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Thermodynamic study of (anthracene + benzo[a]pyrene) solid mixtures

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Abstract

To characterize better the thermodynamic behavior of a binary polycyclic aromatic hydrocarbon mixture, thermochemical and vapor pressure experiments were used to examine the phase behavior of the {anthracene (1) + benzo[a]pyrene (2)} system. A solid-liquid phase diagram was mapped for the mixture. A eutectic point occurs at $x_1 = 0.26$. The eutectic mixture is an amorphous solid that lacks organized crystal structure and melts between $T = (414 \text{ and } 420) \text{ K}$. For mixtures that contain $0.10 < x_1 < 0.90$, the enthalpy of fusion is dominated by that of the eutectic. Solid-vapor equilibrium studies show that mixtures of anthracene and benzo[a]pyrene at $x_1 < 0.10$ sublime at the vapor pressure of pure benzo[a]pyrene. These results suggest that the solid-vapor equilibrium of benzo[a]pyrene is not significantly influenced by moderate levels of anthracene in the crystal structure.

Keywords

Polycyclic aromatic hydrocarbons; Anthracene; Benzo[a]pyrene; Binary mixtures; Phase equilibria; Vapor pressure

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are normally found in mixtures of many similarly structured compounds. The goal of the present research is to understand better PAH mixture thermodynamics by studying the phase behavior of a binary {anthracene (1) + benzo[a]pyrene (2)} system. Anthracene and benzo[a]pyrene are common PAHs and are common components of PAH mixtures, often with considerable environmental significance.

Similar studies have been conducted on binary, organic component mixtures and these principally report the temperatures and enthalpies of solid to liquid phase transitions, often involving one or two eutectic points [1–12]. In addition to analyses of melting temperature, enthalpies of fusion, and microstructure, many of the results presented here will address the sublimation behavior, *i.e.*, vapor pressure of the system given that the (anthracene + benzo[a]pyrene) solid-vapor system is not yet well understood or reported on in the literature. This work is part of broad study on binary PAH mixtures and hence, the experimental procedure is analogous to that previously reported for a mixture of (anthracene + pyrene) [13].

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2. Experimental

2.1. Materials

Anthracene (CAS Reg. No. 120-12-7, with mass fraction purity > 0.99) and benzo[a]pyrene (CAS Reg. No. 50-32-8, with mass fraction purity > 0.96) were obtained from Sigma-Aldrich. Purity was verified by gas chromatography/mass spectrometry (GC-MS) analysis. The anthracene contained trace levels of phenanthrene. Impurities in the benzo[a]pyrene were not detected.

In addition, the melting temperature of each pure compound, $T_{\text{fus},1} = (490 \pm 1) \text{ K}$ and $T_{\text{fus},2} = (449 \pm 1) \text{ K}$, was measured and compared favorably to the literature values [14]. The details of the melting temperature analysis are discussed in section 2.3.

2.2. Mixture Preparation

Mixtures of anthracene and benzo[a]pyrene were prepared using a melt and quench-cool technique. The desired quantities of anthracene (1) and benzo[a]pyrene (2) were measured to $\pm 0.01 \text{ mg}$ and sealed within a brass vessel. The vessel was then heated to $T = (498 \pm 5) \text{ K}$ and agitated, ensuring that both components melted and mixed in a liquid state. After a period of 5 min, the vessel was removed from the heat source and immediately immersed in liquid nitrogen, which provided cooling at an estimated $(70 \text{ to } 80) \text{ K} \cdot \text{s}^{-1}$ for the first 4 s. The preparation technique intended to preserve the disorder of the well-mixed liquid during crystallization. This heating and quench-cool procedure was repeated four additional times before the mixture crystals were removed from the preparation vessel and placed in glass storage vials. Uniformity of the samples was confirmed by visual examination. As it turned out, the results presented below were largely insensitive to the details of the preparation of the mixture (see section 3.1).

