



ENVIRONMENTAL RESEARCH BRIEF

Octanol/Water Partition Coefficients for Eight Phthalate Esters

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Abstract

Octanol/water partition coefficients (K_{ow}) for eight dialkyl phthalate esters were measured by the "slow-stir" method. The K_{ow} s and water solubilities for the esters were also computed by a computational expert system (SPARC). The largest difference between measured and computed values was for bis(2-ethylhexyl) phthalate; the difference was 0.27 log units at a log K_{ow} of >7 . Values for diethyl-, butylbenzyl-, and diamyl phthalate differed by only 0.04 log units.

Background

The Clean Water Act, the Marine Protection, Research, and Sanctuaries Act, the Endangered Species Act, and the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) require EPA to address sediment quality issues. A water quality-based approach is currently used to implement pollution control and prevention strategies for toxics in the water column. A similar approach is under development for sediments. Development of Sediment Quality Criteria (SQC) is an on-going component of the current Office of Research and Development (ORD) sediment research program. The method employed for deriving SQC uses equilibrium partitioning to estimate the amount of bioavailable contaminant(s) in sediment porewater for comparison with the water quality criteria for the contaminant(s). This approach is referred to as the equilibrium partitioning (EqP) model of bioavailability. The EqP method uses partition coefficients for relating the freely dissolved and total concentrations of chemicals in the water column, and pore water concentrations to total sediment concentrations of chemicals in sediments. The EqP method requires

sediment (K_{oc}), particulate (K_{poc}) and dissolved (K_{doc}) organic carbon partition coefficients, and the octanol/water partition coefficient (K_{ow}). Correlations have been developed for log K_{oc} , log K_{poc} , and log K_{doc} with log K_{ow} that allow their calculation from a known value of log K_{ow} . Uncertainties in SQC values for a chemical are closely related to the uncertainties in the log K_{ow} of the chemical.

A proposal by the Phthalate Ester Panel (PEP) of the Chemical Manufacturers Association offered an opportunity for EPA to test the EqP method on dialkyl phthalate esters with log K_{ow} s ranging from 1.5 to 8.5. The Environmental Research Task Group (ERTG) of the Panel drafted a preproposal for a sediment research program designed to evaluate the environmental safety of sediment-associated phthalate esters. The preproposal was submitted to the Sediment Quality Program in the Health and Ecological Criteria Division of the Office of Water of the U.S. Environmental Protection Agency (EPA) for review. After EPA review of the proposal, a joint meeting was held between ERTG and EPA, and consensus was reached on a research plan that would address joint research needs. The ERTG needed to assess the possible effects of phthalate esters on benthic organisms, and therefore required data to characterize potential phthalate ester exposures from contaminated sediments. One EPA objective for the research was to test the EqP method for predicting the toxicity of sediment-associated phthalate esters to benthic organisms. EPA agreed to determine the octanol/water partition coefficients (K_{ow}) of the phthalate esters by the "slow-stir" method (1-3). These log K_{ow} values and water-only toxicity data generated in preliminary experiments will be used to calculate sediment spiking concentrations for use in experiments designed to determine the potential for adverse acute effects at environmentally relevant concentrations. Data generated in these spiked sediment toxicity tests will be used to evaluate or "compare" the extrapo-

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lation of the EqP model across sediments and organisms. A second EPA objective was to compare the laboratory measured "slow-stir" $\log K_{ow}$ to values computed by SPARC (4,5).

Procedure

A detailed description of the method is reported elsewhere (6). Briefly, at the beginning of an experiment, water (0.5-9L) is brought into the equilibration vessel together with a Teflon-coated magnetic stirring bar, and a minimum vortex is initiated through the stirring action. When the water temperature has equilibrated to 25°C, the stirring is stopped and 10 to 25 ml of octanol are carefully layered onto the surface. Stirring is resumed. After 24 hours, stirring is stopped and octanol (30-100 ml) containing one of the esters to be measured is carefully added in a manner that avoids mixing the two phases. The concentration of the ester in the octanol is calculated to yield a final octanol layer concentration of 2 to 4 parts per thousand. Samples of octanol and water are analyzed daily until the ratio of the concentration of the chemical in the octanol divided by the concentration of the chemical in the water is the same for three successive days.

