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Deviations from Ideal Sublimation Vapor Pressure Behavior in Mixtures of Polycyclic Aromatic Compounds with Interacting Heteroatoms

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Abstract

Despite the relatively small atomic fraction of a given heteroatom in a binary mixture of polycyclic aromatic compounds (PAC), the inclusion of heteroatomic substituted compounds can significantly impact mixture vapor pressure behavior over a wide range of temperatures. The vapor pressures of several binary PAC mixtures containing various heteroatoms show varying behavior, from practically ideal behavior following Raoult's law to significant deviations from ideality depending on the heteroatom(s) present in the mixture. Mixtures were synthesized using the quench-cool technique with equimolar amounts of two PAC, both containing heteroatoms such as aldehyde, carboxyl, nitrogen, and sulfur substituent groups. For some mixtures, deviation from ideality is inversely related to temperature, though in other cases we see deviations from ideality increasing with temperature, whereas some appear independent of temperature. Most commonly we see lower vapor pressures than predicted by Raoult's law, which indicates that the interacting heteroatoms prefer the solid mixture phase as opposed to the vapor phase. Although negative deviations predominate from Raoult's Law, the varying mixtures investigated show both higher and lower enthalpies and entropies of sublimation than predicted. In each mixture, a higher enthalpy of sublimation leads to higher entropy of sublimation than predicted, and vice versa.

Introduction

Mixtures of high molecular-weight organic compounds exist throughout the environment. Coal tar-laden soils contain a plethora of polycyclic aromatic compounds (PAC), pollutants resulting from the incomplete combustion of coal, fossil fuels, and other anthropogenic sources. Motor vehicle exhaust comprises a variety of PAC, including oxygenated and halogenated compounds in various compositions [1-3]. Coal tars and other environmental pollutants are complex mixtures of not just pure polycyclic aromatic hydrocarbons, but of compounds containing heteroatoms, including those capable of strong molecular interactions. Although we know these compounds to exist, primarily, as mixtures in the environment, it is confounding how little we know about their thermodynamic behavior as mixtures. They often appear within non-aqueous phase liquids (NAPLs) and in the solid phase; here we investigate the sublimation vapor pressures of mixtures to examine the effect of heteroatom addition to mixtures of PAC, complementing previous work on mixtures of unsubstituted polycyclic aromatic hydrocarbons.

Like Oja and Suuberg [4] and Peters, et al. [5], our laboratory found that mixtures of unsubstituted polycyclic aromatic hydrocarbons (PAH) tend towards ideal behavior according to Raoult's law, especially at temperatures slightly above ambient [6]. However, Oja and Suuberg encountered very different behavior when mixture components experienced interactions with each other. The addition of a heteroatom alone does not imply deviations from ideality, but rather the strength of the intermolecular interactions between

various heteroatomic compounds plays a pivotal role in a mixture's vapor pressure and its deviations from ideality. In their work, the vapor pressure of a mixture of 1-hydroxypyrene and phenanthridine was considerably over-predicted by Raoult's law. The observed decrease in vapor pressure is likely due to the strong electron donor group of the phenanthridine and likewise electron acceptor of the 1-hydroxypyrene. [4]

In a related study on high molecular weight organics, Shim, Oja and Hajaligol examined the vapor pressures of tobacco pyrolysis tar. They found that hexane phase partitioned tar (HPT), as compared to the whole bright tobacco tar (BTT), showed a lower enthalpy of vaporization and a higher vapor pressure. The higher heat of vaporization and boiling point of HPT is attributed to contributions of more polar compounds in BTT yielding stronger intermolecular forces, such as hydrogen bonding. Although molecular weight plays an important role, it is not the only factor determining volatility; the chemical nature of the mixture, such as heteroatoms present, must be considered. [7]

Several groups have found that the experimental partitioning of NAPLs in water is consistent with Raoult's law for PAC constituents of coal tar, diesel fuel and synthetic mixtures of PAC-NAPLs. Deviations from ideality – both positive and negative – result from combinatorial activity coefficients [8-10]. Negative deviations of activity coefficients are predicted for benzene and naphthalene due to their perceived excess solvation tendencies. On the other hand, slightly positive deviations, such as those for ethyl and alkylated PAC are indicative of self-association propensities. On the whole, however, Peters, Mukherji and Weber [11] conclude that the majority of constituents in PAC-containing NAPLs have activity coefficients between 0.9 and 1.1, implying that Raoult's law provides a rough estimate of the partitioning behavior of PAC in complex mixtures.

