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Thermodynamics of Multicomponent PAH Mixtures and Development of Tar-Like Behavior

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Abstract

This study explores the solid/liquid phase behavior of mixtures of polycyclic aromatic hydrocarbons (PAHs), exploring the transition from non-ideal solid mixtures to a relatively ideal liquid behavior characteristic of “tars”. PAH mixtures have been studied using differential scanning calorimetry, melting point analysis and Knudsen effusion. Mixtures of anthracene, pyrene and fluoranthene show behavior that is consistent with other binary PAH mixtures; that is, the initially solid mixture exhibits a significant melting point depression, relative to the pure components, and in a certain range of composition, solid azeotrope behavior on vaporization. As the number of distinct PAH species is increased (by adding in benzo[*a*]pyrene, phenanthrene, fluorene and chrysene) this behavior gradually gives way to liquid phase character at even room temperature, and the vaporization behavior approaches that crudely predictable from ideal mixture theory.

Introduction

Mixtures of polycyclic aromatic hydrocarbons (PAHs) are quite common in many materials, such as petroleum products and various types of tars. There is surprisingly little in the way of reliable phase behavior information on PAH mixtures in the literature, considering the commercial and environmental importance of such mixtures. This laboratory has been engaged in studying the phase behavior of binary mixtures of PAHs and related compounds for some time,^{1–3} and we⁴ and other laboratories^{5–12} have studied some aspects of tar mixtures. Furthermore, solid/liquid equilibrium of systems containing tar components (i.e., PAHs) has been examined by melting temperature analysis that reports the formation of eutectic phases, but does not fully characterize the mixture thermodynamics^{13,14}. The picture that has emerged is that the two component mixtures are generally non-ideal in every respect, but that other results have suggested that the multicomponent mixtures might approach ideal behavior.

Thus this study begins to address the question of how the transition takes place from the non-ideal room temperature solid phase mixture to the usual sorts of room temperature, viscous “tar” liquids that have been claimed to exhibit ideal mixture behavior. There are many approaches that could be brought to bear on this question. Some earlier workers have, for example, been concerned with the water solubility of PAH mixtures, motivated by an interest in dissolution of tars in water.^{6–10} Here, the choice is to instead focus on the solid to liquid and solid to vapor transitions of PAHs with no other components present. The experimental methods employed are those that have been discussed in connection with the earlier studies of binary PAH mixtures.^{1–3}

Experimental

Materials

Anthracene (CAS Reg. No. 120-12-7) and benzo[*a*]pyrene (CAS Reg. No. 50-32-8) were obtained from Sigma-Aldrich. Pyrene (CAS Reg. No. 129-00-0), fluorene (CAS Reg. No. 86-73-7) and fluoranthene (CAS Reg. No. 206-44-0) were obtained from TCI America. Phenanthrene (CAS Reg. No. 85-01-8) was obtained from Acros Organics. Reported minimum mass fraction purities between 0.95 and 0.99 were verified by gas chromatography/mass spectrometry (GC-MS) analysis. Samples were used with no further purification.

Mixture Preparation

PAH mixtures were prepared using a melt and quench-cool technique. The desired quantities of each PAH were measured to ± 0.01 mg and roughly 40 mg were sealed within a brass vessel. The vessel was then heated to the melting temperature of the component with the highest melting point 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 to 80 K·s⁻¹ for the first 4 s. The preparation technique was intended to preserve the disorder of the well-mixed liquid during solidification. This heating and quench-cool procedure was repeated four additional times before the solid mixture was removed from the preparation vessel and placed in a glass storage vial. Uniformity of the samples was confirmed by visual examination. This technique was originally developed in order to ensure that “liquid-like” disorder would be promoted in the solids, so they might better model liquid tars. It was subsequently found, though, that the quench cooling technique has relatively little impact on observed results. Similar results can be obtained by simpler melting procedures.

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. A melting temperature analyzer was used to visually observe and obtain higher resolution melting temperature measurements. These generally agreed with the DSC onset temperatures in that the melting temperatures from each instrument differed by no more than a few degrees Kelvin.

