ADSORPTION BEHAVIOUR AND QSPR STUDIES OF ORGANOTIN COMPOUNDS ON ESTUARINE SEDIMENT

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ABSTRACT

The adsorption behaviour of eight organotin species and Sn^{++} ($SnCl_4$) on estuarine sediments has been reported for the first time. It was found that the adsorption of organotins varies greatly with molecular structure. The order of adsorption coefficient k is Sn^{++} > mono- > di- > tri-organotins. Correlations of log k with eight different structural parameters show that the electronic properties of the Sn atom is the principal factor controlling the adsorption behaviour of organotins. The adsorption mechanism of organotins is mainly an ion-exchange process, with little lipophilic partitioning.

INTRODUCTION

Organotin compounds which are represented by formula R_mSnX_{4-m} (R are groups attached to Sn with C–Sn bonds, X with non C–Sn bonds) are a series of extensively used organometallic compounds. $RSnX_3$ and R_2SnX_2 are mainly used as thermal stabilizers in PVC products and catalysts in the production of polyurethane foams. R_3SnX are applied as biocides in agriculture, antifouling paint and wood preservation.

In the last 30 years, the production of organotins has risen rapidly, the total world production of organotins being $3.5 \times 10^7 kg.yr^{-1}$ in 1989. It was estimated that about 30 percent would eventually enter into the aquatic environment [1] . There have been many reports of pollution caused by organotins in different aquatic ecosystems, especially in harbors with heavy shipping traffic around the world [2] . Many organotins, especially triorganotins are highly toxic. For example, levels of 1 ng or less of tributyltin is toxic to many aquatic organisms in the laboratory [3] . It is thus necessary to understand the distribution and fate of organotins after they enter the aquatic environment.

Distribution between water and sediment is an important process affecting the fate and ecotoxic effects of organotins. If organotins adsorb on suspended particulate matter and settle to the bottom, they may not be available as toxicants in the aqueous phases. However, they may be more dangerous to benthos. There have been some reports on adsorption behaviour of organotins. Uger [4] studied the adsorption and desorption of tributyltin (TBT) under freshwater and estuarine conditions. The adsorption coefficients of TBT are 110 L / kg for estuarine sediment, and 8200 L / kg for freshwater sediment, respectively. Weber et al. [5,6] studied the effects of ion-strength (0-35‰). pH (6.2-8.2) and concentration of suspended particulate matter(0-1000ppm) on the adsorption behaviour of butyltins and methyltins between artificial seawater and a fulvic acid-coated hydrous ion oxide solid. The adsorption order is mono-> tri-> di-butyltin and mono-> di-> tri-methyltin.

QSAR (Quantitative Structure-Activity Relationship) and QSPR (Quantitative Structure-Property Relationship) approaches have been successfully applied in environmental science for organic compounds to predict the activity (or property) of a "new compound" or to illustrate mechanisms of the studied processes. For organometallic compounds, QSAR studies have just been started. Recently, there have been some reports on QSAR studies on organotins for their toxic effects on different kinds of aquatic organisms [7,8]. However, no work is known on QSPR studies for organotins.

We have studied the adsorption behaviour of eight organotin species and Sn^{++} in a water-sediment system consisting of 90mL artificial seawater (15‰) and 2g estuarine sediment. QSPR studies were carried out between adsorption coefficient and eight physicochemical and topological parameters which included two new molecular connectivity indices $^1X^r$ and $^1X^b$. A multi-parameter model was set up and the adsorption mechanism was explained according to the results of QSPR studies.