2.3. Melting Temperature and Enthalpy of Fusion

Melting temperatures and enthalpies of fusion ($\Delta_{\text{fus}}H$) of mixtures and pure samples were measured using a Thermo Scientific melting temperature analyzer and DuPont differential scanning calorimeter (DSC). In the latter case, hermetically sealed DSC pans were filled with (1 to 3) mg of sample and scanned in both 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 produces conveniently integrable peaks, increasing the accuracy of the enthalpy of fusion calculation. However, the values of enthalpy and transition temperatures were generally insensitive to changes in heating and cooling rate in the range of $(2.5 \text{ to } 20) \text{ K} \cdot \text{min}^{-1}$. A melting temperature analyzer was used to visually observe and obtain higher resolution melting temperature measurements. These generally agreed with the DSC in that the melting temperatures from each instrument differed by no more than 4 K, though naturally what is reported from the DSC is a temperature from an endothermic event stretching over several degrees, and hence, these values are less precise than classic melting temperature determination.

Melting behavior was tracked using the melting temperature analyzer to $\pm 1 \text{ K}$. In following the thaw-melt method [5], (1 to 2) mg of each sample was placed inside a glass capillary tube and heated at $(1 \pm 0.5) \text{ K} \cdot \text{min}^{-1}$. The thaw temperature is the temperature at which the first droplet of liquid appears in the capillary tube. The *liquidus* temperature is the maximum temperature at which both solid-crystals and liquid are observed to coexist in the system. Hence, the liquidus temperature is reached when the last crystal melts in the capillary tube. The experimentally measured enthalpies of fusion, thaw temperatures, and liquidus temperatures have been used to build a phase diagram for the (anthracene + benzo[a]pyrene) solid-liquid system.

2.4. Vapor Pressure

The Knudsen effusion technique was used to measure the vapor pressures (P) of (solid anthracene + benzo[a]pyrene) mixtures and pure components. This technique allows for vapor pressure measurement of low volatility compounds. Traditional vapor pressure techniques measure pressure directly and would require unacceptably high experimental temperatures that could degrade both anthracene and benzo[a]pyrene. The Knudsen effusion technique allows measurement of sample mass loss from a confining cell through a small orifice and relates it to vapor pressure by

$$P = \frac{m}{AW} \sqrt{\frac{2\pi RT}{M}}, \quad (1)$$

where m is the mass loss rate, A is the orifice area, R is the universal gas constant, T is the sample temperature, M is the molar mass, and W is the Clausing correction factor. The Clausing correction factor W , is very nearly unity, as noted elsewhere [13]. Vapor pressure experiments must satisfy fundamental effusion theory, which stipulates that vapor molecules escape a confining cell through orifice passages that are much smaller than their molecular mean free path. A detailed explanation of the Knudsen effusion theory and its implementation in this laboratory can be found elsewhere. [15–16]

Samples of {anthracene (1) + benzo[a]pyrene (2)} were placed inside effusion cells prepared from steel shim stock. The cells were sealed except for a single, circular orifice of diameter (0.60 ± 0.01) mm and placed on the arm of a continually recording microbalance contained in a high vacuum chamber. The pressure inside the chamber was reduced to 10^{-4} Pa to achieve the required condition of negligible backpressure outside the orifice. A calibrated, type-K thermocouple was used to measure cell temperature to ± 0.1 K and to verify thermal equilibrium in the system. At equilibrium, the pressure inside the cell is the vapor pressure of the sample and the subliming species leaks from the cell through the small orifice. The leak rate is measured and correlated to vapor pressure with eq 1. The relative instrument uncertainty within the experimental temperature range is $\delta P/P = 0.045$. In the case of a mixture, there is obviously a question of what molar mass must be used for M . In this work, the decision was made to use a weighted average of pure component molar masses. Because the value of molar mass appears as the square root, there is not a particularly great sensitivity to this value. For example, use of the above, assumed value would result in a maximum difference of 1.4 % in measured vapor pressure, if we take an extreme composition at $x_1 = 0.10$ at an experimental temperature of 338 K. Such a small difference is seen to be within the overall uncertainties.

