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Determination of Octanol–Water Partition Coefficients, Water Solubility and Vapour Pressures of Alkyl-lead Compounds

Yun Wang, Andrew G. Allen and Roy M. Harrison*
Institute of Public and Environmental Health/School of Chemistry, University of Birmingham,
Edgbaston, Birmingham B15 2TT, UK

Physico-chemical properties of alkyl-lead compounds, namely aqueous solubility, octanol–water partition coefficient (K_{ow}), vapour pressure and Henry's Law constant, have been determined. Vapour pressures of trialkyl-lead salts at different temperatures were measured by a gas-saturation technique in which air was passed slowly through a glass column packed with pure solid alkyl-lead compounds. K_{ow} of tetra-alkyl-lead (TAL) and trialkyl-lead (TriAL) were determined under different salinity and pH conditions, and the latter were related to the species (R_3Pb^+, R_3PbOH^0 or R_3PbCl^0) dominating under a particular set of conditions. Regression calculations incorporating melting point corrections relate water solubility to K_{ow}, and provide a means of estimating either parameter for a wider range of compounds.

Keywords: alkyl-lead; octanol–water partition coefficient; K_{ow}; water solubility; vapour pressure

INTRODUCTION

Environmental pollution by organic lead has arisen from the worldwide use of tetra-alkyl-lead (R_4Pb) compounds as gasoline (petrol) additives. Whilst many developed countries have phased down or entirely eliminated their use of alkyl-lead in gasoline, the compounds are still widely used in the developing world. Additionally, there is evidence for a slow conversion of inorganic lead to alkyl-lead in the environment by methylation.[1,2] In the environment, R_4Pb compounds decompose to inorganic lead with trialkyl-lead (R_3Pb^+) and dialkyl-lead (R_2Pb^{2+}) compounds as fairly persistent intermediates.[3] The toxicity of these species is well documented.[4]

The behaviour of organoleads as they interact with air, water, soil and biota, and degrade and migrate is dependent on their physico-chemical properties, including solubility in water, vapour pressure and their ability to partition into lipid-rich organic media (which can be defined using the octanol–water partition coefficient, K_{ow}). These properties have been widely used to predict the behaviour of organic compounds in the environment[5–7] and may be used for environment modelling purposes. For example, the Henry's law constant (H) can be determined from the ratio of vapour pressure to water solubility of a compound, and used to predict exchange across an air–water interface.[8] Tetra-alkyl-lead species are highly volatile ($H > 100$ Pa m^3 mol^{-1}) and are expected to be lost rapidly to the atmosphere under normal environmental conditions. Trialkyl-lead species, however, are only slightly volatile ($H < 1$ Pa m^3 mol^{-1}), with an equilibrium concentration in air only approximately 1/2500 of that of water, and may be readily transferred to solution across an air–water interface.

Only limited physical and chemical data are currently available for alkyl-lead species, and their octanol–water partition coefficients are entirely lacking. In this paper, the water solubilities of two trialkyl-lead chloride salts and the octanol–water partition coefficients of four tetra-alkyl-lead and two trialkyl-lead species are presented under different salinity and pH conditions. The vapour pressures of two trialkyl-lead chloride salts were determined by a gas-saturation method.

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* To whom correspondence should be addressed.

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EXPERIMENTAL

Chemicals

Trimethyl-lead chloride and triethyl-lead chloride were obtained from Johnson Matthey Ltd, Royston, UK. Aqueous stock solutions of 100 mg l^{-1} (as Pb) of trialkyl-lead were prepared by dissolving 13.9 mg and 15.9 mg, respectively, of trimethyl-lead chloride and triethyl-lead chloride in 100 ml water. The solutions were stored in the dark at 4 °C. Tetramethyl-lead, tetraethyl-lead and their mixed alkyl derivatives were provided by the Associated Octel Company, London. Octan-1-ol (especially pure for drugs partition coefficient determination) was obtained from Fisons Chemicals. All other reagents employed in the study were obtained from BDH Chemicals. Distilled, deionized water (DDW), from a Milli-Q system, was used throughout the study.

