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Spectrophotometric Studies on Tri-, Di- and Monobutyltin(IV) Oxinates in Different Solvents

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The complex formation of tri-, di- and monobutyltin(IV) chloride with oxine (oxine = 8-quinolinol) was studied spectrophotometrically in methanol, chloroform and hexane (the last two after extraction with buffer pH 9.0) by the molar ratio method. The compositions of the chelates formed were found to some extent to be solvent and molar ratio (C_M/C_L) dependent. The complex formation constants were calculated.

Introduction

Oxine has previously been found to form complexes with tri-, di- and monobutyltin chloride, with absorbance maxima at λ_1 = 258 nm and λ_2 = 368–380 nm. Structural aspects of the organotin oxinates have been examined by several workers [1–7], but general studies of the systems in solution have only been done to a small extent [3, 8]. The use of these types of complex in high performance liquid chromatography showed the need for closer examination in this field. Studies of the absorption of visible and ultraviolet radiation have long been used to obtain information on the composition of a complex in solution.

This paper describes the complex formation in organic solvents between tri-, di- and monobutyltin chloride and oxine. The solvents methanol, chloroform and n-hexane, which have different polarity and solvent properties, were chosen for the present study. (Chloroform and hexane were extracted with a buffer of pH 9.0).

Experimental

Reagents

Chemicals were obtained from the following sources: tri- and dibutyltin chloride from Fluka AG (Switzerland); monobutyltin chloride from ICN Pharmaceuticals; K & K, Rare and Fine Chemicals (New York) and oxine from Merck.

Tri- and monobutyltin chloride were purified by distillation. Dibutyltin dichloride was recrystallized from light petroleum (boiling range 40–60 °C). Oxine was recrystallized from ethanol after sublimation.

Boric Acid Buffer

Boric acid (3.1 g/l, 0.05 *M*) and sodium perchlorate monohydrate (140 g/l, 1.0 *M*) were dissolved in water to 1.0 l solution. pH was adjusted with sodium hydroxide pellets to 9.0.

Apparatus

UV/visible spectra were recorded on a Cary 14 spectrophotometer, while measurements at special wavelengths were taken with a Cary 16 spectrophotometer.

Procedure

The butyltin chlorides and the oxine were dissolved separately in organic solvents. The methanolic solution of monobutyltin trichloride was particularly unstable and was therefore prepared just before use.

With methanol as the solvent various amounts of butyltin chloride were added to a 10 ml volumetric flask, or a separation funnel containing 10 ml of buffer solution when using chloroform and hexane. Appropriate amounts of oxine solution were added in the same way. The total volume of organic solvent was adjusted to 10 ml. When extracting with the buffer solution, the separation funnel was shaken vigorously for 2 min. After separation the absorbance of the layer containing the complex (usually organic) was measured in 1 cm cells. The concentrations of the ligand when measuring the absorbances against molar ratios were $2.00\cdot10^{-5}$ and $3.00\cdot10^{-4}$ *M* at λ_1 = 258 nm and λ_2 = 370 nm, respectively. When measuring the molar absorptivities in excess of ligand the concentrations were five and ten times higher.

UV/visible spectra of all the systems for different molar ratios were taken. It was also examined whether the wavelength of maximum absorbance was molar ratio dependent. Generally the UV spectra were very similar for different butyltin oxinates.

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The Molar Ratio Method

This work is based on the use of the molar ratio method [9, 10]. The ligand concentration was kept constant while changing the metal concentration. Measurements were taken at the wavelength at the absorbance maximum of the complex.

The molar absorptivities were measured in the presence of an excess of oxine. In some cases more than one species was formed with the same solvent. Usually the absorptivity of the 1:1 complex if formed could be determined from maximum absorbance of the molar plot, A_{max}. Otherwise values obtained with other solvents for the same complexes were used. Calculations showed that, except for dibutyltin in methanol and tributyltin in chloroform, the error of assuming that the measured absorptivity in excess of ligand belonged to the complex of highest ligand content formed, was less than one percent. The error for dibutyltin in methanol was calculated to be 2–4 percent. In the case of tributyltin in chloroform the degree of complex formation was too small for measurement of the molar absorptivity in excess of oxine.