EXPERIMENTS

Tributyltin chloride (TBTCl), Dibutyltin chloride (DBTCl$_2$), Monobutyltin chloride (MBTCl$_3$), Trimethyltin chloride (TMTCl), Dimethyltin chloride (DMTCl$_2$), Monomethyltin chloride (MMTCl$_3$), Triphenyltin chloride (TPTCl), Diphenyltin chloried (DPTCl$_2$) were purchased from Alfa and Vertron Chemical Co.. Purity levels of all organotins were 99.9% except DBT (96.5%). All organotins were dissolved in absolute ethanol to make up $1000\mu gSn \cdot L^{-1}$ stock solutions, and stored in a refrigerator (4℃) under darkness. The stock solutions were diluted to suitable concentration before each experiment. SnCl$_4$ was dissolved in 6N HCl, and pH values of the experimental systems must be adjusted to 7.6-8.0 after SnCl$_4$ was added.

The experiments were carried out in 100ml erlenmeyer flasks containing 90mL artificial seawater (15‰) and 2.0g of estuarine sediment (<100mesh). The water-sediment systems was shaken for 2 hours before organotins were added. Seven concentrations were used for each compound, and the experiment of each concentration as well as standard series was replicated twice. Immediately after

organotins were added, the whole system was sealed, and was shaken for 18−24 hours at $21 \pm 1°C$ under darkness. The sediment was then separated from water phase by centrifugation, and the concentrations of organotins in water phase were determined. Concentration of organotins in sediment was determined by subtracting the water content from the initial total content. To allow for the possible loss of organotins ($< 7\%$) adsorbed onto the bottle walls, the standard series were treated under the same condition as the experimental sets. Determination of organotins in water phase was described briefly as follows [9−11] : (1) extraction by 0.1% tropolone−benzene solution; (2) derivatization by Grignard reagents; (3) analysis by GC−MS or GC−AAS techniques.

CALCULATIONS

Eight physicochemical and topological parameters were used in QSPR studies.

Molecular connectivity index (^1X) and valence molecular connectivity index ($^1X^v$): These molecular connectivity indices (MCIs) were calculated from a hydrogen−suppressed graph [12] . ^1X and $^1X^v$ values of organotins were calculated according to the following equations:

$$^1X = \sum (\delta_i \delta_j)^{-\frac{1}{2}} \tag{1}$$

$$^1X^v = \sum (\delta_i^v \delta_j^v)^{-\frac{1}{2}} \tag{2}$$

$$\delta_i^v = (Z^v - h) / (Z - Z^v - 1) \tag{3}$$

where δ is delta value for each atom. It is equal to the number of non−hydrogen atoms attached to the studied atom. δ^v is valence delta value. Z^v, Z and h are the number of valence electrons, atomic number, and the number of hydrogen atoms, respectively.

Radius−corrected MCI ($^1X^r$) and bond−length−corrected MCI ($^1X^b$): Valence molecular connectivity index is the corrected pattern for ^1X to distinguish the contributions of heteroatoms and unsaturation to MCI. However, it has been proved not to be applicable to organometallic compounds [13,14] .Two new MCIs−−$^1X^r$ and $^1X^b$ were used in this study which can be calculated as follows:

$$^1X^r = \sum (\delta_i^r \delta_j^r)^{-\frac{1}{2}} \tag{4}$$

$$\delta^r = r_c / r(Z^v - h) \tag{5}$$

$$^1X^b = \sum b (\delta_i \delta_j)^{-\frac{1}{2}} \tag{6}$$

where r_c and r are covalent radii of the C atom and the atom studied, respectively. For Sn atom, $r_c / r = 0.77 / 1.40 = 0.55$. b is bond−length ratio of the chemical bond studied to C−C bond. For C−Sn, $b = 2.17 / 1.54 = 1.41$. The meaning of Z, Z^v and h is the same as above.

Electronic parameters Hammett constant (σ^*) and Taft constant (σ^*): σ^* and σ^* values for organotins are the sum of σ values of the substituent groups attached to the Sn atom [15] .

Lipophilic parameters total surface area of a molecule (TSA) and Leo fragment constant (π): TSA and π values for organotins are the sum of those of the substituent groups attached to the Sn atom [15,16]

RESULTS AND DISCUSSION

Physicochemical parameters of the sediment.Physicochemical parameters of the sediment were listed in Table 1.

