Solubility of Acenaphthene, Anthracene, and Pyrene in Water At 50 °C to 300 °C

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The aqueous solubilities of acenaphthene, anthracene, and pyrene, three polycyclic aromatic hydrocarbons (PAHs), were measured at temperatures from 50 °C to 300 °C. A dynamic method was used in the production of saturated aqueous solution, and the amount of analyte was determined by gas chromatography−mass spectrometry. In solubility measurements below the melting point of the analyte, a flow-through saturation cell was applied, whereas for measurements above the melting point a new saturation cell was constructed and the experimental setup was optimized. Solubilities below the melting point correlated well with literature values. An exponential relationship between solubility and temperature was found for pyrene and anthracene. The mole fraction solubilities measured at 250 °C and 5 MPa were $(1.25 \pm 0.097) \times 10^{-3}$ for acenaphthene, $(4.97 \pm 0.89) \times 10^{-4}$ for anthracene, and $(2.05 \pm 0.23) \times 10^{-4}$ for pyrene. At 300 °C and 10 MPa, the values were $(3.78 \pm 0.13) \times 10^{-3}$ for anthracene and $(1.41 \pm 0.17) \times 10^{-3}$ for pyrene. Aqueous solubilities of pyrene, anthracene, and acenaphthene at such high temperatures have not been reported previously.

Introduction

Knowing the solubilities of PAHs at elevated temperatures will help us to better understand the mechanisms in pressurized hot water extraction (PHWE). It is also easier to optimize the PHWE conditions if the solubilities are known. The water solubilities of several PAHs have been measured at ambient temperature or slightly above it, and generally, the solubilities are low.[1] Some solubility data exists for higher temperatures too, but little solubility data is available above the melting point of the analytes.

The water solubility (S_w) defines the maximum concentration of analyte in the aqueous phase. Undissolved analyte and dissolved analyte are then in dynamic equilibrium, and the solution is said to be saturated. Solubilities can be determined by static or dynamic methods. For the determination of solubilities, a saturated solution of the analyte is first generated, and the amount of analyte in the saturated solution is then measured. Spectrophotometric,[2,3] gravimetric,[4] chromatographic,[5−7] generator column,[8] and visual[9] methods are commonly used in the measurement of solubilities. Methods based on radionuclides[10] and fluorescence[11] have also been applied.

Earlier, saturated aqueous solutions were prepared by the "shake-flask" method in which an excess quantity of the analyte was added to the water while the solution was stirred.[2] The analysis of the saturated solutions was most often carried out by spectrophotometry. The method is time-consuming and also prone to errors when the solubilities are determined for compounds of only low water solubility.

In the generator column method, saturated solutions are generated either off- or online, with measurement of the amount of analytes by solid-phase extraction liquid chromatography.[8] A solid support is coated with the compound of interest and packed into the generator column. The saturated aqueous solution is obtained by pumping water through the generator column. After the online SPE and a concentration step, the analytes are analyzed online by HPLC with fluorescence detection.

A dynamic system with a flow-through saturation cell is one way to generate saturated solutions. The amount of analyte in the effluent is determined by gas chromatography−mass spectrometry. The system has been applied in the determination of solubilities of solid analytes[5,6] and, with slight modifications, to liquid analytes such as benzene and toluene.[12] In the last case, the setup differs according to whether the analyte is more or less dense than water. The solubilities of liquid organic flavor and fragrance compounds have been measured as well, at temperatures ranging from 25 °C to 200 °C.[13]

The presence of other organic solutes clearly affects the solubility of the individual components at higher temperatures (200 °C), but only a little at 25 °C or 50 °C.[5] Although a change in temperature affects the solubilities, often dramatically, an increase in pressure has only a minor effect on the solubility. When the pressure is increased from 1 bar to 65 bar, the solubility of naphthalene remains virtually unchanged,[6] but when the pressure is increased from 60 bar to 2850 bar, the solubility of anthracene decreases by an order of magnitude.[14] The solubility of 2,4,6-trinitrotoluene (TNT) has been studied as a function of temperature and pH.[15] The solubility drops at high pH, and transformation products of TNT are observed. No transformation products are observed at low pH. Solubilities of triazine pesticides (atrazine, cyanazine, and simazine) have been measured in pure water, and the solubility of atrazine was also measured in water modified with ethanol or urea at temperatures ranging from 50 °C to 125 °C.[16] Both cosolvents increase the solubility of atrazine relative to pure water, but the increase in solubility is more pronounced with ethanol.

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In this study, the solubilities of selected PAHs [acenaphthene (a three-ring PAH), anthracene (a three-ring PAH), and pyrene (a four-ring PAH)] were measured at temperatures ranging from 50 °C to 300 °C using a dynamic system similar to that described by Miller et al.[5,6] for generating saturated aqueous solutions. The collected fractions were analyzed by GC−MS with an internal standard technique. A primary objective of the study was to determine the solubilities at the temperatures used in PHWE (200 °C to 300 °C) to obtain a better understanding of the extraction process in PHWE. Because the solubility measurements had to be done above the melting points of the analytes, the construction of a new saturation cell was required.