Mixtures of PAC have a tendency to degrade at the high temperatures required to measure their vapor pressure directly. As such, we employ the Knudsen effusion technique, an indirect method to measure vapor pressure relating the mass loss through a pinhole leak to the vapor pressure of a given compound or mixture. This enables measurements in the ambient to slightly elevated temperature range, negating the decomposition issue and yielding measurements at temperatures of environmental interest. Data are analyzed using the Clausius-Clapeyron equation, a well-known equation relating the saturation vapor pressure, P^o , absolute temperature, T , enthalpy, $\Delta_{sub}H$, of vaporization (or sublimation) and the universal gas constant, R , of a compound or mixture such that

$$\frac{d[\ln P^o]}{d[1/T]} = \frac{-\Delta_{sub}H}{R} \quad (1)$$

Although we usually encounter this relationship for pure compounds, its application to sublimation mixture thermodynamics is logical given that sublimation enthalpies are not strongly temperature-dependent over a reasonably small temperature range, such that plots of $\ln P^o$ vs. $1/T$ are normally straight lines. The same trend is expected of and indeed encountered with mixtures [4,12].

Following determination of the vapor pressure of a mixture we use Raoult's law, a commonly employed estimation technique, to determine the degree to which a given mixture follows (or deviates from) ideal behavior. The vapor pressure of the mixture, P^{vap} , is equal to the sum of x_i , the components' mole fractions, times P_i^o , their respective pure component vapor pressures through Raoult's law as shown in equation 2.

$$P^{vap} = \sum_i x_i P_i^{\circ} \quad (2)$$

Materials & Methods

Mixture vapor pressures were determined using the Knudsen effusion technique, where we measure the effusive escape rate of the molecules of the evaporating mixture through a small opening in an effusion cell at low to moderate temperatures. The rate of effusion, m , is measured as the mass loss of sample through the effusion cell per unit time and related to the vapor pressure of the effusing substance or mixture via the Knudsen equation (equation 3):

$$P^{vap} = \frac{m}{W_0 A_0} \sqrt{\frac{2\pi RT}{M}} \quad (3)$$

where A_0 is the orifice area, M the molecular weight of the effusing mixture, T the absolute temperature, R the universal gas constant, and W_0 the Clausing correction factor, accounting for the idealized assumptions within Knudsen's original equation. This factor was calculated using a relation between the orifice effusion length, l , and orifice radius (Goldfarb and Suuberg *J Chem. Eng. Data* 2008) and via calibration of the system. Both methods yielded Clausing factors between 0.96 and 0.98 for all effusion cells. The theory behind this method is described in detail elsewhere [13-15].

Experimental Apparatus

The effusion apparatus is described in several previous publications [16, 17] and is discussed here only briefly. In short, the Knudsen effusion sample cell with a pre-drilled, pre-measured orifice size is suspended on one arm of a Cahn 2000 microbalance (sensitivity of 0.5 μg) inside a blackened copper capsule approximately 2.5 cm in diameter and 15 cm in length. Each cell is heated in a propane flame before filling to blacken the exterior to improve heat transfer and to remove surface impurities and fingerprints. The capsule ensures a uniform temperature environment around the sample cell, and is painted black to promote heat transfer via radiation. Inside this capsule is an Omega Type K thermocouple (calibrated against a mercury precision thermometer to ± 0.1 K) positioned directly above the cell orifice. The copper capsule and balance wire are enclosed in pyrex glass. The cell is indirectly heated via radiation from an aluminum block oven surrounding the glass vacuum enclosure. The block is heated using a Watlow cartridge heater, controlled via an Omega CN8202 temperature controller. A BOC Edwards turbomolecular pump holds the backpressure in the glass enclosure at to 10^{-5} Pa; the high vacuum is maintained by a downstream condenser that removes species that effuse out from the cell, preventing them from contaminating the pump.

