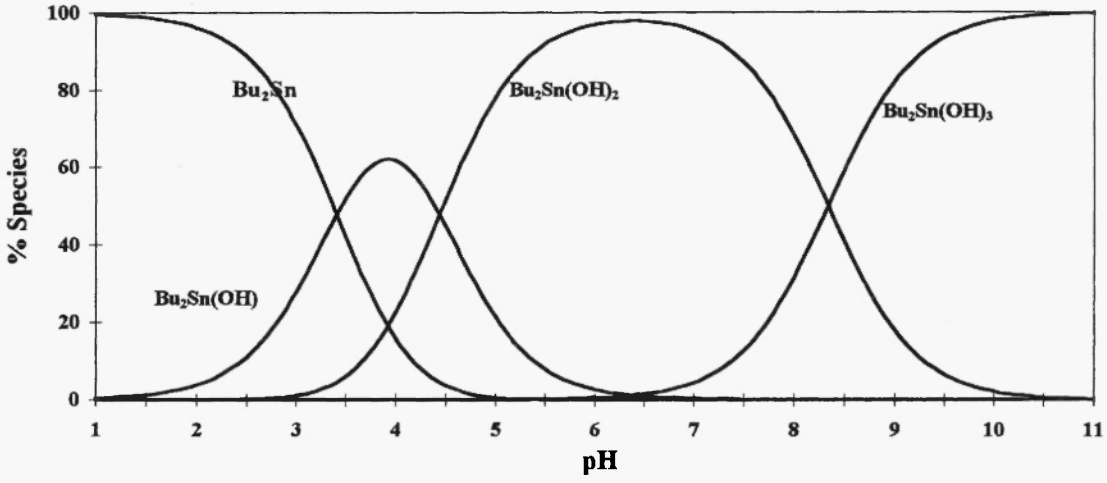


Fig. (1) Concentration distribution of various species as a function of pH in the $Bu_2Sn(OH)$ system.

The potentiometric titration curve of dibutyltin(IV) complex is lowered from the corresponding ligand curve. This corresponds to the formation of a complex species through a release of hydrogen ion. The potentiometric data of the amino acid complexes were fitted with models in which complex-formation of the hydroxo complexes was taken into consideration. The accepted model is consisting of 1:1 and 1:2 (organotin : ligand) complexes. The titration data were also fitted with the model composed of the species 110, 11-1 and 11-2 as assumed by Arena et al[24]. The data fits, however, were very poor and indicated that the hydroxo complexes are weak complex-formation partners. This may be due their poor solubility with the butyltin derivative. The formation of 1:2 complex is supported with the previous investigations on dimethyltin complexes with amino acids[26], diethyltin(IV) complexes with 8-hydroxyquinoline[27] and diorganotin(IV) complexes with N-acetylamino acids[28].

The potentiometric data of serine and threonine complexes may be fitted assuming that the binding of these ligands proceeds in a glycine-like mode and that the alcoholato group is not ionized[29]. The presumption of the participation of the thioether group[30] in the coordination of S-methylcysteine and methionine with $Bu_2Sn(IV)$ seems to be evidently unfavoured, because the stability constants of their complexes are in fair agreement with those of α-amino acids.

The amino acids lysine, ornithine, histidine, aspartic acid, glutamic acid, mercaptoethylamine, cysteine, penicillamine and glutathione form protonated and deprotonated ternary complexes. The acid dissociation constants of the protonated complexes are given by the Eq. (3)[31].

$$pK^{(H)}_{(Bu_2Sn)(L)(H)} = \log K^{(Bu_2Sn)}_{(Bu_2Sn)(L)(H)} - \log K^{(Bu_2Sn)}_{(Bu_2Sn)(L)} \qquad (3)$$

The acid dissociation constant of the protonated ternary complex with histidine is 5.61, which compare favourably with the acid dissociation constant of the protonated imidazole nitrogen (5.75), revealing that histidine binds to $Bu_2Sn(IV)$ in a glycine-like mode, while the imidazole nitrogen atom remains free. The acid dissociation constants of the protonated complexes amounted to 5.17 for aspartic acid and 5.61 for glutamic acid. These values are compared favourably with the acid dissociation constant of the protonated ω-carboxylate group for aspartic acid (5.17) and glutamic acid (5.71), revealing that aspartic acid and glutamic acid bind to $Bu_2Sn(IV)$ in a glycine-like mode, while the ω-carboxylate group remains free. The acid dissociation constants of the protonated complexes amounted to 5.20 for lysine and 5.26 for ornithine. These values are lower than the pK_a of both α-amino and ω-amino group. This indicates that the two amino groups are taking part in the complex formation. This finding is supported by the observation that the stability constant of their 1:1 complexes are higher than those of α-amino acids (N,O donor set). The acid dissociation constants of the protonated complexes obtained with glutathione, cysteine and penicillamine were evaluated as amounting to 5.51, 5.51 and 5.98 respectively. The microscopic acid dissociation constants of -SH and $-NH_3^+$ groups of glutathione, cysteine and penicillamine were previously reported[32,33], as amounting to 8.87 and 9.48 for glutathione, 9.74 and 10.09 for cysteine and 9.70 and 10.29 for penicillamine. Clearly the pK^H values obtained in the present study are lower than the above microscopic acid dissociation constants, showing that the NH_3^+ and -SH groups most likely take part in complex formation. This is supported by observing that the stability constants values of these complexes are in between the stability constant values of complexes with mercaptopropionic acid (S,O donor set) and mercaptoethylamine (N,S donor set).

