

Solubility and Solubility Modeling of Polycyclic Aromatic Hydrocarbons in Subcritical Water

Wen Hui Teoh,[†] Raffaella Mammucari,[‡] Silvio A. B. Vieira de Melo,[§] and Neil R. Foster^{*‡}

[†]Department of Chemical Engineering, University of Malaya, Malaysia

[‡]School of Chemical Engineering, University of New South Wales, Australia

[§]Programa de Engenharia Industrial, Escola Politécnica, Universidade Federal da Bahia, Brazil

S Supporting Information

ABSTRACT: A static analytical equilibrium method was used to measure the binary and ternary solubilities of anthracene and *p*-terphenyl in subcritical water between 393 and 473 K and at 50 and 150 bar. Temperature was found to have the most significant effect on the solubility of polycyclic aromatic hydrocarbons (PAHs) in subcritical water. The effect of pressure, and the combined effect of temperature and pressure on solubility were found to be insignificant, particularly when the range of pressure considered is relatively small. The solubilities of PAHs were found to be governed primarily by sublimation pressure, and only secondarily by the dielectric constant of water. The Peng–Robinson equation of state was used to correlate the aqueous solubilities of PAHs under subcritical conditions, with good agreement between experimental and calculated values obtained for binary systems.

1. INTRODUCTION

The solubilities of a number of hydrophobic solid substances in water at room temperature have been investigated in recent years, and found to be as low as 10^{-6} and even 10^{-7} mole fractions.^{1,2} However, numerous studies have also shown that the solubilities of hydrophobic compounds in liquid water increase dramatically above 100 °C.^{3–7} As a consequence of the dramatic increase in solvating power, subcritical water at relatively higher temperature has been shown to be a good alternative to organic solvents. Subcritical water processing has its advantages in that water is nontoxic, inexpensive, readily available, and easily disposed. In terms of the extraction process, subcritical water has the added advantage of not requiring the drying of samples prior to processing.⁸ Among others, subcritical water technologies have been applied to the removal and decomposition of pollutants, for the extraction of compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls from soils, and recently to the micronization of hydrophobic drugs.^{3,4,7,9–13} The onward desire for sustainability through the reduction in the costs and usage of toxic organic solvents, the search for alternatives that are nonexhaustible, and the need for versatility in extraction techniques became the motivation for the development of subcritical water technologies.^{14,15}

Although the use of subcritical water to process materials is gaining increased interest, many potential applications remain undeveloped due to a lack of fundamental data. An understanding of the thermodynamics of subcritical water phase equilibria is essential and important in the design of separation and extraction processes. In light of the need for accurate thermodynamic data, fundamental solubility studies are necessary as they quantify the ability of subcritical water to act as a solvent, consequently defining the feasibility and economic effectiveness of a particular process.^{16,17} In the present study, a static analytical equilibrium method was employed to measure the solubilities of anthracene and *p*-terphenyl. The present work follows from the experimental work conducted by Carr et al.⁷ with

a number of modifications incorporated to improve the reliability and the relative standard deviation (RSD) of the solubility data obtained. A detailed discussion is given in the following sections.

2. PHASE EQUILIBRIA OF PAHS IN SUBCRITICAL WATER

Solubility measurements conducted in this study are above the normal boiling points of the solvents. Sufficient pressure must be applied to maintain the liquid state of the solvents used. Therefore, an understanding of the VLE of the solvents involved is essential. The saturated vapor pressures of water at various temperatures are shown in Table 1. The data from

Table 1. Vapor Pressures for Water, Anthracene, and *p*-Terphenyl at Various Temperatures

temperature (°C)	water saturated vapor pressure ^a (bar)	anthracene sublimation pressure ^b (bar)	<i>p</i> -terphenyl sublimation pressure ^b
120	1.99	8.97×10^{-4}	8.59×10^{-5}
140	3.61	2.50×10^{-3}	3.15×10^{-4}
150	4.76	3.99×10^{-3}	5.70×10^{-4}
160	6.18	6.22×10^{-3}	9.33×10^{-4}
170	7.92	9.45×10^{-3}	1.68×10^{-3}
180	10.02	1.40×10^{-2}	2.75×10^{-3}
200	15.54	2.92×10^{-2}	6.81×10^{-3}

^aData obtained from Parry et al.¹⁸ ^bData obtained from Zhao et al.¹⁹

Table 1 shows that a minimum pressure of 16 bar is required to ensure water is in the liquid state at temperatures between 120 and 200 °C. The sublimation pressures of anthracene and

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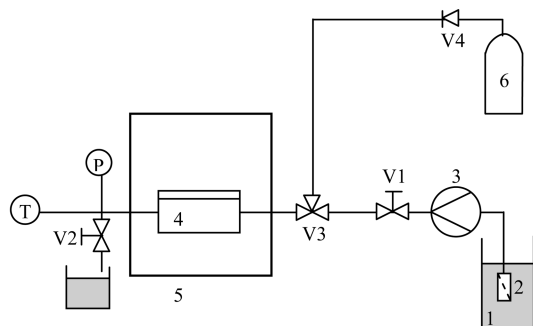
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p-terphenyl are also shown in Table 1 and are lower than the vapor pressure of water. All solubility measurements in the present study were conducted at a pressure of 50 bar to keep a safe range away from the minimum of 16 bar.

The experimental setup for a phase behavior study is shown in Figure 1. Solutes were packed into a Jergusen gage placed in



1: deionized water; 2: filter; 3: syringe pump; 4: Jergusen gage; 5: oven; 6: N₂ cylinder; T: temperature indicator; P: pressure indicator

Figure 1. Schematic diagram of the phase behavior study.

a GC oven with the glass side of the Jergusen gage facing upward. A K-type thermocouple attached to a Jenco temperature indicator was inserted into the Jergusen gage. Water was allowed to flow into the system. Valves V1, V2, and V3 were closed once water dripped out. The temperature of the oven was raised to the maximum desired temperature. As the oven was heated up, the pressure in the system increased. The liquid solution was released via valve V2 to maintain the pressure of the system at 50 bar. When the system had reached the required temperature and pressure, the system was allowed to equilibrate for 45 min. Any physical changes to the solute and the solution were observed.

