Published in final edited form as:

Fluid Phase Equilib. 2013 March 25; 342: . doi:10.1016/j.fluid.2012.12.036.

Thermochemical and Vapor Pressure Behavior of Anthracene and Brominated Anthracene Mixtures

Jinxia Fu^a and Eric M. Suuberg^b

Jinxia Fu: Jinxia_Fu@Brown.edu; Eric M. Suuberg: Eric_Suuberg@Brown.edu

^aBrown University Department of Chemistry, Providence, RI USA 02912

^bBrown University School of Engineering, Providence, RI USA 02912

Abstract

The present work concerns the thermochemical and vapor pressure behavior of the anthracene (1) + 2-bromoanthracene (2) and anthracene (1) + 9-bromoanthracene (3) systems. Solid-liquid equilibrium temperature and differential scanning calorimetry studies indicate the existence of a minimum melting solid state near an equilibrium temperature of 477.65 K at $x_1 = 0.74$ for the (1) + (2) system. Additionally, solid-vapor equilibrium studies for the (1) + (2) system show that the vapor pressure of the mixtures depends on composition, but does not follow ideal Raoult's law behaviour. The (1) + (3) system behaves differently from the (1) + (2) system. The (1) + (3) system has a solid solution like phase diagram. The system consists of two phases, an anthracene like phase and a 9-bromoanthracene like phase, while (1) + (2) mixtures only form a single phase. Moreover, experimental studies of the two systems suggest that the (1) + (2) system is in a thermodynamically lower energy state than the (1) + (3) system.

Keywords

polycyclic aromatic compound; anthracene; 2-bromoanthracene; 9-bromoanthracene; thermochemical behavior; vapor pressure

1. Introduction

The thermodynamic properties of pure polycyclic aromatic compounds (PACs) have been widely studied [1–5]. However, those of PAC mixtures, which are pertinent to petroleum and environmental industries [6, 7], have not been as completely investigated. Traditional studies of such PAC mixtures often involve examining thermochemical properties, aqueous solubility, general phase behavior and microstructure analyses [8–21]. However, vapor pressure, which may also determine the fate and transport of the components of such mixtures, particularly under elevated temperature conditions, has been rarely considered [22–28].

Anthracene, a tricyclic aromatic hydrocarbon produced by incomplete combustion and many fuel processing operations, is widely used to produce coating materials, dyes, insecticides, and various types of wood products. It is also listed as one of the 16 priority PAH pollutants by the US Environmental Protection Agency (USEPA). Although the environmental fate and effects of anthracene have been studied in detail for over 50 years, much less is known about the brominated anthracene derivatives or anthracene derivative mixtures [26, 28].

In this article, solid-liquid equilibrium, enthalpy of phase change, crystal structure, and vapor pressure of the anthracene (1) + 2-bromoanthracene (2) system were experimentally studied. Moreover, the entropies of crystallization and interaction energy were calculated using enthalpies of crystallization obtained via differential scanning calorimetry. Structural features such as the spacing between aromatic planes was also derived from X-ray diffraction data. Thermodynamic properties of the anthracene (1) + 9-bromoanthracene (3) system were similarly studied to investigate the influence of the Br-substituent position on the thermodynamic behaviors of PAC mixtures.

2. Materials and Methods

2.1. Chemicals

Anthracene (CAS Reg. No. 120-12-7, with mass fraction purity > 0.99) was purchased from Aldrich, and 2-bromoanthracene (CAS Reg. No. 7321-27-9, with mass fraction purity > 0.97) and 9-bromoanthracene (CAS Reg. No. 1564-64-3, with mass fraction purity > 0.95) were purchased from TCI America. They were used without further purification. The melting points of anthracene, 2-bromoanthracene and 9-bromoanthracene were found to be 490.05 ± 0.1 K, 493.85 ± 0.1 K, and 374.15 ± 0.1 K, respectively. The data for anthracene and 9-bromoanthracene are in good agreement with corresponding literature values [29–31] while the data for 2-bromoanthracene fall within the literature range 484.15–497.15K [30, 32]. They were used in the measurements without further purification (except during actual vapor pressure measurements, as described below).

2.2. Mixture Preparation

A melt and quench-cool technique was used to prepare mixtures of anthracene + 2-bromoanthracene, and anthracene + 9-bromoanthracene with various compositions. The desired quantities (around 50 mg) of anthracene and 2-bromoanthracene or anthracene and 9-bromoanthracene were measured to ± 0.05 mg and sealed in a brass vessel. The vessel was heated to 498 ± 5 K in a fluidized bath and agitated for 5 min. Then the vessel was immediately placed into liquid nitrogen, which provided cooling at approximately 70–80 K·s⁻¹ for the first 4 sec. The heating and cooling procedure was repeated 4 times.

The melting process provides enough energy to the mixture in order to cross over the energy barrier for forming liquid mixture systems, and the quench cool process is intended to preserve the disorder of the well-mixed liquid during solidification. For the mixtures prepared in this study, since the components do not chemically react with each other, the phase behaviors of mixtures prepared by melt-quench cool are expected to be the same as mixtures prepared by other methods, such as melt-slow cool and ball milling methods, except for any kinetic effects associated with solidifications. Such kinetic effects have not been observed for these or other similar PAC systems.

2.3. Solid-liquid equilibrium temperatures

Melting temperatures of pure samples and mixtures were measured using a Mettler Toledo MP50 melting point system. 1 to 2 mg of each sample were placed in a quartz capillary and heated at 1 ± 0.1 K·min⁻¹. The thaw points were determined according to the method proposed by Pounder and Masson [33]. The thaw temperature is the temperature at which the first droplet of liquid appears in the capillary, which is also the lowest solid-liquid equilibrium temperature characterizing the mixtures. The liquidus point is the temperature at which all solid has finally melted.

2.4. Temperatures and enthalpies of fusion and crystallization

Temperatures and enthalpies of fusion and crystallization were measured using a DuPont 2910 differential scanning calorimeter (DSC). A 1 to 3 mg sample was placed into a hermetically sealed DSC pan and was scanned in heating and cooling modes. The rates of heating and cooling were $10 \text{ K}\cdot\text{min}^{-1}$ and $2.5 \text{ K}\cdot\text{min}^{-1}$, respectively. This procedure provides crystallization enthalpy peaks that are more convenient to integrate than the fusion enthalpy peaks because the baseline of the cooling scan is more stable, making it easy to distinguish the start and end points of phase transition peaks. Since the values of enthalpy and transition temperatures were generally insensitive to changes in heating and cooling rate in the range of $2.5 - 10 \text{ K}\cdot\text{min}^{-1}$, the enthalpy of crystallization was used to characterize the enthalpy of the fusion phase transition. Note that the crystallization typically occurs from a subcooled liquid state in these experiments, hence crystallization temperature does not exactly match melting temperature.