Experimental Section

Solvents and Chemicals. All of the solvents were of HPLC grade. Toluene was from Lab-Scan Analytical Sciences (Dublin, Ireland). Heptane and chloroform were from Rathburn (Walkerburn, Scotland, U.K.). Water was distilled and ion-exchanged with a Millipore Milli-Q system (Molsheim, France). Pyrene (purity ca. 97%, MW 202.26, mp 156 °C, bp 404 °C), anthracene (purity ca. 99%, MW 178.24, mp (214 to 216) °C, bp 342 °C), acenaphthene (purity ≥99%, MW 154.21, mp (92 to 95) °C, bp 279 °C) and fluoranthene (purity ≥97%, MW 202.26, mp (105 to 110) °C, bp 375 °C) were from Fluka (Buchs, Switzerland). Acid-washed sea sand was purchased from Riedel-de Haën (Seelze, Germany). Anhydrous sodium sulfate used in the drying of the samples was from Merck (Darmstadt, Germany).

Instruments. Apparatus for Generating Saturated Solutions. The principle of the system used for generating saturated aqueous solutions has been presented by Miller et al.[5,6] In our study, two Jasco PU-1580 pumps (Tokyo, Japan) were employed, one for pumping water through the saturation cell and the other for pumping the collection solvent. The 3-m-long preheating coil and all the other stainless steel capillaries before the T piece had an inner diameter of 0.5 mm; the stainless steel capillaries after the T piece, including the 1-m-long cooling coil, had an inner diameter of 0.75 mm. The cooling coil was inserted into an ice bath. The flow-through-type saturation cell used below the melting point of the analytes had an internal diameter of 1.0 cm, length of 3.7 cm, and volume of 3 mL. This type of laboratory-made saturation cell was used earlier as an extraction vessel for pressurized hot water extraction.[17,18] The saturation cell used above the melting point of the analytes had an internal diameter of 2.0 cm, length of 3.5 cm, and volume of 11 mL (Figure 1). The i.d. of the cartridge sometimes placed inside the saturation cell was 1.0 cm; the length was 3.0 cm, and the volume was 2.4 mL. All of the saturation cells were made of stainless steel 316L.

A GC oven was modified to heat the saturation cell. The oven temperature was adjusted by changing the heating power with a laboratory-written computer program. A temperature probe (thermocouple) was installed in the oven, and the temperature was monitored by computer with the aid of a Pico TC-08 thermocouple data logger (Pico Technology, Cambridgeshire, U.K.). The temperature of the oven, not the temperature of the water, was measured during the solubility measurements. It can be assumed, however, that the temperature of the water was the same as the temperature of the oven because a stabilization time of (20 or 30) min was allowed at each temperature. The pressure in the equipment was regulated with a manually adjustable pressure restrictor (micrometering valve from Jasco), and the pressure was kept so high that water always existed in the liquid phase. The pressure was 5 MPa in all solubility measurements at 50 °C to 250 °C, but in the solubility measurements at 300 °C, it was 10 MPa. The pressure was read from the two Jasco pumps, and the readings of the two pumps were generally the same during the measurement. During the solubility measurements, the uncertainty in the temperature was ±0.5 °C, and that in the pressure was ±0.5 MPa.

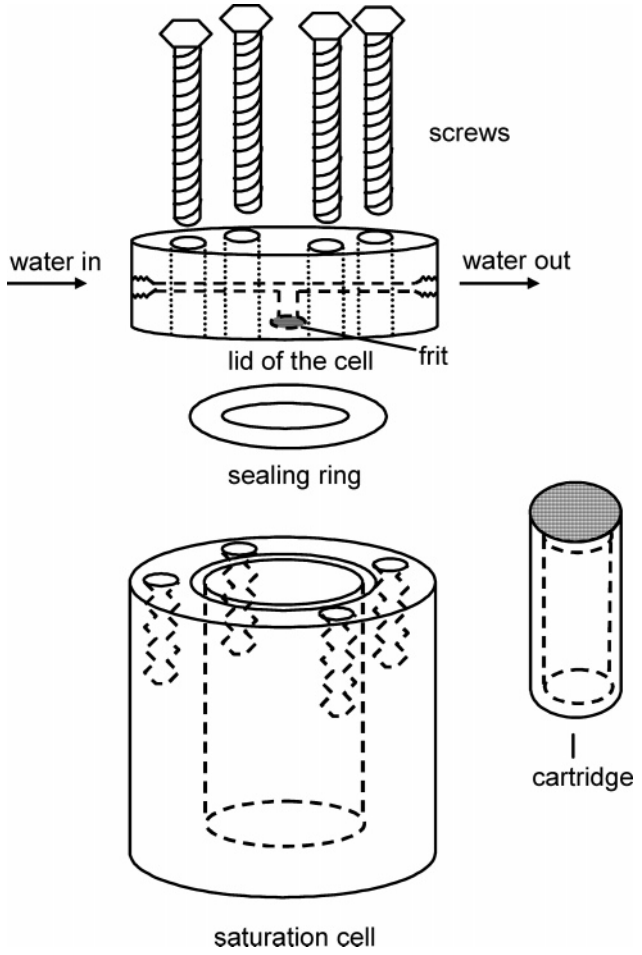

Figure 1. Saturation cell used above the melting point of the analytes.

