

Aqueous Speciation and 1-Octanol–Water Partitioning of Tributyl- and Triphenyltin: Effect of pH and Ion Composition

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Due to their widespread use as antifouling agents in boat paints, tributyltin (TBT), and triphenyltin (TPT) have been found to be present in marine and freshwater ecosystems at concentrations exceeding acute and chronic toxicity levels. In order to assess the environmental behavior and particularly the bioavailability and bioaccumulation of these compounds, their aqueous speciation and partitioning behavior between nonaqueous phases and water need to be known. In this work, the effect of pH and of the concentration of various anions on the 1-octanol–water partitioning of TBT and TPT has been systematically investigated. A simple model is presented that enables a quantitative description of the overall 1-octanol–water distribution ratio of TBT and TPT as a function of pH and salt concentration. Acidity constants of 6.25 and 5.20 were determined for TBT and TPT, respectively. Furthermore, the aqueous phase complex formation constants with chloride, perchlorate, bromide, and nitrate as well as the 1-octanol–water partition constants of the corresponding complexes are reported. In addition, the Setschenov constants of TBT- and TPT-hydroxide have been determined for NaCl (0.6 and 0.4, respectively) and are estimated for other salts.

Introduction

Because of their widespread use as biocides and because of their very high toxicity toward aquatic organisms, triorganotin compounds (TOTs) have to be considered as very hazardous pollutants in aquatic ecosystems (1, 2). In particular tributyltin (TBT) and triphenyltin (TPT) have drawn considerable interest because, as a consequence of their use as antifouling agents in boat paints, these compounds have been found to be present in marine and freshwater ecosystems at concentrations exceeding acute and chronic toxicity levels (1, 3, 4).

In view of these facts, it is somewhat surprising that the aqueous speciation and the partitioning behavior of TOTs between nonaqueous phases and water have not yet been systematically investigated. Recently, Traas et al. (5) pointed

out that one of the critical factors in the assessment of the accumulation of TOTs in water, sediments, and food web is the uncertainty in their reported organic phase–water partitioning behavior, particularly in their 1-octanol–water distribution ratios (D_{ow}). One reason for this lack of reliable data may be that, depending on the solution chemistry (i.e., pH, type and concentration of anions presents), TOTs may exist in water as cationic and/or as various neutral species that may exhibit quite different partitioning behavior, thus rendering the quantification of partitioning processes difficult (6).

As has been demonstrated in numerous studies, the 1-octanol–water system is well suited for assessing the partitioning behavior of neutral organic compounds between natural organic phases and water (7). In addition, the partitioning of organic compounds into a nonaqueous phase liquid (NAPL) may reduce the mineralization rate of these organic compounds in polluted sites containing NAPLs (8). Furthermore, as we have already shown (9), the evaluation of the 1-octanol–water partitioning behavior of ionizable organic compounds may give important insights into their speciation in the aqueous and organic phases and may provide quantitative data on ion pair and/or complex formation in both phases (9–11).

The few results available show that D_{ow} values of TOTs increase with increasing pH (12, 13) and that they are strongly dependent on the type and concentration of the anions present (6). However, the data provided by these studies are not sufficient to determine the aqueous speciation of TOTs, which is essential for the interpretation of the observed partitioning behavior. The chemistry of TOTs in aqueous solution has been studied in detail only for trimethyltin (TMT) (14–21). It has been shown by electrochemical methods (14–18, 20) as well as by ¹¹⁹Sn-NMR spectroscopy (19) that, at low pH values in water, TMT is present as cationic species, TMT⁺ (probably a trigonal bipyramidal cation with water molecules in the axial positions). TMT⁺ may form complexes with different organic and inorganic ligands such as amino acids (18, 20), carboxylic acids (20), phosphate (17, 20), or chloride (21). At higher pH values, TMT⁺ dissociates to the neutral trimethyltin hydroxide (TMTOH). The pK_a values reported for TMT range from 5.79 (in 0.1 M NaNO₃) (17) to 6.60 (in 3 M NaClO₄) (14).

In this work, we have investigated the effects of pH and the type and concentration of several anionic ligands on the 1-octanol–water partitioning behavior of TBT and TPT. We report the acidity constants, the complex formation constants of TBT and TPT with Cl⁻, Br⁻, ClO₄⁻, and NO₃⁻ in water, and the 1-octanol–water partition constants of the corresponding complexes. With these constants, the 1-octanol–water distribution ratio of TBT and TPT can be calculated as a function of pH and concentration of the anions investigated. The results of this study provide an important base for a better understanding and quantification of the speciation, of the solid–water partitioning behavior, and of the bioavailability of TBT and TPT in different aquatic environments including freshwater and seawater.

Theoretical Considerations

Model for the Description of the 1-Octanol–Water Partitioning of TOTs. The partitioning of TOTs can be described by an overall distribution ratio, D_{ow} , that is defined by the quotient of the sum of the concentrations of the different charged and neutral species in 1-octanol, $[TOT]_{tot,org}$, and water, $[TOT]_{tot,aq}$, respectively. The species and equilibrium reactions considered are summarized in Figure 1. In analogy to equilibrium models used to describe the partitioning of

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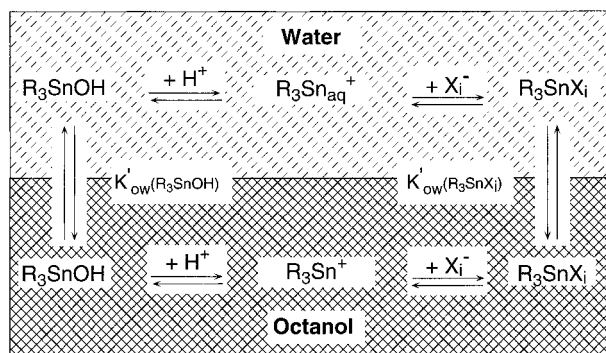


