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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 presence of heteroatoms 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 a range of behavior, from practically ideal behavior following Raoult's law to significant deviations from ideality depending on the heteroatoms present. 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 deviation 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, and *vice versa*.

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1. Introduction

Mixtures of high molar mass 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 only pure polycyclic aromatic hydrocarbons, but also 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 surprising how little we know about their thermodynamic behavior as mixtures. They often appear in non-aqueous phase liquids (NAP-Ls) and in the solid phase; here, complementing previous work on mixtures of unsubstituted polycyclic aromatic hydrocarbons, we investigate the sublimation vapor pressures of mixtures to examine the effect of heteroatom addition to mixtures of PAC.

Like Oja and Suuberg [4] and Peters *et al.* [5], our laboratory found that mixtures of unsubstituted polycyclic aromatic hydro-

carbons (PAH) see relatively minor deviations from ideal behavior as described by 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 the work by Oja and Suuberg, the vapor pressure of (1-hydroxypyrene + phenanthridine) was considerably overpredicted by Raoult's law. The observed decrease in vapor pressure is likely due to the strong electron donor group of the phenanthridine and corresponding electron acceptor of the 1-hydroxypyrene [4].

In a related study on high molar mass organics, Shim *et al.* [7] 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 temperature of HPT is attributed to contributions of more polar compounds in BTT yielding stronger intermolecular forces, such as hydrogen bonding. Although molar mass plays an important role, it is not the only factor determining volatility; the chemical nature of the mixture, such as heteroatoms present, must also be considered.

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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 various intermolecular interactions [8–10]. Negative deviations 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 *et al.* conclude that the majority of constituents in PAC-containing NAP-Ls 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 [11].

Mixtures of PAC have a tendency to degrade at the high temperatures required to measure their vapor pressures directly. As such, we employ the Knudsen effusion technique, an indirect method of vapor pressure measurement relating the mass loss rate of a given compound or mixture through a pinhole leak to its vapor pressure. This enables measurements in the ambient to slightly elevated temperature range, negates the decomposition issue, and yields measurements at temperatures of environmental interest. Data are analyzed using the Clausius–Clapeyron equation, a well-known equation relating saturation vapor pressure, P° (as referenced to the high vacuum in which it is measured herein), absolute temperature, *T*, enthalpy of vaporization (or in this case, sublimation), $\Delta_{sub}H$, and the universal gas constant, *R*, such that

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

Although we usually employ this relationship for pure compounds, its application to sublimation mixture thermodynamics is logical given that sublimation enthalpies are not strongly temperaturedependent over a reasonably small temperature range, such that plots of $\ln P^{\circ}$ versus 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 predicted Raoult's Law vapor pressure of a mixture of *i* components, P_{Raoult}° , their respective pure component vapor pressures through Raoult's law as shown in the following equation:

$$P_{Raoult}^{\circ} = \sum_{i} x_{i} P_{i}^{\circ}.$$
⁽²⁾

2. Materials and methods

Mixture vapor pressures were determined using the Knudsen effusion technique, in which 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

TABLE 1

Pure compounds used to fabricate equimolar non-ideal PAC mixtures (melting temperature, enthalpy, and entropy of sublimation as measured by this laboratory [17,21]).



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 mixture, P_{mix}° , *via* the Knudsen equation (equation (3)):

$$P_{mix}^{\circ} = \frac{m}{W_0 A_0} \sqrt{\frac{2\pi RT}{M}},\tag{3}$$

where A_0 is the orifice area and M the molar mass of the effusing mixture. The molar mass of the mixture is calculated simply as the mole fraction-weighted average molar mass based on conservation of mass principles that (here) equimolar amounts of each component were used and that a homogeneous distribution would result (on average) in an equal number of both molecules in a given sample. In equation (3), W_0 is the Clausing correction factor, which accounts for the idealized assumptions within Knudsen's original equation. This factor was calculated using a relation between the orifice effusion length and orifice radius and *via* experiments with