Both anthracene and *p*-terphenyl in subcritical water were observed to be at solid–liquid equilibria at 200 °C and 50 bar. Melting point depression was not observed for anthracene and *p*-terphenyl in water at temperatures as high as 200 °C. Observations from the phase behavior study also did not indicate the presence of a third gaseous phase.

3. APPARATUS AND EXPERIMENTAL METHOD FOR SOLUBILITY MEASUREMENT

Anthracene and *p*-terphenyl of 99% purity were purchased from Sigma-Aldrich. Degassed deionized water was used in all experiments. A static equilibrium experimental setup was utilized and is shown schematically in Figure 2. Solute was packed into a 6 mL stainless steel equilibrium vessel together with a magnetic stirrer. The amount of solute loaded into the vessel was higher than the amount solubilized during the experiment, and at all times, there was an excess of solute. An external oscillating iron ring magnet attached to a motor via stainless steel rods guided the internal magnet. Filter stones of 2 μm porosity were fitted to each end of the vessel to prevent physical entrainment of the solute in the liquid phase. A Shimadzu GC-8A chromatography oven was used for heating. The temperature indicator in the GC oven was calibrated with a GMC-calibrated K-type thermocouple attached to a Jenco (model 7000CH) temperature indicator.

At the commencement of an experiment, an ISCO model 260D syringe pump was used to supply water to the system. Water was *not* heated and set to the required temperature prior to being pumped into the rig due to the limitations in the equipment available. Valves V1, V2, and V4 were opened.

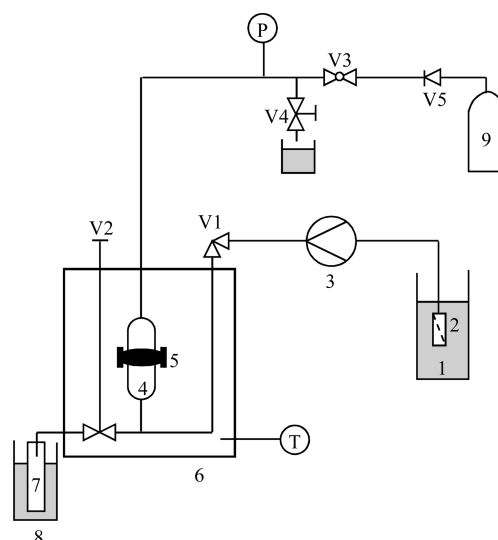


Figure 2. Schematic diagram of the solubility apparatus.

Valve V2 and subsequently valve V4 were closed once water dripped out. At the onset of heating, valve V4 was occasionally opened to relieve pressure generated from thermal expansion. Subsequently, pressure was kept at 50 bar throughout the experiment with an ISCO syringe pump operating in constant pressure mode. Pressures were measured with a Druck pressure transducer (PDCR 911), coupled with a Druck DPI 260 pressure indicator calibrated with a Hydraulic Dead weight Tester (Pressurements Model M2200). Stirring commenced at the onset of heating. Once the system had reached the required temperature, the system was left to equilibrate for a designated amount of time while being stirred by the magnetic stir bar. Equilibration time for each solute in subcritical water at various temperatures is shown in Table 2 and is further discussed in section 3.1.

Table 2. Equilibration Time for Solubility Measurement of Anthracene and *p*-Terphenyl at Various Temperatures and 50 bar

temperature (°C)	equilibration time (min)
120	180
140	40
150	40
160	25
170	25
180	22
200	20

Near the end of the equilibration time, a weighed collection vessel (CV) dipped into a cold water bath was connected to valve V2. All fittings and tubing were made of stainless steel type 316. At the end of equilibration, the magnetic stirrer was stopped. Nitrogen gas preset to 54 bar was allowed to contact the solution in the equilibrium vessel via valve V3. Nitrogen was used to maintain the pressure of the solution in the equilibrium vessel to prevent premature vaporization of the solution. In this way, it was possible to withdraw samples without disturbing the equilibrium condition (constant pressure, temperature, and phase composition). Once V3 was fully opened, V2 was opened to allow decanting of solution into the collection vessel (CV). When N₂ started to flow into the collection vessel, V2 and V3 were shut and the oven was turned off.

When the collection vessel had cooled, it was removed, externally dried, and weighed. The solvent and the precipitated solutes in the collection vessel were collected in a glass vial. Further washings with acetone were conducted to ensure all solutes were collected in the glass vial. Valve V2 was also washed with acetone. The liquid was collected in a glass vial and dried. The solutes were then dissolved in analytical grade methanol and analyzed by UV. Three experimental runs were conducted on each solubility data point with a maximum of 5% relative standard deviation (RSD) obtained. The reported solubility data are expressed as the mean values of three experimental runs and given as mole fractions of the solute in water. The results were compared against the solubility of anthracene in subcritical water from published literature and are discussed in the following sections.

3.1. Equilibration Time. In a static equilibrium method, equilibration is promoted by stirring or rocking, as an effective mixing would allow for a fast equilibration.²⁰ The need for stirring in a static equilibrium method is different from a dynamic continuous flow method where a large amount of solutes is required for short equilibration time. Therefore, in the present study, the amount of PAH soluble in subcritical water was measured at various mixing time intervals until a plateau was observed in the measured data. Saturation was established when a plateau was observed. For example, the measured concentrations of *p*-terphenyl in subcritical water at 120 °C and various equilibration times are given in Figure 3.