It is known that a relationship exists between the dissociation constant of a series of structurally related ligands and the stability constants of their 1:1 complexes with a given metal ion species. Such a relationship can be used to estimate the stability constants of metal complexes of closely related substances if their pK_a and any of K_{ML} values are known. Figure 2, demonstrates such a relationship for the dibutyltin(IV) complexes of amino acids.

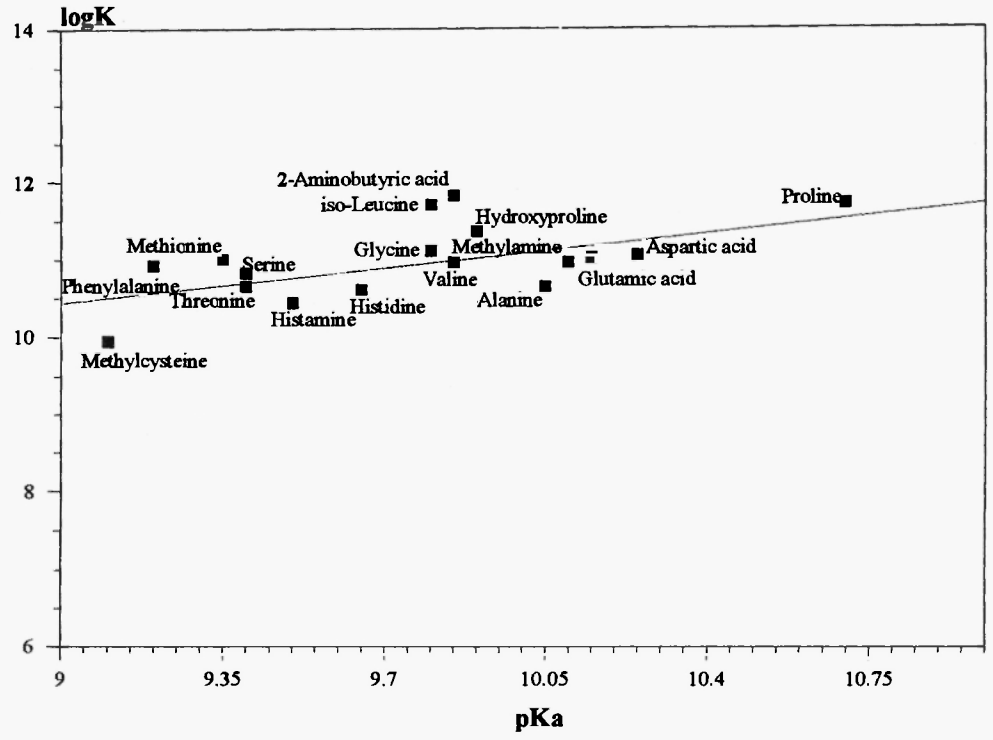
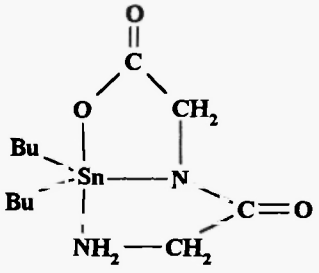


Fig. (2) Correlation of formation constant of Bu_2Sn-amino acid with acid dissociation constant of the amino acid.

Complex Formation Equilibria with Peptides

It was shown by structural studies that the complex formation between $Bu_2Sn(IV)$ and glycylglycine[34] results in a chelate involving the terminal amino moiety, carboxylate oxygen and the amide nitrogen atoms.



In the present study, the best fit of the titration data were obtained when the complexes $(Bu_2Sn)L$ and $(Bu_2Sn)LH_{-1}$ were considered and the results obtained can be explained by the following equilibria

$$Bu_2Sn^{2+} + L^- \overset{K_1}{\rightleftharpoons} (Bu_2Sn)L^+ \quad (4)$$

$$(Bu_2Sn)L^+ \overset{K_a}{\rightleftharpoons} [(Bu_2Sn)LH_{-1}] + H^+ \quad (5)$$

The pK_a of of the ionized amide group is calculated by the relationship[31]:

$$pK_a = \log\beta_{(Bu_2Sn)L^+} - \log\beta_{(Bu_2Sn)LH_{-1}}$$

The values thus obtained are in the range 5.31-7.15. The relative magnitudes of the pK_a values have interesting biological implications. Under normal physiological conditions (pH ca. 7.4) the peptides would coordinate in the entirely deprotonated form. The slight difference in the side chain of the peptide produces dramatic differences in their behaviour toward the $Bu_2Sn(IV)$ species.