FIGURE 1. Schematic representation of the model used to describe the partitioning of triorganotin compounds in the 1-octanol–water system (eqs 1–14).

other ionizable organic compounds in organic phase–water systems (10, 11, 22), the D_{ow} of a given TOT may be expressed by

$$D_{ow} = \frac{[\text{TOT}]_{\text{tot,oct}}}{[\text{TOT}]_{\text{tot,aq}}} = \alpha_{R_3\text{SnOH}} K'_{ow}(R_3\text{SnOH}) + \sum_i \alpha_{R_3\text{SnX}_i} K'_{ow}(R_3\text{SnX}_i) \quad (1)$$

where $K'_{ow}(R_3\text{SnOH})$ and $K'_{ow}(R_3\text{SnX}_i)$ are the conditional 1-octanol–water partition coefficients at given solution conditions of the hydroxide complex and of the neutral complexes formed with other monovalent anions X_i^- (excluding OH^-), and $\alpha_{R_3\text{SnOH}}$ and $\alpha_{R_3\text{SnX}_i}$ are the fractions of the respective species in the aqueous phase. Note that, in this model, the contributions of the TOT cations, $R_3\text{Sn}^+$, negatively charged complexes with multivalent anions, and possible TOT di- or oligomers are neglected (see Results). The conditional 1-octanol–water partition coefficient of a given TOT species, K'_{ow} , is related to its K_{ow} at infinite dilution (i.e., the reference state) by

$$K'_{ow} = \frac{[\text{TOT}]_{\text{org}}}{[\text{TOT}]_{\text{aq}}} = K_{ow} \frac{f_{\text{TOT}}(\text{aq})}{f_{\text{TOT}}(\text{org})} \quad (2)$$

where $f_{\text{TOT}}(\text{aq})$ and $f_{\text{TOT}}(\text{org})$ are the activity coefficients of the species in the aqueous and organic phase, respectively. We assume that $f_{\text{TOT}}(\text{org})$ does not change significantly with electrolyte and TOT concentrations and, therefore, can be set equal to 1 (the effect of ionic strength on the water content of octanol is considered to be negligible). Equation 2 then simplifies to

$$K'_{ow} = \frac{[\text{TOT}]_{\text{org}}}{[\text{TOT}]_{\text{aq}}} = K_{ow} f_{\text{TOT}}(\text{aq}) \quad (3)$$

For any charged species i (i.e., $R_3\text{Sn}^+$, X_i^-) the activity coefficient in aqueous solution can be estimated using the Davies equation (23):

$$\log f_i^c = \frac{-z_i^2}{2} \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \quad (4)$$

where, f_i^c is the activity coefficient of the charged species i , z_i is its charge, and I is the ionic strength.

For uncharged TOT species (i.e., $R_3\text{SnOH}$, $R_3\text{SnX}_i$), the effect of a given salt on the activity coefficient in water, f_i^n , can be described by (see also ref 7)

$$f_i^n = 10^{K^S[\text{salt}]} \quad (5)$$

where K^S is the Setschenov or salting constant for a given

electrolyte, and $[\text{salt}]$ is the total molar concentration of that electrolyte. Insertion of eq 5 into eq 3 yields

$$K'_{ow} = K_{ow} \times 10^{K^S[\text{salt}]}$$

or

$$\log K'_{ow} = \log K_{ow} + K^S[\text{salt}] \quad (6)$$

Hence, K^S of a given neutral TOT species can be determined experimentally by measuring K'_{ow} as a function of the salt concentration. Additionally, as will be discussed later, K^S can also be estimated from known K^S values of other hydrophobic compounds.

The fractions $\alpha_{R_3\text{Sn}^+}$, $\alpha_{R_3\text{SnOH}}$, and $\alpha_{R_3\text{SnX}_i}$ of the different TOT species present in the aqueous phase at a given pH and solution composition may be expressed by

$$\alpha_{R_3\text{Sn}^+} = \frac{1}{1 + 10^{\text{pH} - \text{p}K'_a} + \sum_i K'_i [X_i^-]} \quad (7)$$

$$\alpha_{R_3\text{SnOH}} = \frac{10^{\text{pH} - \text{p}K'_a}}{1 + 10^{\text{pH} - \text{p}K'_a} + \sum_i K'_i [X_i^-]} \quad (8)$$

$$\alpha_{R_3\text{SnX}_i} = \frac{K'_i [X_i^-]}{1 + 10^{\text{pH} - \text{p}K'_a} + \sum_i K'_i [X_i^-]} \quad (9)$$

In these equations, K'_a is the mixed acidity constant of the dissociation reaction



and is given by

$$K'_a = \frac{[R_3\text{SnOH}][\text{H}^+]}{[R_3\text{Sn}^+]} = K_a \frac{f_{R_3\text{Sn}^+}^c}{f_{R_3\text{SnOH}}^n} \quad (11)$$

where K_a is the mixed acidity constant at infinite dilution, $\{\text{H}^+\}$ is the activity of the proton (directly measured by the pH electrode), and $f_{R_3\text{Sn}^+}^c$ and $f_{R_3\text{SnOH}}^n$ are the activity coefficients of $R_3\text{Sn}^+$ and $R_3\text{SnOH}$, respectively, for the given solution conditions. These activity coefficients can be estimated and/or determined as discussed above. The K'_i values in eqs 7–9 represent the formation constants of $R_3\text{SnX}_i$ due to exchange of a water molecule by X_i^- :



K'_i is defined as

$$K'_i = \frac{[R_3\text{SnX}_i]}{[R_3\text{Sn}^+][X_i^-]} = K_i \frac{f_{R_3\text{Sn}^+}^c f_{X_i^-}^c}{f_{R_3\text{SnX}_i}^n} \quad (13)$$

where, again, K_i is the corresponding equilibrium constant at infinite dilution, and the f_i values are the activity coefficients of the species under the given solution conditions.