Water solubility

A preliminary test of water solubility was first performed according to the following procedure. To approximately 0.05 g of pure trimethyl-lead or triethyl-lead salt (TriAlCl) in a 25-ml glass-stoppered cylinder, increasing volumes (0.5, 1, 2, 10 and 25 ml) of DDW were added. After each addition the mixture was shaken vigorously for 10 min and visually checked for any undissolved material. It was found that almost complete solution was achieved with 0.5 ml and 25 ml of water for trimethyl-lead chloride and triethyl-lead chloride, respectively. In a second experiment, trimethyl-lead chloride (5 g) and triethyl-lead chloride (0.2 g) were added to 25 ml DDW in each of two glass bottles with glass stoppers. The mixtures were continuously agitated in an ultrasonic water bath at 30 °C for 24 h, and then re-equilibrated at the test temperature (20±2 °C) in the dark. After 1-, 3-, 7- and 14-day intervals, 1 ml of the saturated solution from each of the bottles was centrifuged to remove any remaining solid material, and an aliquot analysed using an alkyl-lead-specific method based on extraction, derivatization and gas chromatography–atomic absorption spectrometry.[9] Full equilibrium was found to be achieved within 14 days. Trimethyl-lead and triethyl-lead standards were prepared by dilution of their corresponding stock solution, and analysed according to the same procedure as described above. Recoveries of trimethyl-lead and triethyl-lead spiked into DDW were 104% and 100%, respectively. Analytical precision (RSD) was 4.7% (trimethyl-lead), and 7.2% (triethyl-lead).

Octanol–water partition coefficient

Before a partition coefficient was determined, a mixture of n-octanol and DDW was mechanically shaken together for 1 h and then separated by centrifugation to presaturate the two phases. The octanol-saturated water was then distributed into four 100-ml glass bottles and salinity and pH were adjusted to (a) $\mathrm{Cl^-}=0$ M, pH=7; (b) $\mathrm{Cl^-}=0.55$ M; pH=8; (c) $\mathrm{Cl^-}=2.0$ M, pH<8; (d) $\mathrm{Cl^-}=0$ M; pH=10 by adding NaCl and NH_4OH. All partition coefficient measurements were made at 20±2 °C.

Approximately 0.1 mg (as Pb) of each of four tetra-alkyl-lead compounds was dissolved in 10 ml of water-saturated octanol in a 60-ml brown glass bottle having an airtight closure. The octanol-saturated water (20 ml) was then added, and the mixture of two phases alternately shaken and equilibrated for 3 h, after which the two layers were separated by centrifugation and analysed. The octanol fraction was diluted with hexane and the water fraction was extracted into hexane before analysis. Extraction efficiencies from DDW into hexane for the four tetra-alkyl-lead species were between 96 and 102%.

Small amounts of the stock aqueous solutions

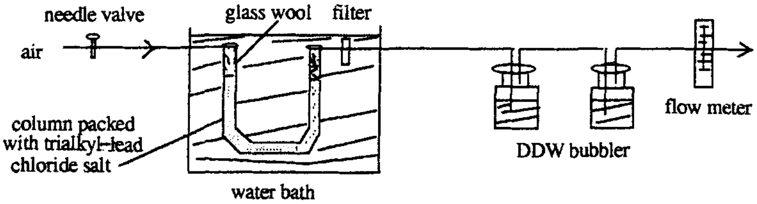

Figure 1 Schematic diagram of the gas-saturation technique to determine vapour pressure.