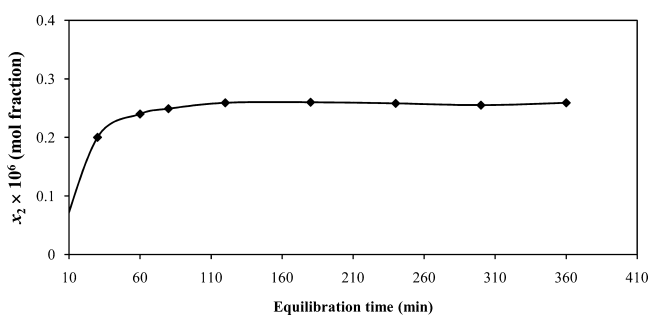


Figure 3. Measured concentrations of *p*-terphenyl in subcritical water at 120 °C and different equilibration times via the static equilibration method.

The concentration of *p*-terphenyl in water was observed to approach a plateau after equilibrating for 120 min. While a minimum equilibration time of 120 min was required, an additional 60 min of mixing was conducted to ensure saturation for *p*-terphenyl in subcritical water. The total equilibration time of 180 min for a solubility measurement at 120 °C was not extended to other higher temperatures, since the tendency for solutes to degrade at higher temperatures would be compounded by a long mixing time. Instead, the same principle was applied to other investigated temperatures and solutes, which are shown in Table 2.

3.2. Stability of Solid Solutes under Experimental Conditions. Solubility measurements at relatively high temperatures for an extended amount of time necessitate stability studies on the investigated solutes. Solute reaction and/or degradation in subcritical water would render experimentally determined solubility data inaccurate. Literature surveys on the stability of PAHs in subcritical water reveal contrasting results.^{5,21–24} In the solubility study by Karasek et al.,⁵ analysis of PAHs extracted at temperatures between 40 and 210 °C did not reveal noticeable degradation. However, in a study by Yang

and Hildebrand,²⁴ a portion of phenanthrene in subcritical water was degraded to several organic compounds that include phenol, naphthalene, and benzoic acid.²⁴ Degradation and reduced recovery of extracted PAHs using water at high temperatures and pressures have also been observed.^{25,26}

The detailed study by Yang and Hildebrand²⁴ showed that temperature and concentrations of phenanthrene and dissolved oxygen in subcritical water played significant roles in phenanthrene degradation. The proportion of degraded phenanthrene was found to be higher at higher temperatures. For a relatively high concentration of phenanthrene in subcritical water, an insignificant amount of degradation was obtained with the proportion of phenanthrene that degraded ranging from 0.2 to 5.6% between 150 and 350 °C.²⁴ At lower concentrations of phenanthrene, the proportion of phenanthrene that degraded increased to 61.9% at 350 °C.²⁴ Compounds obtained from the degradation of phenanthrene were found to be mostly byproducts of oxidation. The oxidizing power of subcritical water in the investigated phenanthrene–water system was attributed by the authors to the presence of dissolved oxygen in water.²⁴ Therefore, in solubility/extraction studies where the degassing of water was carried out, no significant degradation was observed. The reduction in the amount of dissolved oxygen, thus, reduces the oxidizing power of water. Also, in most literature studies, relatively large quantities of organic compounds are used. The small quantity of oxygen available in the degassed water could only oxidize a small fraction of the large quantity of organic compounds present, reducing the degradation percentage to unnoticeable levels.²⁴

In order to reduce solute degradation in the present study, water was degassed prior to the conduct of solubility measurements, while a substantial amount of solutes was added into the equilibrium vessel. FTIR (Fourier transformed infrared spectroscopy) recorded with a Thermo Nicolet 370 FTIR spectrometer on a KBr disc was used to observe the degradation of anthracene and *p*-terphenyl under the experimental conditions used in this study. No noticeable degradation was found in both anthracene and *p*-terphenyl from the IR spectra obtained. The IR spectra for both solutes are shown in Figures A1 and A2 in the Appendix.

4. RESULTS AND DISCUSSION

4.1. Rig Validation. The ability of the apparatus designated for solubility study in this work, to accurately measure solubility, was validated by measuring and comparing the solubility of anthracene in subcritical water with published literature data. Solubility data of anthracene in subcritical water measured at 50 bar was compared with the solubility values obtained by Miller et al.,⁶ Andersson et al.,²¹ and Karasek et al.⁵ shown in Figure 4 and Table 3. The differences in the experimental setup are also shown in Table S1 (Supporting Information).

Figure 4 illustrates that most of the solubility data were in reasonable agreement with each other with slight variations found in anthracene solubility data at 200 °C. Despite the fact that the solubility values were compiled at similar temperatures, the pressures of the system used by different authors to maintain the liquid state of water were dissimilar. However, both Figure 4 and Table 3 demonstrate that the relatively small range of pressure (47–77 bar) poses no significant effects on the solubility of a solute in subcritical water, concurring with the observations made in the literature.^{6,27} Hence, the comparisons made among the four studies in this paper are still relevant and valid.

4.2. Preliminary Study on the Effect of Temperature and Pressure on the Solubility of a PAH in Subcritical Water. In a preliminary solubility study, the effects of pressure

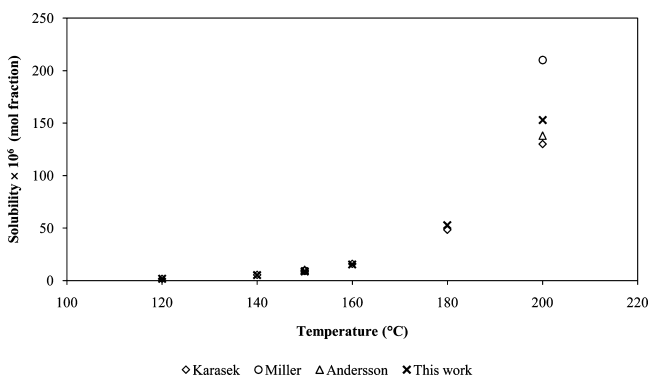


Figure 4. System validation: Solubility data of anthracene in subcritical water together with their standard deviations at various temperatures from various sources. Pressure ranges from 47 to 77 bar. The standard deviation for some data points may be too small to appear in the graph.