Gas Chromatograph−Mass Spectrometer. The fractions collected from the solubility apparatus were analyzed with an Agilent model 6890N gas chromatograph connected to a model 5973 mass-selective detector. All analyses were done in scan mode. The ions used for the quantification were 202 for pyrene, 178 for anthracene, 153 for acenaphthene, and 202 for the internal standard fluoranthene. On-column injection was applied, and the injection volume was 1 μL. The injector was operated in oven tracking mode. The pressure of helium used as a carrier gas was 100 kPa. The analytical column was a 30 m × 0.25 mm i.d. HP-5 column (Agilent Technologies) with a phase thickness of 0.25 μm, and it was connected to a 3 m × 0.53 mm i.d. DPTMDS-deactivated retention gap (Agilent Technologies) via a glass pressfit connector (BGB Analytik AG, Rothenfluh, Switzerland). When the samples were in heptane or toluene, the GC oven was programmed from 80 °C (4 min) at 20 °C/min to 300 °C (10 min). However, when chloroform was used as sample solvent, the temperature program was started from 40 °C. The mass spectrometer was operated in EI mode (70 eV). The temperatures of the transfer line, quadrupole, and ion source were 300 °C, 150 °C, and 230 °C, respectively.

Measurement Procedure. The basic idea in the measurements was as follows. The saturation cell was packed either with PAH and sea sand or with PAH only. In the beginning of the measurement, water was pumped at 1 mL/min to pressurize the system, and the oven was heated to the desired temperature. After the equilibration period, the fractions were collected. The water saturated with the PAH was mixed with the collection solvent, usually toluene, in the T piece placed in the hot oven, and the PAHs partitioned to toluene as the water cooled. Finally, the toluene fractions containing the analytes were analyzed by GC−MS. The overall procedure used in the solubility measurements has been described by Miller et al.[5,6] In our procedure, however, the collection solvent was toluene. In some experiments, heptane or chloroform was used instead. The equilibration period at each temperature was 20 min when the measurements were done below the melting point of the analyte and 30 min when the measurements were done above the melting point. The time used for the collection of one fraction was 10 min (Miller et al.[5,6] used 3 min). Below the melting point of the analytes, six fractions were collected in one measurement; above the melting point, five fractions were collected. In other words, each measurement ($n = 1$) is a mean of five or six fractions, and thus standard deviations (SD) could be calculated for single measurements. The solubility values reported are the average values from four separate measurements ($n = 4$), which increases the reliability of the results. The solubilities reported by Miller et al. were for a single measurement at each temperature, with each measurement based on five[6] or ten[5] fractions.

The flow rate of water was 0.1 mL/min, and the flow rate of toluene was 0.4 mL/min. However, the flow rate of toluene was 1 mL/min in the solubility measurements with anthracene at 300 °C and with acenaphthene at 250 °C. The saturation cell was packed with a 20 mass % mixture of PAH in sea sand in the measurements below melting point. The mixture of PAH and sea sand was homogenized with a spatula before packing into the saturation cell. In the measurements above the melting point, the PAH was usually packed in the saturation cell without sea sand. When the water eluting from the oven cooled, the analyte was partitioned into toluene, which was used as a collection solvent. If necessary, the fractions were diluted. Then 100 μL of fluoranthene was added as an internal standard at a concentration of 50 μg/mL, 100 μg/mL, or 250 μg/mL depending on the measurement, and toluene and the water phases were separated. The toluene phase was dried by elution through a Pasteur pipet packed with sodium sulfate.

All of the solubilities in this work were calculated as mole fraction solubilities (x_2). Labfit (version 7.2.2 by Wilton and Cleide Pereira da Silva, Paraíba, Brasil) software was used for the treatment and analysis of experimental data.

Results and Discussion

1. Solubility Measurements below the Melting Point. The effect of the collection solvent on the results was studied using pyrene; in addition to toluene, chloroform and heptane were also tested. The repeatability between the different measurements was clearly better with toluene: at 50 °C and 5 MPa, the RSD with toluene was 23% ($n = 4$), whereas with heptane it was 81% ($n = 5$) and with chloroform it was 109% ($n = 3$). Toluene was chosen as the collection solvent because it gave the most repeatable results but also because, in general, toluene is a better solvent for PAHs and also less volatile than chloroform or heptane.