Melting behavior was tracked from thaw to liquidus temperatures using the melting temperature analyzer to ± 1 K. In following the thaw-melt method¹⁵ 1 to 2 mg of each sample was placed inside a glass capillary tube and heated at 1 ± 0.5 K·min⁻¹. The thaw temperature is the temperature at which the first droplet of liquid appears in the capillary tube. The liquidus temperature is reached when the last crystal in the tube melts.

Vapor Pressure

The Knudsen effusion technique was used to measure the vapor pressures (*P*) of solid PAH 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 the PAHs. The Knudsen effusion technique measures 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 molecular weight, and W is the Clausing correction factor. The Clausing correction factor W , is very nearly unity, as noted elsewhere.¹ 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.^{16,17}

Samples of the PAH mixtures 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. The equilibrium pressure inside the cell is the vapor pressure of the sample, and the leak rate is measured and related 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 molecular weight must be used for M . In this work, the decision was made to use a weighted average of pure component molecular weights. Because the value of molecular weight appears as the square root, there is not particularly great sensitivity to this value.^{1,2}

With respect to the values of measured vapor pressures for mixtures, it is important to recognize that if the fundamental condition of thermodynamic equilibrium in the sample cell is fulfilled (as must be considered reasonable), then equilibrium must be satisfied for all phases that might be present. What this means is that the vapor pressure of the system cannot exceed the sum of the vapor pressures of the pure components that make up the system, since any component can nucleate its own pure solid phase in the cell, should the vapor pressure of that component in the mixture exceed its pure phase vapor pressure.

Gas Chromatography – Mass Spectrometry

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.¹⁸

Results and Discussion

Ternary Solid Azeotropy of Anthracene, Pyrene, and Fluoranthene

Previous studies from this laboratory have examined the phase behavior of binary PAH mixtures, reporting the formation of eutectic points, solid azeotropy, and non-ideal phase equilibrium.^{1–3} In establishing a better understanding of PAH systems that generally contain multiple components, the next logical step was to study the behavior of a ternary PAH system. The experimental data for an equimolar, three-component system of anthracene(1) + pyrene(2) + fluoranthene(3) are given in Figures 1–3. The results are quite similar to those of the binary anthracene(1) + pyrene(2) system in that the ternary system exhibits the solid

azeotropy, depressed melting temperature, and multiple phases associated with complicated binary phase behavior.¹

Figure 1 shows the continuously measured vapor pressure as a function of mass loss of an initially equimolar 1 + 2 + 3 system held first at 318.15 K and subsequently at 328.15 K. In the case of a thermodynamically ideal mixture that follows Raoult's law, except for the unlikely situation of equal pure component vapor pressures, the mixture will become progressively enriched in the less volatile components and the total mixture vapor pressure (eq 2) will continuously decrease as the mixture loses mass through vaporization or sublimation.

$$P = \sum_i x_i P_i^{\text{sat}} \quad (2)$$

In eq 2, P is the total system vapor pressure, x_i is the condensed-phase mole fraction, and P_i^{sat} is the vapor pressure of pure species i at a given system temperature.

Vapor pressure results for the ternary mixture shown in Figure 1 do not indicate ideal mixture behavior, since the vapor pressure of the mixture is relatively constant for the first 65% of sample mass loss by sublimation. This is analogous to liquid azeotropic behavior, which in this instance involves a subliming solid, as opposed to the more usual liquid azeotropic phase. Following the loss of 65% of initial sample mass, a different behavior is seen, consistent with the existence of a second phase that exhibits more usual mixture behavior of declining vapor pressure with mass loss. Further evidence for the existence of this second phase will be presented below. Continued sublimation of this second mixture phase involves a progressive decrease in vapor pressure, although a brief period of relatively stable vapor pressure is seen when the phase composition approaches that of pure pyrene. It should also be kept in mind that both phases initially present in the mixture are subliming in parallel, but that the higher vapor pressure azeotropic phase initially dominates the observed behavior.