Table 1. Physicochemical parameters of the sediment

pH	C%	Content of organic matter	Ion—exchange capacity
8.04	11.33%	1.43%	191.34m mol / 100g

Adsorption isotherm. The adsorption isotherm of the nine tin compounds (see Table 2.) follows both the Langmuir equation (equation 7.) and the Freundlich equation (equation 8.). The Freundlich isotherm are often used to describe the adsorption behaviour for nonpolar organic matters. However, the adsorption behaviour of most heavy metal ions follows the Langmuir isotherm. Organotins have both centric Sn atom and organic substituent group, therefore they are well correlated by both equations.

Table 2. The adsorption isotherm constants for organotins

Compd	Langmuir isotherm			Freundlich isotherm		
	K	M	r*	1 / n	logk	r*
MBT	5.49	6.33×10^2	0.9930	0.622	2.92	0.9957
DBT	0.12	1.87×10^2	0.9840	0.969	1.33	0.9774
TBT	10.52	1.25×10^1	0.9904	0.359	1.07	0.9779
Sn^{4+}	5.15	8.40×10^3	0.9908	0.938	4.49	0.9855
MMT	36.43	3.49×10^2	0.9725	0.613	3.20	0.9714
DMT	0.78	9.35	0.9946	1.27	1.15	0.9934
TMT	0.88	9.52	0.9962	0.764	0.69	0.9983
MPT	9.29	1.47×10^3	0.9899	0.636	3.49	0.9927
TPT	0.66	1.53×10^2	0.9625	0.793	1.81	0.9631

* r is correlation coefficient of isotherm equation

Langmuir isotherm

$$C_s = M \frac{KC_w}{1 + KC_w} \qquad (7)$$

Freundlich isotherm

$$C_s = kC_w^{1/n} \qquad (8)$$

where Cs and Cw are solute concentrations in sediment phase and water phase, respectively. k is adsorption coefficient. K, M and n are constants.

It can be seen clearly that the adsorption behaviour of organotin compounds varies dramatically with the molecular structure. k values vary from $10^{0.5}$ to $10^{4.5}$, covering 4 orders of magnitude. The order of k is $Sn^{4+} >$ mono- $>$ di- $>$ tri-organotins. In the same substituent series, the k value of the organotin with an aromatic group is larger than that with an aliphatic group.

QSPR studies of log k. All parameters of organotins applied to QSPR studies are shown in Table 3. Simple—parameter linear correlations were analyzed in the relationship between each structural parameter as an independent variable and log k as a dependent variable. The results of the regression analyses are shown in Table 4.

Table 3. Parameters of organotin compunds

Compd	logk	^1X	$^1X^v$	$^1X^b$	$^1X^r$	σ^*	$\sigma^{\bullet}$	TSA	π
MPT	3.49	4.605	14.664	5.277	3.115	9.48	2.31	192.8	4.09
MMT	3.20	2.000	14.764	3.033	1.541	8.88	1.83	133.2	2.69
MBT	2.92	3.561	15.488	4.533	3.051	8.75	1.57	195.9	4.26
TPT	1.81	9.826	13.566	9.623	7.032	4.76	−0.51	322.2	6.59
DBT	1.33	5.121	15.764	5.963	4.946	5.66	−0.58	263.7	5.68
DMT	1.15	2.000	14.315	2.961	1.926	5.92	−0.06	138.3	2.54
TBT	1.07	6.682	16.040	7.392	6.841	2.57	−2.73	331.5	7.10
TMT	0.69	2.000	13.866	2.890	2.312	2.96	−1.15	143.4	2.39