Mixture Fabrication

Because physically agitating two or more solid phase components will not result in a continuous phase, known mixtures of PAC were fabricated using a quench-cool technique. Mixtures of high molecular weight organics are commonly synthesized by two methods – melt-growth and solution-growth techniques. Solution-growth techniques are not easily applied to mixtures of PAC and other semi-volatile organics; there is not a good option for a solvent to dissolve the materials, and the evaporation of the solvent often degrades the PAC present or evaporates the PAC with the solvent [12]. Conversely, with the quench-cool technique, known quantities of each component are placed into a stainless steel vessel. The PAC used in this investigation were obtained from TCI America at minimum purities of

95%, detailed in Table 1. Compounds with minimum purities below 97% underwent fractional sublimation using the Knudsen effusion technique until at least 5%, by mass, of each compound was lost to account for volatile impurities.

After filling the mixing vessels with desired amounts of compounds, the vessels were placed into an oven and heated slightly above the melting point of the most volatile component for fifteen minutes, entering the liquid state. The transition to liquid state assures the compounds are well mixed. This is followed by quench-cooling in liquid nitrogen to retain the molecular-level mixing of the components, as the time for phase separation to occur is minimized [4]. After opening the mixing vessels, no visible separation of the compounds was noted. To ensure homogeneity of the mixtures, the melting points of each were measured using a Differential Scanning Calorimeter (DuPont DSC 2910) in a hermetically sealed aluminum pan calibrated with pure indium (Instrument Specialists, Inc.) at a heating rate of 10°C/min. We were able to successfully reproduce the melting points of each mixture three times to within ± 1.8 K, indicating the mixtures are homogeneous. These measurements also ensured that the vapor pressures measured were sublimation vapor pressures by keeping the temperature of each mixture below its melting point.

Approximately 10 to 20 mg of each mixture was loaded into at least three different effusion cells, each following their own temperature profile effusion experiment. For example, one experiment involved only an increase in cell temperature from one data point to another while another started with the sample at a high temperature then was cooled and re-heated as data were taken. Each data point was reproducible independent of the temperature path followed. In order to preserve the known composition of the mixture in the effusion cell, a maximum of 10% (by mass) is sublimed out of each effusion cell.

Results & Discussion

The measured vapor pressure data from each mixture as compared to Raoult's law predictions at each temperature are given in Table 2. The data show an array of deviations from the ideal behavior predicted by Raoult's Law as discussed in the following sections.

Equimolar Anthraquinone and 2-Anthracenecarboxylic Acid

For an equimolar mixture of anthraquinone and 2-anthracenecarboxylic acid, Figure 1 shows modest negative deviations from the vapor pressure predicted by Raoult's law. Measured mixture vapor pressures are slightly lower than the predicted values, as enumerated in Table 2. At 389.5 K, the Raoult's law predicted vapor pressure is 0.251 Pa, whereas the actual vapor pressure is 0.092 Pa. By contrast, at 330.3 K, Raoult's law only over-predicts the vapor pressure by 25%. Although we have seemingly large deviations from ideality in terms of measured vapor pressure, the enthalpy of sublimation calculated from the vapor pressure data for the mixture is 105.5 ± 4.0 kJ·mol⁻¹, compared to the 115.1 kJ·mol⁻¹ predicted by Raoult's law. This is because the slope of the Clausius-Clapeyron plot of the experimental data is very close to that predicted by Raoult's law, whereas the entropy for the experimental data is 0.254 ± 0.01 kJ·mol⁻¹K⁻¹ compared to that predicted by Raoult's law at 0.284 kJ·mol⁻¹K⁻¹.

Equimolar Anthraquinone and 9-Anthracenecarboxylic Acid

The vapor pressures calculated from Raoult's law also slightly over-predict the measured values for the equimolar mixture of anthraquinone and 9-anthracenecarboxylic acid. At 310 K the predicted vapor pressure is over a full order of magnitude larger than the measured vapor pressure. This difference decreases to 1.7 times larger at 344 K. Table 3 details the enthalpy and entropy of sublimation for the two anthraquinone and anthracenecarboxylic

acid mixtures. The measured enthalpy of sublimation of the 9-anthracenecarboxylic acid mixture, at $117.9 \pm 5.9 \text{ kJ} \cdot \text{mol}^{-1}$ is quite close to that predicted by Raoult's law, at $115.3 \text{ kJ} \cdot \text{mol}^{-1}$. Both this mixture and the previous mixture containing anthraquinone and an anthracenecarboxylic acid show higher deviations from ideality as temperature increases, the opposite trend noted previously for mixtures of pure PAH [6]. This indicates a higher energy barrier to sublime than predicted at these high temperatures – predictions indicate the more volatile component, the anthraquinone, should dictate the thermodynamic behavior of the mixture, yet the less volatile component, the anthracenecarboxylic acids, appear to have a stronger influence - leading to the lower observed vapor pressures at higher temperatures. Because each mixture was run with several effusion cells at different temperature profiles, we know this is not merely an experimental artifact of depleting the more volatile component. For example, the data point at 339.7 K in Figure 2 was taken as the first data point in a series of decreasing temperature points, where as the point at 344.1 K was the last in a series of increasing temperature points.