2.5. Vapor pressure

The Knudsen effusion technique was used to measure the vapor pressures of pure anthracene, 2-bromoanthracene, 9-bromoanthracene and their mixtures. This is an indirect measurement technique based on the molecular effusion of a vapor through an orifice into a high vacuum chamber. These results are generally used to measure the vapor pressure of low volatility substances. The vapor pressure of a substance can be obtained from effusion data using

$$P = \frac{\omega}{tAW} \sqrt{\frac{2\pi RT}{M}} \quad (1)$$

where ω is the weight loss during the effusion time interval t , A is the orifice area, R is the universal gas constant, T is the sample temperature, M is the molecular weight of the effusing species, and W is the Clausing correction factor. W ranges from 0 to 1 and quantifies the probability of molecular escape from the effusion cell [34]. W is calculated from the empirical formula

$$W = \frac{1}{1 + (3l/8r)} \quad (2)$$

where l is the orifice effusion length and r is the orifice radius. In these experiments, W was always very close to unity, both by calculation using (2) and from experimental calibration.

Samples were placed inside effusion cells prepared from steel shim stock. The cells were sealed except for a single, circular orifice $0.61 \pm 0.02 \text{ mm}$ in diameter, and then placed on one arm of a continuously recording microbalance in a high vacuum chamber. The pressure inside of the chamber was reduced to 10^{-4} Pa in the experiments. The measurements were made under isothermal conditions. Temperatures were measured using a type K thermocouple located directly right above the effusion cell, accurate to $\pm 0.1 \text{ K}$, calibrated with a National Institute of Standards and Technology traceable thermometer. The temperature and mass were recorded continuously in order to obtain an average mass loss rates over an extended period. Therefore, the relative instrument uncertainty within the experimental temperature range is about $\varepsilon_P = \delta P/P = \pm 0.05$. Before commencing data collection, over 5 % of the compound in the cell was sublimed to ensure removal of any volatile impurities, and this has also been observed by mass spectrometry to be sufficient to obtain pure compound results even when starting with commercial purity samples [4].

Additionally, the data collection was stopped before 95 % of the sample in the cell sublimed in case there were any nonvolatile impurities present. To verify the reliability of the experimental technique, the reference compound anthracene was periodically employed to test the performance of the Knudsen effusion apparatus and the results were in good agreement with literature values [3, 35–37]. More details of this technique can be found in [26–28, 38, 39].

2.6. Other Characterization

Powder X-ray diffraction patterns were obtained using a Bruker AXS D8-Advanced diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned with 2θ angle $10^\circ - 60^\circ$ and a step-size 0.02° .

The composition of mixtures was determined by GC-MS. The samples were dissolved in dichloromethane to about $100 \mu\text{g}\cdot\text{mL}^{-1}$ and analyzed using a Varian CP3800 gas chromatograph and Saturn 2200 mass spectrometer. The Varian analytical procedure for the EPA Method 8270C was followed [40].

3. Results and Discussion

3.1. Solid-liquid equilibrium diagram

The phase diagram of the anthracene (1) + 2-bromoanthracene (2) system is shown in Figure 1 (A). The diagram suggests the non-ideality of the anthracene + 2-bromoanthracene system. The melting temperature range (thaw to liquidus) of these mixtures at any given composition is observed to be 1.1 – 2.6 K. The lowest solid-liquid equilibrium temperature (LSLET) for this system is found at 477.6 K and $x_1 = 0.74$, and is about 15 K lower than that of either pure compound. The melting temperature range of this mixture is 1.8 K.

The melting behavior of the anthracene (1) + 9-bromoanthracene (3) system is different from that of the anthracene (1) + 2-bromoanthracene (2) system. Figure 1 (B) displays the phase diagram of the anthracene (1) + 9-bromoanthracene (3) system. This system exhibits solid-solution-like phase diagram, but it is not a real solid solution system. The thaw temperatures of mixtures with $x_1 < 0.5$ are about 5 – 10 K lower than the melting point of the pure 9-bromoanthracene, while the thaw temperatures of mixtures with $x_1 > 0.5$ tend to be significantly higher and increase almost linearly towards the melting point of anthracene with an increase of the mole fraction of anthracene in the mixtures.

3.2. Temperature of crystallization and enthalpy of fusion and crystallization

The heating, cooling and reheating scans of the anthracene (1) + 2-bromoanthracene (2) mixture and the anthracene (1) + 9-bromoanthracene (3) mixture at $x_1 = 0.50$ are shown in Figure 2 (A) and (B), respectively.

For the equimolar anthracene + 2-bromoanthracene mixture (see Figure 2(A)), during the initial heating scan, only a single peak appears at 481.7 K, which is quite close to the melting temperature of the mixture determined in the separate melting experiments. Similarly, one peak appears at 475.8 K in the cooling scan. The temperature difference between the melting and crystallizing processes is 12.4 K indicating crystallization from a subcooled liquid state. When reheated, the phase transition enthalpy and associated temperature match those in the initial heating scan showing that initial quench cooling gives behavior no different than slowing cooling. The temperature difference between the melting and crystallizing events during heating and cooling varies from 6 – 24 K, for the full range of composition examined (results not shown).

For the equimolar anthracene (1) and 9-bromoanthracene (3) mixture (see Figure 2(B)), two peaks appear during both the heating and cooling scan, which indicates the existence of two phases in that mixture. The high temperature crystallization peak at 421.8 K indicates the existence of one phase, while the low temperature crystallization peak, at 328.4 K indicates the existence of a second. It should be noted that the melting peak at about 370 K is associated with the low-melting phase. At $x_1 < 0.50$, this phase may be described as a 9-bromoanthracene-like phase, but it is not true 9-bromoanthracene. There is no clear high temperature melting peak visible in Figure 2(B), because this other higher melting phase dissolves into the melt phase over a range of temperature. This higher melting phase is associated with the broad peak near 440 K (corresponding with the liquidus temperatures in Figure 1(B)). It is this phase that crystallizes at around 420 K upon cooling (421.7 K for $x_1 = 0.5$). The shape of Figure 1(B) suggests that the properties of this second phase vary continuously with composition, unlike the 9-bromoanthracene-like phase that defines the thaw point at $x_1 < 0.50$.

Figure 3 (A) and (B) show the thaw and crystallization temperatures, and enthalpies of crystallization of the two mixture systems as a function of composition. For the anthracene (1) + 2-bromoanthracene (2) system (Figure 3(A)), the diagram can be crudely divided into 3 regions. The mixtures with relatively low mole fraction of anthracene ($x_1 < 0.10$), in region A, not surprisingly behave like 2-bromoanthracene. The enthalpies of crystallization are near the values of pure 2-bromoanthracene. When the mole fraction of anthracene is between 0.10 – 0.90, in region B, the fusion enthalpies fluctuate, but are lower than that of either 2-bromoanthracene or anthracene. The lowest enthalpy value is obtained at $x_1 = 0.70$ which suggests that this mixture is in a less stable, higher energy state relative to other nearby compositions. This composition is notably near the LSLET. In region C ($x_1 > 0.90$), the enthalpies increase towards the enthalpy of pure anthracene.