Liphophilic parameters log K_{ow} and TSA have high predicting ability in adsorption behaviour for nonpolar organic pollutants. MCIs are also often used in the studies of the adsorption behaviour for nonpolar organic pollutants because MCIs have good correlation relationship with log K_{ow}. However, for organotins satisfactory linear correlations can not be obtained ($r < 0.3082$) using these parameters. The two new MCIs $^1X^r$ and $^1X^b$, which had been proven to be very effective in QSAR studies for the toxicity of organotins, also failed. Hence, those rules, which have been used successfully in the studies of organic pollutants, can not be adopted in the studies of these organometallic com-

pounds. However, electronic parameters σ^* and $\sigma^\bullet$ show satisfactory correlations with log k, and log k increases with the increasing σ^* (b > 0). The larger σ^* is, the stronger the electron−withdrawing effect of the substituent groups from the centric Sn atom is, and accordingly the Sn atom is more strongly electropositive. Thus the adsorption of organotins increases with the positive charge on Sn atom, which is analogous to that of heavy metal ions. Hence, the adsorption mechanism is believed to be mainly ion exchange.

Table 4. Simple−parameter correlation of log k

and structural parameters

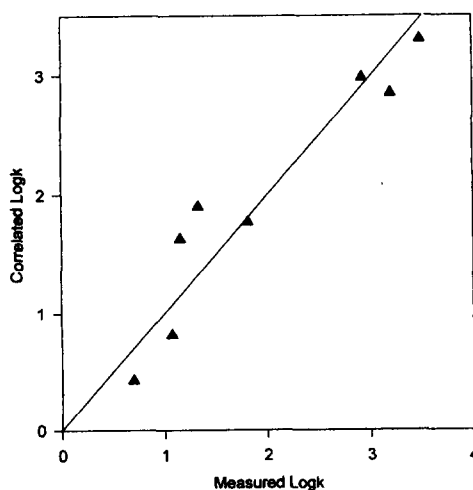| Parameter	log k = a+bp(parameter)		correlation coefficient
	a	b	r
π	2.40	-1.32×10^{-1}	0.2102
TSA	2.78	-4.39×10^{-2}	0.3082
$^1X^r$	2.59	-1.96×10^{-1}	0.3680
$^1X^v$	−3.12	3.30×10^{-1}	0.2120
$^1X^b$	2.11	-5.69×10^{-2}	0.1160
^1X	2.03	-4.80×10^{-2}	0.1119
σ^*	−0.347	3.76×10^{-1}	0.9374
$\sigma^\bullet$	1.93	5.52×10^{-1}	0.9134

Correlated Logk vs Measured Logk

Figure.1 Relationship between correlated and measured log k values. The estimated values were obtained by the following equation: logk = −1.129+0.124$^1X^r$+0.426σ^*

Diparametric and triparametric approaches have been attempted by various combinations of the eight parameters. In triparametric approaches, the best correlation is between log k and σ^*, π and $^1X^r$:

$$log k = -1.108 + 0.297\,^1X^r + 0.452\sigma^* - 0.192\pi \qquad (9)$$

$$r = 0.9571 \quad F = 54.552 \quad t(^1X^r) = 0.650 \quad t(\sigma^*) = 4.967 \quad t(\pi) = 0.394$$

However, the coefficient before π is not significant (t test $t_{1,1}^3 = 1.476$). When π was not considered, we obtained the following diparametric equation:

$$log k = -1.129 + 0.124\,^1X^r + 0.426\sigma^* \qquad (10)$$

$$r = 0.9554 \quad F = 37.406 \quad t(^1X^r) = 1.557 \quad t(\sigma^*) = 7.339$$

According to t values, log k is mainly controlled by σ^* and to a small extent by $^1X^r$. The adsorption mechanism is principally are of ion-exchange process with a small lipophilic contribution.

The relationship between experimental log k and correlated log k according to the regression formulae with two independent variables as shown in Fig.1 shows a fairly reliable correlation.

CONCLUSION

The adsorption behaviour of organotin compounds to sediment varies greatly with the molecular structure. The adsorption coefficient k varies from $10^{0.5}$ to $10^{4.5}$, covering 4 magnitude orders: $Sn^{4+} > $ mono- > di- > tri-organotins. From QSPR studies, it is concluded that log k increases with σ^* and $^1X^r$. Adsorption mechanism is mainly an ion-exchange process with little lipophilic partitioning.

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