The solubilities obtained at 100 °C and 5 MPa, when 10 mass %, 20 mass %, and 30 mass % pyrene in sea sand were packed in the saturation cell, were compared. Almost identical results were obtained with the different percentages, indicating that saturated solutions could be obtained with all amounts of pyrene. The mole fraction solubilities measured under the different conditions were $(7.18 \pm 0.61) \times 10^{-7}$ (10 mass % pyrene, $n = 1$), $(6.37 \pm 0.25) \times 10^{-7}$ (20 mass % pyrene, $n = 4$), and $(6.46 \pm 0.80) \times 10^{-7}$ (30 mass % pyrene, $n = 1$). Within the SD values, there were no differences among the solubilities, but because the standard deviation was lower with 20 mass %, this level was used in the following experiments.

The effect of the geometry of the saturation cell on the results was studied at 100 °C and 5 MPa, and it was found that a short and broad cell (length 1.3 cm, i.d. 1.5 cm, and volume 2 mL) and the longer cell generally used in solubility measurements (length 3.7 cm, i.d. 1.0 cm, and volume 3 mL) gave very similar results. The solubilities measured with the short and broad cell and the conventional cell were $(6.79 \pm 0.61) \times 10^{-7}$ ($n = 1$) and $(6.37 \pm 0.25) \times 10^{-7}$ ($n = 4$), respectively. A somewhat smaller solubility value was obtained when a longer and narrower cell (length 7.7 cm, i.d. 0.7 cm, and volume 3 mL) was used: $(5.40 \pm 0.041) \times 10^{-7}$ ($n = 1$). Again, the results were at the same level, indicating, however, that the geometry of the saturation cell does not appreciably affect the results.

For pyrene and anthracene, the solubilities measured below the melting point are presented in Table 1. The values agree with literature values obtained with the same technique.[5] Our values are also compared in a subsequent paragraph to the solubilities measured with another technique by Rössling et al.[14] Note that our solubilities are based on 4 separate measurements at the same temperature, whereas the literature values with the same technique are the results of single measurements in which 10 fractions were collected. The solubility of pyrene was greater than that of anthracene at 100 °C and 5 MPa, but the solubility of anthracene increased more rapidly with temperature than did that of pyrene. With increasing temperature from 100 °C to 150 °C, the solubility of anthracene was enhanced 31-fold, whereas with increasing temperature from 100 °C to 140 °C the solubility of pyrene increased only 8-fold.

Rössling et al.[14] have also determined solubilities for anthracene at high temperatures. We converted the solubilities measured by Rössling et al. to mole fraction solubilities to be able to compare our results to their results. At 100 °C and at a pressure of 7 MPa, Rössling et al. obtained a mole fraction solubility of 3.06×10^{-7} (1.70×10^{-5} mol/L), and at 150 °C and a pressure of 6 MPa, they obtained mole fraction solubility of 5.75×10^{-6} (3.19×10^{-4} mol/L). The solubility at 100 °C compares well with our value [$(3.25 \pm 0.34) \times 10^{-7}$], whereas our value is twice as high at 150 °C [$(1.02 \pm 0.13) \times 10^{-5}$]. At 200 °C and at a pressure of 80 MPa, Rössling et al. measured a mole fraction solubility of 2.74×10^{-5} (1.52×10^{-3} mol/L) for anthracene. This value is smaller than our value [$(1.38 \pm 0.19) \times 10^{-4}$], but the solubilities at 200 °C should not be compared because the pressures differed considerably and an increase in pressure decreases the solubilities.

2. Solubility Measurements above the Melting Point. It was not possible to use the flow-through saturation cell in measurements above the melting point of the analytes because most of the melted analyte would then have moved forward in the equipment with the water flow and the amount of analyte in the collected fractions would not

Table 1. Solubilities Measured (at 5 MPa) below the Melting Point for Pyrene and Anthracene ($n = 4$) and Comparison with Literature Values Obtained by a Similar Method