Samples from the vapor pressure experiments of Figure 1 were occasionally removed from the effusion cells, dissolved in dichloromethane, and analyzed by GC-MS. Reported mole fractions are accurate to ± 0.01 . Accounting for the approximately 65% of solid in the azeotropic phase, the GC-MS data allowed calculation of a ternary azeotrope composition of $x_1 = 0.38$, $x_2 = 0.42$, and $x_3 = 0.20$. The result suggests a 2:2:1 packing in this phase.

It was also possible to extract from the data such as that of Figure 1 vapor pressure data for the azeotrope as function of temperature and these are shown in Figure 2. The pure component and maximum possible vapor pressures (representing the summed contributions of the three pure phases) have been plotted along with the measured azeotrope data for comparison.

Based upon the integrated form of the Clausius-Clapeyron equation given below, the enthalpy of sublimation for each compound can be determined. This of course depends on the assumptions that enthalpy of sublimation is independent of temperature in the given range and that the vapor is an ideal gas. These assumptions are quite plausible given the limited temperature range, low system pressure, and moderate temperature.

$$\ln P^{\text{vap}} = \frac{-\Delta_{\text{sub}}H}{RT} + \frac{\Delta_{\text{sub}}S}{R} \quad (3)$$

The sublimation enthalpies (Table 1) obtained from the slopes of the curves in Figure 2 are virtually identical, indicating that the cohesive energy density in the azeotropic mixture is not very different than that of the pure components themselves. On the other hand, the entropy of sublimation (given in Table 1, as calculated from eq 3) shows that the entropy change from the solid phase to the vapor phase is greater for the azeotropic mixture state than for the pure components. This indicates a more ordered state for the azeotrope, bearing in mind that the pure components are crystalline solids.

In addition to literature values^{19,20} (previously obtained and reported in this laboratory), the pure component enthalpies and entropies of sublimation that were measured and used in this recent study are also provided in Table 1. The results from this study are in fair agreement with the literature. However, there is reason to suspect that the previously reported enthalpy of sublimation of phenanthrene was slightly high due to sample impurities; a purer sample was now used.

The vapor pressure of compounds with a relatively high vapor pressure, i.e., phenanthrene and fluorene, must be measured in a low temperature range where sample mass loss from the effusion cell does not exceed allowable experimental design. For these reasons, the vapor pressure of fluorene and the higher purity phenanthrene (97%) were now measured at lower temperatures with a more precise microbalance, and the new values are improvements to the previously reported results.

Roux et al. have summarized the thermodynamics of all of the pure compounds of interest in this study.²¹ In general the values reported in our study agree with the summarized literature. Note that our sublimation enthalpies often fall below those recommended by Roux et al. for 25 °C, but it should be noted that our experimental results were generally measured at higher than ambient temperatures, and that the enthalpies decrease with increasing temperature.

Figure 3 displays the DSC heating, cooling, and reheating scans of the ternary 1 + 2 + 3 mixture and of pure pyrene. Heating and cooling scans were conducted between 298 and 523 K at 10 K·min⁻¹ and 2.5 K·min⁻¹, respectively. Peaks in the scans represent phase transitions and can be integrated to determine the enthalpy of fusion of the sample with a relative uncertainty of $\delta\Delta_{\text{fus}}H/\Delta_{\text{fus}}H = 0.07$. Focusing first on the behavior of a typical pure compound (pyrene), the reproducible peak that occurs during the heating scan represents an endothermic solid to liquid phase transition at 426 K with $\Delta_{\text{fus}}H = 80 \pm 5.6 \text{ J}\cdot\text{g}^{-1}$. The exothermic peak that occurs at 402 K during the cooling scan represents the crystallization of pyrene from a subcooled state, as is typically observed in such experiments. This and other pure compound DSC scans have been noted to be in good agreement with literature values.^{1,2, 22}

The DSC scan in Figure 3 for the ternary 1 + 2 + 3 mixture of Figure 1 shows that the initial mixture is comprised of two distinct, solid phases. The first melts with a sharp, endothermic peak at 379 K with $\Delta_{\text{fus}}H = 47 \pm 3.3 \text{ J}\cdot\text{g}^{-1}$ (this is the enthalpy per mass of total mixture). The poorly defined peak associated with the second mixture phase is observed between 398 and 432 K and it may be approximately integrated to show a solid to liquid enthalpy $\Delta_{\text{fus}}H$ between 20 and 30 J·g⁻¹. This behavior is likely a result of both true melting and dissolution of the second, solid phase into the first, melted phase. Information from the cooling scan confirms that this solid system actually forms two distinct phases.