With respect to the values of measured vapor pressures for mixtures, it is important to recognize that what is being examined is a solid sublimation system. The temperatures are always so low that there will be no formation of a liquid phase. This is important to keep in mind, insofar as the behavior of this system is inherently different than that of a liquid mixture system. If the fundamental condition of thermodynamic equilibrium in the sample cell is fulfilled (as must be considered reasonable), then it is important to recognize that equilibrium must be satisfied for all phases that might be present. What this means is that if a molecular component of a particular solid mixture were to have a sublimation pressure above the sublimation pressure of that pure component, a new pure component phase would be nucleated, even if it were not present in the quench-cooled mixture. In other words, the vapor pressure of the system would be bounded on the upper side by the sum of pure component vapor pressures. This is different from the situation in liquid systems, in which mixing would be more favored and the same sort of phase separation would not necessarily be possible.

2.5. Other Sample Characterizations

The crystal structures of anthracene, benzo[a]pyrene, and their mixtures were qualitatively investigated using powder X-ray diffraction (XRD). Samples were reduced to a fine powder and dusted onto glass slides that were coated with a thin petroleum film. A Siemens X-ray diffractometer (model D5000) was used to measure the diffraction patterns of each sample between (10 and 60) deg.

GC-MS was used to determine the composition of mixtures before, during, and after vapor pressure experiments. Analytes were dissolved in dichloromethane to an approximate concentration of $100 \mu\text{g}\cdot\text{mL}^{-1}$ and analyzed by a calibrated Varian combined gas chromatograph (model CP3800) and mass spectrometer (model Saturn 2200). The Varian analytical procedure for EPA Method 8270C was followed [17].

3. Results and discussion

3.1. Phase Diagram and Enthalpy of Fusion

Enthalpies of fusion for all samples were measured using temperature-controlled differential scanning calorimetry. Results from typical DSC scans are given in figure 1. All four scans were conducted in heating-mode at $10 \text{ K}\cdot\text{min}^{-1}$. The full heating, cooling, and reheating scan is given for pure benzo[a]pyrene. The DSC results here show heat input ($\Phi/W\cdot\text{g}^{-1}$) as the system is both heated and cooled. Endothermic peaks in the DSC scan reveal solid to liquid phase changes and can be integrated to determine the enthalpy of fusion of the sample with a relative uncertainty of $\delta\Delta_{\text{fus}}H/\Delta_{\text{fus}}H = 0.07$. Pure anthracene melts at $T = 490 \text{ K}$ with $\Delta_{\text{fus}}H = (156 \pm 11.9) \text{ J}\cdot\text{g}^{-1}$. This result is in fair agreement with Domalski and Hearing who report that pure anthracene melts at $T = 489 \text{ K}$ with $\Delta_{\text{fus}}H = 164.8 \text{ J}\cdot\text{g}^{-1}$ [18]. In the case of pure benzo[a]pyrene, two phase transitions were observed in the initial heating sequence. It was determined that the first peak in the scan is not that of a melting endotherm. Rather, it is attributable to a crystal transition and is previously reported by Casellato *et al.* [19]. The second peak in the benzo[a]pyrene scan at $T = 449 \text{ K}$ corresponds to the true solid to liquid phase transition and indicates a $\Delta_{\text{fus}}H = 44.6 \text{ J}\cdot\text{g}^{-1}$. As the liquid benzo[a]pyrene sample is subsequently cooled and reheated, a single subcooled fusion exotherm and single melting endotherm are repeatedly observed. This indicates that the initial crystal structure is not recovered during fusion and is likely a result of synthesis and purification. The commonly reported fusion enthalpy of benzo[a]pyrene contains both the crystal transition and melting endotherms [19,20] However, since all mixture samples were melted and quench cooled prior to analysis, this study reports the fusion enthalpy of pure benzo[a]pyrene to be $(44.6 \pm 3.1) \text{ J}\cdot\text{g}^{-1}$, corresponding only to the true melting behavior in the DSC scan. It is worth noting that the enthalpy of crystallization from the subcooled fusion exotherm matches the reported enthalpy of fusion within the relative uncertainty.

Mixture compositions are given in terms of x_1 as it is understood that $x_1 + x_2 = 1$. The DSC results indicate that {anthracene (1) + benzo[a]pyrene (2)} quench-cooled mixtures within the indicated composition range undergo a phase transition between $T = (414 \text{ and } 420) \text{ K}$, well before either of the pure phases melts. This indicates the existence of a eutectic mixture. In some cases, such as the one shown for a mixture at $x_1 = 0.70$, there appear to be two phase transitions as the sample is heated.