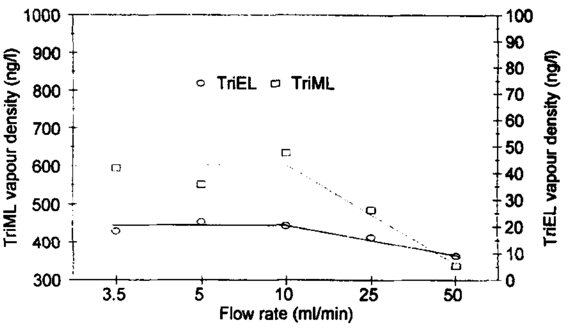

Figure 2 Influence of air flow rate on vapour pressure.

of trimethyl-lead and triethyl-lead chloride were dissolved in 20 ml of octanol-saturated water, and then 20 ml of water-saturated octanol was added. The same procedures were followed as given above for tetra-alkyl-lead. Trialkyl-lead in the water layer was extracted into hexane in the presence of NaCl and sodium diethyldithiocarbamate. The extraction efficiencies of trimethyl-lead and triethyl-lead were 98% and 96%, respectively. Trialkyl-lead in the octanol layer was first extracted into water, and then back-extracted into hexane. The extraction efficiency was 94% for trimethyl-lead and 88% for triethyl-lead. Further details of this analytical method have been published.[9]

The octanol–water partition coefficient (K_{ow}) was then given by the ratio of the equilibrium concentrations of the dissolved material in this two-phase system.

Vapour pressure

Approximately 0.8 g of solid trialkyl-lead chloride was packed into a clean U-shaped glass column (28 cm long × 6 mm i.d.) with glass-wool plugs at each end (Fig. 1). Gas-saturation measurements were then made by placing the column in a water bath to achieve a constant temperature, and slowly passing air (from a cylinder) through at 5–8 ml min^{-1}. Sufficient time (1 h) was allowed to attain a vapour-saturation state in the column, before the vapour-pressure measurement was started. Figure 2 illustrates the influence of air flow rate on vapour density, from which an upper limit of 10 ml min^{-1} is obtained in order that both trialkyl-lead compounds should reach saturation. The output was filtered through a 0.5-μm PTFE membrane, and gas-phase alkyl-lead was collected into two bubblers in series, each containing 100 ml DDW. That no losses of vapour-phase material occurred onto the particulate filter was confirmed by the collection of identical quantities of material in the bubblers when (a) the filter was positioned in the constant-temperature bath and (b) when it was maintained at ambient temperature. Flow rates were regulated by a needle valve, and measured with a soap-bubble flowmeter. After sampling was completed the solutions from the two bubblers were combined before determination of ionic alkyl-lead content. Previous work had shown that the use of two bubblers in series was sufficient to ensure 100% collection of gaseous trialkyl-lead species.[3] The vapour pressure was calculated from the measured vapour density by application of the ideal gas law (Eqn [1]),

$$P=dRT/M \qquad [1]$$

where P is the vapour pressure, d is the saturation vapour density, M is the molecular weight, T is the absolute temperature and R is the gas constant.

RESULTS AND DISCUSSION

Octanol–water partition coefficients, vapour pressures and water solubilities determined at

Table 1 Physico-chemical properties of alkyl-lead compounds (at 20 °C)

	Vapour pressure (mm Hg)	Water solubility (mg Pb l^{-1})	log K_{ow} Cl$^-$=0 M, pH=7	Henry's law constant (Pa m^3 mol^{-1})
Tetramethyl-lead	26[a]	15[a]	3.67	4.7×10^4
Trimethylethyl-lead	7.3[a]	—	3.88	—
Dimethyldiethyl-lead	2.2[a]	—	4.04	—
Tetraethyl-lead	0.26[a]	0.2–0.3[a]	4.15	6.9×10^4
Trimethyl-lead chloride	2.9×10^{-5}	96 870	−2.06	8.1×10^{-6}
Triethyl-lead chloride	7.4×10^{-7}	11 180	−1.76	1.8×10^{-6}

[a] Reference [2].