The exothermic peaks in the cooling scan for the ternary mixture occur at 402 K and 374 K with $\Delta_{\text{fus}}H = 26.4 \text{ J}\cdot\text{g}^{-1}$ and $48.7 \text{ J}\cdot\text{g}^{-1}$, respectively. These crystallization peaks correspond to the fusion peaks noted above and are consistent with the two-phase behavior implied by the vapor pressure data. The enthalpy associated with the azeotrope represents about 66% of total fusion enthalpy, consistent with the conclusion from the vapor pressure data that the azeotropic phase represents 65% of the total mixture mass, though there is no particular reason to a priori believe that the enthalpies of fusion of the two phases should, on a mass basis, be equal. Also it is worth noting that since the enthalpy of fusion of the larger, lower temperature crystallization peak (that due to what is believed to be the phase that gives rise to the azeotrope behavior on sublimation) represents about 65% of the total mixture mass, the actual azeotrope phase crystallization/fusion enthalpy may be estimated to be approximately $75 \text{ J}\cdot\text{g}^{-1}$ for that phase alone, and the same value emerges for the other phase that is present. In other words, the enthalpies of these phases are comparable, and not very much different than the fusion enthalpies of pure components that make up these phases. Moreover, the azeotrope phase must then have a higher entropy of fusion than the second mixture phase.

It is also worth noting here that melting point analysis was used to substantiate the DSC results found above and to verify that the endothermic peaks in the DSC scan do not represent solid crystal transitions of pure phases.²³ Results from the melting point analysis show that the equimolar 1 + 2 + 3 mixture has a thaw point at $377 \pm 1 \text{ K}$ and liquidus point at $433 \pm 1 \text{ K}$. This is consistent with the DSC scans for this mixture. Hence, it is clear that there exist only two true mixture phases in this system.

Quaternary System of Anthracene, Pyrene, Fluoranthene, and Benzo[a]pyrene

Benzo[a]pyrene was then added to the previous components to create an equimolar 4-component mixture of anthracene(1) + pyrene(2) + fluoranthene(3) + benzo[a]pyrene(4). The pure phase vapor pressure of benzo[a]pyrene is considerably lower than that of the other mixture components and it has exhibited complicated phase behavior when mixed with anthracene to form the binary 1 + 4 system.²

Figure 4 shows the full DSC scan of the 4-component mixture. In contrast to the binary and ternary mixtures, addition of benzo[a]pyrene as a fourth component has allowed the mixture to form a single phase. This is evidenced by single, well-defined, broad endothermic and exothermic peaks in the DSC scan. A separate melting point analysis (not shown) illustrates that the mixture melts in the range of 353 to 369 K, further indicating that the single phase, solid mixture has formed.

A notable trend has begun to appear at this point in the study, in which the enthalpies of fusion and melting temperatures, listed in Table 2, appear to be decreasing with the number of components added to the mixture. The 4-component mixture is approaching a liquid, that is, tar behavior in which $\Delta_{\text{fus}}H = 0$ and discrete melting is not observed. In other words, addition of benzo[a]pyrene has limited the energetically favorable interaction of the pure species. It is important to clarify that the 4-component mixture has not yet reached the liquid state and is only approaching liquid behavior. Also note that the enthalpies of fusion are much lower than those associated with sublimation.

In reference to the enthalpies reported in Table 2, it should be noted that the available equipment limits the accuracy of this DSC technique and the comparatively larger reported uncertainties here compared with other literature result from the inherent uncertainty in peak integration. Except for pure benzo[a]pyrene, which has a complicated DSC signature, the enthalpies of fusion of pure components reported in Table 2 are in fair agreement with those recommended in the literature. In the case of benzo[a]pyrene, two peaks are initially

observed in the DSC scan (not shown).^{2,23} The first peak is not associated with melting. Rather, it is attributed to a crystal transition associated with preparation and is only observed when heating a sample for the first time. It has been shown in this laboratory and in others that the benzo[a]pyrene transition peak is not recovered when reheating a previously melted sample.^{2,23} Since the mixtures from this study are melted during preparation, the lower value of 11.3 kJ·mol⁻¹ is appropriate.