Estimation of the concentration distribution of various species in solution provides a useful picture of organotin(IV) binding in the biological system. In all the species distributions the concentration of the complex increases with increasing pH; thus making the complex formation more favoured in the physiological pH range. Distribution curves for dibutyltin(IV) complexes with glycine and with glycylglycine are given in Figures (3,4). Formation of 1:1 glycine complex begins at pH = 1.0, and with increasing pH its concentration reaches 78.6%. Further increase of pH leads to an increase of the 1:2 complex concentration, predominating with formation degree of 3.3% at pH ≈ 6.8. The concentration distribution diagram for all $Bu_2Sn(IV)$-peptide systems in the present study shows the same qualitative features namely a progressive increase of $Bu_2Sn(IV)L$ complex concentration with pH reaching a maximum of 88.2% at pH ≈ 3.8. Further increase of pH, the $Bu_2Sn(IV)LH_{-1}$ concentration increases accompanied by a corresponding decrease in the concentration of free $Bu_2Sn(IV)$ and $Bu_2Sn(IV)L$ species. The $Bu_2Sn(IV)LH_{-1}$ concentration reaches a limiting value of 43.0% at pH ≈ 7.0.

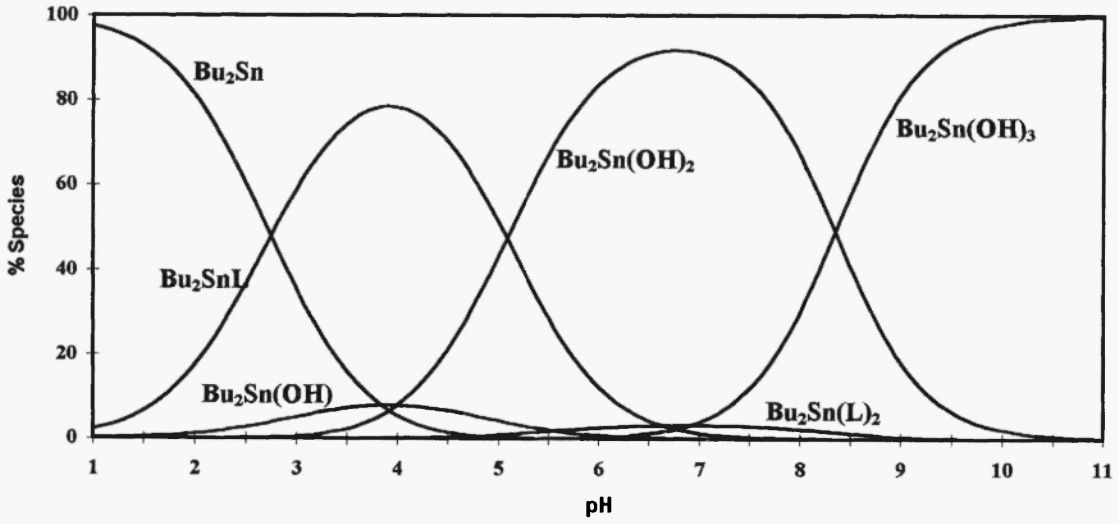


Fig. (3) Concentration distribution of various species as a function of pH in the Bu_2Sn-glycine system.

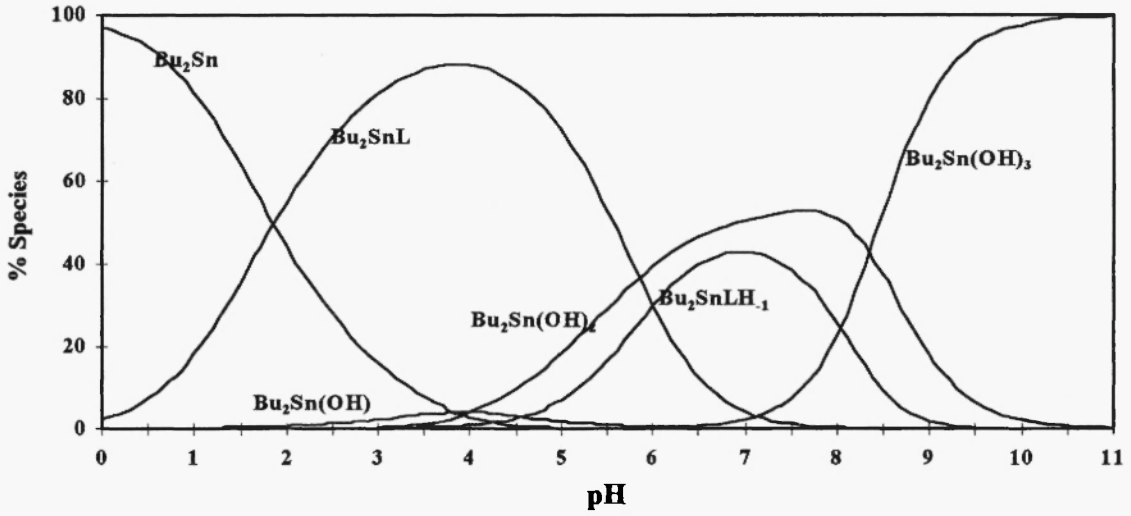


Fig. (4) Concentration distribution of various species as a function of pH in the Bu_2Snglycylglycine system.

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