and temperature and the joint effect of the two factors on the solubility of anthracene in water were studied. A two-level, two-factorial experimental design with three replicates was designed to investigate the effects of temperature and pressure on solubility. Solubility measurements were conducted at 140 and 180 °C and at pressures of 50 and 150 bar. The results of the solubility measurements are shown in Table 4. The interaction plots between the two factors are shown in Figure 5. The interaction plots indicate a strong interaction between temperature and the solubility of anthracene in subcritical water. The calculation of the main effect, shown in Table 5, confirms that temperature has the most significant effect on solubility in subcritical water, while pressure and the combined effect of temperature and pressure (i.e., density) are not significant. The results shown in Table 5 are consistent with observations made in the literature,^{6,27} in that the effect of pressure on the solubility of organic compounds in subcritical water is minimal, particularly when the range of pressure considered is relatively small. The preliminary two-factor experimental design was not extended to *p*-terphenyl, as the PAH solute is expected to exhibit the same cause-and-effect behavior as anthracene. The similarity in the solubility behavior observed between *p*-terphenyl and anthracene can be found in a solubility study by Karasek et al.⁵ via the dynamic equilibrium method, and confirmed by the results obtained in the present study, described in section 4.3.

4.3. The Effect of Temperature on the Solubility of PAHs in Subcritical Water: Binary Systems. In the preliminary study discussed in section 4.2, solubility measurements were conducted at high and low temperatures of 180 and 140 °C. In a more detailed

Table 4. Solubility Data of Anthracene in Subcritical Water at 140 and 180 °C and at Pressures of 50 and 150 bar

factor: temperature, <i>T</i>	factor: pressure, <i>P</i>	
	<i>P</i> low (50 bar)	<i>P</i> high (150 bar)
<i>T</i> low (140 °C)	5.26×10^{-6}	4.87×10^{-6}
<i>T</i> high (180 °C)	5.48×10^{-5}	5.83×10^{-5}

Table 5. Main Effects That Contribute to the Solubility of Anthracene in Subcritical Water

parameter	main effect	sum of squares
temperature	5.15×10^{-5}	2.65×10^{-9}
pressure	1.54×10^{-6}	2.39×10^{-12}
combined pressure and temperature	-1.94×10^{-6}	3.76×10^{-12}

investigation on the effect of temperature, temperature measurements were extended to 120 and 200 °C. The pressure of the system was kept constant at 50 bar. The solubilities of pure anthracene and *p*-terphenyl in subcritical water are shown in Table 6 and Figure 6. The relative standard deviations for all of the solubility data were found to be less than 5%.

In accordance with previous reports,^{3–6,21} the solubilities of anthracene and *p*-terphenyl were found to increase exponentially with temperature. The dramatic increase is generally attributed to the reduced dielectric constant of water as a consequence of temperature increase.^{3,6,8} However, the exponential increase observed in PAH solubility with temperature does not correspond with the rate of decrease in the dielectric constant of water, particularly the sharp increase in solubility observed above 150 °C. In fact, the observed exponential solubility trend shown in Figure 6 is more similar to the change in sublimation pressure with temperature for both PAHs, shown in Figure 7. The change in the dielectric constant of water is also included in Figure 7, to provide a comparison with the change in sublimation pressure. Attributing the increase in PAH solubilities in subcritical water to the change in their sublimation pressure is reasonable, since the solubilities of solid hydrocarbons in supercritical fluids have also been shown to be heavily influenced by their sublimation pressures.^{28,29} Table 7 shows the ratios of the dielectric constant, the sublimation pressures, and the PAH solubilities at various temperatures. The increment rate in solubility can be found to mirror that of the sublimation pressures of the solid solutes, rather than that of the dielectric constant.

With regard to the dielectric constant playing a smaller role in solubility, a further observation can be made by comparing the solubility of anthracene in subcritical water with that in nitrobenzene, shown in Table 8. While both solvents exhibit

Table 3. Solubility (x_2) of Anthracene (Mole Fraction) in Subcritical Water Measured Using Various Methods^a

temperature	120 °C	140 °C	150 °C	160 °C	180 °C	200 °C
Miller et al. ⁶ [dynamic]	$x_2 \times 10^6$		9.20 ± 0.60 [<i>P</i> = 47 bar]			210 ± 25.0 [<i>P</i> = 48 bar]
	RSD		6.5%			11.9%
Andersson et al. ²¹ [dynamic]	$x_2 \times 10^6$		10.2 ± 1.30 [<i>P</i> = 50 bar]			138 ± 19.0 [<i>P</i> = 50 bar]
	RSD		12.7%			13.8%
Karasek et al. ⁵ [dynamic]	$x_2 \times 10^6$	1.54 ± 0.10 [<i>P</i> = 52 bar]	5.37 ± 0.10 [<i>P</i> = 47 bar]	15.9 ± 0.44 [<i>P</i> = 54 bar]	48.40 ± 1.21 [<i>P</i> = 63 bar]	130 ± 2.87 [<i>P</i> = 77 bar]
	RSD	6.49%	1.86%	2.77%	2.50%	2.21%
this work [static]	$x_2 \times 10^6$	1.59 ± 0.04 [<i>P</i> = 50 bar]	5.34 ± 0.08 [<i>P</i> = 50 bar]	8.75 ± 0.24 [<i>P</i> = 50 bar]	15.5 ± 0.29 [<i>P</i> = 50 bar]	52.9 ± 1.01 [<i>P</i> = 50 bar]
	RSD	2.51%	1.49%	2.74%	1.90%	1.91%
						0.88%

^a x_2 = solubility in mole fraction, *P* = pressure, RSD = relative standard deviation.