Although still very complicated, the solid-vapor equilibrium study for the 4-component system demonstrates a trend towards liquid mixture behavior. Figure 5 shows the continuously measured vapor pressure of the solid mixture for the first 21% of sample mass loss, first at T = 318 K and then at T = 333 K. There is a brief period of vapor pressure stability between 5 and 10 % mass loss. The system composition in this region of constant sublimation pressure was found to be $x_1 = 0.21$, $x_2 = 0.24$, $x_3 = 0.26$, and $x_4 = 0.29$. Although this behavior might initially appear similar to the previously discussed solid azeotropy, the brevity of the segment and sudden decrease in pressure at 10 % mass loss indicate otherwise. It should be understood that the system composition is not yet significantly changed during the first 10% of sample mass loss and consequently, the rate of sublimation appears steady. It needs to be remembered that the DSC indicated existence of a single phase.

In the experiment of Figure 5, the vapor pressure of the system decreases with increasing mass loss beyond 10% mass loss, as the more volatile components decrease in concentration. This behavior resembles more ideal mixture behavior, but does not yet follow ideal, Raoult's law thermodynamics. For instance, at 21% mass loss and 333 K, the experimentally measured vapor pressure is $P = 0.026$ Pa. However, composition here was determined to be $x_1 = 0.14$, $x_2 = 0.26$, $x_3 = 0.26$, and $x_4 = 0.34$ and the calculated Raoult's law vapor pressure for a mixture at this composition is $P = 0.039$ Pa. This means that the system vapor pressure is slightly below that predicted by Raoult's law.

As the vapor pressure decreases, the mass loss rate from the effusion cell can become so low that impractically long times are needed to measure the vapor pressures. This can be addressed in many cases by simply increasing the temperature of the experiment. However, since this 4-component mixture has a low melting temperature of 355 K, this fact limited the ability to study vapor pressures in the sublimation regime that was of main interest here to below this temperature. Figure 6 shows the complex behavior that can be observed when phase changes are permitted to occur in these types of sublimation/vaporization experiments.

Figure 6 shows the continuously measured vapor pressure of the 4-component equimolar mixture as temperature is increased from 318 to 368 K at 0.3 K·min⁻¹. In region A of Figure 6, the mixture vapor pressure increases with temperature, reaches a maximum, and begins to decrease as the less volatile constituents are exhausted. This is consistent with the behavior from Figure 5. When, in region B of Figure 6, the temperature of the mixture reaches 355 K, the mixture melts. This causes an increase in vapor pressure as the process changes from solid sublimation to liquid vaporization. The liquid then undergoes the expected decline in vapor pressure consistent with composition change associated with loss of more volatile components.

Upon reaching region C of Figure 6, the mixture becomes concentrated in benzo[a]pyrene, and it appears that a solid phase crystallizes. As the remaining liquid is vaporized from the system, the vapor pressure of a solid, benzo[a]pyrene rich mixture begins to dominate and is shown in region D. The concentration of this stable phase is $x_1 = 0$, $x_2 = 0.07$, $x_3 = 0.07$, and $x_4 = 0.86$. DSC results (not shown) indicate that this new phase begins to melt at $T_{\text{fus}} = 388$

K and this corroborates the conclusion that the mixture must have crystallized in region C of Figure 6. This observation of relatively stable vapor pressure in region D does not necessarily represent true azeotropy. Rather, it is suggested that solid phase structure is defined by the majority benzo[a]pyrene component, and this defines the system's behavior. In other words benzo[a]pyrene can accommodate moderate pyrene and fluoranthene impurities within its crystal structure without significant concentration or enthalpy variation.