For the anthracene (1) and 9-bromoanthracene (3) system (see Figure 3(B)), the diagram can also be roughly divided into three regions. The mixtures with relatively low concentration of anthracene ($x_1 < 0.20$), in region A, behave like 9-bromoanthracene and show only one crystallization peak during the cooling scan, consistent with the phase diagram in Figure 1(B) though seemingly extending to just slightly higher values of x_1 . For mixtures with moderate concentrations of anthracene ($0.20 < x_1 < 0.90$), in region B, two phases exist, one low-melting and the other high-melting, as is indicated by the existence of low and high temperature crystallization peaks. The crystallization temperatures (T_{cry}) of the low-melting phases do not fluctuate much, 328–342 K, while the T_{cry} of the high-melting phase increases with an increase of the mole fraction of anthracene in the mixture. It is also worth mentioning that with the increase of mole fraction of anthracene in the mixtures, the enthalpy of crystallization ($\Delta_{\text{cry}} H$) of the high-melting phase increases almost linearly, while ($\Delta_{\text{cry}} H$) of the low-melting phase decreases linearly. The total enthalpies of crystallization of the mixtures are however nearly constant. It is important to note that $\Delta_{\text{cry}} H$ in Figure 3(B) is based on total moles in the mixture, so the linear profiles reflect a change in amount of a given phase, as opposed to properties of the phase.

Since the amount of the high temperature melting phase increases from 0% to 100% between $x_1 = 0.20$ and $x_1 = 0.90$, the slope of the enthalpy for that curve provides an estimate of the enthalpy of fusion for that phase. This is roughly $22.8 \text{ kJ}\cdot\text{mol}^{-1}$. Meanwhile, the curve for the low temperature melting phase shows the opposite trend. Taking $x_1 = 0.10$ as a definitive point of 100% of the low temperature phase, by $x_1 = 0.90$ it disappears. Again, the enthalpy of crystallization of this phase is then roughly $19.3 \text{ kJ}\cdot\text{mol}^{-1}$. The similarity of these values is why there is little variation in the total enthalpy of crystallization in region B.

In region C ($x_1 > 0.90$), the mixtures approach anthracene-like phase behavior and properties abruptly change. It is not understood why in region B at $x_1 > 0.50$ the thaw temperature of the mixture increases from 370K with composition (see Figure 1(B)), while the crystallization of the mixture always takes place at relatively constant much lower temperature of 340 K (Figure 3(B)). This appears to be some kind of kinetic effect associated with delayed nucleation of the low temperature phase.

In summary, the characteristics of the two mixture systems, (1)+(2) and (1) + (3), are very different. Anthracene and 2-bromoanthracene tend to form a single phase whose properties vary smoothly with composition, while anthracene and 9-bromoanthracene form at least two phases (in region B), and tend towards pure component behavior outside that region.

3.3. Entropy and interaction energy

The interaction energy and entropy of these two systems can be calculated from the enthalpy and temperature of crystallization data in Figure 3.

The entropy of crystallization is defined by

$$\Delta_{\text{cry}} S = (\Delta_{\text{cry}} H)_{\text{exp}} / T_{\text{cry}} \quad (3)$$

where $\Delta_{\text{cry}} S$ is the entropy of crystallization in the subcooled state, $(\Delta_{\text{cry}} H)_{\text{exp}}$ is the measured enthalpy of crystallization of the mixtures, and T_{cry} is the temperature of crystallization.

An excess interaction energy for the mixture is calculable from,

$$E_{\text{inter}} = (\Delta_{\text{fus}} H)_{\text{exp}} - (\Delta_{\text{fus}} H)_{\text{cal}} \quad (4)$$

in which

$$(\Delta_{\text{fus}} H)_{\text{cal}} = X_1 (\Delta_{\text{fus}} H)_1 + X_2 (\Delta_{\text{fus}} H)_2 \quad (5)$$

where $(\Delta_{\text{fus}} H)_1$ and $(\Delta_{\text{fus}} H)_2$ are the enthalpies of fusion of pure anthracene and 2-bromoanthracene, respectively, and $(\Delta_{\text{fus}} H)_{\text{cal}}$ is the ideal enthalpy of fusion for the mixtures, defined by x_1 and x_2 and the respective pure phase enthalpies. This interaction energy is arbitrarily defined, referencing the pure solid state. The interaction energy is an enthalpy of mixing, but conflates contributions in the solid and liquid states.

It has been reported in several studies that Raoult's law can be successfully employed to estimate the partitioning of PAHs into water from multicomponent immiscible liquids, such as diesel fuel [41], coal tars [42, 43], and multicomponent nonaqueous phase liquid (NAPL) [20]. In the liquid state, the Raoult's law is usually a reasonable approximation for PAC-containing mixtures due to PAC's chemical similarity. Raoult's law implies that the molecular interactions of a constituent in the liquid mixture solution are the same as for that compound in a liquid of pure material, which implies that the enthalpy of mixing in the liquid state is zero. Therefore, for the solid state PAC mixtures, the interaction energy, i.e. enthalpy of mixing, is mainly attributable to the enthalpy of mixing in the solid state, which can be calculated from the enthalpy of fusion of the mixtures. This will be assumed here.

Assuming that the total enthalpies of crystallization from the cooling scans are numerically equivalent to the total enthalpies of fusion, Eq. (4) and (5) can be rewritten as

$$E_{\text{inter}} = |(\Delta_{\text{cry}} H)_{\text{exp}}| = |(\Delta_{\text{cry}} H)_{\text{cal}}| \quad (6)$$

$$|(\Delta_{\text{cry}} H)_{\text{cal}}| = x_1 |(\Delta_{\text{cry}} H)_1| + x_2 |(\Delta_{\text{cry}} H)_2| \quad (7)$$

where $(\Delta_{\text{cry}} H)_1$ and $(\Delta_{\text{cry}} H)_2$ are the enthalpies of crystallization of pure anthracene and 2-bromoanthracene, respectively, and $(\Delta_{\text{cry}} H)_{\text{cal}}$ is the calculated total enthalpy of crystallization of the mixtures. The use of absolute values indicates that the enthalpy of crystallization is of course negative.

The results for the anthracene (1) + 2-bromoanthracene (2) system are shown in Figure 4 (A). The interaction energy curve suggests that anthracene and 2-bromoanthracene generally form mixtures in a higher energy state relative to that of pure components (i.e. $E_{\text{inter}} < 0$). This of course could have also been anticipated, since the enthalpies of fusion of the pure component phases are higher than those of the mixtures. The entropies and interaction energies in region B are somewhat constant and do not vary much with composition except at x_1 greater than around 0.60. There is clearly great complexity in the region $0.7 < x_1 < 0.8$, where the minimum thaw temperature is encountered. It is not known why the minimum in thaw temperature at $x_1 = 0.74$ does not exactly correspond to the minimum in entropy and excess energy at $x_1 = 0.70$. A maximum appears at $x_1 = 0.80$ (region B) in both the entropy and the interaction energy curves, which indicates that this (1) + (2) mixture is in a more ordered state and has stronger interaction than the mixtures with nearby concentrations. Conversely, a minimum appears at $x_1 = 0.70$ in both curves, which suggests that this (1) + (2) mixture is in a more disordered state with weaker interaction energy.