Equimolar Anthraquinone and 2-Fluorenicarboxaldehyde

Another binary mixture including anthraquinone again displayed negative deviations from ideality. The vapor pressures of equimolar anthraquinone and 2-fluorenicarboxaldehyde, shown in Figure 3, are lower than Raoult's Law with a fairly constant offset for the measurable temperature range. The calculated sublimation enthalpy and entropy are slightly higher than those predicted by Raoult's law, as shown in Table 3.

Because of the uniqueness of this behavior, in order to ensure that we were not experiencing any experimental artifacts, four different effusion cells were used for measurements. The first cell was progressively increased in temperature, the second was progressively decreased in temperature, the third was started at a low temperature, and cycled from high to low, and the fourth was started at higher temperatures and then cycled between lower and higher temperatures. As seen with the first two mixtures, regardless of the experimental temperature path followed the same results emerged.

Equimolar 2-Fluorenicarboxaldehyde and Phenanthridine

An equimolar mixture of 2-fluorenicarboxaldehyde and phenanthridine exhibited strong nonideality. In this case, the vapor pressures measured at both 307.8 and 309.3 K were well below Raoult's law predictions. At 311.2 K the vapor pressure is equal to that predicted by Raoult's law, and then from 312.9 to 335.1 K the measured vapor pressures trend higher than that predicted by ideality as temperature increases. Above 320 K the vapor pressures are very close to that of pure phenanthridine, as shown in Figure 4. The measured enthalpy and entropy of sublimation for this mixture are both higher than predicted by Raoult's law. Regardless of temperature path taken, it appears that the more volatile component, the phenanthridine, is driven out of the mixture phase. To ensure this was not an artifact of failing to enter the liquid phase, we remade this mixture twice and still recovered the same results. Both times we fabricated this mixture we fractionally sublimed at least 5 wt% of each compound before measuring into the mixing vessel in equimolar quantities, such that any volatile components that could potentially push the mixture vapor pressure higher were removed.

Equimolar 2-Fluorenicarboxaldehyde and 9-Fluorenone

Figure 5 shows an equimolar mixture of 2-fluorenicarboxaldehyde and 9-fluorenone; here we found only slightly negative deviations from ideality. The slope of the Clausius-Clapeyron line for the experimental data was 11.68, compared to 11.15 for the Raoult's law prediction. There were no strong specific energetic interactions between the mixture components, and any small interactions were in the direction of reducing vapor pressures.

The calculated value of $\Delta_{\text{sub}}S/R$ for the actual mixture was 34.0 and for the ideal mixture it is 32.7. The higher entropy change for the actual mixture shows it has a more ordered structure precipitated by the need to accommodate the functional groups on the PAC, leading to the lower vapor pressures than predicted.

Equimolar Phenanthridine and 9-Fluorenone

Again, we see an inverse trend than that encountered for unsubstituted PAH mixtures with an equimolar mixture of phenanthridine and 9-fluorenone (Figure 6). At lower temperatures, the vapor pressure of the mixture is very close to Raoult's law. However, from 310 to 340 K the vapor pressure continues to decrease from Raoult's law. At 340 K the predicted vapor pressure is 1.1 Pa and the measured vapor pressure is only 0.87 Pa. However, although it appears that the deviations from ideality increase with temperature, we note that at the highest measurable temperature range (such that the mass loss was consistent with the Knudsen effusion theory) the deviations were still quite small.

As seen in Table 3, the enthalpy and entropy of mixture sublimation in this case are actually less than would be predicted from an ideal, non-interacting 9-fluorenone and phenanthridine mixture. This shows that the decrease in vapor pressure is not attributable to any energetically favorable interactions of the electron donating groups on the mixture partners. Instead, the vapor pressure is decreased due to a less favorable entropy of sublimation than would be predicted based upon simply summing the contributions of the two components. We surmise that the mixture must have assumed a more disordered structure, as a result of the presence of the heteroatoms, encouraging it to remain in the solid phase.