 TABLE 2

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

PvapMix/Pa P^{vap}Raoult/Pa PvapMix/Pa P^{vap}Raoult/Pa T/K T/K (Anthraquinone + 2-anthracenecarboxylic acid) (Phenanthridine + 9-fluorenone) 0.000208 304.8 0.0677 3247 0 000157 0.0217 328.3 0.000251 0.000332 307.3 0.0333 0.0233 3303 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 0.00744 0.955 361.8 0.0165 317.5 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 0 4 4 0 0.0810 325.2 0 2 0 4 0 2 4 0 0.0600 3283 0 284 0334 381 5 0119 381.6 0.0606 0.120 329.0 0.294 0.359 0.0920 333.0 389.5 0.251 0.424 0.544 336.2 0.591 0.752 (2-Fluorenecarboxaldehyde + phenanthridine) 339.9 0.871 1.09 0.00892 307.8 0.00452 0.00864 (Phenanthridine + phenoxathiin) 309.3 0.0108 311.2 0.0134 0.0137 309.7 0114 0 320 0.164 0.0197 0.0169 313.2 0.424 312.9 314.6 0 0247 0.0208 314.7 0175 0.478 316.6 0.0349 0.0264 315.5 0.201 0.509 318.4 0.0438 0.0328 316.7 0.250 0.560 0.0406 0.591 320.2 0.0574 317.4 0.257 321.3 0.0646 0.0461 318 9 0 2 9 0 0 664 0.0931 0.0602 323.6 321.0 0.366 0.781 324.9 0.108 0.0699 322.5 0.425 0.875 327.4 0.0927 326.2 0.621 0.135 1.16 328.8 0.157 0.108 328.7 0.766 1.39 331.6 0.230 0.148 329.6 0.787 1.49 332.4 0.243 0.161 332.2 1.20 1.80 335.1 0.329 0.216 335.9 1.41 2.35 336.9 1.52 2.52 (2-Fluorenecarboxaldehyde + 9-fluorenone) 278.6 0.000339 0.00062 (Anthraquinone + 2-fluorenecarboxaldehyde) 289.3 0.00173 0.00272 318.1 0.00374 0.00554 0.0203 0.0251 0 00544 307.0 324.0 0.0111 310.7 0.0283 0.0387 325.7 0.00696 0.0135 314.8 0.0370 0.0618 327.0 0.00823 0.0156 0.0661 0.0954 328.7 0.00912 0.0189 318.7 0.109 0.140 335.2 0.0246 0.0386 322.2 335.4 0 0249 0.0394 (Anthraquinone + 9-anthracenecarboxylic acid) 338.9 0.0366 0.0573 309.8 8.55E-06 2 07E-05 340 6 0.0394 0.0685 9.47E-05 0.0460 0.0792 320.7 8.51E-05 342.0 324.6 0.000133 0.000159 343.8 0.0625 0.0953 0.000216 0.000264 328.5 345.4 0.0639 0.112 332.2 0.000335 0.000423 347.0 0.0820 0.132 0.000415 0.000686 336.1 339.7 0.000624 0.00106 0.00103 0.00179 344.1

known compounds and known orifice area. 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].

2.1. Experimental apparatus

The effusion apparatus is described in several previous publications [16,17]. Briefly, the Knudsen effusion sample cell with a predrilled, pre-measured orifice is suspended on one arm of a Cahn 2000 microbalance (sensitivity of 0.5 μ g) 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; it 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 below 10^{-5} Pa; the high vacuum is maintained by a downstream condenser that traps species that effuse out from the cell, preventing them from contaminating the pump.