It is important to recall that the results are all for quench-cooled samples. If similar DSC experiments are performed on physical {anthracene (1) + benzo[a]pyrene (2)} mixtures, the measured values of melting temperature and fusion enthalpy are in fair agreement with those of the quench-cooled samples. This suggests that vapors interdiffuse in the vapor-solid system

and that a thermodynamically favored eutectic exists for this (anthracene + benzo[a]pyrene) system, irrespective of initial preparation.

It is worth noting with regard to the results of figure 1 that all evidence of anthracene and benzo[a]pyrene solid phase disappear in the presence of the lower temperature eutectic phase peak, irrespective of the magnitude of that latter peak. In other words, it appears as though neither pure anthracene nor benzo[a]pyrene is in a stable phase in such mixture systems. Figure 2 shows the full heating, cooling, and reheating scan of an (anthracene + benzo[a]pyrene) mixture at $x_1 = 0.70$. As previously discussed, the mixture at $x_1 = 0.70$ undergoes two endothermic phase transitions upon heating. Then cooling at a rate of $2.5 \text{ K} \cdot \text{min}^{-1}$ induces crystallization at $T = 440 \text{ K}$ of what is most probably an inhomogeneous phase that has limited solubility in the eutectic. This is followed by crystallization of the eutectic phase itself at $T = 411 \text{ K}$. Each of these phase transitions represents the crystallization of a subcooled liquid. When reheated, the phase transitions and associated temperatures match those of the initial heating sequence (Figure 2). Additionally, when nucleation of the eutectic phase is prevented by cooling to only $T = 423 \text{ K}$, the eutectic melting peak is no longer present in the reheating step (not shown). These results indicate that the two exothermic transition peaks definitively correspond to those of the two endothermic phase transitions.

In order to explore more completely phase behavior, it was necessary to use a melting temperature analyzer. Although the DSC measures the energy of a phase transition, it is not possible to observe visually the processes. Melting temperatures were measured for all pure components and mixtures and are given in table 1. The melting temperatures were measured in heating mode at $(1 \pm 0.5) \text{ K} \cdot \text{min}^{-1}$. This relatively slow rate allows for more precise measurement of melting temperatures. The results show that solid, quench-cooled {anthracene (1) + benzo[a]pyrene (2)} mixtures form a eutectic phase that melts between $T = (414 \text{ and } 420 \pm 1) \text{ K}$ at $x_1 = (0.26 \pm 2 \cdot 10^{-4})$. For all other compositions, only a portion of the crystals melts in the eutectic temperature range. Consequently, both solid and liquid coexist until the liquidus temperature is reached. Thus, figure 3 represents a phase diagram for the {anthracene (1) + benzo[a]pyrene (2)} system in which only solid phases exist below the thaw curve and only a liquid phase exists above the liquidus curve. The areas between these curves show the equilibrium coexistence of both solid and liquid phases. The point at which the liquidus curve meets the eutectic temperature range is the (anthracene + benzo[a]pyrene) eutectic point. Since the eutectic mixture does not melt at a singular temperature, defining this as a eutectic point is confusing and requires further explanation. So it is suggested here that mixtures of anthracene and benzo[a]pyrene form a single, amorphous, solid eutectic phase at $x_1 = 0.26$ that lacks any organized crystal structure and which melts throughout the $(414 - 420) \text{ K}$ temperature range. This region of phase transition, represented by the shaded region of figure 3, is not rate dependant and is observed in both the DSC and melting temperature analyzer for all combinations of (anthracene + benzo[a]pyrene), providing assurance that the region represents the melting temperature of a single, amorphous, solid phase. Further evidence supporting this conclusion will be presented in a later X-ray diffraction section.