Equimolar Phenanthridine and Phenoxathiin

Finally, strong non-ideality was noted for an equimolar mixture of phenanthridine and phenoxathiin, as seen in Figure 7. In this case, the measured vapor pressures of the mixture were all much lower than that predicted by Raoult's law. However, as temperature increases the vapor pressure of the mixture very slowly approaches the Raoult's law prediction. The Clausius-Clapeyron equation for the actual mixture data in the temperature range of 310 to 337 K yielded an enthalpy of sublimation of $84.8 \pm 6.9 \text{ kJ}\cdot\text{mol}^{-1}$ compared to that predicted by Raoult's law at $65.7 \text{ kJ}\cdot\text{mol}^{-1}$. This suggests that the compounds interact in an energetically favorable way in the condensed phase. The entropy of sublimation from measurements is also seen to be much higher than that for the ideal mixture. The entropy of sublimation was measured at $0.256 \pm 0.021 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and predicted at $0.203 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The greater entropic disorder of the mixture compared with the ideal summation value helps to keep the vapor pressure nearer to the ideal mixture line than would be the case given the strength of the specific interactions.

Oja and Suuberg [4] noted similar trends with other mixtures. The vapor pressure of a nearly equimolar mixture of 1-hydroxypyrene and phenanthridine was far less than that predicted by Raoult's law. Such deviations were attributed to the strong interactions between the basic nitrogen of the phenanthridine ring and the acidic phenolic hydroxyl of the 1-hydroxypyrene. This interaction of a strong electron donor (N) with a good electron acceptor (OH) is expected to result in the observed decrease in vapor pressure.

Through these mixture experiments, we see various deviations from ideality depending on the mixture in question. The somewhat variable deviations from ideality are a result of simultaneous enthalpic and entropic effects. This implies a limiting value of mixture activity coefficients, which Aoulmi *et al.* [18] note is especially true of mixtures with strong hydrogen bonding. Hydrogen bonding generally entails a stronger decrease in the entropy of the interacting molecules than those with van der Waals interactions, which are relatively

unaffected by the orientation of the interacting molecules. Therefore, a mixture dominated by such interactions has a vastly different relationship between entropy and enthalpy than mixtures of molecularly similar species characterized by relatively weak bonding [19]. As we saw through the various mixtures presented herein, there is often a decrease in entropy and corresponding increase in enthalpy (a “more negative” slope of the Clausius-Clapeyron curve) as mixtures tend further from ideal behavior, especially at lower temperatures, which illustrates this balancing act between the two thermodynamic driving forces.

There is no obvious correlation between the deviations observed and specific compounds in the mixture. The mixtures of (phenanthridine/9-fluorenone), and (phenanthridine/2-fluorene-carboxaldehyde) are all pairs with potential intermolecular interactions. There is a nitrogen in phenanthridine, which gives these mixtures a lone pair of electrons [20]. The 9-fluorenone and 2-fluorene-carboxaldehyde each contain a single double-bonded oxygen, whereas anthraquinone has two. Yet despite their similarities in terms of molecular structure, the deviations in terms of vapor pressure are widely varying for each mixture. The phenanthridine/9-fluorenone mixture sees a direct relationship between temperature and relative deviations – as temperature increases, so do the deviations from Raoult’s law. Yet, the phenanthridine/2-fluorene-carboxaldehyde mixture has negative deviations from Raoult’s law at low temperatures and positive deviations at higher temperatures, though this mixture seems to be an anomaly of the nonideal mixtures investigated as it is the only one to cross the Raoult’s line on the Clausius-Clapeyron plot.

Conclusions

One trend noted throughout almost all of the nonideal PAC mixtures was that the measured vapor pressures are often lower than those predicted by Raoult’s law in the measurable temperature range. Overall, these negative deviations from Raoult’s law are attributed to strong attractive forces between the electron donor-acceptor pairs as mentioned above, as well as to hydrogen bonding between molecules containing heteroatoms. Such strong forces are absent from those mixtures of unsubstituted PAH, in which deviations from ideality tend to be positive and err on the side of the more volatile component at lower temperatures. Although we see deviations from ideality, for most cases the measured enthalpy and entropy of sublimation are within 15% of the values predicted by Raoult’s Law. Given the paucity of models that incorporate mixtures of these compounds, Raoult’s Law appears to be an applicable tool for modeling their behavior, keeping in mind that it most often tends to slightly over-estimate vapor pressures.