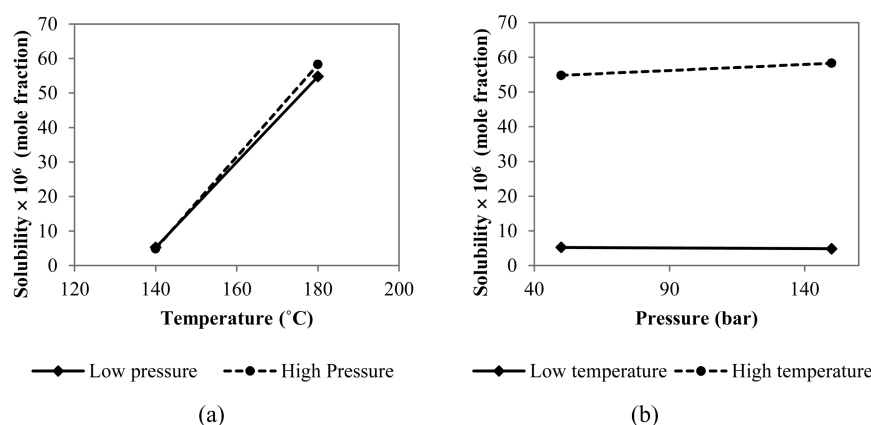


Figure 5. Interaction plots: the effects of temperature and pressure on the solubility of anthracene in subcritical water.

Table 6. Solubility Data (in Mole Fraction) for Binary Water–Anthracene and *p*-Terphenyl–Water Systems

T (°C)	anthracene, x_2	<i>p</i> -terphenyl, x_2
120	$(1.59 \pm 0.04) \times 10^{-6}$	$(1.95 \pm 0.08) \times 10^{-7}$
140	$(5.34 \pm 0.08) \times 10^{-6}$	$(5.90 \pm 0.05) \times 10^{-7}$
150	$(8.75 \pm 0.24) \times 10^{-6}$	$(1.05 \pm 0.03) \times 10^{-6}$
160	$(1.55 \pm 0.03) \times 10^{-5}$	$(1.96 \pm 0.06) \times 10^{-6}$
170	$(3.04 \pm 0.16) \times 10^{-5}$	$(3.71 \pm 0.12) \times 10^{-6}$
180	$(5.29 \pm 0.10) \times 10^{-5}$	$(7.14 \pm 0.24) \times 10^{-6}$
200	$(1.53 \pm 0.01) \times 10^{-4}$	$(2.43 \pm 0.03) \times 10^{-5}$

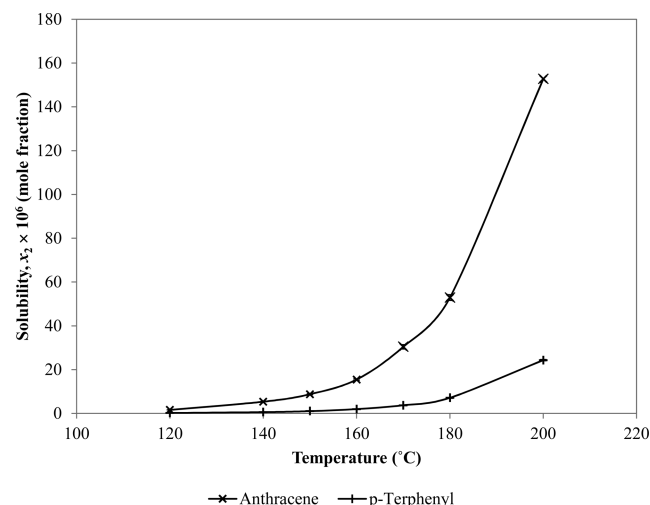


Figure 6. Solubility data of anthracene and *p*-terphenyl in subcritical water together with their standard deviations at 50 bar and various temperatures. The standard deviation for some data points may be too small to appear in the graph.

similar dielectric constant values, the solubility of anthracene in nitrobenzene is approximately 670 times higher. Moreover, the solubility of anthracene in nitrobenzene is 31 times higher than that in methanol even though methanol has a lower dielectric constant. It is, thus, evident that the dielectric constant is not the main determinant of PAH solubility in solvents. Therefore, with temperature bearing considerable influence on the dielectric constant of water and the sublimation pressure of the solutes, the contrast in the trends observed points to solubility in subcritical water being predominantly governed by the sublimation pressures. The effect from mixture density has been established (in section 4.2) as insignificant within the temperature and pressure range considered in the present study.

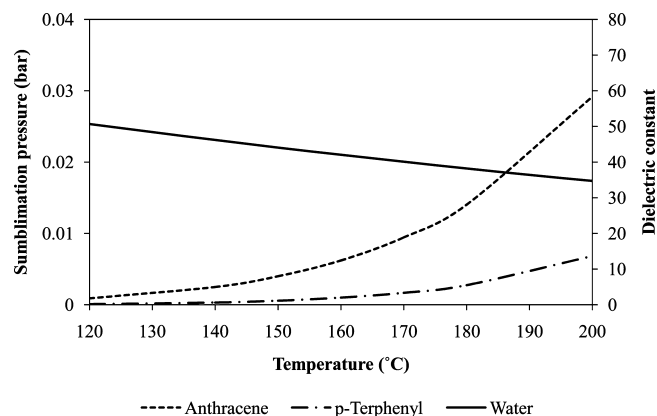


Figure 7. The sublimation pressures of solid anthracene and *p*-terphenyl and the dielectric constant of subcritical water at various temperatures, reproduced from refs 19 and 30.