Finally, insertion of eqs 7–9 into eq 1 yields the model used in this work to describe the 1-octanol–water partitioning

behavior of TOTs as a function of pH and major ion composition in the aqueous phase:

$$D_{ow} = \frac{10^{\text{pH}-\text{p}K'_a} K'_{ow}(\text{R}_3\text{SnOH}) + \sum_i K'_i [\text{X}_i^-] K'_{ow}(\text{R}_3\text{SnX}_i)}{1 + 10^{\text{pH}-\text{p}K'_a} + \sum_i K'_i [\text{X}_i^-]} \quad (14)$$

Experimental Section

Chemicals. Tributyltin chloride (97%, pract.), triphenyltin chloride (97%, pract.), 1-octanol (99.5%, puriss.), morin (Fluka standard), Triton X-100, sodium bromide (99.5%, purum p.a.), citric acid monohydrate (>99.5%, puriss p.a.), lithium hydroxide (>99%, puriss p.a.), hydrobromic acid (48%, puriss p.a.), and the organic buffers [MES (2-(*N*-morpholino)ethanesulfonic acid, $\text{p}K_a = 6.15$), MOPS (3-(*N*-morpholino)propanesulfonic acid, $\text{p}K_a = 7.2$), HEPPS (*N*-(2-hydroxyethyl)piperazine-*N*-3-propanesulfonic acid, $\text{p}K_a = 8.0$), CAPS (3-cyclohexylamino-1)propanesulfonic acid, $\text{p}K_a = 10.4$), all at least 99% purity] were obtained from Fluka Chemie AG (Buchs, Switzerland). Sodium chloride (>99.5%, p.a.), sodium perchlorate monohydrate (>99%, p.a.), sodium dihydrogen phosphate monohydrate (99%, p.a.), orthophosphoric acid (85%, p.a.), hydrochloric acid (32%, p.a.), nitric acid (65%, p.a.), perchloric acid (60%, p.a.), acetic acid (100%, p.a.), sodium hydroxide (Titrisol 1 M), and sodium nitrate (>99.5, p.a.) were purchased from E. Merck (Darmstadt, Germany). Methanol (99.8%, HPLC prep grade) was obtained from Scharlau (Sentmenat, Spain). All chemicals were used without further purification. All water was doubly distilled in quartz.

Experimental Procedure. All glassware used was washed and rinsed with ethanol or methanol, with deionized water, and again with ethanol or methanol. Aqueous solutions were prepared with the appropriate buffer (MES, MOPS, HEPPS, or CAPS, 10 mM) and the appropriate amount of the sodium salt of the respective anion. The experiments at $\text{pH} < 5$ were conducted without pH buffer. In these cases, the pH was adjusted with HClO_4 for the study of the pH dependence of D_{ow} or with the corresponding acid for the study of the anion dependence of D_{ow} . The pH of the aqueous solutions was measured before and after the partitioning experiments with an Orion 720A pH meter with an Orion Ross-Sure-Flow 81-72 electrode (Orion, Boston, MA). To prevent significant volume changes, the respective 1-octanol and aqueous phases were mutually saturated prior to the partitioning experiments (10).

Partitioning Experiments. Experiments were conducted by adding between 0.15 and 1 mL (depending on the expected D_{ow} value) of 1-octanol saturated with the corresponding aqueous solution to 100 mL of 1-octanol-saturated aqueous solution in a 100-mL separatory funnel. A 12- μL aliquot of a 1 M TBT methanol stock solution or 20, 10, and 5 μL of an 0.1 M TPT acetone stock solution were injected into the aqueous phase. The two phases were equilibrated for 12 h at 25 °C in the dark on a horizontal Lab Shaker (A. Kühner, Basel, Switzerland). The two phases were then allowed to separate (typically for 24 h), and the total TBT or TPT concentrations were determined in each phase. TBT experiments were run in triplicate, and TPT experiments were run in duplicate. The partitioning of TBT as a function of the nitrate concentration was studied in duplicate at initial aqueous concentrations of 20, 10, and 5 μM . Mass balances were always determined and varied typically between 67 and 80% for TBT experiments and between 95 and 105% for TPT experiments. The low mass balance in the TBT experiments was probably due to sorption to the silanol functional groups of the glass surface (24). The standard deviation of the mean D_{ow} value was always less than 11%.

Analytical Procedures. The concentrations of TBT and TPT in the aqueous and 1-octanol phases were determined with isocratic cation exchange HPLC with fluorescence detection after post-column derivatization with morin in a micellar solution (25, 26). The HPLC equipment consisted of a Jasco pump 880-PU (Japan Spectroscopic Co. Ltd., Tokyo, Japan), a GINA 50 autosampler (Gynkotec, Germering, Germany), and a 200 \times 4 mm Nucleosil 100 5 SA column (Macherey-Nagel, Düren, Germany) (TBT analysis) or a 125 \times 4.6 mm Metrosep Cation 1-2 column (Metrohm AG, Herisau, Switzerland) (TPT analysis). The eluent, 150 mM ammonium acetate in 85/15 methanol–water (v/v) (TBT analysis) or 37.5 mM citric acid and 10 mM lithium hydroxide in 80/20 methanol–water (v/v) (TPT analysis), was pumped at a flow rate of 1 mL/min. The reagent solution [0.7% (w/v) Triton X-100, 20 μM morin, and 7.5 mM acetic acid in water (TBT analysis) or 1.8% (w/v) Triton X-100, 133 μM morin, 180 mM citric acid, and 342 mM lithium hydroxide (TPT analysis)], was pumped by a Synkam S 1000 (Synkam, Gilching, Germany) at a flow rate of 2 (TBT analysis) or 3 mL/min (TPT analysis). The mobile phase and the reagent solution were then combined using a T-piece (Valco, Houston, TX). A 2 m \times 0.3 mm PTFE reaction coil (ict, Frankfurt, Germany) ensured good mixing prior to fluorescence detection (Jasco 821 FP, Japan Spectroscopic Co. Ltd., Tokyo, Japan). The excitation wavelengths were 410 nm for TBT and 409 nm for TPT, and the detection wavelengths were 520 and 525 nm, respectively. Excitation and emission slits were set at a band width of 18 nm. The 1-octanol samples containing TBT or TPT were diluted by a factor of 100–1000 in methanol or in the mobile phase, respectively, prior to analysis. The sample volume was 100 μL . Peak areas (TBT) or the peak heights (TPT) were determined using Chrom-Card software (Fisons Ltd., Manchester, United Kingdom). TBT and TPT were quantified with external standards. Aqueous standards were prepared in solutions with the same composition as in the partitioning experiments. Standards for the nonaqueous solutions were prepared in methanol (TBT) or in the mobile phase (TPT). For the low TBT concentration in the water phase in the experiments at $\text{pH} 10$ and $[\text{NaCl}] > 0.1$ M, a newly developed analytical method was used that involved on-line concentration of 10-mL aliquots on a 20 \times 4 mm Metrosep Cation 1-2 precolumn (Metrohm AG, Herisau, Switzerland) followed by gradient elution on a 125 \times 4.6 mm Metrosep Cation 1-2 column (Metrohm AG, Herisau, Switzerland) (27).