2.2. Mixture fabrication

Physically agitating two or more solid phase components will not result in a continuous phase. As such, we fabricate mixtures of PAC using a guench-cool technique. Mixtures of high molar mass organics are commonly synthesized by two methods - meltgrowth and solution-growth techniques. Solution-growth techniques are not easily applied to mixtures of PAC and other semivolatile organics since 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 was obtained from TCI America at minimum mass fraction purity of 0.95, as detailed in table 1. Compounds with minimum mass fraction purity below 0.98 underwent fractional sublimation using the Knudsen effusion technique until at least 5%, by mass, of each compound was lost to account for volatile impurities. This was shown by our laboratory to produce compounds of mass fraction purity >0.99 [16,21].

After filling the stainless steel mixing vessels with the desired amounts of each purified compound, the vessels were sealed and placed into an oven and heated slightly above the melting temperature of the most volatile component for 15 min to enter the liquid state. The transition to the 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 temperatures 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 $10 \text{ K} \cdot \text{min}^{-1}$. We were able to successfully reproduce the transition points of each mixture at least three times to within 1.4 K. These measurements also ensured that the vapor pressures measured were sublimation vapor pressures by keeping the temperature of each mixture below its transition point.

Approximately 10–20 mg of each mixture was loaded into at least three different effusion cells, each following their own temperature profile. 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 and 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.

3. Results and 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. We advise the reader that the pure compound data and ensuing Raoult's law predictions are all from measurements on our Knudsen effusion apparatus. Several other research groups present data on some of these pure compounds, for which ours is within a reasonable range in the literature. However, we have chosen here to present the mixture vapor pressures with our pure compound data as a gauge of deviations as all data were taken on the same apparatus by the same experimenter. Other experimental methods may present slightly higher or lower pure compound vapor pressures, but as we cannot measure our mixtures on their apparatuses, we feel this data presents a good basis for analysis of trends within the data.

3.1. Equimolar anthraquinone and 2-anthracenecarboxylic acid

For an equimolar mixture of (anthraguinone + 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 T = 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 T = 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 $(105.5 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$, compared to the $115.1 \text{ kJ} \cdot \text{mol}^{-1}$ 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 $(0.254 \pm 0.01) \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ compared to that predicted by Raoult's law at $0.284 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Of course, we note that the Clausius-Clapeyron equation employed here for the experimental data assumes a constant enthalpy and entropy of sublimation over the temperature range employed. It is given here as a gauge of non-ideality and to explore the potential causes for this non-ideality, be they entropic or enthalpic in nature.

3.2. Equimolar anthraquinone and 9-anthracenecarboxylic acid

The vapor pressures calculated by Raoult's law also slightly over-predict the measured values for the equimolar mixture of (anthraquinone + 9-anthracenecarboxylic acid). At *T* = 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 *T* = 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 + anthraquinone) mixture, at (117.9 ± 5.9) kJ · mol⁻¹ is quite close to that predicted by Raoult's law, at 115.3 kJ · mol⁻¹. Both this mixture and the previous mixture 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 higher temperatures. Predictions indicate the more volatile component, the anthraquinone, should dictate the thermodynamic behavior of the mixture of the



FIGURE 1. Plot of vapor pressure against reciprocal temperature for pure anthraquinone (long dash [21]) and 2-anthracenecarboxylic acid (dotted [17]) and experimental equimolar mixture (\bullet) compared to Raoult's law prediction (solid line).

TABLE 3

Measured and predicted enthalpy and entropy of sublimation for equimolar non-ideal PAC mixtures.