The absorbance measured at a given wavelength is

$$A_x = \Sigma(\epsilon_n \cdot [Bu_xSnCl_{(4-x-n)}Ox_n]) + \epsilon_L \cdot [HOx] + A_{bl}$$

where ϵ_n is the molar absorptivity of the complex $Bu_xSnCl_{(4-x-n)}Ox_n$ (Ox = oxinate), ϵ_L the absorptivity of oxine and A_{bl} the absorbance of the blank solution containing neither the butyltin chloride nor the oxine, at the wavelength of measurement (butyltin chlorides have no absorbance at these wavelengths). The sample path length is 1 cm.

In general the equation for complex formation at equilibrium is

$$m \cdot M + n \cdot L \rightleftharpoons M_mL_n$$

Complexes between butyltin chlorides and oxine were assumed to contain only one organometallic group and to be monomeric in solution. The expression for butyltin oxines is then

$$n \cdot HOx + Bu_xSnCl_{(4-x)} \rightleftharpoons Bu_xSnCl_{(4-x-n)}Ox_n + n \cdot HCl$$

The complex formation constants of butyltin oxines given in this paper are calculated according to the equation

$$K_n = \frac{[Bu_xSnCl_{(4-x-n)}Ox_n]}{[Bu_xSnCl_{(4-x)}]\,[HO_x]^n}$$

where the index n in K_n gives the number of oxine groups bounded to butyltin. It is in fact the oxinate ion that reacts with the butyltin compound; the dissociation constant of oxine and the butyltin chloride have to be parts of the given formation constant of the complex. The concentration of HCl is also left out of the equation of the formation constant which is not completely correct. When shaking with a buffer solution the by-products H^+ and Cl^- from the complex formation were extracted away from the organic phase into the buffer solution. This simplification makes the formation constant solvent- (and to some extent) buffer-dependent. When shaking with a buffer this expression only holds when the metal, ligand and complexes formed almost entirely are found in the organic phase. Tri- and dibutyltin compounds are sparingly soluble in water [11, 12], while monobutyltin chloride was found to be moderately soluble. More than 99% of oxine is in the chloroform phase when extracted with buffer at pH 9.0 [13, 14]. The distribution of the complexes were checked by measuring the absorbance of the buffer solution. Except for monobutyltin oxine in the hexane/buffer system, no extra absorption of the aqueous phase could be measured.

By making these simplifications the formation constants can be calculated from the molar ratio curves. Closer examinations of the composition of the butyltin oxines formed in solutions are then possible. The formation constants giving the least standard deviation were calculated by a computer program. The standard deviation was calculated from the equation

$$s = \sqrt{\Sigma(A_x - A_o)^2/(M - N)}$$

where A_x and A_o represents the measured and calculated absorbance respectively, N the total number of measurements in the set and M is the number of formation constants K_n different from zero.

The molar absorptivities were also calculated from the molar ratio plots, which gave alternative values to those measured in excess of oxine.

Results and Discussion

Composition of the Buffer

A buffer system with pH 9.0 containing diethanolamine and a very high concentration of sodium perchlorate has been recommended [11] for spectrophotometric determination of organotin compounds with dithizone or 3-hydroxyflavone as chelating agents. Experiments showed however that this buffer system was difficult to handle, and not all systems gave reproducible results.

A buffer containing boric acid at pH 9.0 proved to be more suitable. Preliminary experiments indicated the necessity of high ionic strength, and 1.0 *M* sodium perchlorate proved to be suitable. The results given in this paper were obtained with the boric acid buffer system. The degrees of complexation were in no case found to be higher by using the diethanolamine buffer.

TABLE I. Molar Absorptivities and Complex Formation Constants of Butyltin Oxinates Determined by the Molar Ratio Method.[a]

Organotin Chloride	Solvent	λ_{max}	ϵ_1	ϵ_2	ϵ_3	ϵ_4	K_1	K_2	K_3	K_4	s^b
			(10^3 mol^{-1} cm^{-1})								
Bu_3SnCl	MeOH										
Bu_3SnCl	$CHCl_3$	376	2.82				$1.57 \cdot 10^3$				0.010
Bu_3SnCl	Hexane	368	2.77				$5.2 \cdot 10^4$				0.019
Bu_2SnCl_2	MeOH	258(254)	33.6	51.6	96.3		$2.8 \cdot 10^5$	$6 \cdot 10^8$	$5 \cdot 10^{14}$		0.016
		368	1.97	5.23	7.92		$1.4 \cdot 10^5$	$6 \cdot 10^8$	$4 \cdot 10^{12}$		0.008
Bu_2SnCl_2	$CHCl_3$	258		57.0				$2 \cdot 10^{11}$			0.009
		379		5.23				$2 \cdot 10^{11}$			0.007
Bu_2SnCl_2	Hexane	258		60.1				$6 \cdot 10^{11}$			0.022
		387		5.29				$4 \cdot 10^{11}$			0.011
$BuSnCl_3$	MeOH	258	33.6	51.6	96.3	136.3	$5.3 \cdot 10^6$	$1 \cdot 10^5$	$1 \cdot 10^{11}$	$1 \cdot 10^{22}$	0.053
		258		66.4				$1 \cdot 10^{12}$			0.019
		376	2.18	5.23	7.95	9.16	$2.4 \cdot 10^6$	$1 \cdot 10^5$	$2 \cdot 10^{11}$	$3 \cdot 10^{19}$	0.014
$BuSnCl_3$	$CHCl_3$	258(260)		56.0				$5 \cdot 10^{10}$			0.034
		380		5.41				$3 \cdot 10^8$			0.036