compound (temperature)	measured solubility ($x_2 \pm$ SD[a])	literature value[b] ($x_2 \pm$ SD)
pyrene (50 °C)	$(8.63 \pm 3.58) \times 10^{-8}$	
	$(7.80 \pm 1.50) \times 10^{-8}$	
	$(5.43 \pm 0.55) \times 10^{-8}$	
	$(5.63 \pm 0.59) \times 10^{-8}$	
average of averages	$\mathbf{(6.87 \pm 1.59) \times 10^{-8}}$	$(3.8 \pm 0.1) \times 10^{-8}$
pyrene (100 °C)	$(6.17 \pm 0.51) \times 10^{-7}$	
	$(6.32 \pm 0.31) \times 10^{-7}$	
	$(6.73 \pm 0.35) \times 10^{-7}$	
	$(6.25 \pm 0.29) \times 10^{-7}$	
average of averages	$\mathbf{(6.37 \pm 0.25) \times 10^{-7}}$	$(9.0 \pm 0.5) \times 10^{-7}$
pyrene (140 °C)	$(7.16 \pm 0.23) \times 10^{-6}$	
	$(3.80 \pm 0.33) \times 10^{-6}$	
	$(4.40 \pm 0.64) \times 10^{-6}$	
	$(6.24 \pm 0.52) \times 10^{-6}$	
average of averages	$\mathbf{(5.40 \pm 1.57) \times 10^{-6}}$	
anthracene (100 °C)	$(2.89 \pm 0.12) \times 10^{-7}$	
	$(3.58 \pm 0.44) \times 10^{-7}$	
	$(3.03 \pm 0.20) \times 10^{-7}$	
	$(3.48 \pm 0.30) \times 10^{-7}$	
average of averages	$\mathbf{(3.25 \pm 0.34) \times 10^{-7}}$	$(3.2 \pm 0.5) \times 10^{-7}$
anthracene (150 °C)	$(1.06 \pm 0.077) \times 10^{-5}$	
	$(1.14 \pm 0.0067) \times 10^{-5}$	
	$(1.05 \pm 0.061) \times 10^{-5}$	
	$(0.83 \pm 0.021) \times 10^{-5}$	
average of averages	$\mathbf{(1.02 \pm 0.13) \times 10^{-5}}$	$(9.2 \pm 0.6) \times 10^{-6}$
anthracene (200 °C)	$(1.55 \pm 0.10) \times 10^{-4}$	
	$(1.25 \pm 0.13) \times 10^{-4}$	
	$(1.52 \pm 0.039) \times 10^{-4}$	
	$(1.18 \pm 0.057) \times 10^{-4}$	
average of averages	$\mathbf{(1.38 \pm 0.19) \times 10^{-4}}$	$(2.1 \pm 0.25) \times 10^{-4}$

[a] The standard deviation in one measurement is calculated for the six fractions collected. The standard deviation for the average of averages (bolded) is calculated from the four average solubility values. [b] Each literature value is a result of 1 measurement in which 10 fractions were collected.[5]

reflect the solubility in water. In view of this, a new saturation cell was constructed for solubility measurements above the melting point of the analytes (Figure 1). In this cell, the water flows through the lid of the cell. The analytes diffuse into the water flow through the frit and the small opening in the lid. Where an inner cartridge was used in the measurements, it was inserted upside down into the saturation cell, with PAH or the PAH + sea sand mixture packed inside. In some measurements, the space between the saturation cell and the cartridge was filled with sea sand. As it turned out, the cartridge hindered the diffusion of PAHs into the water flow. There were grooves in the bottom of the cartridge because otherwise the cartridge would have been too tight against the lid of the cell, totally preventing the diffusion of PAHs into the water. There were also four small grooves at the top end of the cartridge to allow the analytes to diffuse from the cartridge to the saturation cell and into the water. The whole assembly was tightened with four screws and a sealing ring.

Search for Optimum Measurement Conditions and Setup. In the optimization of the new cell, it was assumed that solubilities obtained with the new saturation cell and the flow-through saturation cell should be similar for measurements below the melting point of the analyte. The solubility values and RSDs (in one measurement and between measurements) were the criteria used for choosing the best setup. Solubilities should also follow some reasonable relationship as a function of temperature. For example, exponential increases in the solubility of atrazine in water have been observed with increases in temperature and with increases in the amount of ethanol in water.[16] In addition, it was important to ensure that saturation was reached in the measurements after an equilibration period of 20 min, not just the steady state. To be sure of that, the amount of the test solute in the cell was increased (discussed in more detail later).

Pyrene was used as a test solute in optimizing the conditions and setup. First, the new cell was tested at 140 °C and 5 MPa. In an attempt to ensure that the analytes moved only by diffusion, the cartridge was filled with a 20 mass % mixture of pyrene in sea sand and placed upside down in the saturation cell. The space between the cartridge and the saturation cell was filled with sea sand, and a frit (10 μm) was fixed in the lid of the cell. Some pyrene eluted at the beginning of the solubility measurement, but the amount decreased markedly in subsequent fractions. Evidently this setup presented too much hindrance to allow pyrene to be eluted properly. Different cell constructions were then tested, one by one, with pyrene at 300 °C and 10 MPa, to find the setup giving the best and most repeatable results.

First, two setups were tested, one with a frit in the lid of the saturation cell (Table 2, column a) and one without (Table 2, column b). There was no cartridge in the saturation cell, and 0.6 g of pyrene was packed into the bottom of the cell. The kinetics of the measurements (Figure 2) as well as the solubilities and RSDs of the measurements (Table 2) were used in judging which setups performed best. In the kinetic measurements (Figure 2), the collection of the fractions was started immediately after the oven reached the temperature of 300 °C without any stabilization time, and that is why the amount of pyrene was small and increased in the first fractions. When the solubilities of PAHs were calculated, the first fractions corresponding to the stabilization time were never taken into account to allow the saturation conditions to be reached. The configuration with the frit gave lower solubilities than that without a frit, and the amount of pyrene in the fractions decreased noticeably in the course of the measurement (Figure 2). Quite clearly then, saturated solutions are not obtained when a frit is assembled in the lid of the cell because, in the attempt to ensure diffusion, the setup creates too much hindrance.