Table 2 Vapour pressures of TriML and TriEL measured at different temperatures

	Trimethyl-lead chloride		Triethyl-lead chloride	
Temperature (°C)	Vapour density ($\mu g\ m^{-3}$)	Vapour pressure (mm Hg)	Vapour density ($\mu g\ m^{-3}$)	Vapour pressure (mm Hg)
25	594	3.9×10^{-5}	20.4	1.2×10^{-6}
30	800	5.3×10^{-5}	33.8	1.9×10^{-6}
35	1017	6.8×10^{-5}	51.2	3.0×10^{-6}
40	1400	9.5×10^{-5}	78.8	4.7×10^{-6}

20±2 °C are presented in Table 1 (as means of paired experiments). Vapour pressures for trialkyl-lead species determined at 25, 30, 35 and 40 °C are listed in Table 2, and the relationship between log P and $1/T$ (the reciprocal absolute temperature) is illustrated in Fig. 3. The regression lines obtained were extrapolated to estimate the vapour pressures at 20 °C given in Table 1. The vapour concentration reported here for trimethyl-lead chloride at 25 °C is similar to that reported previously (450 $\mu g\ m^{-3}$) at ambient temperature,[10] although saturation was not obtained in the latter case and the concentration quoted in that study should therefore be considered a lower-limit value.

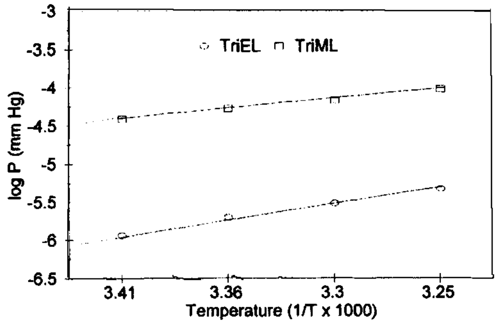

Figure 3 Relationship between vapour pressure and temperature (K).

Table 3 K_{ow} (for TAL) in simulated freshwater and seawater

	Freshwater ($Cl^-=0$ M pH=7)		Seawater ($Cl^-=0.55$ M pH=8)	
Compound	K_{ow}	log K_{ow}	K_{ow}	log K_{ow}
Tetramethyl-lead	4.7×10^3	3.67	1.3×10^4	4.10
Trimethylethyl-lead	7.6×10^3	3.88	2.7×10^4	4.43
Dimethyldiethyl-lead	1.1×10^4	4.04	3.2×10^4	4.51
Tetraethyl-lead	1.4×10^4	4.15	4.2×10^4	4.62

It is known that pH and salinity strongly affect the distribution of organomercury and organotin species between water and octanol.[11-13] Similarly, K_{ow} for TAL and TriAL will vary in natural waters having different conditions of salinity and pH. In the present work, K_{ow} was measured for sodium chloride concentrations of 0–2 M and pH 7–10 (Tables 3, 4), including conditions equivalent to those typical of freshwater and seawater. Paired two-sample comparison, using the t-test, between K_{ow} means for each TAL species showed statistically significant differences ($P<0.01$) according to the medium used. Thus the K_{ow} of TAL in saline water is rather higher than that in freshwater. An increase in chloride concentration of the solution also caused a large increase in the K_{ow} of trimethyl-lead and triethyl-lead (Table 4). In the aqueous phase, trialkyl-lead species present include R_3Pb^+, R_3PbOH^0 and R_3PbCl^0;[14] the fractions of these species present, determined from theoretical calculations (N. Mikac, Centre for Marine Research, Zagreb, Croatia, personal communication), according to salinity and pH, are given in Table 4. K_{ow, R_3Pb^+}, K_{ow, R_3PbOH^0} and K_{ow, R_3PbCl^0}, can be estimated from values obtained under conditions where individual species dominated. The smallest value of K_{ow} was obtained for freshwater, where R_3Pb^+ is the dominant species, in which the positive charge reduces affinity for the octanol phase. The lower K_{ow} for conditions where R_3PbOH^9 is dominant, as compared with those which favour the existence of R_3PbCl^0 is probably due to (a) the formation of stronger hydrogen bonds with water in the case of R_3PbOH^0 and (b) enhancement of the interaction of the trialkyl-lead species with the 'hydrocarbon tail' of octanol due to the presence of the Cl group of R_3PbCl^0 relative to the OH group of R_3PbOH^0. Theoretical values of K_{ow} under differ-