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Figure 1. Vapor pressure of pure anthraquinone (long dash [21]) and 2-anthracenecarboxylic acid (dotted; [17]) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Figure 2. Vapor pressure of pure anthraquinone (long dash [21]) and 9-anthracenecarboxylic acid (dotted; [17]) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Figure 3. Vapor pressure of pure anthraquinone (long dash [21]) and 2-fluorencarboxaldehyde (dotted [17]) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Figure 4. Vapor pressure of pure phenanthridine (long dash; [14]) and 2-fluorencarboxaldehyde (dotted [17]) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Figure 5. Vapor pressure of pure 9-fluorenone (long dash [21]) and 2-fluorencarboxaldehyde (dotted; this laboratory) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Figure 6. Vapor pressure of pure 9-fluorenone (long dash [21]) and phenanthridine (dotted; [14]) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Figure 7. Vapor pressure of pure phenoxathiin (long dash [21]) and phenanthridine (dotted; [14]) and experimental equimolar mixture (●) compared to Raoult's law prediction (solid line)

Table 1

Pure compounds used to fabricate equimolar nonideal PAC mixtures (enthalpy and entropy of sublimation as measured by this laboratory via Knudsen Effusion)

Components	Min. Purity/%	CAS Reg. Num.	Molecular Weight/ g·mol ⁻¹	Average Melting Point/K	Enthalpy of Sublimation / kJ·mol ⁻¹	Entropy of Sublimation/ kJ·mol ⁻¹ ·K ⁻¹	Molecular Structure
2-Anthracenecarboxylic Acid C ₁₅ H ₁₀ O ₂	>98	613-08-1	222.2	509	134.9	0.301	
9-Anthracenecarboxylic Acid C ₁₅ H ₁₀ O ₂	>97	723-62-6	222.2	492	120.1	0.278	
2-Fluorencarboxaldehyde C ₁₄ H ₁₀ O	>95	30084-90-3	194.2	357	100.0	0.277	
9-Fluorenone C ₁₃ H ₈ O	>98	486-25-9	180.20	356	88.5	0.258	
Anthraquinone C ₁₄ H ₈ O ₂	>98	84-65-1	208.21	557	111.3	0.287	
Phenanthridine [14] C ₁₃ H ₉ N	>97	229-87-8	179.22	380	100.1	0.290	
Phenoxathiin C ₁₂ H ₈ OS	>98	262-20-4	200.26	330	96.3	0.296	

Table 2

Vapor pressure data for PAC mixtures compared to Raoult's law prediction at each temperature

Temp/K	P ^{vap} Mix/Pa	P ^{vap} Raoult/Pa	Temp/K	P ^{vap} Mix/Pa	P ^{vap} Raoult/Pa
<i>anthraquinone and 2-anthracenecarboxylic acid</i>			<i>phenanthridine and 9-fluorenone</i>		
324.7	0.000157	0.000208	304.8	0.0217	0.0677
328.3	0.000251	0.000332	307.3	0.0333	0.0233
330.3	0.000342	0.000428	310.1	0.0433	0.0316
342.6	0.00131	0.00193	310.8	0.0491	0.0440
346.8	0.00237	0.00315	313.8	0.0581	0.0478
351.0	0.00294	0.00508	314.3	0.0668	0.0717
355.2	0.00421	0.00809	317.5	0.973	0.103
361.8	0.00744	0.0165	317.5	0.955	0.103
365.9	0.0144	0.0253	320.9	0.129	0.151
370.0	0.0183	0.0385	321.2	0.129	0.156
374.1	0.0338	0.0580	324.8	0.202	0.230
377.5	0.0440	0.0810	325.2	0.204	0.240
381.5	0.0600	0.119	328.3	0.284	0.334
381.6	0.0606	0.120	329.0	0.294	0.359
389.5	0.0920	0.251	333.0	0.424	0.544
			336.2	0.591	0.752
			339.9	0.871	1.09
<i>2-fluoreneboxaldehyde and phenanthridine</i>			<i>phenanthridine and phenoxathiin</i>		
307.8	0.00452	0.00892			
309.3	0.00864	0.0108	309.7	0.114	0.320
311.2	0.0134	0.0137	313.2	0.164	0.424
312.9	0.0197	0.0169	314.7	0.175	0.478
314.6	0.0247	0.0208	315.5	0.201	0.509
316.6	0.0349	0.0264	316.7	0.250	0.560
318.4	0.0438	0.0328	317.4	0.257	0.591
320.2	0.0574	0.0406	318.9	0.290	0.664
321.3	0.0646	0.0461	321.0	0.366	0.781
323.6	0.0931	0.0602	322.5	0.425	0.875
324.9	0.108	0.0699	326.2	0.621	1.16
327.4	0.135	0.0927	328.7	0.766	1.39
328.8	0.157	0.108	329.6	0.787	1.49
331.6	0.230	0.148	332.2	1.20	1.80
332.4	0.243	0.161	335.9	1.41	2.35
335.1	0.329	0.216	336.9	1.52	2.52
<i>2-fluoreneboxaldehyde and 9-fluorenone</i>			<i>anthraquinone and 2-fluoreneboxaldehyde</i>		
278.6	0.000339	0.00062	318.1	0.00374	0.00554
289.3	0.00173	0.00272	324.0	0.00544	0.0111
307.0	0.0203	0.0251			