It is believed that the trends described here are general, in that the ternary mixture has been observed to behave much like the binary systems earlier studied¹⁻³; azeotrope behavior is observed, and multiple phases exist. With the ternary system and 4-component systems examined here, there is a continuation of the decrease in melting temperature and enthalpy of fusion from the binary mixtures and pure components.

Five and Six Component PAH Mixtures

The five-component system includes all components 1 + 2 + 3 + 4 in addition to phenanthrene(5). The pair of six component mixtures consists of 1 + 2 + 3 + 4 + 5 and either fluorene(6), or chrysene(7). All mixtures are again initially equimolar.

Figure 7 shows DSC scans for the five and six component mixtures between 310 and 420 K. As the number of components in the mixture increases, the peaks begin to lose definition and the baseline appears to lack stability, in part because the scale has been expanded to show the relatively smaller heat effects. The fusion enthalpies continue to approach the liquid limit of $\Delta_{\text{fus}}H = 0$ with addition of each new component (Table 2).

All of these five and six component mixtures have become black in color and inhomogeneous, meaning that solid inclusions are observed amongst a tacky and glass-like semisolid – in short, the mixture is already visually indistinguishable from a tar in appearance. Hence, melting point analysis can no longer be used to discern either a thaw or a liquidus point because visual differentiation between true melting, dissolution, or change in viscosity is not possible. This is in stark contrast to the mixtures with fewer components, and to the pure PAHs, which are generally white or yellow, homogenous, solid, crystalline powders.

Solid/liquid/vapor equilibrium (i.e., vapor pressure) results for five and six component mixtures are provided in Figure 8. In the case of the six component mixture, it was that containing components 1 through 6. These data are plotted in Clausius-Clapeyron form, but the experiments were carried out using a different procedure than in the case of the experiments reported above. In this instance, system temperature was held constant only long enough to allow equilibration and measurement of 30 minutes of mass loss data, before raising the temperature to the next higher value. Thus each data point represents the result of an isothermal measurement.

Beginning with the 6-component mixture at low temperatures (i.e., high $1000/T$), the results closely follow the predicted Raoult's law behavior for the initial composition. In other words, the system has approached ideal solution behavior. Because of how these experiments were performed, the mixture gradually lost the more volatile components in preference to the less volatile, and the vapor pressures dropped as temperatures were increased ($1000/T$ decreases). A new limit was achieved at high temperatures, which was suggestive of a constant vapor pressure system. The GC-MS analysis of the mixture recovered after these experiments indicated that the mixture still contained fluorene, the most volatile compound, at $x_6 = 0.07$, so it was still a 6-component mixture. The solid line in Figure 8 shows what Raoult's law would predict for a 5-component mixture of the measured composition, if the presence of fluorene were disregarded. There is not necessarily any

physical significance to the relatively good fit, but the Raoult's law prediction for the actual measured mixture composition (including fluorene) is considerably higher, as shown in Figure 8. It is not known whether the 6-component system approached some azeotrope behavior (given the constancy of vapor pressure as temperature was raised to high values) or if there was some other complex phase behavior involved in giving the observed results. What is important to note is that the earlier reported and assumed ideal mixture behavior of multicomponent PAH systems was observed with this 6-component mixture until it approached a 5-component system in composition.

The experiments of the initially equimolar 5-component mixture give a vapor pressure that is near that predicted from Raoult's law for that composition, but also close to the final limit for the initially 6-component mixture (if the presence of fluorene in that latter mixture is ignored). It is presently unclear why this is the case. The final compositions of the 6-component mixture is $x_1 = 0.08$, $x_2 = 0.23$, $x_3 = 0.23$, $x_4 = 0.24$, $x_5 = 0.15$, $x_6 = 0.07$ and for the 5-component mixture $x_1 = 0.17$, $x_2 = 0.22$, $x_3 = 0.18$, $x_4 = 0.23$, $x_5 = 0.20$. This means that the 6-component mixture transitioned to something relatively close to the 5-component mixture. The question of whether these mixtures transition towards some new azeotrope has not been explored in detail. It should be noted that the Raoult's Law predicted vapor pressure for the initially equimolar 5-component mixture (dot-dash line in Figure 8) is indistinguishable from that for the final GC-MS measured composition (not shown). Essentially, if plotted together, the lines would overlap.

