Available online at www.sciencedirect.com
ScienceDirect
Journal of Chromatography A, 1140 (2007) 195–204
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Aqueous solubility data for pressurized hot water extraction for solid heterocyclic analogs of anthracene, phenanthrene and fluorene

Pavel Karásek, Josef Planeta, Michal Roth [*]

Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 60200 Brno, Czech Republic

Received 27 September 2006; received in revised form 16 November 2006; accepted 17 November 2006
Available online 1 December 2006

Abstract

We report the aqueous solubilities of phenanthrene and several solid three-ring aromatic heterocycles (phenanthridine, acridine, phenazine, thianthrene, phenothiazine, phenoxathiin, phenoxazine, carbazole, dibenzofuran, dibenzothiophene, and 4,6-dimethyldibenzothiophene) at temperatures ranging from 313 K to the solute melting point and at a pressure of 5 MPa. The data were measured by dynamic saturation method using an in-house-assembled apparatus for pressurized hot water extraction (PHWE). The solute from a known mass of the saturated aqueous solution was transferred to an organic solvent (hexane or toluene), and the organic phase was analyzed by GC/MS. In any of the solutes, the GC/MS records did not indicate any noticeable decomposition within the temperature range of the measurements. The resultant solubilities were converted to activity coefficients of the individual solutes in saturated aqueous solutions, and the results are discussed in terms of temperature and type/number of heteroatoms.

Keywords: Pressurized hot water; Solubility; Aromatic heterocycle; Extraction; Sample preparation; Activity coefficient

1. Introduction

The needs for sustainable development and for environmentally benign processes result in growing use of tunable green solvents [1], with water providing the greenest alternative available. Here, "tunability" means the possibility to achieve significant variations in solvent power and properties through changes in the operating temperature and pressure. The properties that control the solvating abilities of water, i.e., the static relative permittivity (dielectric constant), the cohesive energy density, and the ion product, vary widely with temperature and pressure [2–4]. Consequently, water is not only the greenest but also the most tunable solvent [5].

Liquid water at temperatures between the normal boiling point and the critical point, often referred to as pressurized hot water (PHW) [6], can even be used as a benign alternative solvent for organic reactions [7,8]. Since its first reported use as a solvent in analytical extractions [9], PHW has seen many interesting applications in sample treatment procedures for analytical chemistry [10–12], extractions of plant materials [13–16], environmental remediation processes [17–19], decomposition of non-biodegradable polymers [20], or hydrothermal degradation of silk protein to amino acids [21]. The reactions in PHW are a complement to the reactions conducted under more drastic conditions in supercritical water [22–26].

In spite of the frequent applications of pressurized hot water extraction (PHWE) as a sample treatment method, the underlying fundamental data available to date seem far from being of satisfactory amount and diversity. Most previous measurements of solubilities of heavy organic solids in PHW were focused on polycyclic aromatic hydrocarbons (PAHs) [27–32], and a predictive correlation with pure component properties has recently been developed [33] to estimate PAH solubilities in PHW as functions of temperature and pressure. Solubility data for other classes of important organic solid solutes, however, are scarce [28–30]. Therefore, to strengthen the rational background for PHWE process design and to improve understanding of the solvent properties of PHW, extension of the solubility measurements in PHW to other classes of heavy organic solutes is necessary. Given the data base already available for PAHs, nitrogen- and sulfur-containing aromatic heterocycles are natural candidates in this respect, both because of their importance

---

[*] Corresponding author. Tel.: +420 532 290 171; fax: +420 541 212 113.
E-mail address: roth@iach.cz (M. Roth).