In addition to the melting temperatures, the results from the thermal analyses are given in table 1 and shown in figure 3. The $\Delta_{\text{fus}}H$ observed at the eutectic temperature characterizes the necessary heat input for the initial melting to occur. The total $\Delta_{\text{fus}}H$ is a summation of both endothermic phase transition peaks observed in the DSC scan. It is worth noting that the total $\Delta_{\text{fus}}H$ is very similar to that of the eutectic mixture over a wide range of compositions. What this means is that when the mixture contains only modest amounts of anthracene and benzo[a]pyrene, the energetics of the eutectic phase are favored and characterize the mixture system. It is not until the mixtures are enriched in either anthracene or benzo[a]pyrene beyond the eutectic composition that the fusion enthalpy shifts towards that of the pure components. This

indicates that the ability of anthracene to reach a lower energy crystalline configuration is significantly impeded by the presence of relatively small amounts of benzo[a]pyrene.

In Figure 3, the data for $\Delta_{\text{fus}}H$ at the eutectic temperature clearly establish that the eutectic is a thermodynamically preferred phase, whose formation is limited by the system stoichiometry. At low concentrations of anthracene, eutectic formation is limited by the availability of anthracene. Since the actual eutectic composition occurs near $x_1 = 0.26$, at low anthracene concentrations, addition of N_1 moles anthracene produces $(N_1 + (74/26) \cdot N_1 = 3.85 \cdot N_1)$ moles of eutectic. This means that as an approximation for small additions of anthracene,

$$\frac{d\Delta H_{\text{eutectic peak}}}{dN_1} = 3.85 \cdot \overline{\Delta H_e}, \quad (2)$$

in which the $\overline{\Delta H_e}$ represents the molar enthalpy of fusion of the pure eutectic phase. If the addition of anthracene is done while keeping the total moles in the system roughly constant, then since $d(N_1/N_{\text{tot}}) = dx_1$ it is possible to see that

$$\frac{d\Delta H_{\text{eutectic peak}}}{dx_1} = 3.85 \cdot \Delta H_{e,\text{max}}, \quad (3)$$

where $\Delta H_{e,\text{max}}$ is now the maximum enthalpy of fusion at the eutectic point. Integration gives as a result (for the relevant range of anthracene-limited eutectic formation)

$$\Delta H_{\text{eutectic peak}} = 3.85 \cdot 60.7 \text{ J} \cdot \text{g}^{-1} \cdot x_1 = 234 \cdot x_1 \text{ J} \cdot \text{g}^{-1} \quad (4)$$

This is valid only for $x_1 < 0.26$. So for example at $x_1 = 0.10$, the predicted enthalpy for the eutectic peak is $23.4 \text{ J} \cdot \text{g}^{-1}$, whereas the measured value is just slightly lower than this.

Beyond the eutectic composition, $x_1 > 0.26$, the concentration of benzo[a]pyrene is assumed to limit the ability to form the eutectic phase. Again, for the eutectic, it is true that $(x_{1,e}/x_{2,e} = 0.26/0.74 = 0.351)$. The fraction of moles involved in forming the eutectic can be expressed as $(x_e = x_{1,e} + x_{2,e})$, but since benzo[a]pyrene is assumed to be the limiting component, it is possible to say that $(x_2 = x_{2,e})$, i.e., all of the benzo[a]pyrene is in the eutectic phase. It is true that $(x_1 + x_2 = 1)$, which means

$$x_e = x_{1,e} + (1 - x_1) = 0.351 \cdot x_{2,e} + (1 - x_1) = 1.351 \cdot (1 - x_1) \quad (5)$$

This in turn means that for $x_1 > 0.26$

$$\frac{d\Delta H_{\text{eutectic peak}}}{dx_1} = -1.351 \cdot \Delta H_{e,\text{max}} \quad (6)$$

Upon integration, this yields

$$\Delta H_{\text{eutectic peak}} = 60.7 \text{ J} \cdot \text{g}^{-1} - 1.351 \cdot 60.7 \text{ J} \cdot \text{g}^{-1} \cdot (x_1 - 0.26) = 60.7 \text{ J} \cdot \text{g}^{-1} - 82 \cdot (x_1 - 0.26) \text{ J} \cdot \text{g}^{-1} \quad (7)$$

So for example, at $x_1 = 0.50$, the enthalpy of fusion at $T = 414 \text{ K}$ is predicted to be about $41 \text{ J} \cdot \text{g}^{-1}$. This is in agreement with the observed value.