Modeling of the D_{ow} Values. In order to determine the values of $K_{ow}(\text{R}_3\text{SnOH})$, K^s , K_a , K_i , and $K_{ow}(\text{R}_3\text{SnX}_i)$ for both TBT and TPT, the measured D_{ow} values were modeled according to eqs 1–14, with the weighted nonlinear least-squares regression procedure of Matlab (Matlab Version 4.2c, The MathWorks Inc., Natick, USA), using the Levenberg–Marquardt algorithm (28).

Results

Acidity Constants, K_{ow} , and K^s Values of the R_3SnOH Species.

Figure 2 shows the D_{ow} of TBT and TPT as a function of pH in the presence of 10 mM NaClO_4 . For both TBT and TPT, D_{ow} increased by about 2 orders of magnitude between pH 3 and pH 7 and remained constant at higher pH values. Since at high pH values and low electrolyte concentration only the R_3SnOH species were present and any salting out effects can be neglected (see below), the K_{ow} of the R_3SnOH species can be obtained directly by averaging the corresponding D_{ow} values (see Table 1). Furthermore, from the data in the pH range in which R_3SnOH is the dominant species in determining D_{ow} , the $\text{p}K_a$ of the R_3Sn^+ (aq) species can be determined by fitting the experimental data points to eqs 11 and 15:

$$D_{ow} = \alpha_{\text{R}_3\text{SnOH}} K_{ow}(\text{R}_3\text{SnOH}) = \frac{10^{\text{pH}-\text{p}K'_a} K_{ow}(\text{R}_3\text{SnOH})}{1 + 10^{\text{pH}-\text{p}K'_a}} \quad (15)$$

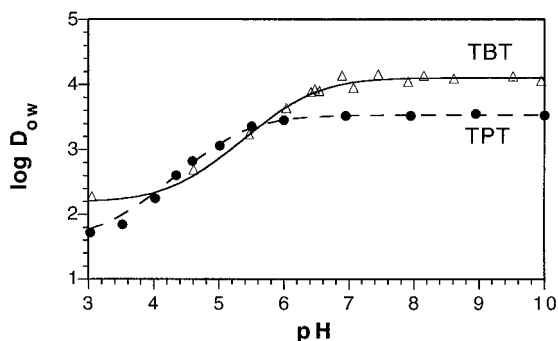


FIGURE 2. pH dependence of the 1-octanol-water distribution ratio, D_{ow} , of TBT and TPT; the aqueous solution contained 10 mM NaClO₄ and 10 mM buffer (for pH \geq 5). The lines represent the calculated D_{ow} values (eqs 1–14) using the constants listed in Tables 1 and 2.

TABLE 1. Acidity Constants (pK_a), Octanol-Water Partition Constants of the Hydroxide Complexes ($K_{ow}(R_3SnOH)$), and K^S Values of TBTOH and TPTOH for Various Salts

	TBT	TPT
pK_a	6.25 (0.05) ^{a,b}	5.20 (0.02) ^{a,c}
$\log K_{ow}(R_3SnOH)$	4.10 (0.07) ^{a,d}	3.53 (0.01) ^{a,e}
$K^S(R_3SnOH)$ in M ⁻¹ for		
NaCl	0.61 (0.04) ^{a,f}	0.36 (0.03) ^{a,g}
NaBr ^{h,i}	0.48	0.29
NaClO ₄ ^{h,i}	0.33	0.20
NaNO ₃ ^{h,i}	0.37	0.22
NaH ₂ PO ₄ ^{h,j}	0.65	0.39
Na ₂ HPO ₄ ^{h,k}	2.1	1.3

^a Standard deviation in parentheses. ^b Number of measurements, $n = 9$, see Figure 2. ^c $n = 6$, see Figure 2. ^d $n = 4$, see Figure 2. ^e $n = 3$, see Figure 2. ^f $n = 5$. ^g $n = 6$. ^h Estimated values using eq 16. ⁱ Reference compound: benzene ($K^S(\text{NaCl}) = 0.195$, $K^S(\text{NaBr}) = 0.155$, $K^S(\text{NaClO}_4) = 0.106$, $K^S(\text{NaNO}_3) = 0.119$; data from ref 49). ^j Reference compound: iodine ($K^S(\text{NaCl}) = 0.00575$, $K^S(\text{NaH}_2\text{PO}_4) = 0.0062$; data from ref 50). ^k Reference compound: nitrous oxide ($K^S(\text{NaCl}) = 0.103$, $K^S(\text{Na}_2\text{HPO}_4) = 0.362$; data from ref 51).