For the anthracene (1) and 9-bromoanthracene (3) system (see Figure 4(B)), the interaction energy calculated by Eq. (6) for the system falls in the range of -8.35 to $+0.77$ $\text{kJ}\cdot\text{mol}^{-1}$. The weakest interaction (i.e. highest energy state) appears at $x_1 = 0.70$. A positive interaction energy appears at $x_1 = 0.10$, which indicates that the mixture $x_1 = 0.10$ is relatively more stable than the pure phases. For other (1) + (3) mixtures, the interaction energies are lower than those of any mixtures in the anthracene + 2-bromoanthracene system. Therefore, anthracene and 9-bromoanthracene form mixtures that are more displaced (towards a high energy state relative to pure compounds) than the anthracene and 2-bromoanthracene mixtures.

3.4. Powder XRD analysis

The powder X-ray diffraction method was used to study the crystal structures of the two mixture systems (Figure 5 (A) and (B)). The lattice structure of anthracene crystals is monoclinic with $a = 8.44$ Å, $b = 5.99$ Å, $c = 11.11$ Å, $\beta = 125.4^\circ$ [44]. The strong diffraction peak at 19.58° in pure anthracene corresponds to the (002) plane, and the spacing between the 002 planes is 4.53 Å. Although only one hydrogen atom is substituted by a bromine atom, the crystal structures of 2-bromoanthracene and 9-bromoanthracene are significantly different from that of anthracene. However, it is also worth noting that all these three compounds have a diffraction peak close to 19.5° .

For the anthracene (1) + 2-bromoanthracene (2) system, with the increase of the mole fraction of 2-bromoanthracene, x_2 , in the mixture, the (002) plane spacing starts to shift to lower values (Figure 6). Moreover, a new diffraction peak occurs near $2\theta = 17^\circ$ with increasing x_2 in the mixture. This indicates that new mixture crystal structure evolves. The new peak appears at $2\theta = 16.38^\circ$ when $x_1 = 0.70$ roughly corresponding to the lowest solid-

liquid equilibrium melting point (Figure 1(A)). With increase of x_1 , the peak position increases from 16.38° to 17.06° and disappears in pure anthracene.

The diffraction data for mixtures with x_1 between 0.50 and 0.10 indicate relatively amorphous structures, since the peaks are not very strong. Nonetheless, some peak structures are visible, and allow analysis of structure.

The distance between 002 planes in the pure anthracene, pure 2-bromoanthracene and mixture can be calculated by Bragg's law

$$n\lambda = 2d\sin\theta \quad (8)$$

where n is an integer, λ is the wavelength of the incident wave, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

Figure 6 shows changes of the 2θ angle of (002) plane and distance between 002 planes in the (1) + (2) system, which demonstrates that the spacings between 002 planes are significantly stretched by adding 2-bromoanthracene into anthracene. The distance between 002 planes reaches a maximum when the mixture is near the lowest melting solid-liquid equilibrium point, which is in good agreement with the thermodynamic data above, indicating the formation of the highest energy solid state near the lowest solid-liquid equilibrium melting point. Interestingly, the mixture at $x_1 = 0.18$ gives a local minimum in the (002) plane spacing, despite the higher energy nature of this mixture (see Figure 4(A)). What this demonstrates is that there is no one structural aspect, such as that characterized by the 002 spacing, that determines system energetics.

As distinct from the anthracene (1) + 2-bromoanthracene (2) system, for the anthracene (1) + 9-bromoanthracene (3) system, the intensity of the diffraction peak corresponding to 002 is significantly weakened upon adding 9-bromoanthracene into the system (see Figure 5(B)). For some of the mixtures, for example mixtures with $x_1 = 0.70$ and 0.80 , the intensity of the peak is too low to be distinguished from background noise in the XRD scan.

3.5. Vapor pressure

The Knudsen effusion technique was used to measure the vapor pressure of anthracene (1) + 2-bromoanthracene (2) mixtures and anthracene (1) + 9-bromoanthracene (3) mixtures in two different types of experiments, i.e. non-isothermal and isothermal.

Figure 7 shows the vapor pressure of pure anthracene and 9-bromoanthracene measured here and these results are consistent with literature values [3, 4]. Figure 7 also shows the vapor pressure of pure 2-bromoanthracene, for which no literature values were found. The enthalpies of sublimation of 2-bromoanthracene and 9-bromoanthracene are almost identical, $101.3 \text{ kJ}\cdot\text{mol}^{-1}$ and $100.9 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, while the vapor pressure of 9-bromoanthracene is about one order of magnitude higher than that of pure 2-bromoanthracene and very similar to that of unsubstituted anthracene. The enthalpy of sublimation of anthracene is about $95.0 \text{ kJ}\cdot\text{mol}^{-1}$. The similarity of the sublimation enthalpies of the pure compounds is apparent from Figure 7, in which all curves have similar slopes.

Figure 8 shows the vapor pressure of the mixture and the change in composition of anthracene in the condensed phase (x_1) and vapor phase (y_1) with the sample mass loss in an experiment which begins with a (1) + (2) mixture at $x_1 = 0.83$ and $T = 338.15 \text{ K}$. The composition of anthracene in the condensed phase is measured before, during, and after

vapor pressure experiments by taking a 0.10 – 0.40 mg solid sample out of the effusion cell. Analytes were then dissolved in dichloromethane to an approximate concentration of 40–100 ppm and analyzed by GC-MS. The composition of the anthracene in the vapor phase, y_1 , can be calculated from how much of component 1 vaporized compared to the total amount vaporized,

$$y_1 = \frac{n_{1-V}}{n_{1-V} + n_{2-V}} \quad (9)$$

in which,

$$n_{1-V} = n_{1-0} - n_{1-F} \quad n_{1-0} = \frac{m_{1-0}}{Mw_1} \quad n_{1-F} = \frac{m_{1-F}}{Mw_1} \quad (10)$$

$$n_{2-V} = n_{2-0} - n_{2-F} \quad n_{2-0} = \frac{m_{2-0}}{Mw_2} \quad n_{2-F} = \frac{m_{2-F}}{Mw_2} \quad (11)$$

where n_V is the calculated amount of the compounds in the vapor phase, n_0 and n_F are the amount of the compounds in the solid before and after each step of the experiment, m_{i-0} and m_{i-F} is the mass of the component in the solid before and after each step of the experiment, and Mw is the molecular weight of the component. The mass ratio of the mixture components remaining in the solid phase at any time is calculable from:

$$\frac{m_{2S}}{m_{1S}} = \frac{Mw_1}{Mw_2} (1/x_{1S} - 1) \quad (12)$$

and by mass balance,

$$m_{0-total} - \Delta m_{total} = \left[1 + \left(\frac{m_{2S}}{m_{1S}} \right)_F \right] m_{1-F} \quad (13)$$

which allows calculation of m_{1-F} from the initial mass of the sample ($m_{0-total}$), measured mass loss of the sample (Δm_{total}), and measured mass ratio of mixtures after each step of experiments ($(m_{2S}/m_{1S})_F$) from Eq.(12). Then, all the other quantities are easily obtained.