The water sample for each analysis is removed through a stopcock at the base of the equilibration vessel. The ester is extracted from the water sample by either methylene chloride or Empore™ extraction disks (acetonitrile extraction solvent). The extract is usually concentrated to a final volume of 0.5 to 1 ml by blowdown with a gentle stream of nitrogen. The concentration factors usually range from 10 to 8,000. Analysis of the octanol layer is performed by removing 1 ml and successively diluting it with solvent until gas or liquid chromatographic analysis of equal volume (1 μ l gas chromatograph and 10 μ l liquid chromatograph) injections of both the final octanol dilution and the water extract concentrate yield the same (within a factor of two) detector response. The K_{ow} is then calculated:

$$K_{ow} = \frac{(\text{Detector response, octanol}) \times \text{Dilution factor}}{(\text{Detector response, water}) \div \text{Concentration factor}}$$

Computed Data

SPARC (SPARC Performs Automated Reasoning in Chemistry) is a computational expert system that predicts chemical reactivity. The system has the capability of crossing chemical class boundaries to cover all organic chemicals and using algorithms based on fundamental chemical structure theory to estimate parameters. SPARC quantifies reactivity by classifying molecular structures and selecting appropriate "mechanistic" models. It uses an approach that combines principles of quantitative structure-activity relationships, linear free energy theory (LFET), and perturbed molecular orbital (PMO) or quantum theory to describe quantum effects such as delocalization energies or polarizabilities of π electrons. SPARC computes the log of the octanol/water partition coefficient from activity coefficients in the octanol (γ_o^∞) and water (γ_w^∞) phases:

$$\log K_{ow} = \log \frac{\gamma_w^\infty}{\gamma_o^\infty} + \log \frac{M_o}{M_w}$$

where M_o and M_w are solvent molecularities of octanol and water, respectively. Activity coefficients for either solvent or solute are computed by solvation models that are built from structural constituents requiring no data besides the structures. Water solubilities are computed in a similar manner.

A goal for SPARC is to compute values that are as accurate as values obtained experimentally for a fraction of the cost required to measure them. Because SPARC does not depend on laboratory measurements conducted on compounds with structures closely related to that of the solute of interest, it does not have, for instance, the inherent problems of phase separation encountered in measuring highly hydrophobic compounds ($\log K_{ow} > 5$). For these compounds, SPARC's computed value should, therefore, be more reliable than a measured one. However, at this time, no SPARC version number has been assigned for the physical property calculator. Data computed after future refinement in the calculator may, therefore, be slightly different.

Results and Discussion

Table 1 contains the list of phthalate esters studied and their $\log K_{ow}$ s measured by the "slow-stir" method and computed by SPARC. Because the water solubility of a chemical is an important physico-chemical parameter, the SPARC computed water solubilities are also listed. Three equilibration vessels were used in the "slow-stir" measurements of each phthalate ester. For the esters with $n > 3$ in Table 1, multiple samples were withdrawn from each flask. For example, each dimethyl phthalate vessel was sampled 4 times to yield a total of 12 determinations. For bis(2-ethylhexyl) phthalate (DEHP) and dioctyl phthalate (DOP) the contents of a single vessel were sampled on days 5, 6 and 8. The measured values and calculated values are in close agreement. The greatest difference between the SPARC-computed value and the mean of the "slow-stir" values is 0.27 log units for DEHP. Log K_{ow} values reported in the literature for DEHP range from 5.11 to 9.61. Computed and measured values for diethyl-, butylbenzyl-, and diamyl phthalate differ by only 0.04 log units.

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Table 1. Log K_{ow} Values for Eight Phthalate Esters

Chemical Name	CAS Number	Log K_{ow}		Water Solubility (SPARC), mg/L
		"Slow-Stir"	SPARC	
Dimethyl phthalate	131-11-3	1.60 ± 0.04 (n=12)	1.48	3.3E3
Diethyl phthalate	84-66-2	2.42 ± 0.04 (n=9)	2.51	4.0E2
Dibutyl phthalate	84-74-2	4.50 ± 0.03 (n=9)	4.63	4.9E0
Butylbenzyl phthalate	85-68-7	4.73 ± 0.06 (n=6)	4.77	2.4E0
Diamyl phthalate	131-18-0	5.62 ± 0.04 (n=6)	5.66	4.9E-1
Dihexyl phthalate	84-75-3	6.82 ± 0.10 (n=5)	6.67	4.9E-2
Bis(2-ethylhexyl) phthalate	117-81-7	7.27 ± 0.04 (n=3)	7.54	2.6E-3
Diocetyl phthalate	117-84-0	8.10 ± 0.11 (n=3)	8.30	4.6E-4

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