Thus, pK_a values of 6.25 for TBT⁺(aq) and of 5.20 for TPT⁺(aq) were obtained.

Since sodium chloride mimics quite well the properties of seawater with respect to the salting out of hydrophobic organic compounds (7), the corresponding K^S values of R_3SnOH species were determined by measuring K'_{ow} at pH 10 as a function of the sodium chloride concentration (see eq 6). Note that at pH 10, even at 1 M NaCl, both TBT and TPT are still present primarily as hydroxide species (see below). The linear correlation between $\log(K'_{ow}/K_{ow})$ versus $[\text{NaCl}]$ yielded K^S values of 0.61 for tributyltin hydroxide (TBTOH) and 0.36 for triphenyltin hydroxide (TPTOH), respectively (data not shown). With regard to the K^S values of TBT and TPT species for other salts, as a first approximation, it can be assumed that for two different compounds, the ratio of their K^S values for two different salts is approximately constant (29). Hence, if for a reference compound (e.g., benzene) the K^S values are known for salt i and for NaCl (reference salt), the K^S for the R_3SnOH species can be calculated as

$$K^S_{R_3SnOH}(\text{salt } i) = \frac{K^S_{\text{ref}}(\text{salt } i)}{K^S_{\text{ref}}(\text{NaCl})} K^S_{R_3SnOH}(\text{NaCl}) \quad (16)$$

The estimated K^S values for TBTOH and TPTOH for the various salts used in this study are summarized in Table 1.

Formation Constants, K_i , and K_{ow} Values of R_3SnX_i Species. Because both TBT and TPT form relatively strong complexes with OH⁻ (see K_i values for OH⁻ in Table 2), experiments for determining K_i and K_{ow} values for other R_3SnX_i species had to be carried out at low pH. However, at low pH values, the minimal ionic strength is determined by

TABLE 2. Octanol-Water Partition Constant ($K_{ow}(R_3SnX_i)$) and Formation Constant (K_i) of Some R_3SnX_i Species

ligand	TBT		TPT	
	$\log K_{ow}(\text{TBTX}_i)$	$\log K_i$	$\log K_{ow}(\text{TPTX}_i)$	$\log K_i$
Cl ⁻	4.76 ^a	0.60 ^b	4.19 (0.04) ^c	0.66 (0.05) ^c
Br ⁻	5.07 ^a	0.43 ^b	4.50 (0.31) ^c	0.36 (0.33) ^c
ClO ₄ ⁻	4.18 ^a	0.09 ^b	3.61 (0.07) ^c	0.10 (0.11) ^c
NO ₃ ⁻	3.49 (0.12) ^c	0.62 (0.17) ^c	2.97 (0.16) ^c	0.26 (0.26) ^c
OH ⁻	4.09 (0.02)	7.75 (0.05) ^d	3.53 (0.01)	8.80 (0.02) ^d

^a Calculated assuming $\log K_{ow}(\text{TBTX}_i) - \log K_{ow}(\text{TBTOH}) = \log K_{ow}(\text{TPTX}_i) - \log K_{ow}(\text{TPTOH})$, see text for details. ^b Error not calculated due to the uncertainty of the above assumption. ^c Standard deviation in parentheses, for number of measurements see Figure 3. ^d $K_i = K_w/K_a$; K_w (25 °C) = 10^{-14} ; the K_a values are given in Table 1.

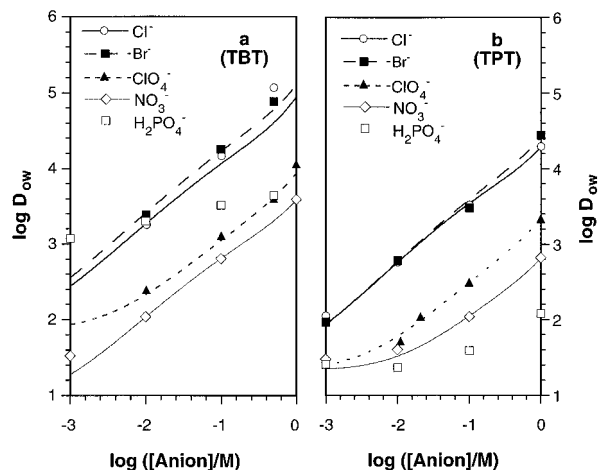


FIGURE 3. Dependence of the 1-octanol-water distribution ratio, D_{ow} , on the concentration of several sodium salts. The lines represent the fitted curves applying eqs 1–14 (a) TBT data, pH = 4 (except for nitrate: pH = 3). (b) TPT data, pH = 3.

the acid concentration, and thus the pH cannot be chosen too low in order to cover a reasonable concentration range of X_i^- . This puts severe constraints on the pH range available for such experiments. Figure 3 shows the effect of the concentration of various anions on the D_{ow} of TBT and TPT at pH 4 and pH 3, respectively. Depending on the type and concentration (10^{-3} to 1 M) of anions present, the formation of uncharged R_3SnX_i species led to an increase in D_{ow} of between 1 and 3 orders of magnitude.

Table 2 summarizes the K_i and K_{ow} values determined by fitting the data shown in Figure 3 to the model described by eqs 1–14. Note that in the calculation of the activity coefficients, f_i^{\pm} , of the other R_3SnX_i species, K^S values determined for the R_3SnOH species were used. This approximation is based on the assumption that the K^S value of hydrophobic organic compounds is primarily determined by the hydrophobic surface area of the molecules (7, 29). Furthermore, the parameters K_i and $K_{ow}(R_3SnX_i)$ of the TBT complexes with chloride, bromide, and perchlorate could not be fitted simultaneously, either because the formation constants K_i were too small or because the available data set was too small and did not consist of sufficiently precise data. Thus, in the calculation of $K_i(\text{TBTCl})$, it was assumed that the difference between $\log K_{ow}(\text{TBTCl})$ and $\log K_{ow}(\text{TPTCl})$ was the same as the difference between $\log K_{ow}(\text{TBTOH})$ and $\log K_{ow}(\text{TPTOH})$. A similar procedure was used in the case of bromide and perchlorate complexes of TBT. This procedure is based on the observation that, for a given class of compounds, the effect of a substituent on the $\log K_{ow}$ is approximately constant (see also refs 7, 30, and 31). The validity of this approach was confirmed by the observed

differences between the log K_{ow} of TBT and TPT nitrate complexes.

