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Aqueous solubility (in the range between 298.15 and 338.15 K), vapor pressures (in the range between 10^{-5} and 80 Pa) and Henry's law constant of 1,2,3,4-dibenzanthracene and 1,2,5,6-dibenzanthracene

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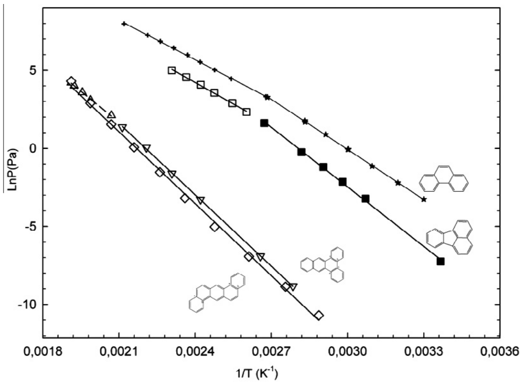
HIGHLIGHTS

- Vapor pressures of heavy polycyclic aromatic hydrocarbons (PAHs) were determined by chromatographic method.
- Aqueous solubility of PAH were determined by a saturation technique.
- Henry's law constant and partition of PAH between atmosphere and water was deduced from solubility and volatility data.

GRAPHICAL ABSTRACT

Comparison of vapor pressures of 4 PAHs from top: phenanthrene, fluoranthene, 1,2,3,4-DBA and 1,2,5,6-DBA.



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ABSTRACT

Aqueous solubility and vapor pressures of 1,2,3,4-dibenzanthracene and 1,2,5,6-dibenzanthracene were determined using dynamic saturation methods. For the two isomers, aqueous solubility is in the range between 10^{-10} and 10^{-2} in molar fraction corresponding to temperature between 298.15 and 338.15 K. Vapor pressures of the pure solutes range from 10^{-5} to 80 Pa. Prior to the study of the two dibenzanthracenes and in order to check the experimental procedures, solubility of fluoranthene (between 298 and 338 K) and vapor pressures of phenanthrene and fluoranthene (between 300 and 470 K) were measured.

From aqueous solubility data coupled with the vapor pressures of the pure solutes, partition coefficient air-water, K_{AW}, and Henry's constant, K_H, of environmental relevance were calculated.

1. Introduction

Polyaromatic hydrocarbons (PAHs) are a particular class of organic compounds, studied for their carcinogenic and mutagen character. The PAH's physical properties vary according to their

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molecular mass and structure. Due to their stability in the environment and their toxicity, several of them (sixteen) were declared priority pollutants by the EPA (Environmental protection agency) and the EEA (European environmental agency). PAH are biologically active molecules once accumulated in the organic tissues. The metabolites thus formed can have a toxic effect while binding to fundamental biological molecules such as proteins causing cellular dysfunction such as carcinogenic properties or mutagen character depending on the chemical structure of the formed metabolites (Baek et al., 1991; INERIS, 2003; Luch, 2005).

The effects of pollutants released to the environment are strongly influenced by their physical–chemical properties. Some of the most important properties controlling the partitioning between different environmental compartments are solubility of the solute in water (X), vapor pressures (P), octanol–water partition coefficient (K_{OW}), air–water partition coefficient (K_{AW}) and Henry's law constant (K_H).

The aim of the present study is to extend the knowledge of PAH by determining experimentally the vapor pressures (from 303 to 525 K) and aqueous solubility (at 298.15; 308.15; 318.15; 328.15 and 338.15 K) of 1,2,3,4-dibenzanthracene (1,2,3,4-DBA) and 1,2,5,6-dibenzanthracene (1,2,5,6-DBA) using two dynamic apparatuses. From the latter determinations were derived other thermodynamic properties such as sublimation and vaporization enthalpies beside the environmental partitioning parameters quoted previously, namely K_{AW} and K_H. Prior to dibenzanthracenes study, the experimental protocol used for both apparatuses was checked by studying fluoranthene and phenanthrene already studied by some authors. The experimental results were compared with the literature data.

2. Materials

The molecular configuration of the PAH along with the CAS number are detailed in Table 1.

The chemicals are from Sigma–Aldrich and present the highest purity available. The purity stated by the manufacturer is as follows: 1,2,3,4-DBA (98%), 1,2,5,6-DBA (99+%), phenanthrene (98%) and fluoranthene (98+%). Water used for aqueous solubility determination was bidistilled and ultrapure. The extraction solvent, dichloromethane, was supplied by Sigma–Aldrich with purity of 99.9% (HPLC grade). All compounds were used without any further purification.

3. Aqueous solubility

3.1. Experimental method

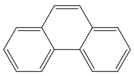
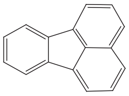
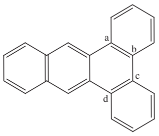
The used apparatus is shown in Fig. 1. It has been described in detail in previous papers (Saab et al., 2010, 2008). The principle for solubility measurement is based on the saturation of a known quantity of water flowing through a cell (*b*) packed with a stationary phase, Chromosorb W 60/80 mesh (Interchim, France), previously coated by the organic solute (5% by mass). The saturated water flows into the extraction column (*d*) where the sample is trapped for analysis after a cooling step (*c*). Water exempt of solute is recovered in a flask for weighting (*f*). Water delivery is assured by a liquid chromatography pump. The used flow rate is low, 0.5 ml/min, to ensure liquid–liquid equilibria.

The final step is the extraction of the solute by an adequate solvent in order to perform a quantitative analysis. In the present case the elution solvent is dichloromethane. Prior to the use of this solvent which is not miscible with water, methanol was used to remove water in the circuit downstream the sample cell (PAH are practically nonmiscible with methanol and remain in the extraction cartridge). Anyhow, used methanol was recovered and analyzed by GC–MS to ensure it is free from any trace of sample. To evacuate the residual water, gas nitrogen stream at flow rate of 20 mL/min was sent in the elution circuit. Thus, this supplementary step eliminate the risk of cohabitation of water with dichloromethane and loose of sample while recuperation.

3.2. Validation of the procedure – study of fluoranthene

Although the experimental procedure was checked previously (Saab et al., 2008), the very low solubility study of PAH and the modification over the experimental procedure led us to validate the entire process using a polyaromatic molecule. Fluoranthene ($C_{16}H_{10}$) was chosen as some values are available in the literature. Solubility of fluoranthene was studied in pure water in a temperature range between 298.15 K and 338.15 K. The analysis of the trapped compound was carried out by gas chromatography coupled to mass spectrometer using internal calibration method (benzo(a)pyrene was used as internal standard). Each measurement was repeated three times. The relative standard deviation do not exceed 3% overall the temperature range, Table 2.

Table 1
Structure and properties of the studied PAHs.

Compound	Formula	CAS number	Molecular weight (g mol^{-1})	Structure
Phenanthrene	$C_{14}H_{10}$	85-01-8	178.23	
Fluoranthene	$C_{16}H_{10}$	206-44-0	202.25	
1,2,3,4-Dibenzanthracene	$C_{22}H_{14}$	215-58-7	278.34	
1,2,5,6-Dibenzanthracene	$C_{22}H_{14}$	53-70-3	278.34