Table 7. Ratio of the Dielectric Constant (ϵ_r) of Water and the Ratios of Sublimation Pressures (P_T^{sub}) of PAHs and PAH Solubility (x_T) at Various Temperatures

T_1 (°C)	T_2 (°C)	$(\epsilon_{r,T1}/\epsilon_{r,T2})_{\text{water}}$	$(P_{T2}^{\text{sub}}/P_{T1}^{\text{sub}})_{\text{PAH}}$		$(x_{T2}/x_{T1})_{\text{PAH}}$	
			anthracene	<i>p</i> -terphenyl	anthracene	<i>p</i> -terphenyl
120	140	1.10	2.79	3.67	3.36	3.03
140	150	1.05	1.60	1.81	1.64	1.78
150	160	1.05	1.56	1.74	1.77	1.87
160	170	1.05	1.52	1.69	1.96	1.89
170	180	1.05	1.49	1.64	1.74	1.92
180	200	1.05	2.08	2.48	2.89	3.40

4.4. The Effect of Temperature on the Solubility of PAHs in Subcritical Water: Ternary Systems. Subcritical water has been used to remove or decompose pollutants such as polycyclic aromatic hydrocarbons (PAHs), pesticides, and polychlorinated biphenyls from contaminated soils. While systematic solubility study on PAHs in subcritical water has been widely conducted, most studies were carried out for binary systems and very few data are available for solvent–solid–solid systems.^{3–6,21,35,36} However, as pollutants rarely exist as a single component, solubility studies conducted on multicomponent systems would be beneficial. While the study on the effects of a cosolute on another solute in subcritical water is scarce, Miller et al.⁶ studied the solubilities of mixed ternary PAHs in subcritical water. The solubilities of a mixture

Table 8. Solubility of Anthracene in Various Solvents and Temperatures and the Corresponding Dielectric Constant of the Solvents

solvent	dielectric constant	conditions	anthracene solubility	references
nitrobenzene	34.8	25 °C	1.03×10^{-2}	31, 32
methanol	32.6	25 °C	3.26×10^{-4}	33, 34
water	34.7	200 °C, 50 bar	1.53×10^{-5}	30

of carbazene, anthracene, and chrysene in subcritical water were measured between 25 and 200 °C. Miller et al.⁶ premised that the PAHs behaved as separate solids at relatively lower temperatures, as the solubilities of the PAHs in the quaternary system were found to be similar to their individual solubilities in subcritical water between 25 and 50 °C. However, as the temperatures increased above 50 °C, solubility depressions were found to occur in the three solutes.

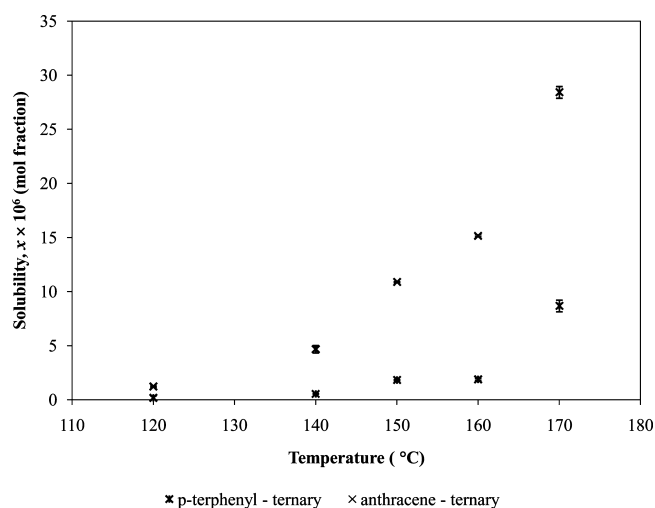
In this study, additional experiments were conducted to determine the effects of a cosolute PAH on another PAH when the two solutes are mixed together in subcritical water. The present work is a continuing study on solid–liquid equilibrium (SLE) in ternary systems consisting of solid–solid–solvent at different temperatures. This is the first known study conducted on a mixture of two solutes in subcritical water at the invariant point where the solution is saturated with both solutes. In this section, the solid–solid–liquid ternary systems of *p*-terphenyl–anthracene–water at temperatures between 120 and 170 °C are presented.

In the conduct of the solid–solid–liquid equilibrium (SSLE) experiments, an equimolar mixture of anthracene and *p*-terphenyl was packed into the equilibrium vessel prior to the start of the experiment. All other parts of the experiment were conducted similar to the experiment conducted for binary systems. The amount of solutes collected were dried and dissolved in acetonitrile. Separation and analysis of solutes were conducted using a Waters RP-HPLC (reverse-phase high pressure liquid chromatography) system with a Lichrosorb RP18 analytical column. The solubilities of the mixed solutes are shown in Table 9. The natural logarithm solubilities of solutes in binary and ternary subcritical water systems are compared in Figure 8.

Table 9. Solubility Data (Mole Fractions) in the Subcritical Water (1)–Anthracene (2)–*p*-Terphenyl (3) System

<i>T</i> (°C)	x_2	x_3
120	$(1.22 \pm 0.06) \times 10^{-6}$	$(1.82 \pm 0.07) \times 10^{-7}$
140	$(4.68 \pm 0.35) \times 10^{-6}$	$(5.60 \pm 0.35) \times 10^{-7}$
150	$(1.09 \pm 0.06) \times 10^{-5}$	$(1.83 \pm 0.05) \times 10^{-6}$
160	$(1.52 \pm 0.06) \times 10^{-5}$	$(1.89 \pm 0.09) \times 10^{-6}$
170	$(2.84 \pm 0.07) \times 10^{-5}$	$(8.67 \pm 0.54) \times 10^{-6}$

Solubility depression was observed for anthracene at 50 bar and all temperatures, except at 150 °C, while depression was observed for *p*-terphenyl at 120 and 140 °C. The solubility depressions observed in the present study are in agreement with the observations made by Miller et al. (1998). However, the increased solubilities of mixed anthracene and *p*-terphenyl at several temperatures show the unpredictable effects of having a cosolute in subcritical water systems. The significance of the addition of a cosolute to the solubility of a PAH was determined with a paired *t* test, compared between the solute's solubilities in ternary and binary systems. The results of the paired *t* test, shown in Table 10, demonstrate that generally the presence of a PAH