The maximum possible vapor pressure that any mixture can exert may be calculated assuming that each component exists in its own separate phase, such that

$$P_{max} = \sum_i P_i^* \quad (14)$$

where P^* is the saturated vapor pressure for each compound. Pressures above the maximum possible vapor pressure are not possible at equilibrium, because this would result in the nucleation of a pure solid phase [24].

If a mixture were an ideal mixture, the vapor pressure of the mixture would obey Raoult's law. Thus,

$$P_{\text{RL}} = \sum_i x_i P_i^* \quad (15)$$

where x is the mole fraction of each component in the mixture.

At the beginning of the experiment in Figure 8, the vapor pressure of the mixture is close to, but not exactly the vapor pressure of pure anthracene (which is also close to the maximum, non-interacting phases vapor pressure). The mixture vapor pressure would logically be close to the vapor pressure of anthracene, because $P_2 \ll P_1$.

The vapor pressure of the (1) + (2) mixture falls slowly with mass loss between the vapor pressure of anthracene and a Raoult's law value corresponding to $x_1 = 0.83$ until the mixture loses approximate 60% of the mass. Of course, the vapor pressure clearly really cannot follow Raoult's law, as the mixture composition is much below $x_1 = 0.83$ for much of that period (see Figure 8). Thus, the choice to plot the Raoult's law value at $x_1 = 0.83$ is somewhat arbitrary, but it is a useful frame of reference since it corresponds to the initial mixture composition. Meanwhile, the estimated composition of anthracene in the vapor phase is close to 1.0 until over 50% mass loss from the sample, which illustrates that the vapor pressure of the mixture is dominated by the vapor pressure of anthracene.

When x_1 , the remaining mole fraction of anthracene, is about 0.60, the vapor pressure starts to quickly decrease. At this point, about 70 % of anthracene in the original mixture has evaporated, and the mixture vapor pressure decreases towards that of 2-bromoanthracene. The final point is at a 25% content of anthracene in the solid, and the vapor pressure is near $\ln P/\text{Pa} = -4.8$, which is very near the vapor pressure of pure 2-bromoanthracene at this temperature.

Figure 9 shows for a (1) + (2) mixture how the vapor pressure and composition in the condensed phase and vapor phase change starting from an initial composition of $x_1 = 0.30$ again at about the same temperature $T = 338.6$ K. The vapor pressure of the mixture with an initial anthracene mole fraction of 0.30 again falls continuously to the vapor pressure of 2-bromoanthracene, and the composition of anthracene in the vapor phase decreases from 0.76 to 0.20. In essence, this continues the behavior seen in Figure 8 to lower values of x_1 . The vapor pressure finally falls to the 2-bromoanthracene value, even when there remains about $8 \pm 2\%$ anthracene in the mixture. Thus the mixture accommodates this amount of anthracene under this condition, while not allowing the bulk phase behavior of the anthracene to manifest itself in terms of preferential escape of this more volatile component. This does not mean that the anthracene is nonvolatile, as Figure 9 clearly demonstrates, but only that the mixture vapor pressure is dominated by that of 2-bromoanthracene, even as this small remaining amount of anthracene is lost.

The vapor pressure behavior is consistent with the XRD results of Figure 5 (A) at $x_1 = 0.10$, which begins to approach closely the XRD pattern of pure 2-bromoanthracene, even while there is a significant residual content of anthracene. The composition of the initial mixture ($x_1 = 0.30$) is in region B of Figure 3(A), while that of the final mixture ($x_1 \approx 0.10$) is in region A.

In summary, the x - y diagram for sublimation of the anthracene (1) + 2-bromoanthracene (2) system at $T=338\text{K}$ may be prepared, and this is shown in Figure 10. At higher concentrations of anthracene, the evaporation process of the (1) + (2) mixtures is dominated by the evaporation of anthracene. These are the mixtures that in the XRD show transition in the crystal phase towards pure anthracene (region C). On the other hand, (1) + (2) mixtures that are not as anthracene-rich follow the more usual trajectory of decreasing vapor pressure

with mass loss, until the concentration of anthracene becomes so low that its contribution becomes negligibly low.

Vapor pressures of the (1) + (2) mixtures with $x_1 = 0.70$ and $x_1 = 0.90$ are shown as a function of temperature in Figure 11. The vapor pressures of the mixture with $x_1 = 0.90$ is very near the vapor pressure of anthracene, and based on the results of Figure 10, the vapor pressure will be very near pure anthracene at all temperatures near ambient, even up to 71% mass loss (or a 62 mol% anthracene remaining in the solid). This is crudely consistent with the point at which the vapor pressure curve began to sharply decline. The mixture with $x_1 = 0.70$ gives a vapor pressure closer to a Raoult's law value until losing about 33% of its initial mass (if all the mass loss were anthracene, this would correspond to $x_1 = 0.52$ as the final composition). Then the vapor pressure starts to quickly drop towards the vapor pressure of 2-bromoanthracene (data points not shown). So again, mixtures that start out in region C show a behavior that indicates that only the more volatile anthracene evaporates at the beginning, and after significant loss of mass, the existence of the less volatile component begins to influence results. Starting in region B, the mixture properties are more immediately apparent, though still very much dominated by anthracene.

Figure 12 shows the vapor pressure of (1) + (2) mixture with initial $x_1 = 0.50$. The vapor pressure drops with mass loss during measurement, though it stays somewhere between the Raoult's law predictions for $x_1 = 0.50$ and 2-bromoanthracene vapor pressure until losing about 75 % of its mass. This continuous decrease with composition is consistent with what is shown in Figure 10, for composition at $x_1 < 0.50$ (i.e., in region B). The temperature dependence of vapor pressure suggested by the curvature in the data of Figure 12 is, of course, influenced by the sample composition change. There is every reason to believe that at any particular composition, a straight line, corresponding to Clausius – Clapeyron behaviour with constant $\Delta_{\text{sub}} H$, would describe the data, just as in the other cases. Mixtures continuously decrease in vapor pressure as the more volatile anthracene is lost, but in this case, some 2-bromoanthracene is also continually lost right from the start as well, as shown by Figure 10.