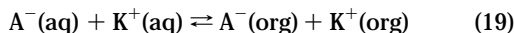
Effect of Phosphate on D_{ow} . Because phosphate is a polydentate ligand and may form negatively charged complexes with TOTs as well as TOT dimers (20, 32), it is rather difficult to quantify the contribution of such species to the overall D_{ow} . Figure 3 illustrates the effect of the dihydrogen phosphate concentration on the D_{ow} of TBT at pH 4 and of TPT at pH 3. The relatively high D_{ow} of TBT at a 1 mM phosphate concentration (Figure 3a) may indicate the formation of a relatively hydrophobic complex of TBT, most probably tributyltin dihydrogen phosphate (TBT·H₂PO₄). This hypothesis is supported by the fact that a log K_i value of 1.35 has been reported for the formation of trimethyltin dihydrogen phosphate (TMT·H₂PO₄) (20), which is significantly higher than the values obtained for TBT and TPT complexes with the monovalent anions investigated. In contrast to TBT, the D_{ow} of TPT at a 1 mM phosphate concentration is lower than or equal to the D_{ow} values observed for the other studied anions (Figure 3b). At a 1 M phosphate concentration, the D_{ow} of TPT is almost 1 order of magnitude smaller than in presence of weak complexing anions such as nitrate or perchlorate. This behavior suggests the formation of a relative weak and/or hydrophilic (i.e., charged) complex, i.e., triphenyltin hydrogen phosphate (TPT·HPO₄⁻).

Significance of Free Ion Partitioning. As pointed out in the theoretical section, the partitioning of the TOT cations has not been considered in the model used to evaluate the experimental data (eqs 1–14). Since in previous work with other ionizable organic compounds (10, 11) it has been shown that, especially at low ionic strength (33), the contribution of the free ion to the overall 1-octanol–water distribution ratio cannot always be neglected, the validity of our assumption has to be checked. To this end, it is useful to estimate the magnitude of the partitioning constant, K_{ion}^{TOT} , for the partitioning of the TOT cations in the presence of a given counterion:



$$K_{ion}^{TOT} = \frac{[R_3Sn^+]_{org}[X_i^-]_{org}}{[R_3Sn^+]_{aq}[X_i^-]_{aq}} \quad (18)$$

where X_i^- is a monovalent anion that is transferred with the TOT cations to maintain the electroneutrality of both aqueous and 1-octanol phases. Jafvert et al. (11) have determined values for anionic organic acids, A⁻, of similar hydrophobicities to those of TBTOH and TPTOH, in the presence of K⁺ counterions:



$$K_{ion}^A = \frac{[A^-]_{org}[K^+]_{org}}{[A^-]_{aq}[K^+]_{aq}} \quad (20)$$

These values varied between 10^{-4.5} and 10^{-2.5}. Considering that the partitioning behavior of Cl⁻ and K⁺ ions are very similar (33), the reported K_{ion}^A were used to estimate K_{ion}^{TOT} in the presence of chloride counterions. Thus, concentrations of free TOT cations between 0.02 and 2 μM in 1-octanol were obtained for a typical TOT(aq) concentration of 10 μM at pH 4 and 0.1 mM Cl⁻(aq) concentration. Under the same solution conditions, TBTCI and TPTCI concentrations of 230 and 70 μM, respectively, in 1-octanol were calculated from eqs 3 and 9 using the data reported in Table 2. The partitioning of TOT cations is not expected to differ significantly in the presence of other counterions. Thus, even at 0.1 mM ionic strength, the partitioning of TOT cations can be assumed to be negligible.

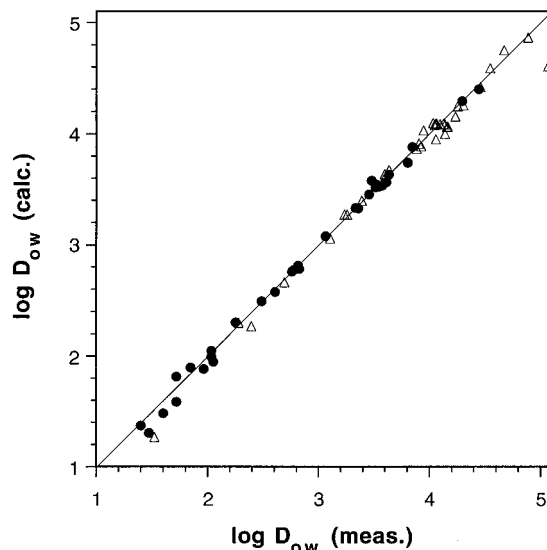


FIGURE 4. Comparison of 74 calculated (eqs 1–14, Tables 1 and 2) and experimentally determined 1-octanol–water distribution ratios, D_{ow} , of TBT (Δ) and TPT (●).