Enthalpies and entropies of sublimation for these mixtures and for actual coal tar fractions⁴ are given in Table 1. The results presented here are consistent with those previously reported for real coal tars⁴, though the enthalpies are a bit lower for the present mixtures than for the coal tars. The coal tars have significant heteroatomic (oxygen and nitrogen) contents, particularly in the case of Wyodak and Pittsburgh coal tars and it is known that heteroatomic substituted PAHs can have higher enthalpies of sublimation compared with their parent PAHs.²⁴ In addition, it should be noted that the present mixtures are also of somewhat lower molecular weight than the reported averages for the lowest molecular weight fractions of the coal tars, and this would also lead to the enthalpies of vaporization being higher for the latter materials. Hence, the Upper Freeport tar fraction is closest to the presently studied materials and it is not surprising that it approaches most closely the presently obtained values.

Conclusions

These results show that the thermodynamic behavior of multicomponent low molecular weight PAH mixtures is determined by the number of components in the mixture. Tar-like visual appearance begins to manifest itself when the number of components exceeds 5. The approach to tar-like behavior in such systems is supported by the gradual transition from distinct solid melting behavior to a much more ill defined "melting" behavior in 5 and 6-component mixtures. The near-ambient vapor pressure and phase behavior of 3-component systems show a continuation of non-ideal solid mixture behavior that also characterizes binary PAH mixtures. As the number of mixture components increases, the non-ideal solid mixture behavior of 2 and 3-component systems gives way to the commonly assumed ideal mixture behavior, and is clearly seen in a 6-component mixture examined here. The present results also warn of complicated phase behavior that can be encountered as components are lost to evaporation. In some instances, the phase behavior has been observed to approach that of a system with fewer components, in which small amounts of a lower molecular weight component appear to no longer significantly influence the vapor pressure behavior of the mixture. The vapor pressure behavior of the tar-model system examined here is consistent with that observed for real coal tar systems.

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Figure 1.
Vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene mixture.

Figure 2.

Vapor pressure of the solid azeotrope ($P_{\text{AZEOTROPE}}$) at $x_1 = 0.38$, $x_2 = 0.42$, and $x_3 = 0.20$. The vapor pressures of each pure component are given for reference. The maximum possible vapor pressure (P_{MAXIMUM}) is the sum of the pure component vapor pressures.

Figure 3.
Differential scanning calorimetry results of pyrene and an equimolar ternary PAH mixture.

Figure 4. Differential scanning calorimetry results of an equimolar, 4-component PAH mixture.

Figure 5.
Vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene + benzo[a]pyrene mixture versus sample mass loss. Raoult's law is calculated for measured concentrations noted in the text.

Figure 6. Vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene + benzo[a]pyrene mixture versus time during a continuous temperature ramp and subsequent period of temperature stability.

Figure 7. Differential scanning calorimetry results of one, 5-component and two, 6-component, PAH mixtures.

Figure 8.

Vapor pressure of initially equimolar 5 & 6-component PAH mixtures, with Raoult's Law (P_{RL}) estimates for both equimolar and GC-MS measured mole fractions. The transitional region of $P_{6\text{-COMPONENT}}$ maps the loss of more volatile components and is experimentally path dependent. It does not represent the equilibrium vapor pressure of an equimolar mixture.

Table 1

Enthalpies and entropies of sublimation of pure PAHs, mixtures, and real coal tars.