Figure 13 shows the vapor pressure behavior of equimolar anthracene (1) + 9-bromoanthracene (3) mixtures. Since the vapor pressures of anthracene and 9-bromoanthracene are similar, the maximum possible vapor pressure is contributed to by the vapor pressures of both anthracene and 9-bromoanthracene. In the isothermal run (Figure 13 (A)) at 328.15 K, the vapor pressure is close to the maximum possible vapor pressure until just over 65% of the total mass is lost. This is consistent with the non-isothermal data (Figure 13 (B)). It is also consistent with the continuous decrease of anthracene in the vapor phase, in which it is around 65% mass loss that the mixture vapor pressure significantly drops. During the non-isothermal run (Figure 13 (B)), the vapor pressure stays at its maximum possible value until losing about 75% of the total mass, which is different from the vapor pressure behavior of equimolar anthracene + 2-bromoanthracene mixtures (Figure 12). This is consistent with these (1) + (3) mixtures behaving like two phase systems in region B.

Figure 14 also shows the vapor pressure behavior of equimolar anthracene (1) + 9-bromoanthracene (3) mixtures at 328.15 K, based on the data from Figure 13 (A). This further demonstrates that the anthracene and 9-dibromoanthracene mixtures show separated phase behaviors, as already suggested in Figure 3(B). Hence, no simple x-y diagram can be plotted, as was for the single phase anthracene (1) + 2-bromoanthracene system.

4. Conclusions

Two PAC mixture systems are investigated to study the influence of bromine substitution on anthracene on phase behavior and vapor pressure. The anthracene (1) + 2-bromoanthracene (2) system is a single phase system, but not ideal. It is not a eutectic system, but does have a minimum solid-liquid equilibrium melting temperature of 477.65 K at $x_1 = 0.74$. The melting and crystallization studies show that the energetics of the (1) + (2) mixtures is composition dependent and that the least stable state forms somewhere between $x_1 = 0.7$ and $x_1 = 0.8$. This is verified by entropies of crystallization and interaction energies, and XRD analysis shows that it is reflected in the crystal structure. The vapor pressure measurements on this system show that the phase behavior of the mixtures depends on the composition in a complicated way. For (1) + (2) mixtures with high mole fraction of anthracene ($x_1 > 0.7$), the sublimation of the mixtures is dominated by loss of anthracene. For (1) + (2) mixtures with $x_1 \approx 0.70$, the vapor pressure falls slowly towards that of 2-bromoanthracene, achieving this value while there is still a significant amount of anthracene left in the mixture ($x_1 = 0.08 \pm 0.02$). The anthracene (1) + 9-bromoanthracene (3) system behaves quite differently from (1) + (2) system. The (1) + (3) system shows a solid solution like phase diagram, but forms two separate phases, i.e. an anthracene like and a 9-bromoanthracene like phase.

Acknowledgments

This project was supported by Grant Number P42 ES013660 from the National Institute of Environmental Health Sciences (NIEHS), NIH and the contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIEHS/NIH.

I express my gratitude to my colleague, James Rice, for valuable research collaboration, discussion and editorial advice.

References

1. Shiu WY, Ma KC. J Phys Chem Ref Data. 2000; 29:41–130.
2. Roux MV, Temprado M, Chickos JS, Nagano Y. J Phys Chem Ref Data. 2008; 37:1855–1996.
3. Goldfarb JL, Suuberg EM. J Chem Eng Data. 2008; 53:670–676.
4. Goldfarb JL, Suuberg EM. Journal of Chemical Thermodynamics. 2008; 40:460–466. [PubMed: 20376299]
5. Goldfarb JL, Suuberg EM. Environmental Toxicology and Chemistry. 2008; 27:1244–1249. [PubMed: 18220445]
6. Paumen ML, Borgman E, Kraak MHS, van Gestel CAM, Admiraal W. Environmental Pollution. 2008; 152:225–232. [PubMed: 17644226]
7. Van Metre PC, Mahler BJ. Environ Sci Technol. 2005; 39:5567–5574. [PubMed: 16124288]
8. Gupta RK, Singh RA. Journal of Crystal Growth. 2004; 267:340–347.
9. Gupta RK, Singh SK, Singh RA. Journal of Crystal Growth. 2007; 300:415–420.
10. Szczepanik, Richard; Skalmowski, Włodzimierz; Bitumen, Teere; Asphalte, Peche. 1963; 14:506,508–512,514.
11. Szczepanik, Ryszard. Chem Stosowana Ser A. 1963; 7:621–660.
12. Rastogi RP, Rama Varma KT. Journal of the Chemical Society. 1956:2097–2101.
13. Rastogi RP, Bassi PS. The Journal of Physical Chemistry. 1964; 68:2398–2406.
14. Singh NB, Giri DP, Singh NP. J Chem Eng Data. 1999; 44:605–607.
15. Singh NB, Srivastava MA, Singh NP. J Chem Eng Data. 2001; 46:47–50.
16. Singh NP, Singh NB. Progress in Crystal Growth and Characterization of Materials. 2006; 52:84–90.
17. Singh NB, Srivastava A, Singh NP, Gupta A. Molecular Crystals and Liquid Crystals. 2007; 474:43–54.

18. Singh NB, Das SS, Singh NP, Agrawal T. *Journal of Crystal Growth*. 2008; 310:2878–2884.
19. Singh NB, Das SS, Gupta P, Dwivedi MK. *Journal of Crystal Growth*. 2008; 311:118–122.
20. Peters CA, Mukherji S, Knightes CD, Weber WJ. *Environ Sci Technol*. 1997; 31:2540–2546.
21. Peters CA, Wammer KH, Knightes CD. *Transport Porous Med*. 2000; 38:57–77.
22. Fu J, Rice JW, Suuberg EM. *Fluid Phase Equilibria*. 2010; 298:219–224. [PubMed: 21076624]
23. Burks GA, Harmon TC. *J Chem Eng Data*. 2001; 46:944–949.
24. Rice JW, Fu J, Suuberg EM. *Journal of Chemical & Engineering Data*. 2010; 1021:je100208e
25. Rice JW, Suuberg EM. *The Journal of Chemical Thermodynamics*. 2010; 42:1356–1360. [PubMed: 20814451]
26. Fu J, Rice JW, Suuberg EM. *Fluid Phase Equilibria*. 2010; 298:219–224. [PubMed: 21076624]
27. Fu J, Suuberg EM. *The Journal of Chemical Thermodynamics*. 2011; 43:1660–1665. [PubMed: 22021935]
28. Fu J, Suuberg EM. *Environmental Toxicology and Chemistry*. 2012; 31:486–493. [PubMed: 22139714]
29. Bogdal D, Lukaszewicz M, Pielichowski J. *Green Chem*. 2004; 6:110–113.
30. Netka J, Crump SL, Rickborn B. *The Journal of Organic Chemistry*. 1986; 51:1189–1199.
31. Lide, DR.; Baysinger, G.; Kehiaian, HV.; Berger, LI.; Kuchitsu, K. *Handbook of Chemistry and Physics*. 90. CRC Press; 2010.
32. Porzi G, Concilio C. *Journal of Organometallic Chemistry*. 1977; 128:95–98.
33. Pounder FE, Masson I. *J Chem Soc*. 1934:1357–1360.
34. Oja V, Suuberg EM. *Analytical Chemistry*. 1997; 69:4619–4626.
35. Bender R, Bieling V, Maurer G. *The Journal of Chemical Thermodynamics*. 1983; 15:585–594.
36. Hansen PC, Eckert CA. *J Chem Eng Data*. 1986; 31:1–3.
37. Sonnefeld WJ, Zoller WH, May WE. *Anal Chem*. 1983; 55:275–280.
38. Fu J, Suuberg EM. *Environ Toxicol Chem*. 2012; 31:574–578. [PubMed: 22213441]
39. Fu JX, Suuberg EM. *Environ Toxicol Chem*. 2011; 30:2216–2219. [PubMed: 21766320]
40. *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)* Varian Inc., 2001–2004.
41. Lee LS, Hagwall M, Delfino JJ, Rao PSC. *Environ Sci Technol*. 1992; 26:2104–2110.
42. Lee LS, Rao PSC, Okuda I. *Environ Sci Technol*. 1992; 26:2110–2115.
43. Liu LH, Endo S, Eberhardt C, Grathwohl P, Schmidt TC. *Environmental Toxicology and Chemistry*. 2009; 28:1578–1584. [PubMed: 19309178]
44. Jo S, Yoshikawa H, Fujii A, Takenaga M. *Appl Surf Sci*. 2006; 252:3514–3519.