[a] ϵ_1, ϵ_2, ϵ_3 and ϵ_4 are the molar absorptivities of 1:1, 1:2, 1:3 and 1:4 complexes, respectively, and K_1, K_2, K_3 and K_4 their respective complex formation constants. [b] Standard deviation (see the text for further information).

Tributyltin Chloride

Spectrophotometric measurements of the complexes formed between tributyltin chloride and oxine were only made with chloroform and hexane as solvents, at about 370 nm. Investigation of Bu_3SnOx in methanol by the molar ratio method has no value since the absorption bands are nearly identical with those of oxine alone [4].

From the molar ratio curves tributyltin chloride was found to form a 1:1 complex with oxine, which is in accordance with the results generally observed for triorganotin compounds [3, 4] (see Table I).

Measurement of the molar absorptivity in excess of ligand has only been possible in hexane. Calculations of the value in chloroform from the molar ratio plot give about the same values in hexane and chloroform, which is equal to that of Ox^- in water (pH = 12) [15]. The absorptivity as well as the wavelength of maximum absorption could be expected to be lower in chloroform because of a lesser degree of chelate structure [3, 4, 16]. Disagreement about whether trialkyltin oxinates are chelates at all does however exist [8].

Dibutyltin Dichloride

A 1:2 complex of the form Bu_2SnOx_2 seemed to be formed when chloroform and hexane were used as solvents.

Rather high absorptivities were measured at both wavelengths in methanol, which may indicate the formation of a 1:3 complex between dibutyltin dichloride and oxine. Good correspondence between experimental and calculated molar ratio curves is only achieved when complexes having the molar ratios 1:3, 1:2 and 1:1 are assumed to be formed (see Fig. 1). As can be seen from Table I the formation constant K_3 differs with a factor of up to 100 for the two wavelengths. This value is however based on very few measurements, $Bu_2SnClOx$ being the main complex in methanol solution for most molar ratios.

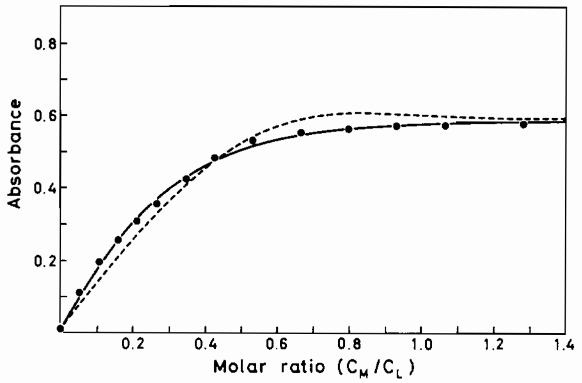

Fig. 1. Molar ratio plot for dibutyltin dichloride in methanol at the wavelength 368 nm. ● measured values. —— calculated curve when K_1, K_2 and K_3 are set different from zero. – – – calculated curve when only K_1 and K_2 are set different from zero ($K_3 = 0$).

The absorptivity at 368 nm is equal to the value found [9] for a synthetic product in methanol, given the formula Bu_2SnOx_2. Determination of the absorptivity of synthetic dibutyltin dioxinate however gave the same value in all three solvents.

Neutrality of the complex and six-coordination of the tin atom are satisfied by two oxinate groups. A higher coordination number of tin, 7 or 8, is known, for instance for $BuSnOx_3$ [5, 7]. The possibility of enlarging the coordination number from six to seven does however decrease with increasing number of alkyl groups bounded to the tin atom [17].