**Figure 8.** Solubility of anthracene and *p*-terphenyl together with their standard deviations in binary and ternary subcritical water systems at 50 bar and various temperatures. The standard deviation for some data points may be too small to appear in the graph.**Table 10. The Results of Paired *t*-Tests Compared between the Solubility of PAHs in the Ternary and Binary Systems for a 95% Confidence Level**

temperature (°C)	<i>p</i> -value	null hypothesis: <i>t</i> test of mean difference = 0	effect of the presence of a cosolute
Anthracene			
120	0.007	null hypothesis rejected	significant
140	0.003	null hypothesis rejected	significant
150	0.043	null hypothesis rejected	significant
160	0.365	null hypothesis accepted	not significant
170	0.044	null hypothesis rejected	significant
<i>p</i> -Terphenyl			
120	0.010	null hypothesis rejected	significant
140	0.196	null hypothesis accepted	not significant
150	0.000	null hypothesis rejected	significant
160	0.023	null hypothesis rejected	significant
170	0.003	null hypothesis rejected	significant

Table 11. Pure Component Physical Properties

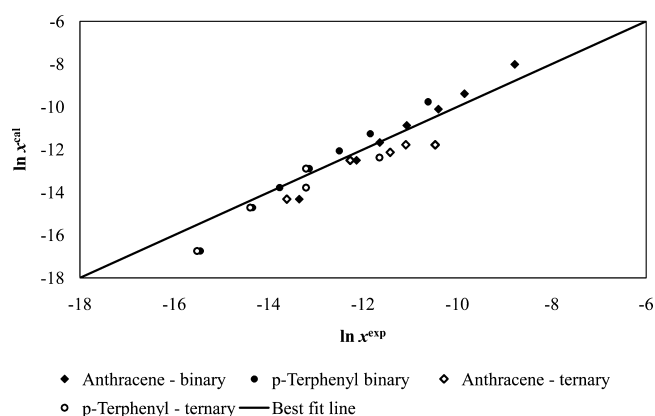
compound	<i>T_c</i> (K)	<i>P_c</i> (bar)	acentric factor, ω	solid density (g/cm ³)	ref
water	647.14	220.64	0.344		38
anthracene	869.3	31.24	0.3531	1.25	39
<i>p</i> -terphenyl	926.0	33.20	0.6426	1.23	40, 41

cosolute has a significant effect on the solubility of another PAH in water. The Pearson correlation coefficients for temperature for anthracene and *p*-terphenyl in the ternary systems are 0.838 and 0.779, respectively, demonstrating a strong correlation between the temperature and solubility of both solutes in the ternary system.

In the present study, it was assumed that the mixing in the equilibrium vessel was sufficient to make both solutes available to the solvent, and that there was no significant interaction between anthracene and *p*-terphenyl. Therefore, both anthracene and *p*-terphenyl were treated as two pure solids in the ternary mixtures. While it was assumed that two pure solid phases and a single liquid mixture exist in the ternary systems, the reasons for the augmented solubility values of *p*-terphenyl at 150 and 170 °C were unknown. It is possible that at these temperatures the dissolved anthracene acts as a cosolute that enhances the solubility of *p*-terphenyl.

Table 12. Regressed k_{ij} Values, the Correlation Coefficient, and the AASD Obtained for PAH in Subcritical Water

system	k_{ij}	AASD (%)	correlation coefficient, r
anthracene (1)–water (2)	$k_{12} = k_{21} = 0.0251$	4.09	0.9957
<i>p</i> -terphenyl (1)–water (2)	$k_{12} = k_{21} = 0.1533$	4.22	0.9979
anthracene (1)– <i>p</i> -terphenyl (2)–water (3)	$k_{13} = k_{31} = 0.0251$	5.47	0.8995
	$k_{23} = k_{32} = 0.1533$		
	$k_{12} = k_{21} = 0$		

Figure 9. Deviation between experimental and calculated values for anthracene and *p*-terphenyl in binary and ternary subcritical water systems.

5. THERMODYNAMIC MODELING

In the present thermodynamic modeling, the Peng–Robinson equation of state³⁷ (PR-EOS) was used together with the classical mixing rules and one adjustable parameter, k_{ij} , was fitted to experimental data. The compressibility factor, Z , was obtained through iteration via the Newton–Raphson method. An objective function (OF) was used in this work to obtain the optimal values of the adjustable parameter, k_{ij} , given by

$$OF = \sum_N \frac{(\ln x_i^{\text{exp}} - \ln x_i^{\text{cal}})^2}{N} \quad (1)$$

The pure component physical properties used in this work are summarized in Table 11. The values of k_{ij} , the correlation coefficient, r , and the average absolute standard deviation (AASD) from experimental values are shown in Table 12. The absolute standard deviation (ASD) is given by eq 2.

$$ASD = \left| \frac{\ln x_i^{\text{exp}} - \ln x_i^{\text{cal}}}{\ln x_i^{\text{exp}}} \right| \times 100\% \quad (2)$$

In this work, the k_{ij} values for PAH–water were regressed from experimental data, while the k_{ij} values for anthracene–*p*-terphenyl were set to zero, since neither solid was assumed to have any interactions with each other in the ternary system. In fact, changes made to the a_{ij} value for anthracene–*p*-terphenyl were found to have no impact on the calculated solubilities of both solids in the ternary system. The AASD and the correlation coefficient, r , shown in Table 12 demonstrate that the PR-EOS can be used as a predictive tool to calculate the solubility of binary PAH–subcritical water systems, although slightly higher deviations were observed at higher temperatures. While the AASD between calculated and experimental values in the ternary system was low, the lower correlation coefficient shows moderate forecast ability of the PR-EOS. Comparisons between the PR-EOS calculated and experimental values can be seen in Figure 9.

6. CONCLUSION

A static equilibrium method was used to determine solute solubility in subcritical water, of which highly reproducible solubility results were obtained. The solubilities of anthracene and *p*-terphenyl in subcritical water were successfully measured and found to increase exponentially with temperature. The solubilities of PAHs in subcritical water were found to be governed primarily by sublimation pressures of the solutes and only secondarily by the dielectric constant of water. The Peng–Robinson EOS was found to provide good representation of PAH solubilities in subcritical water while giving adequate representation of PAHs in ternary subcritical water systems consisting of two solid solutes.