Having established that the configuration without the frit (Table 2, column b) worked better, we went on to test whether the cartridge should be used at all and whether the saturation cell should be right side up or upside down. For this test, 0.6 g of pyrene was packed into the cartridge, and the cartridge was inserted upside down in the saturation cell. In two measurements with the cartridge, the saturation cell was right side up (Table 2, column c), and in two measurements, it was upside down (Table 2, column d). It was found that the setup without the cartridge (Table 2, column b) worked better: the solubility was higher and the RSDs were generally lower than with the cartridge. With the cartridge applied, the setup in which the saturation cell was right side up gave higher solubilities than that with the saturation cell turned upside down. However, as Figure 2 illustrates, with the saturation cell right side up the solubilities drop off quite sharply in the last fractions. The setups with the frit and cartridge gave solubilities for pyrene that were too low because the hindrance to diffusion was too great. Thus, the configuration without the frit,

Table 2. Solubilities and RSDs of the Solubility Measurements for Pyrene at 300 °C and 10 MPa Using Different Setups

	(a) frit, no cartridge, 0.6 g pyrene ($n = 4$)	(b) no frit, no cartridge, 0.6 g pyrene ($n = 4$)	(c) no frit, cartridge, 0.6 g pyrene ($n = 2$)	(d) no frit, cartridge, saturation cell upside down, 0.6 g pyrene ($n = 2$)	(e) no frit, no cartridge, 1.2 g pyrene ($n = 4$)
solubility (x_2)	5.65×10^{-5}	1.21×10^{-3}	4.86×10^{-4}	1.07×10^{-5}	1.41×10^{-3}
RSD (%) of different solubility measurements	29	36	123	4	12
average RSD (%) of single measurement in which five fractions (10 min) were collected	56	31	48	64	8

without the cartridge, and with the saturation cell right side up was selected as the best setup.

Repeatability was still a problem, however. A test was accordingly made of how the amount of pyrene in the saturation cell affects the repeatability. Doubling the amount of pyrene from 0.6 g (Table 2, column b) to 1.2 g (Table 2, column e) improved the repeatability markedly, and 1.2 g was chosen for further studies. The solubilities with these two amounts of pyrene were nevertheless very similar (Table 2), indicating that saturated solutions can also be obtained with 0.6 g of pyrene. The same effect as was obtained by doubling the amount of pyrene in the saturation cell could have been obtained by decreasing the volume of the saturation cell. After the solubility measurement, a ring of precipitated pyrene was often encountered halfway up the wall of the saturation cell, indicating that the melted pyrene had risen to that level during the measurement. However, the melted pyrene did not escape from the cell in the course of the measurement because otherwise the amount of pyrene would have been very large in the first fractions and then it would have decreased. Also, it has to be pointed out that because of the experimental setup there is a small possibility that water flowing through the lid of the saturation cell may not always be fully saturated with the PAH under all conditions, which may lead to solubility values that are slightly too low.

Measurements under Optimized Conditions. The setup and conditions selected on the basis of the optimization of the solubility measurements above the melting point of PAHs were 1.2 g of PAH and neither frit nor cartridge in an upright saturation cell. The equilibration time used in measurements above the melting point was 30 min.

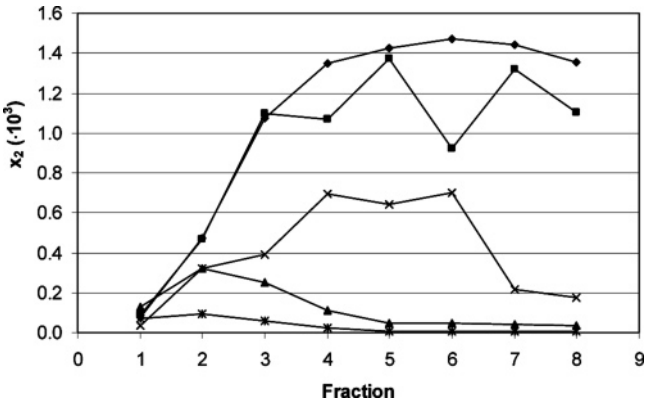

Figure 2. Kinetics of the solubility measurements at 300 °C and 10 MPa using different setups and pyrene [−◆−, no frit, no cartridge, 1.2 g pyrene ($n = 4$); −■−, no frit, no cartridge, 0.6 g pyrene ($n = 4$); −▲−, frit, no cartridge, 0.6 g pyrene ($n = 4$); −×−, no frit, cartridge, 0.6 g pyrene ($n = 2$), −*−, no frit, cartridge, 0.6 g pyrene, saturation cell upside down ($n = 2$)]. In these kinetic measurements, the collection of the fractions was started immediately after the oven reached the temperature of 300 °C without any stabilization times.