Description	MW	$\Delta_{\text{sub}}H$ This Laboratory	$\Delta_{\text{sub}}S$ This Laboratory	$\Delta_{\text{sub}}H$ Published
Pure Components	(g·mol ⁻¹)	(kJ·mol ⁻¹)	(J·mol ⁻¹ K ⁻¹)	(kJ·mol ⁻¹)
Anthracene(1)	178.23	97.1 ± 1.1 (300–373 K)	267.8 ± 0.2	98.5 ± 3.3 ¹⁹ (288–323 K)
Pyrene(2)	202.25	97.1 ± 1.2 (333–375 K)	262.5 ± 0.2	97.8 ± 3.3 ¹⁹ (322–381 K)
Fluoranthene(3)	202.25	94.2 ± 0.9 (308–338 K)	262.0 ± 0.1	96.9 ± 2.8 ¹⁹ (327–359 K)
Benzo(a)pyrene(4)	252.31	116.2 ± 7.5 (398–430 K)	272.7 ± 0.4	113.3 ± 3.1 ¹⁹ (392–424 K)
Phenanthrene(5)	178.23	88.5 ± 1.0 (296–308 K)	264.6 ± 0.1	95.0 ± 4.4 ²⁰ (303–333 K)
Fluorene(6)	166.22	82.6 ± 2.5 (296–317 K)	256.2 ± 0.2	87.1 ± 3.8 ¹⁹ (298–324 K)
PAH Mixtures – This Study				
3 comp. Mixture (1–3 azeotrope)	194.2	97.8 ± 6.0 (308–328 K)	277.3 ± 0.4	N/A
5 comp. Mixture (1–5 equimolar)	202.6	89.6 ± 3.1 (308–323 K)	254.7 ± 0.3	N/A
6 comp. Mixture(1–6 equimolar)	196.6	84.2 ± 3.0 (278–288 K)	248.8 ± 0.3	N/A
Real Coal Tars⁴				
Pittsburgh No. 8 Coal Tar ⁴	230	143.7 (360–400 K)	368.4	N/A
Upper Freeport Coal Tar ⁴	215	106.5 (360–400 K)	274.4	N/A
Wyodak Coal Tar ⁴	240	143.7 (360–400 K)	360.3	N/A

Table 2
Melting temperatures and fusion enthalpies of pure PAHs and multicomponent PAH mixtures.

Description	T_{onset} DSC (K)	T_{melt} Visual (K)	T_{melt} Technique	$\Delta_{\text{fus}}H$ This Laboratory (kJ·mol ⁻¹)	$\Delta_{\text{fus}}H$ Recommended ²¹ (kJ·mol ⁻¹)
Pure Components					
Anthracene(1)	487.0	489	DSC/Visual	27.8 ± 1.9	29.4 ± 0.1
Pyrene(2)	422.0	423	DSC/Visual	16.2 ± 1.1	17.36 ± 0.04
Fluoranthene(3)	382.5	384	DSC/Visual	18.2 ± 1.3	18.73 ± 0.02
Benzo(a)pyrene(4)	442.2	449	DSC/Visual	11.3 ± 0.8	17.3 ± 0.6
Phenanthrene(5)	371.1	372	DSC/Visual	16.3 ± 1.1	16.46 ± 0.04
Fluorene(6)	386.7	388	DSC/Visual	19.4 ± 1.4	19.58 ± 0.06
Chrysene(7)	525.3	526	DSC/Visual	23.3 ± 1.6	26.2 ± 0.2
Binary Mixtures ¹⁻²	T_{thaw}	T_{liquidus}			
1 + 2 at $x_1 = 0.10$	404	419	Visual	16.6 ± 1.2	N/A
1 + 2 at $x_1 = 0.50$	404	453	Visual	18.6 ± 1.3	N/A
1 + 2 at $x_1 = 0.90$	404	485	Visual	19.2 ± 1.3	N/A
1 + 4 at $x_1 = 0.10$	414	438	Visual	8.1 ± 0.6	N/A
1 + 4 at $x_1 = 0.50$	414	440	Visual	14.6 ± 1.0	N/A
1 + 4 at $x_1 = 0.90$	414	486	Visual	19.0 ± 1.3	N/A
Ternary Mixture					
1 + 2 + 3 (equimolar)	377	433	Visual	14.6 ± 1.0	N/A
Quaternary Mixture					
1-4 (equimolar)	353	369	Visual	6.9 ± 0.5	N/A
Five Component Mixture					
1-5 (equimolar)	342	358	DSC	6.3 ± 0.4	N/A
Six Component Mixtures					
1-6 (equimolar)	321	348	DSC	4.5 ± 0.3	N/A
1-5 + 7 (equimolar)	333	353	DSC	5.8 ± 0.4	N/A