0021-9673/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2006.11.061

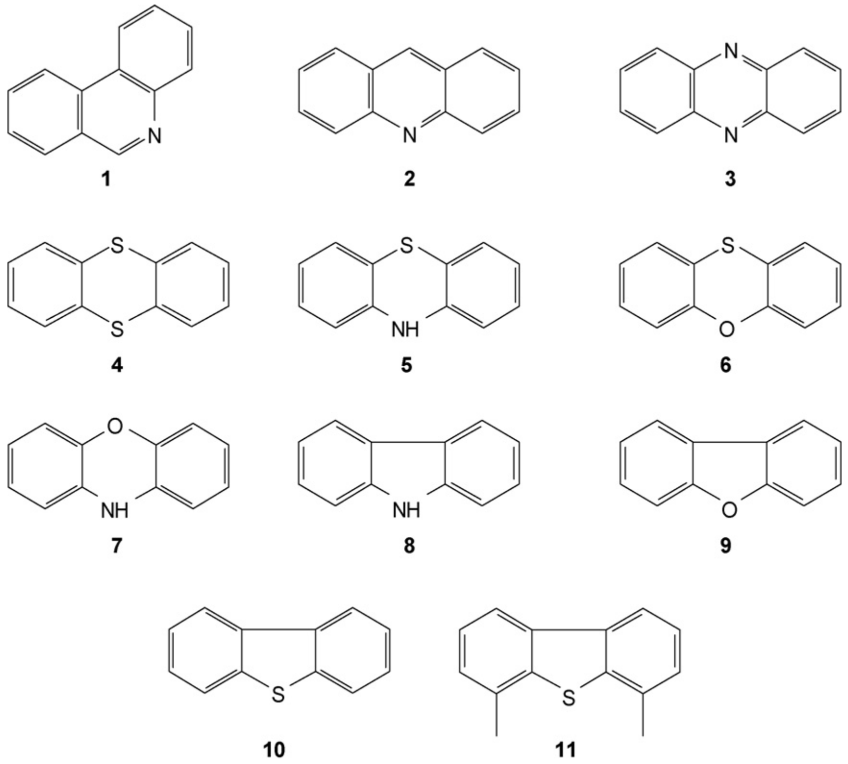

Fig. 1. Structures of heterocyclic solutes: (1) phenanthridine, (2) acridine, (3) phenazine, (4) thianthrene, (5) phenothiazine, (6) phenoxathiin, (7) phenoxazine, (8) carbazole, (9) dibenzofuran, (10) dibenzothiophene, (11) 4,6-DMDBT.

as components of crude oil and potential pollutants and because of future use of solubility data in thermodynamic model development for PHWE processes. From the specific angle of applications in analytical chemistry, solubility data can also be useful as reference values for investigations of sample matrix effects in PHWE.

This contribution presents new data on aqueous solubilities of several solid nitrogen-, sulfur- and oxygen-containing heterocyclic analogs of anthracene, phenanthrene and fluorene at temperatures from 313 K to the solute melting point and at a pressure of 5 MPa.

2. Experimental

2.1. Solutes and solvents

Phenanthrene (>99%), phenanthridine (98%), acridine (97 %), phenazine (98%), thianthrene (97%), phenothiazine (>98%), phenoxathiin (97%), phenoxazine (97%), carbazole (99 %), dibenzofuran (>99%), dibenzothiophene (>99%) and 4,6-dimethyldibenzothiophene (4,6-DMDBT, 97%) were purchased from Sigma–Aldrich (Prague, Czech Republic). Fig. 1 shows an overview of the structures of heterocyclic solutes. Prior to use, the heterocyclic compounds were recrystallized two times from methanol. Methanol (HPLC grade, 99.8%) and toluene (HPLC grade, 99.8%) were obtained from Penta (Chrudim, Czech Republic). Hexane (Pestanal grade, >95%) was supplied by Riedel deHaën (Prague, Czech Republic). Water was purified with a reverse osmosis system Ultra Clear UV (Wasseraufbereitung und Regenerierstation, Barsbüttel, Germany). Immediately before use of water, care was taken to remove the dissolved air by bubbling a stream of helium.

2.2. Experimental arrangement

The experimental setup was essentially the same as in our previous work with PAHs [32,33]. Briefly, the dynamic saturation method was employed to prepare the aqueous solution of the solute at the particular temperature and pressure, a known mass of the aqueous solution was allowed to cool down to room temperature, the solute was transferred to an organic solvent, and the organic solution was analyzed by GC/MS employing a suitable internal standard (see Section 2.4).

Fig. 2 shows a photograph of the in-house-assembled extraction apparatus. The flow-through extraction cell (length 110 mm, I.D. 4 mm) was packed with a mixture of the solid solute with glass beads. The solution left the cell through a fused-silica capillary restrictor, and it was collected in a preweighed vial containing a known amount of water. The presence of water at the start of collection was needed to prevent boiling of the cell effluent at elevated operating temperatures. The flow rate of water through the system had to be sufficiently small to make sure that the composition of the cell effluent really corresponded to equilibrium between the solid solute and the liquid solution. On the basis of equilibration tests in our previous work [32], the maximum mass flow rate of water in the present study did not exceed 0.017 g s^{-1}.

The restrictor dimensions had to be optimized to secure the desired flow rate and, simultaneously, to prevent the outlet end of the restrictor from getting clogged with the solid solute