The solubilities obtained for pyrene at 140 °C and 5 MPa with the new saturation cell and the optimized conditions were compared with the results obtained earlier with the flow-through cell to confirm that the new saturation cell was working well. The new saturation cell gave similar results to the flow-through saturation cell when 0.6 g of pyrene was packed into the cell, indicating that it was working well. The solubility measured for pyrene at 140 °C and 5 MPa was $(3.45 \pm 1.07) \times 10^{-6}$ ($n = 3$) with the new cell and $(5.40 \pm 1.57) \times 10^{-6}$ ($n = 4$) with the flow-through cell.

The solubilities measured for pyrene, anthracene, and acenaphthene above their melting points are presented in Table 3. As can be seen, the solubilities for the different PAHs at 250 °C decrease as the molar mass increases and polarity of PAH decreases. Thus, the solubility is higher for acenaphthene than for anthracene and higher for anthracene than for pyrene. The same trend has been observed for acenaphthene, fluoranthene, and pyrene in several organic solvents.[19] In nonpolar solvents such as hexane, acenaphthene was more soluble than fluoranthene, and pyrene was the least soluble.

Rössling et al.[14] have also measured the solubility of anthracene in water above its melting point at 250 °C (523 K), but the pressure was much higher (80 MPa) so their results and our results cannot be directly compared because the pressure has an effect on solubility when the differences in the pressures are very large. However, we converted the solubilities measured by Rössling et al. to mole fraction solubilities to compare our results roughly to their results. At 250 °C (pressure 80 MPa), Rössling et al. had a mole fraction solubility of 1.84×10^{-4} (1.02×10^{-2} mol/L), whereas our value was $(4.97 \pm 0.89) \times 10^{-4}$. This is in agreement with the fact that solubility decreases as the pressure is increased.

It is worth noticing that at 100 °C pyrene was more soluble than anthracene. The same result was found in an earlier study where a similar method was applied in the determination of solubilities, though otherwise the solubility decreased as the ring size and molar mass of the PAHs increased.[5] Many parameters such as molar mass, polarity, vapor pressure, and shape of the molecule affect the solubility, and it is difficult to predict the effect of an individual parameter. As the temperature is increased, the enhancement in solubility is more pronounced for the nonpolar compounds that have low ambient aqueous solubility because the water gradually becomes more and

Table 3. Solubilities for Pyrene, Anthracene, and Acenaphthene above the Melting Point ($n = 4$)[a]

compound (temperature)	measured solubility ($x_2 \pm$ SD[b])
pyrene (200 °C)	$(5.74 \pm 0.24) \times 10^{-5}$
	$(7.76 \pm 0.56) \times 10^{-5}$
	$(2.96 \pm 0.76) \times 10^{-5}$
	$(3.22 \pm 0.37) \times 10^{-5}$
average of averages	$\mathbf{(4.92 \pm 2.27) \times 10^{-5}}$
pyrene (250 °C)	$(1.90 \pm 0.21) \times 10^{-4}$
	$(1.92 \pm 0.66) \times 10^{-4}$
	$(2.39 \pm 0.51) \times 10^{-4}$
	$(1.99 \pm 0.37) \times 10^{-4}$
average of averages	$\mathbf{(2.05 \pm 0.23) \times 10^{-4}}$
pyrene (300 °C)	$(1.32 \pm 0.085) \times 10^{-3}$
	$(1.23 \pm 0.22) \times 10^{-3}$
	$(1.62 \pm 0.082) \times 10^{-3}$
	$(1.47 \pm 0.050) \times 10^{-3}$
average of averages	$\mathbf{(1.41 \pm 0.17) \times 10^{-3}}$
anthracene (250 °C)	$(5.79 \pm 0.38) \times 10^{-4}$
	$(5.59 \pm 0.54) \times 10^{-4}$
	$(4.62 \pm 0.85) \times 10^{-4}$
	$(3.88 \pm 0.91) \times 10^{-4}$
average of averages	$\mathbf{(4.97 \pm 0.89) \times 10^{-4}}$
anthracene (300 °C)	$(3.67 \pm 0.20) \times 10^{-3}$
	$(3.96 \pm 0.15) \times 10^{-3}$
	$(3.69 \pm 0.27) \times 10^{-3}$
	$(3.78 \pm 0.16) \times 10^{-3}$
average of averages	$\mathbf{(3.78 \pm 0.13) \times 10^{-3}}$
acenaphthene (250 °C)	$(1.23 \pm 0.17) \times 10^{-3}$
	$(1.37 \pm 0.062) \times 10^{-3}$
	$(1.24 \pm 0.12) \times 10^{-3}$
	$(1.14 \pm 0.24) \times 10^{-3}$
average of averages	$\mathbf{(1.25 \pm 0.097) \times 10^{-3}}$

[a] Pressure was 5 MPa at 200 °C and at 250 °C and 10 MPa at 300 °C. [b] The standard deviation in one measurement is calculated for the five fractions collected. The standard deviation for the average of averages (bolded) is calculated from the four average solubility values.