Temp/K	P ^{vap} Mix/Pa	P ^{vap} Raoult/Pa	Temp/K	P ^{vap} Mix/Pa	P ^{vap} Raoult/Pa
310.7	0.0283	0.0387	325.7	0.00696	0.0135
314.8	0.0370	0.0618	327.0	0.00823	0.0156
318.7	0.0661	0.0954	328.7	0.00912	0.0189
322.2	0.109	0.140	335.2	0.0246	0.0386
			335.4	0.0249	0.0394
<i>anthraquinone and 9-anthracenecarboxylic acid</i>			338.9	0.0366	0.0573
309.8	8.55E-06	2.07E-05	340.6	0.0394	0.0685
320.7	8.51E-05	9.47E-05	342.0	0.0460	0.0792
324.6	0.000133	0.000159	343.8	0.0625	0.0953
328.5	0.000216	0.000264	345.4	0.0639	0.112
332.2	0.000335	0.000423	347.0	0.0820	0.132
336.1	0.000415	0.000686			
339.7	0.000624	0.00106			
344.1	0.00103	0.00179			

Table 3

Measured and predicted enthalpy and entropy of sublimation for equimolar nonideal PAC mixtures

Mixture	Temperature Range Measured/ K	Deviations from Raoult's Law	Measured Enthalpy of Sublimation/ kJ·mol ⁻¹	Raoult's Predicted Enthalpy of Sublimation/ kJ·mol ⁻¹	Measured Entropy of Sublimation/ kJ·mol ⁻¹ K ⁻¹	Raoult's Predicted Entropy of Sublimation/ kJ·mol ⁻¹ K ⁻¹
Anthraquinone and 2-anthracenecarboxylic acid	325-390	Negative deviations increase as temperature increases	105.5 ± 4.0	115.1	0.254 ± 0.010	0.284
Anthraquinone and 9-anthracenecarboxylic acid	310-344	Negative deviations throughout	117.9 ± 5.9	115.3	0.287 ± 0.030	0.282
Anthraquinone and 2-fluorene-carboxaldehyde	318-347	Negative deviations throughout	104.5 ± 4.4	100.7	0.280 ± 0.012	0.273
Phenanthridine and 2-fluorene-carboxaldehyde	308-335	Negative deviations at low temperatures, positive deviations at higher temperatures	124.2 ± 10.5	100.1	0.363 ± 0.031	0.286
9-fluorenone and 2-fluorene-carboxaldehyde	278-322	Negative deviations throughout	97.1 ± 2.1	92.7	0.282 ± 0.006	0.271
9-fluorenone and phenanthridine	305-340	Ideal at low temperatures, negative deviations at higher temperatures	87.9 ± 8.7	94.2	0.257 ± 0.025	0.278
Phenanthridine and phenoxathiin	310-337	Negative deviations decrease as temperature increases	84.8 ± 6.9	65.7	0.256 ± 0.021	0.203