The agreement between the values obtained from this simple modeling of system behavior and experiment is shown in figure 3 and strongly support the conclusion that formation of a eutectic phase at $x_1 = 0.26$ is thermodynamically favored. What this means is that the enthalpy of fusion per gram of the non-eutectic phase is increasing proportionally with anthracene fraction, since overall, the enthalpy of fusion of the whole mixture does not vary much with composition. The enthalpy of fusion of the non-eutectic anthracene-rich phase is not the same as that of pure anthracene, meaning that there must be some contribution of benzo[a]pyrene to this phase until the mixture approaches truly pure anthracene.

3.2. X-Ray Diffraction

Powder X-ray diffraction studies were conducted to study the crystal structures of {anthracene (1) + benzo[a]pyrene (2)} mixtures in comparison to those of the pure components. The results are qualitative. The peak intensity from one spectrum to another has no significance and was related only to the quantity of sample used (mixtures were used more sparingly).

Peak positions from the mixture results can be compared to those of the pure component X-ray diffraction patterns. Figure 4 shows that the eutectic mixture lacks any organized crystal structure, because the few peaks that exist in the X-ray pattern are not well defined and do not rise much above the baseline. Additionally there is no real similarity between the eutectic mixture scan and those of the pure components. This result is consistent with the DSC and melting point studies that imply that the mixtures form a single, amorphous solid phase at the eutectic composition.

Figure 4 also shows that the crystal structure of a mixture at $x_1 = 0.10$ is comparable to that of pure benzo[a]pyrene because peaks at (16.8, 23.4, 23.8 and 26.4) degrees are all retained in the mixture diffraction pattern. This suggests that the crystal structure of benzo[a]pyrene is approached at low levels of anthracene. When X-ray patterns are reviewed at higher magnification, it is possible to see the minor differences in the peaks for a benzo[a]pyrene rich mixture and pure benzo[a]pyrene. This means that although the mixture retains much of the crystal structure of pure benzo[a]pyrene, the pure component characteristics are not completely preserved in the mixture. Again, this is consistent with the results of the thermal analysis that suggest that the energetics of the pure components are only approached when mixtures are highly enriched in either anthracene or benzo[a]pyrene.

3.3. Vapor Pressure

Knudsen effusion experiments were conducted by measuring the vapor pressure of various initial quench-cooled mixtures and pure components. The measured vapor pressure of pure anthracene $\ln P_1/\text{Pa} = 32.211 - 11683 \cdot T/\text{K}^{-1}$ at $T = (300 \text{ to } 373) \text{ K}$, and benzo[a]pyrene $\ln P_2/\text{Pa} = 32.802 - 13971 \cdot T/\text{K}^{-1}$ at $T = (358 \text{ to } 428) \text{ K}$, compare favorably to literature values [21]. Based on the notion that anthracene and benzo[a]pyrene were individual organic compounds, it was originally hypothesized that mixtures of the two components would behave ideally and sublime according to a weighted average of pure component vapor pressures, *i.e.*, Raoult's law would be followed. Figure 5 shows that this did not hold true. Continuous vapor pressure measurements were performed on samples of known initial composition. Instead of approaching the ideal mixture values, the vapor pressures of the {anthracene (1) + benzo[a]pyrene (2)} mixtures initially behaved as a sum of the two pure species vapor pressures. Again, this summation represents the maximum possible pressure in the effusion cell because the vapor pressure cannot exceed that of the pure, equilibrated species. It is worth noting that, due to the relatively high vapor pressure of anthracene, the maximum possible vapor pressure is essentially that of pure anthracene.