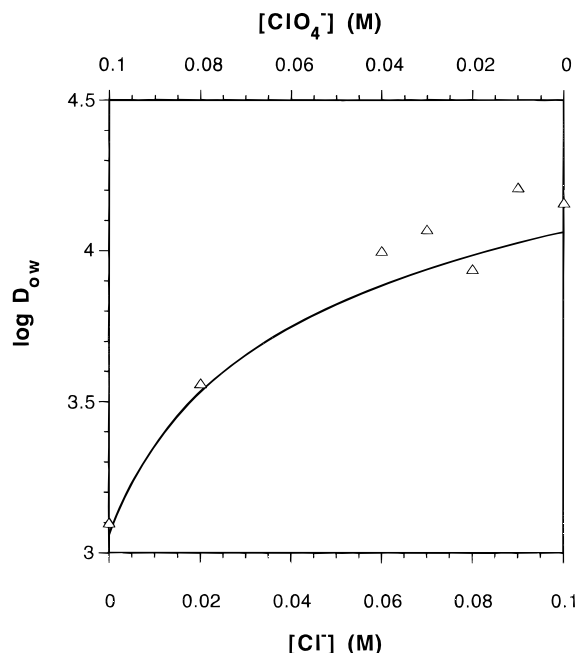


FIGURE 5. Comparison of calculated (eqs 1–14, Tables 1 and 2) and experimentally determined D_{ow} values of TBT at pH 4 and 0.1 M ionic strength at various NaCl/NaClO₄ concentration ratios.

Consistency of the Data and Validation of the Model. In total, 74 D_{ow} values were determined experimentally for TBT and TPT at various solution conditions. From subsets of these data, the constants given in Tables 1 and 2 were derived. Figure 4 shows that, using these constants, all of the available experimental data can be well described by the modeling approach taken, indicating that the whole data set is very consistent. The validity of the model was further tested with additional experiments at pH 4 with TBT in the presence of various mixtures of two salts (NaCl and NaClO₄) at a total concentration of 0.1 M. As can be seen from Figure 5, the experimental data are in good agreement with the modeled curve (solid line) that was calculated using the constants given in Tables 1 and 2.

Discussion

Comparison of TBT and TPT: pK_a , K^S , K_i , and $K_{ow}(R_3SnX_i)$ Values. The pK_a of TBT (6.25) is one unit above that of TPT

(5.20). This difference may be explained by the stronger negative inductive effect of phenyl in comparison with butyl substituents (16). Slightly higher pK_a values but the same pK_a difference of approximately 1 pH unit ($pK_a(\text{TBT}) = 6.58$, $pK_a(\text{TPT}) = 5.48$) were determined by acid–base titration of a 44/56 (w/w) ethanol–water mixture ($I = 0.01 \text{ M}$) (16). More recently, Shoukry (34) obtained a pK_a value of 6.51 for TBT (50/50 ethanol–water (v/v), $I = 0.1 \text{ M}$) using a similar titration method. Enhanced solvation of the TOT species by ethanol and the difference in the activity of H_2O may be the reason for the observed pK_a difference of approximately 0.3 pH unit between data determined in ethanol–water mixtures and the results of this study. The pK_a of TBT is also very similar to that of tripropyltin ($pK_a = 6.3$, $I = 10 \text{ mM}$) determined using 1-octanol–water partitioning experiments (9). Schweitzer and McCarty (32) determined a formation constant of $10^{9.2}$ for TPTOH at 30°C and $I = 0.1 \text{ M}$ using benzene–water partitioning experiments. A pK_a value of 4.4 may be calculated from eq 4 and the dissociation constant of water, K_w , at 30°C ($\log K_w = 13.8$, see ref 35). However, Schweitzer and McCarty neglected the influence of the 0.1 M NaNO_3 background electrolyte on the TPT partitioning behavior. Since the pK_a value was determined from partitioning experiments at pH values between 4.3 and 1.2, this approximation is questionable (see also Figure 3b).

The K^s value of NaCl for TBT (Table 1) is very high as compared to values reported in the literature for other organic compounds (36, 37). As mentioned previously, the K^s value for nonpolar organic compounds is proportional to the molar volume of the compounds (29). Thus, the K^s values of TBT or TPT should be comparable to the K^s value of aliphatic or aromatic organic compounds, respectively, with a similar molar volume. TBTCI (the molar volume of TBTCI is taken as a good approximation for the molar volume of TBTOH, which has not yet been determined) has a molar volume of 0.27 L/mol (38), and its K^s value of 0.61 M^{-1} is on the order of the K^s of hexadecane in seawater ($K^s = 0.65 \text{ M}^{-1}$, see ref 36), which has a molar volume of 0.29 L/mol (36). TPTOH has a molar volume (in the solid phase) of 0.24 L/mol (39), and its K^s value of 0.36 M^{-1} is in the order of the K^s of chrysene ($K^s = 0.34 \text{ M}^{-1}$, see ref 37) which has a molar volume of 0.19 L/mol (37). These comparisons support the validity of the K^s values determined in this study.

Except for OH^- , all monovalent anions studied form relatively weak complexes ($0 < \log K_i < 1$) with both TBT and TPT (Table 2). Nevertheless, the formation constants of these complexes are larger than expected for outer-sphere complexes between a negatively charged ligand ($z = -1$) and a positively charged metal ($z = +1$) carrying two water ligands and three other substituents (40); the $\log K_i$ value for such a complex should be approximately -0.5 . Thus, the reported formation constants indicate the formation of inner-sphere complexes. The formation constant of TBTCI ($\log K_i = 0.6$) is higher than that determined for trimethyltin chloride ($\log K_i = -0.17$) (21). This indicates that the alkyl chain length influences the strength of the complex formation. The formation constants determined for TPTCl ($\log K_i = 0.7$) and triphenyltin bromide (TPTBr; $\log K_i = 0.4$) are 2 orders of magnitude lower than those reported by Schweitzer and McCarty (32). However, their partitioning data were interpreted using a pK_a value of 4.4 for TPT (see above discussion) and are therefore not comparable to our data.

Qualitatively, the affinity sequence of TOTs for the different anions, i.e., $\text{Br}^- \leq \text{Cl}^- \ll \text{OH}^-$ is identical to the one observed for $\text{Sn}^{2+}(\text{aq})$: $\log K_i = 0.74, 1.05$, and 10.1 for the formation of the bromide ($I = \text{M}$), chloride ($I = 1 \text{ M}$) and hydroxide complexes ($I = 0.5 \text{ M}$) (41). Due to the scatter in our data, a more refined analysis of the complexation constants given in Table 2 is inappropriate.