Figure 1 (A)

Figure 1(B)

FIGURE 1.

(A) Phase diagram of anthracene (1) + 2-bromoanthracene (2) mixtures: —○—, thaw temperature; - - △ - -, liquidus temperature. (B) Phase diagram of anthracene (1) + 9-bromoanthracene (3) mixtures: —●—, thaw temperature; - - △ - -, liquidus temperature.

Figure 2 (A)

Figure 2 (A)

Figure 2(B)

FIGURE 2.

(A) DSC of anthracene (1) + 2-bromoanthracene (2) mixture with $x_1 = 0.50$. (B) DSC of anthracene (1) + 9-bromoanthracene (3) mixture with $x_1 = 0.50$. The figure shows two heating cycles and one cooling cycle.

Figure 3 (A)

Figure 3(B)

FIGURE 3.

(A) Thaw temperature and $\Delta_{\text{cry}} H$ of anthracene (1) + 2-bromoanthracene (2) mixtures: -- $\blacktriangle$ --, ΔH ; — $\bullet$ —, thaw temperature. (B) Crystallization temperature and $\Delta_{\text{cry}} H$ of anthracene (1) + 9-bromoanthracene (3) mixtures: — $\bullet$ —, $\Delta_{\text{cry}} H$ at high crystallization T; -- $\blacksquare$ --, $\Delta_{\text{cry}} H$ at low crystallization T; — $\blacktriangle$ —, total $\Delta_{\text{cry}} H$; — $\circ$ — high crystallization peak temperature; -- $\square$ -- low crystallization peak temperature.

Figure 4(A)

Figure 4(B)

FIGURE 4.

(A) Entropy and interaction energy of anthracene (1) and 2-bromoanthracene (2) mixtures: —▲—, entropy of crystallization, $\Delta_{\text{cry}} S$; --●--, interaction energy, E_{inter} . (B) Interaction energy of anthracene (1) and 9-bromoanthracene (3) mixtures: --●--, interaction energy, E_{inter} .

Figure 5(A)

Figure 5(B)

FIGURE 5.

(A) X-ray diffraction patterns of anthracene (1) + 2-bromoanthracene (2) system. (B) X-ray diffraction patterns of anthracene (1) + 9-bromoanthracene (3) system.

FIGURE 6. 2θ angle of (002) plane and distance between (002) planes of pure compound and mixtures of the anthracene (1) + 2-bromoanthracene (2) system: —●—, 2θ angle of (002) plane; --▲--, distance between 002 planes.

FIGURE 7. Vapor pressures of pure anthracene (1), P_1 , 2-bromoanthracene (2), P_2 , and 9-bromoanthracene (3), P_3 : ●, anthracene; ◆, 2-bromoanthracene; □, 9-bromoanthracene.

FIGURE 8.

Vapor pressure and composition change of a mixture with initial anthracene (1) mole fraction of 0.83 + 2-bromoanthracene (2) mole fraction of 0.17 versus sample mass loss at 338.2 K: —○—, measured mixture P ; —●—, measured x_1 of solid mixture; —○—, calculated y_1 ; - - - - -, P , vapor pressure of anthracene; — - - - -, P , Raoult's law prediction at $x_1 = 0.83$; - - - - -, P , pure 2-bromoanthracene.

FIGURE 9.

Vapor pressure and composition change of a mixture with initial anthracene (1) mole fraction of 0.30 + 2-bromoanthracene (2) mole fraction of 0.70 versus sample mass loss at 338.6 K: —, measured mixture P ; —●—, measured x_1 of solid mixture; —○—, calculated y_1 ; - - - - -, P , Raoult's law prediction at $x_1 = 0.30$; - - - - -, P , Raoult's law prediction at $x_1 = 0.10$; - - - - -, P , pure 2-bromoanthracene.

FIGURE 10.

x - y diagram and vapor pressures for sublimation of anthracene (1) + 2-bromoanthracene (2) mixtures at $T = 338$ K. The y points were interpolated from the vapor composition data in Figure 8 and 9. In x - y diagram, ●, calculated y_1 from Figure 8; ▲, calculated y_1 from Figure 9; — — — —, Raoult's law calculation curve assuming $P_1^* = P_2^*$. In the x - $\ln P$ diagram, ●, measured mixture P from Figure 8; ▲, measured mixture P from Figure 9; — — — —, P , Raoult's law calculation of anthracene (1) + 2-bromoanthracene (2) mixtures; - - - - -, P , pure anthracene; — - — -, P , pure 2-bromoanthracene.

FIGURE 11.

Vapor pressure measurements of anthracene (1) + 2-bromoanthracene (2) mixtures with $x_1 = 0.70$ and 0.90 at start of experiment: — — —, P , Raoult's law prediction at $x_1 = 0.90$; - - - -, P , Raoult's law prediction at $x_1 = 0.70$; ●, measured mixture P with $x_1 = 0.70$ at start of experiment; Δ, measured mixture P with $x_1 = 0.90$ at start of experiment; - - - - -, P , pure anthracene; —, P , pure 2-bromoanthracene.

Figure 12 (A)

Figure 12 (B)

FIGURE 12.

Vapor pressure measurements of anthracene (1) + 2-bromoanthracene (2) mixtures with $x_1 = 0.50$ at start of experiment: - - -, P , Raoult's law prediction at $x_1 = 0.50$; ●, measured mixture P ; —, P , pure 2-bromoanthracene.

FIGURE 13.