These data could be interpreted as indicating that mixtures of anthracene and benzo[a]pyrene are phase-separated systems in which the pure species do not interact. However, the aforementioned phase diagram and X-ray data show that the species are interacting in a complicated, non-ideal way. It needs to be kept in mind that upon vaporization, unless both components vaporize at exactly the same rate, composition, and with that, vapor pressure, will continuously change. With reference to figure 5, as anthracene (the more volatile component) is then preferentially lost in the experiment, the vapor pressure would drop, unless the two components behave as separate pure phases. The decreasing vapor pressure shown in figure 5 establishes that for the purposes of vapor pressure, there is interaction between components. The decreasing vapor pressure in figure 5 is path dependent, based on mass loss and is not meant to represent the equilibrium vapor pressure of the mixture. This region of transient vapor pressure is shown only for an initially eutectic mixture, but is observed for all {anthracene (1) + benzo[a]pyrene (2)} mixture compositions. Interestingly, a subsequent, stable vapor pressure was ultimately achieved and is shown for an assortment of mixtures with varied initial composition. This stable vapor pressure approaches that of pure benzo[a]pyrene even though the measurements are for an (anthracene + benzo[a]pyrene) mixture system.

These experiments required that the composition of the mixture be known throughout the sequence. Thus, samples were occasionally removed from the effusion cells, dissolved in dichloromethane, and analyzed by GC-MS. Reported mole fractions are given in table 2 and are accurate to ± 0.01 . The GC-MS analysis showed that the vapor pressure of the system approached that of pure benzo[a]pyrene as the mole fraction of anthracene in the solid was reduced from any given initial value to $x_1 \approx 0.10$. Once this stable vapor pressure was reached, it remained unchanged for the remainder of the experiments. Interestingly, the mixture compositions changed only gradually throughout the final stage of these experiments in which the mole fraction of anthracene never decreased below $x_1 \approx 0.03$. The vapor pressure of anthracene is roughly three orders of magnitude greater than that of benzo[a]pyrene in this temperature range. Hence, if the system were behaving ideally, the composition of the mixture would change significantly and the experimental vapor pressure would shift accordingly. This non ideal behavior indicates that mixtures of anthracene and benzo[a]pyrene at $x_1 < 0.10$ act similarly to a solid-azeotrope. It must be kept in mind that this system does not represent true azeotropy because the mixture concentration does, in fact, change slightly during sublimation. It is suggested instead, that this low a level of anthracene impurity can be retained in the benzo [a]pyrene crystallographic structure without any significant impact on measured solid-vapor equilibrium. It is important to bear in mind the distinction between the eutectic mixture and an azeotrope. The eutectic mixture exhibits a minimum melting temperature at $x_1 = 0.26$. The pseudo azeotrope is a nearly constant subliming mixture at $x_1 < 0.10$. There is no particular reason that a eutectic and an azeotrope should occur at the same composition.

4. Conclusions

The {anthracene (1) + benzo[a]pyrene (2)} mixture system is complicated and non-ideal. The solid-liquid equilibrium study shows that mixtures of anthracene and benzo[a]pyrene have a minimum melting temperature, *i.e.*, eutectic point, at $x_1 = 0.26$ that melts in the range (414 – 420) K. Additionally, for a wide range of composition, the crystal structure and energetics of the (anthracene + benzo[a]pyrene) mixtures are controlled by that of the eutectic mixture. The eutectic behavior is a solid-liquid equilibrium phenomenon and should not be confused with the pseudo azeotropy observed at solid-vapor equilibrium. The observed solid-vapor equilibrium behavior indicates only that benzo[a]pyrene can accommodate low levels of anthracene in its crystal structure and not that the mixture is behaving as a true azeotrope. Future work will aim to characterize other binary and multicomponent mixtures of polycyclic aromatic compounds.

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Figure 1.

Differential scanning calorimetry results of pure components and mixtures: —, pure (2); ---, pure (1); -.-, mixture at $x_1 = 0.30$; ..., mixture at $x_1 = 0.70$.

Figure 2.
Differential scanning calorimetry of an anthracene (1) + benzo[a]pyrene (2) mixture at $x_2 = 0.70$.

Figure 3.

Plot of $\Delta_{\text{fus}}H$ and temperature against mole fraction to show the phase diagram of the {anthracene (1) + benzo[a]pyrene (2)} system: ---, thaw curve; -□-, liquidus curve; ▲, $\Delta_{\text{fus}}H_{\text{eutectic peak}}$; -.-.-, estimated $\Delta_{\text{fus}}H_{\text{eutectic peak}}$ from eq 4 and 7; ..Δ.., $\Delta_{\text{fus}}H_{\text{tot}}$, with error bars representing uncertainty; shaded region, eutectic melting range.