A neutral complex of the form $Bu_2SnOx_2 \cdot HOx$ (*I*) or $Bu_2SnClOx \cdot 2HOx$ (*II*) or an oligomer complex seem to be the most obvious alternatives for a 1:3 complex between dibutyltin dichloride and oxine. Complexes of the form $MOx_n \cdot HOx$ (where n is the charge of the metal) are well known [14]. $Bu_2SnClOx \cdot H_2O$ is found to have a mol weight eight times that of the monomer [18]. In a methanolic solution containing a complex of form *I* or *II*, in excess of oxine, MeOH seems to be the only possible bridging species.

$Bu_2SnClOx$ is formed for higher concentrations of dibutyltin dichloride, which is in agreement with the results obtained by Huber [18].

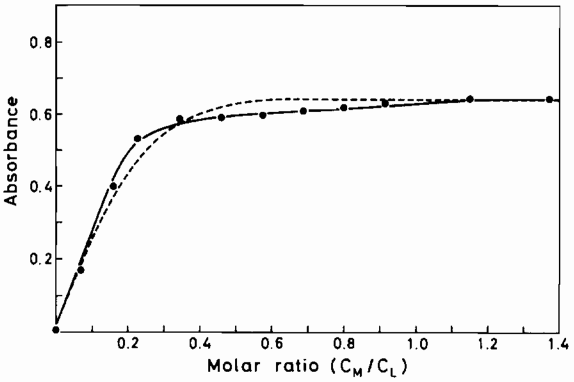

Fig. 2. Molar ratio plot for monobutyltin trichloride in methanol at the wavelength 376 nm. ● measured values. —— calculated curve when K_1, K_2, K_3 and K_4 are set different from zero. – – – calculated curve when only K_1, K_2 and K_3 are set different from zero ($K_4 = 0$).

Monobutyltin Trichloride

$BuSnClOx_2$ seems to be the main complex formed when using chloroform as solvent. The absorption measured at 258 nm decreases with high concentration of monobutyltin trichloride. Maximum absorption is also reached very slowly at 380 nm. This may indicate the formation of a 1:1 complex. The formation constant K_1 was however calculated to be about 10 for both wavelengths, which indicates that the contribution of absorption from $BuSnCl_2Ox$ is insignificant.

The reproducibility of the measurements were poorer than for the other systems. The irregularities may be due to the higher solubility of monobutyltin in the aqueous phase.

When a mixture of monobutyltin trichloride and oxine in hexane is extracted with a buffer solution, a complex is formed in the aqueous phase. The slope of the molar ratio curve was found to be $1.21 \cdot 10^4$ for molar ratios less than 0.3 (λ_1 = 258 nm), which may imply the formation of a 1:1 complex. An ion association complex is probably formed. The necessity of high ionic strength (1.0 *M* sodium perchlorate) supports this assumption. A complex with the composition $(BuSnXOx \cdot nH_2O)^+ClO_4^-$. (X = OH or Cl, n = 1 or 2) may be formed. Determination of the formation constants however have not been possible.

The rather high molar absorptivities measured for the monobutyltin complex in methanol indicate the formation of a 1:4 complex (see Table I). The same discussion applies to mono- as to the dibutyltin oxinates. Steric factors play however a more significant part. A complex of the form $BuSnCl_yOx_{(3-y)} \cdot (y + 1)HOx$ (y = 0, 1, 2) seems reasonable, but the possibility of condensated complexes must not be excluded.

Good correspondence was achieved between experimental and calculated molar ratio curves at 376 nm when all four species are assumed to be formed, the 1:4 and 1:1 being the dominant ones (see Fig. 2). The situation is however different for measurements at 258 nm. A 1:2 complex may seem to be the only existing complex in the methanol solution, having an absorptivity $\epsilon_2 = 6.64 \cdot 10^4$. Deviations from the experimental curve do exist however. The high value of ϵ_2 does not seem reasonable.

Conclusion

The same complexes are formed in chloroform and hexane for tri- and dibutyltin. Monobutyltin does however form an aqueous soluble complex when mixed in hexane, which is not the case in chloroform.

Closer examination of the methanol and hexane/buffer systems (monobutyltin trichloride) are necessary before more exact structures of these complexes can be predicted.

The degree of complex formation was found to be highest in hexane and lowest in methanol for the tri- and dibutyltin complexes, the difference being largest for the tributyltin oxinate. The opposite is however found for monobutyltin oxinates, which can be explained by higher polarity of the complexes, and less hydrophobic groups.

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