Table 4 K_{ow} (for TriAL) in different media

		Percentage of each species (%)				
		R_3Pb^+	R_3PbOH^0	R_3PbCl^0	K_{ow}	$\log K_{ow}$
Freshwater conditions	TriML:	98	2	—	8.7×10^{-3}	−2.06
$Cl^-=0$ M pH=7	TriEL:	99	1	—	1.7×10^{-2}	−1.76
Salt-water conditions	TriML:	42.5	8.5	49	1.8×10^{-1}	−0.74
$Cl^-=0.55$ M pH=8	TriEL:	32	3	65	2.6×10^{-1}	−0.58
	TriML:	—	—	81	3.9×10^{-1}	−0.41
$Cl^-=2.0$ M pH<8	TriEL:	—	—	88	4.7×10^{-1}	−0.33
	TriML:	—	95	—	7.8×10^{-2}	−1.11
$Cl^-=0$ M pH=10	TriEL:	—	90	—	1.5×10^{-1}	−0.82

ent pH and chloride-ion concentration conditions can be calculated using Eqn [2].[12]

$$K_{ow}=(f_{R_3PbCl^0})(K_{ow,\,R_3PbCl^0})+(f_{R_3PbOH^0})(K_{ow,\,R_3PbOH^0})+(f_{R_3Pb^+})(K_{ow,\,R_3Pb^+}) \qquad [2]$$

where $f_{R_3PbCl^0}$, $f_{R_3PbOH^0}$, and $f_{R_3Pb^+}$ represent the aqueous-phase equilibrium fractions of the trialkyl-lead species R_3PbCl^0, R_3PbOH^0 and R_3Pb^+, respectively. In seawater, trialkyl-leads are partly in ionic form and partly in chloride form. Estimated K_{ow} values for trimethyl-lead and triethyl-lead, under seawater conditions, were determined from Eqn. [2], and are in excellent agreement with measurement data (Table 5).

K_{ow} can also be estimated from water-solubility and melting-point data. A theoretical inverse relationship exists between K_{ow} and water solubility (S),[15, 16] while the K_{ow}–S correlation for solids is greatly improved by the inclusion of a melting-point correction having the form of Eqn [3].

$$\log K=a(\log S)+b(\mathrm{mp})+c \qquad [3]$$

where a, b and c are constants, and mp is the melting point of the solid. The regression equations for tetra-alkyl-lead and trialkyl-lead compounds, based on our data, given by Eqns [4] and [5].

$$\log K_{ow}=3.35-0.26\,(\log S)\ \text{for liquids} \qquad [4]$$

$$\log K_{ow}=3.35-0.26\,(\log S)-0.026\,(\mathrm{mp})\ \text{for solids} \qquad [5]$$

Table 5 Comparison of estimated and measured K_{ow} (simulated seawater)

Compound	$\log K_{ow}$ Measured	$\log K_{ow}$ Estimated	Error in estimated value (%)
Trimethyl-lead	−0.74	−0.70	5.7
Triethyl-lead	−0.58	−0.51	13.7

Comparisons of measured K_{ow} with estimated values obtained using the above formulae, together with the percentage errors in the estimated value, are listed in Table 6 for four alkyl-lead compounds. The melting points used were 190 °C and 166 °C for trimethyl-lead chloride and triethyl-lead chloride, respectively.[4] Measured and estimated log K_{ow} are in good agreement, with the uncertainty in estimated data less than 0.3% for tetra-alkyl-lead and 16% for trialkyl-lead compounds. The greater error for trialkyl-lead compounds may be result of the reported melting point being attributable, in part, to thermal decomposition, rather than solely a change of phase. It is proposed that these two regression equations may therefore be used to estimate K_{ow} or S for other alkyl-lead species likely to be present in the environment.

Table 6 Comparison of estimated and measured K_{ow} for TAL and TriAL

Compound	$\log K_{ow}$ Measured	$\log K_{ow}$ Estimated	Error in estimated value (%)
Tetramethyl-lead	3.67	3.66	0.27
Tetraethyl-lead	4.15	4.14	0.24
Trimethyl-lead chloride	−2.06	−2.43	13.8
Triethyl-lead chloride	−1.76	−1.52	15.8

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