Figure 4. X-ray diffraction patterns of pure components and mixtures: D, pure (1); C, pure (2); B, eutectic mixture; A, benzo[a]pyrene rich mixture at $x_1 = 0.10$.

Figure 5. Plot of vapor pressure against reciprocal temperature for {anthracene (1) + benzo[a]pyrene (2)} mixtures with varied initial composition: —, $P_{\max} \approx P_{(1)}$; ---, $P_{(2)}$; □, $P_{(1)} + (2)$ at $x_{1,\text{initial}} = 0.30$; ●, $P_{(1)} + (2)$ at $x_{1,\text{initial}} = 0.10$; +, $P_{(1)} + (2)$ at $x_{1,\text{initial}} = 0.70$.

Table 1

Measured melting temperatures and enthalpies of fusion of the {anthracene (1) + benzo[a]pyrene (2)} system.

x_1	$T_{\text{fus,thaw}}/\text{K}$	$T_{\text{fus,liquidus}}/\text{K}$	$\Delta_{\text{fus}}H_{\text{e}}/\text{J}\cdot\text{g}^{-1}$	$\Delta_{\text{fus}}H_{\text{tot}}/\text{J}\cdot\text{g}^{-1}$
0.00 ± 0	449 ± 1	449 ± 1	0 ± 0	44.6 ± 3.1
$0.10 \pm 1 \cdot 10^{-4}$	414 ± 1	438 ± 1	21.1 ± 1.5	33.0 ± 2.3
$0.20 \pm 1 \cdot 10^{-4}$	414 ± 1	425 ± 1	45.0 ± 3.2	56.9 ± 4.0
$0.22 \pm 2 \cdot 10^{-4}$	414 ± 1	424 ± 1	55.0 ± 3.9	60.0 ± 4.2
$0.24 \pm 2 \cdot 10^{-4}$	414 ± 1	421 ± 1	56.0 ± 3.9	56.0 ± 3.9
$0.26 \pm 3 \cdot 10^{-4}$	414 ± 1	420 ± 1	60.7 ± 4.2	60.7 ± 4.2
$0.28 \pm 3 \cdot 10^{-4}$	414 ± 1	421 ± 1		
$0.30 \pm 3 \cdot 10^{-4}$	414 ± 1	421 ± 1	57.9 ± 4.0	57.9 ± 4.0
$0.34 \pm 3 \cdot 10^{-4}$	414 ± 1	423 ± 1	51.0 ± 3.6	51.0 ± 3.6
$0.38 \pm 3 \cdot 10^{-4}$	414 ± 1	429 ± 1	46.6 ± 3.3	46.6 ± 3.3
$0.42 \pm 4 \cdot 10^{-4}$	414 ± 1	433 ± 1	47.4 ± 3.3	61.9 ± 4.3
$0.50 \pm 5 \cdot 10^{-4}$	414 ± 1	440 ± 1	40.4 ± 2.8	68.0 ± 4.8
$0.70 \pm 8 \cdot 10^{-4}$	414 ± 1	468 ± 1	21.2 ± 1.5	79.4 ± 5.6
$0.90 \pm 9 \cdot 10^{-4}$	414 ± 1	486 ± 1	5.37 ± 0.4	103 ± 7.2
1.00 ± 0	490 ± 1	490 ± 1	0 ± 0	156 ± 10.9

Table 2

Composition of {anthracene (1) + benzo[a]pyrene (2)} solid mixtures, measured during vapor pressure experiments by GC-MS

$x_{1,\text{initial}}$	$x_{2,\text{initial}}$	<i>mass loss/%</i>	$x_{1,\text{solid}}$	$x_{2,\text{solid}}$
0.1	0.9	14	0.049	0.951
0.1	0.9	44	0.030	0.970
0.1	0.9	80	0.032	0.968
0.3	0.7	15	0.102	0.899
0.3	0.7	18	0.104	0.897
0.3	0.7	50	0.040	0.961
0.5	0.5	23	0.168	0.832
0.5	0.5	37	0.068	0.932
0.5	0.5	45	0.049	0.951
0.7	0.3	56	0.048	0.952
0.7	0.3	74	0.051	0.949