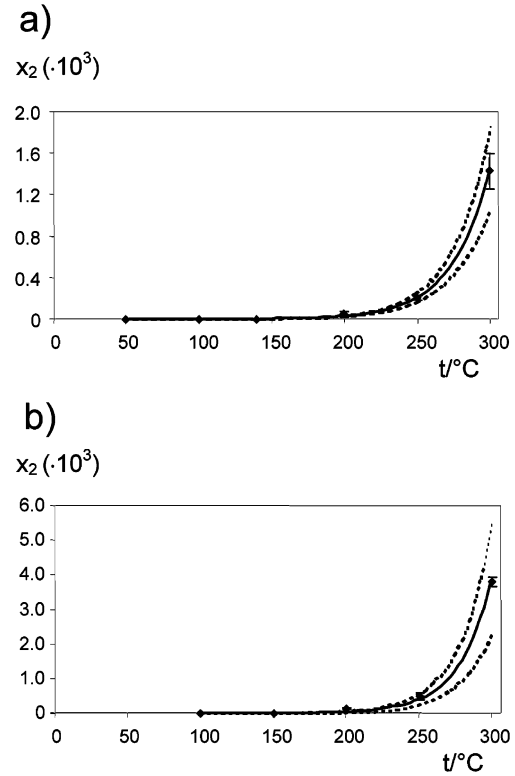

Figure 3. Exponential plots of solubility x_2 as a function of temperature for (a) pyrene and (b) anthracene. Pressure was 5 MPa at (50 to 250) °C and 10 MPa at 300 °C. The 95% confidence limits are shown. Both plots were generated by the Labfit program. The parameters for the exponential equation $Y = A \times 10^{(BX)}$ were for pyrene (a) $A = 0.1313 \times 10^{-07}$ (uncertainty $\sigma a = 0.9673 \times 10^{-09}$), $B = 0.3870 \times 10^{-01}$ (uncertainty $\sigma b = 0.4961 \times 10^{-03}$), and $R^2 = 0.9998162$ and for anthracene (b) $A = 0.3724 \times 10^{-08}$ (uncertainty $\sigma a = 0.4917 \times 10^{-09}$), $B = 0.4615 \times 10^{-01}$ (uncertainty $\sigma b = 0.4698 \times 10^{-03}$), and $R^2 = 0.9988203$.

more nonpolar as the critical temperature of water is reached.

From 200 °C to 300 °C, the solubility of pyrene increased 29-fold, and the solubility of anthracene increased 27-fold. There are no literature values available for these temperatures, but Figure 3 (generated by the Labfit program) shows that the solubilities of pyrene and anthracene change exponentially with temperature when all measurements, both below and above the melting point, are taken into account. The exponential relationship is followed very well: the R^2 values were over 0.99 for both pyrene and anthracene.

Where the solubility measurements were carried out at high temperature, the possible degradation of PAHs had to be considered. The GC−MS chromatograms were studied to determine if there were extra peaks in the chromatograms, but with a few exceptions, no extra peaks were seen.

In the beginning, when the measurements above the melting point of the analytes were started with the new saturation cell, some extra peaks appeared in the chromatogram, but they were most likely contamination because they disappeared later. Clearly, it is advisable to condition a new saturation cell by heating it in an oven before using it for the first time

In our earlier stability studies at 300 °C with heating times as short as 10 min, degradation of PAHs was observed, but in those studies, the amount of PAH in the measurement was much smaller than in the measurements in this work.[20] When the amount of PAH is small (empty reaction vessel spiked with PAH), the contact of the PAH with the walls of the vessel (can catalyze the degradation) and subsequent degradation can be more pronounced.

Conclusions

The aqueous solubilities of anthracene and pyrene measured below the melting point were close to values obtained earlier with similar equipment. A new saturation cell was constructed for measurements above the melting point of the analytes, and the setup for those measurements was optimized. At 140 °C and 5 MPa, values obtained with the new saturation cell were close to those measured with the flow-through saturation cell, indicating that the new saturation cell was working well. The solubilities measured after the optimization above the melting points of the PAHs appeared to be reasonable because for both pyrene and anthracene they followed an exponential relationship with temperature with high R^2 value. Aqueous solubilities were also measured for acenaphthene at 250 °C and 5 MPa. For all three PAHs, the repeatability of the high-temperature measurements was good. Except for the value measured for anthracene at 250 °C, this is the first time that aqueous solubilities have been reported for acenaphthene, anthracene, and pyrene above their melting points and at temperatures as high as 300 °C. The solubility values that were measured will help us to understand the mechanisms in pressurized hot water extraction.

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