A comparison of the K_{ow} values of the various R_3SnX_i species (see Table 2) shows that the K_{ow} values increased in the order

TABLE 3. Comparison of D_{ow} Model Calculation with Reported Data

solution conditions	log D_{ow}			
	TBT		TPT	
	exptl	calcd ^a	exptl	calcd ^a
pH 6, 0.1 M phosphate	3.3 ^b	3.6	3.1 ^b	3.5
pH 8, 0.1 M phosphate	4.1 ^b	4.3	3.6 ^b	3.7
pH 2–4, 0.1 M NaCl	3.4 ^c –4.2 ^d	4.1	2.9 ^c –3.5 ^d	3.5
pH 7–12, 0.1 M NaCl	4.2 ^c	4.2	3.6 ^c	3.6
seawater (0.5 M NaCl, pH 8)	4.4 ^e	4.4	3.8 ^e	3.7

^a From model eqs 1–14. ^b Ref 12. ^c Figure 4, p 157 ref 13. ^d This work (see Figure 3). ^e Ref 13.

$\text{NO}_3^- < \text{OH}^- \leq \text{ClO}_4^- < \text{Cl}^- < \text{Br}^-$, which qualitatively agrees with predictions made using hydrophobic substituent constants (30, 31). The absolute differences found between the various K_{ow} values are however smaller than the predicted ones. This is not too surprising because the substituent constants have been derived for substituents covalently bound to a carbon atom and, therefore, cannot be expected to directly describe the effects of substituents bound (perhaps not even covalently) to a Sn atom.

Comparison of Model Calculations with Data Reported in the Literature. Table 3 summarizes some D_{ow} values reported in the literature for TBT and TPT under various solution conditions together with the corresponding D_{ow} values calculated with our model (eqs 1–14) and the parameters given in Tables 1 and 2. The literature data (Table 3) were selected according to the following criteria: (i) clearly defined composition of solution (i.e., pH and ionic strength), (ii) concentration of TOTs measured in both aqueous and organic phases (to account for errors due to incomplete mass balance), and (iii) ability of the utilized analytical technique to distinguish between inorganic tin, mono-, di-, and triorganotin compounds (to avoid errors due to degradation, especially for experiments performed in natural waters). As can be seen from Table 3, most of the experimental D_{ow} values match the results of the model calculation quite well. The model calculations slightly overestimated the D_{ow} values for a system containing 0.1 M phosphate buffer, especially at low pH values. This behavior is a further indication of the formation of a hydrophilic phosphate complex, i.e., $\text{TOT} \cdot \text{HPO}_4^-$ (20). Because of the observed effect of phosphate on D_{ow} (see also Figure 3), its use as a pH buffer is not recommended. Instead, we recommend to work with zwitterionic buffers for toxicological and other studies dealing with TOTs. These buffers are known to only weakly interact with metal cations and biological material (42, 43). Furthermore, we did not observe any influence of these buffers on the partitioning of TBT and TPT (see Figure 2). This suggests that zwitterionic buffers do not strongly complex with TOTs.

The largest discrepancy between experimental and calculated D_{ow} values was found for the D_{ow} values reported by Tas (13) for low pH values and 0.1 M NaCl , namely $0.6 \log$ unit. However, the experimental D_{ow} values of TBT and TPT determined in this work at similar solution conditions (0.1 M NaCl and pH 4 and pH 3, respectively) are in very good agreement with our calculations.

The data presented in this paper enable one not only to predict D_{ow} values but also the speciation of TBT and TPT in the aqueous and octanol phase. For example, in seawater ($\text{pH} \approx 8$, $I \approx 0.5 \text{ M}$), the model predicts that 93% of the TBT in solution is TBTOH, 2–3% TBTCI, and 4–5% tributyltin cation, while, due to its lower pK_a value, TPT is predicted to be present almost exclusively as TPTOH (>99%). In the octanol phase equilibrated with seawater, the model predicts 89% TBTOH and 11% TBTCI. These model calculations are in agreement with the following observation of Laughlin et

al. (6). In a chloroform extract of a bis(tributyltin) oxide dispersion in 30‰ seawater (pH ≈ 8), both TBTOH and TBTCI were identified with ¹¹⁹Sn-NMR spectroscopy. Further, an undefined species with a ¹¹⁹Sn-NMR chemical shift similar to that of an undefined TBT carbonate species was reported to be present in the chloroform extract. The presence of a carbonate species is, however, questionable because in natural seawater the concentration of free HCO₃⁻ is only about 2 mM (44); the complexation constant for HCO₃⁻ would have to be approximately 250 times that of chloride, and the complex formed would have to exhibit a chloroform-water partition constant similar to that of TBTCI in order to be detectable in the chloroform extract. It seems more likely that the unidentified species was an impurity of the bis(tributyltin)oxide (e.g., dibutyltin) that had been used without purification.

Environmental Significance. The results of this work are important from an environmental point of view in that they provide the basis for assessing the speciation and the partitioning behavior of TBT and TPT in the aquatic environment. As is demonstrated in a companion paper (24), such knowledge is a prerequisite for understanding and quantifying the mineral-water and natural organic material-water distribution of organotin compounds. In addition, the data presented here should help in the interpretation of observed pH and salinity effects on the bioaccumulation (12, 13, 45-47) and toxicity (45) of TBT and TPT. However, this has to be done with great care since for ionizable organic compounds, such as weak acids and bases, we have recently shown that the *D*_{ow} value of the ionic species may significantly underestimate the sorption of such species to, for example, biological membranes (48) and may thus lead to an underestimation of both bioaccumulation and toxicity.

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