(A) Vapor pressure and composition change of a mixture with initial anthracene (1) mole fraction of 0.50 + 9-bromoanthracene (3) mole fraction of 0.50 versus sample mass loss at 328.2 K: —, measured mixture P ; —●—, measured x_1 of solid mixture; —○—, calculated y_1 ; - - -, P , maximum possible vapor pressure; — · — · —, P , Raoult's law prediction at $x_1 = 0.50$; at start of experiment: — — —, P , pure anthracene; — · — · — · —, P , pure 9-bromoanthracene. (B) Vapor pressure measurements of anthracene (1) + 9-bromoanthracene (3) mixtures with $x_1 = 0.50$ at start of experiment: —, P , maximum possible vapor pressure; ●, measured mixture P ; - - -, P , pure 9-bromoanthracene.

FIGURE 14.

Vapor pressure and composition change for sublimation of anthracene (1) + 9-bromoanthracene (3) mixtures at $T = 328 \text{ K}$: ●, measured mixture P from Figure 13(A); — — — —, P , maximum possible vapor pressure; - - - - -, P , pure anthracene; — - — —, P , pure 2-bromoanthracene.

Table 1

Polycyclic aromatic compounds examined

CAS Reg. No.	Compound	Min. Purity	MW/g·mol ⁻¹	Melting point/K	Manufacturer	Molecular Structure
120-12-7	anthracene	0.99	178.23	490.0	Sigma-Aldrich
7321-27-9	2-bromoanthracene	0.97	257.13	493.8	TCI America
1564-64-3	9-bromoanthracene	0.95	257.13	374.1	TCI America

^a Standard uncertainty is $u(T) = \pm 0.1$ K. Samples were used in the measurements without further purification (except during actual vapor pressure measurements-see text).

Table 2

Thermochemical properties of anthracene (1) + 2-bromoanthracene (2) mixtures.

x_1	Liquidus			
	Thaw T/K	T/K	$(\Delta_{\text{cry}}H)_{\text{exp}}/\text{kJ}\cdot\text{mol}^{-1}$	T_{cry}/K
0.00	493.8	493.8	24.09	481.0
0.10	489.4	491.2	23.76	475.1
0.18	488.0	489.1	22.12	478.5
0.30	485.0	486.1	22.40	471.7
0.40	481.9	483.5	22.19	473.6
0.50	480.3	482.1	22.01	468.5
0.60	478.8	480.2	22.78	465.4
0.65	478.4	479.7	22.95	465.1
0.70	478.1	479.5	21.12	466.7
0.72	477.8	479.6	23.16	464.5
0.73	477.9	479.7	22.45	468.3
0.74	477.6	479.4	22.70	462.1
0.75	477.6	479.5	22.51	462.8
0.76	477.9	479.9	22.60	471.9
0.78	478.5	480.1	23.24	467.0
0.80	478.8	480.4	23.73	462.0
0.90	480.4	483.0	22.84	477.0
1.00	490.0	490.0	26.49	466.3

Standard uncertainties are $u(x) = \pm 0.01$, $u(T) = \pm 0.1$ K, and $u(\Delta_{\text{cry}}H) = \pm 5 \text{ J}\cdot\text{g}^{-1}$, i.e. 0.89–1.29 kJ·mol^{−1}.

Table 3

Thermochemical properties of anthracene (1) + 9-bromoanthracene (3) mixtures.

x_1	Thaw T/K	Liquidus T/K	T_{cry} (High)/K	$\Delta_{\text{cry}}H(\text{high})/\text{kJ}\cdot\text{mol}^{-1}$	T_{cry} (low)/K	$\Delta_{\text{cry}}H(\text{high})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cry}}H(\text{total})/\text{kJ}\cdot\text{mol}^{-1}$
0.00	374.1	374.1			336.7	14.33	14.33
0.10	366.3	369.5			340.3	16.32	16.32
0.20	367.5	405.2			337.7	13.42	13.42
0.30	367.7	424.4	397.4	2.94	340.7	11.61	14.55
0.40	368.7	438.4	408.5	5.14	333.9	8.90	14.04
0.50	370.7	451.9	421.8	7.10	328.4	7.47	14.57
0.60	403.5	457.8	428.2	8.57	334.1	6.04	14.61
0.70	424.2	466.9	439.5	10.69	331.9	3.79	14.48
0.80	443.3	475.9	451.3	14.30	342.7	1.99	16.29
0.90	455.7	483.2	465.4	16.77	336.6	0.62	17.39
1.00	490.0	490.0	466.4	26.49			26.49

^a T_{cry} (High) and T_{cry} (low) is high and low temperature crystallization peak positions, respectively, and $\Delta_{\text{cry}}H(\text{high})$ and $\Delta_{\text{cry}}H(\text{low})$ are corresponding enthalpy of crystallization.^b Standard uncertainties are $u(x) = \pm 0.01$, $u(T) = \pm 0.1$ K, and $u(\Delta_{\text{cry}}H) = \pm 5$ J·g⁻¹, i.e. 0.89–1.29 kJ·mol⁻¹.

Table 4

Vapor pressure of pure compounds

<i>T/K</i>	<i>P/Pa</i>	<i>T/K</i>	<i>P/Pa</i>	<i>T/K</i>	<i>P/Pa</i>
Anthracene					
322.9	1.82E-02	333.0	5.58E-02	343.1	1.46E-01
328.0	2.97E-02	338.1	8.91E-02	348.2	2.33E-01
2-bromoanthracene					
334.8	5.41E-03	355.0	4.15E-02	375.3	2.87E-01
339.8	9.21E-03	360.1	7.18E-02	380.4	4.37E-01
344.9	1.56E-02	365.2	1.14E-01	385.4	6.52E-01
350.0	2.61E-02	370.4	1.84E-01	390.4	8.87E-01
9-bromoanthracene					
314.8	5.10E-03	329.8	3.26E-02	345.0	1.58E-01
319.8	1.06E-02	334.9	5.32E-02	350.0	2.61E-01
324.8	1.71E-02	339.9	9.30E-02	355.0	4.18E-01

Standard uncertainty is $u(T) = \pm 0.1$ K, and the uncertainty for P is $\varepsilon_P = \delta P/P = \pm 0.05$.

Table 5

Vapor Pressures of anthracene (1) + 2-bromoanthracene (2) and anthracene (1)+ 9-bromoanthracene(3) mixtures.

Mixture	Initial x_1	T/K	Range of P/Pa	Change range of x_1
(1) + (2)	0.83	338.2	1.05E-01 2.66E-02	0.83–0.25
(1) + (2)	0.30	388.6	1.85E-02 7.10E-03	0.30–0.08
(1) + (3)	0.50	328.2	6.96E-02 – 2.81E-02	0.50–0.07

^a Standard uncertainties are $u(x) = \pm 0.01$, $u(T) = \pm 0.1$ K, and the uncertainty for P is $\varepsilon_P = \delta P/P = \pm 0.05$.