APPENDIX

FT-IR Spectra of Anthracene and *p*-Terphenyl prior to and after Being Subjected to Experimental Conditions

Figures A1 and A2 show the FTIR spectra of anthracene and *p*-terphenyl pre- and post-solubility measurements. The IR

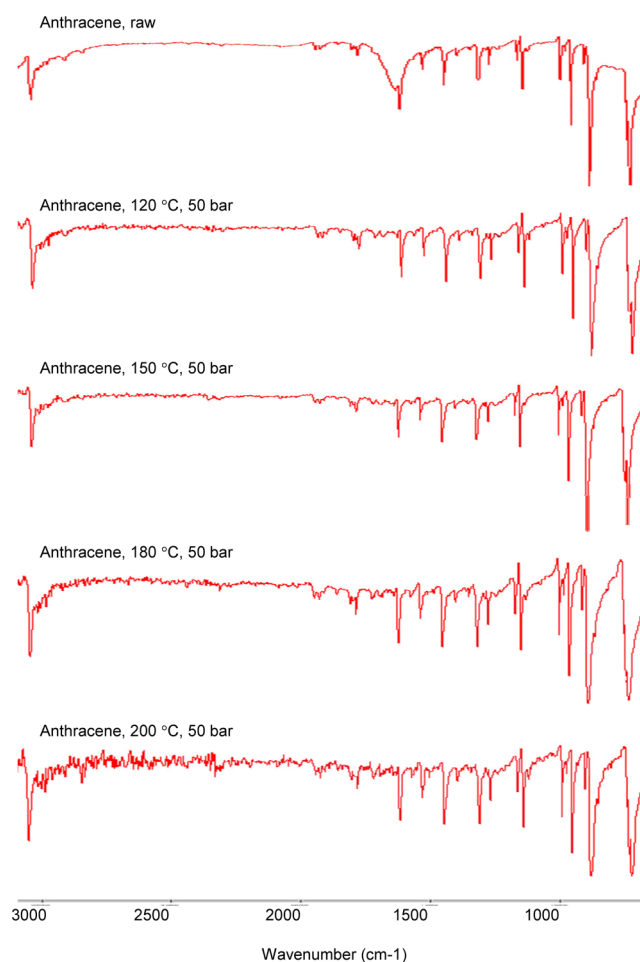


Figure A1. FTIR spectra of anthracene pre- and postprocessing.

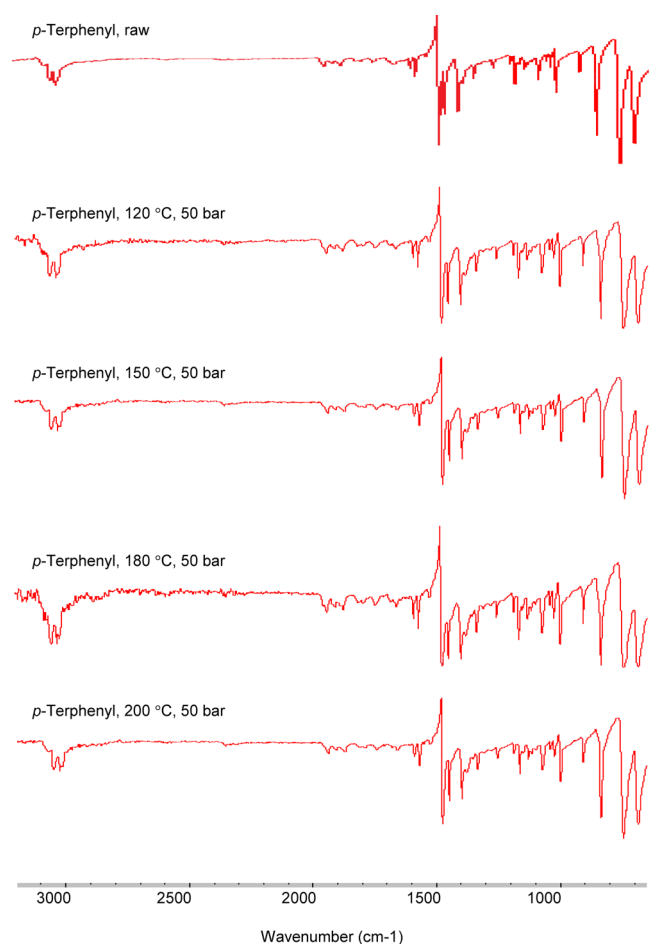


Figure A2. FTIR spectra of *p*-terphenyl pre- and postprocessing.

spectra at 140, 160, and 170 °C were not measured with the reason being that the total mixing time at 140 °C was similar to 150 °C, while the total mixing times at 160 and 170 °C were similar to that of 180 °C. Since no noticeable changes were observed at a higher temperature, it was expected that similar spectra would be observed for lower temperatures with similar mixing times.

Nomenclature

k_{ij}	unlike-pair interaction parameter
OF	objective function
P	pressure
P_c	critical pressure
r	correlation coefficient
T	temperature
T_c	critical temperature
x_i	solubility (or mole fraction) of solute i

Greek Symbols

ϵ	dielectric constant
ω	acentric factor

Abbreviations

AASD	average absolute standard deviation
PAHs	polycyclic aromatic hydrocarbons
PR-EOS	Peng–Robinson equation of state
RP-HPLC	reversed-phase high pressure liquid chromatography
RSD	relative standard deviation
SLE	solid–liquid equilibria

SSLE	solid–solid–liquid equilibria
UV	ultraviolet
VLE	vapor–liquid equilibria

Subscripts

i, j	component i or j
m	mixture

Superscripts

exp	experiment
cal	calculation
L	liquid
S	solid
sub	sublimation

■ ASSOCIATED CONTENT

Supporting Information

Additional figures and tables as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Address: School of Chemical Engineering, Chemical Sciences Building (F10), the University of New South Wales, Sydney, NSW 2052, Australia. E-mail: n.foster@unsw.edu.au.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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