Mixture	Temperature range measured/K	e 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 · K ⁻¹ · mol ⁻¹	Raoult's predicted entropy of) sublimation/ (kJ · K ⁻¹ · mol ⁻¹)
(Anthraquinone + 2- anthracenecarboxylic acid)	325 to 390	Negative deviations increase as temperature increases	105.5 ± 4.0	115.1	0.254 ± 0.010	0.284
(Anthraquinone + 9- anthracenecarboxylic acid)	310 to 344	Negative deviations throughout	117.9 ± 5.9	115.3	0.287 ± 0.030	0.282
(Anthraquinone + 2- fluorenecarboxaldehyde)	318 to 347	Negative deviations throughout	104.5 ± 4.4	100.7	0.280 ± 0.012	0.273
(Phenanthridine + 2- fluorenecarboxaldehyde)	308 to 335	Negative deviations at low temperatures, positive deviations at higher temperatures	5 124.2 ± 10.5	100.1	0.363 ± 0.031	0.286
(9-Fluorenone + 2- fluorenecarboxaldehyde)	278 to 322	Negative deviations throughout	97.1 ± 2.1	92.7	0.282 ± 0.006	0.271
(9-Fluorenone + phenanthridine) 305 to 340	Ideal at low temperatures, negative deviations at higher temperatures	87.9 ± 8.7	94.2	0.257 ± 0.025	0.278
(Phenanthridine + phenoxathiin)	310 to 337	Negative deviations decrease as temperature increases	84.8 ± 6.9	65.7	0.256 ± 0.021	0.203

ture, yet the less volatile component, the anthracenecarboxylic acids, appears 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 T = 339.7 K in figure 2 was taken as the first data point in a series of decreasing temperature points, whereas the point at T = 344.1 K was the last in a series of increasing temperature points.

3.3. Equimolar anthraquinone and 2-fluorenecarboxaldehyde

Another binary mixture including anthraquinone again displayed negative deviations from ideality. The vapor pressures of equimolar anthraquinone and 2-fluorenecarboxaldehyde, shown in figure 3, are lower than Raoult's Law with a fairly constant offset for the measurable temperature range. The measured vapor pressures tend slightly closer to Raoult's Law as temperature increases, as noted by the slightly higher enthalpy of sublimation. The calculated sublimation entropy is also slightly higher than predicted by Raoult's Iaw, as shown in table 3.

Because of the uniqueness of this behavior, four different effusion cells were used for measurements in order to ensure that we were not experiencing any experimental artifacts. The first cell was progressively increased in temperature,



FIGURE 2. Plot of vapor pressure against reciprocal temperature of pure anthraquinone (long dash [21]) and 9-anthracenecarboxylic acid (dotted [17]) and experimental equimolar mixture (\bullet) compared to Raoult's law prediction (solid line).

the second was progressively decreased in temperature, the third was started at a low temperature, and then 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.

3.4. Equimolar 2-fluorenecarboxaldehyde and phenanthridine

An equimolar mixture of (2-fluorenecarboxyaldehyde + phenanthridine) exhibited strong non-ideality. In this case, the vapor pressures measured at both T = (307.8 and 309.3) K were well below Raoult's law predictions. At T = 311.2 K the vapor pressure is roughly equal to that predicted by Raoult's law, and then from T = (312.9 to 335.1) K the measured vapor pressures trend higher than that predicted by ideality as temperature increases. Above T = 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 during mixture fabrication, we remade this mixture twice and still reproduced the same results. Both times we fabricated this mixture we fractionally sublimed at least 5 wt% of each



FIGURE 3. Plot of vapor pressure against reciprocal temperature for pure anthraquinone (long dash [21]) and 2-fluorenecarboxaldehyde (dotted [17]) and experimental equimolar mixture (\bullet) compared to Raoult's law prediction (solid line).



FIGURE 4. Plot of vapor pressure against reciprocal temperature for pure phenanthridine (long dash [14]) and 2-fluorenecarboxaldehyde (dotted [17]) and experimental equimolar mixture (\bullet) compared to Raoult's law prediction (solid line).

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.

3.5. Equimolar 2-fluorenecarboxaldehyde and 9-fluorenone

Figure 5 shows an equimolar mixture of (2-fluorenecarboxaldehyde + 9-fluorenone); here we found only slightly negative deviations from ideality. The slope of the Clausius–Clapeyron line for the experimental data is 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 $\Delta_{sub}S/R$ for the actual



FIGURE 5. Plot of vapor pressure against reciprocal temperature for pure 9-fluorenone (long dash [21]) and 2-fluorenecarboxaldehyde (dotted [17]) and experimental equimolar mixture (\bullet) compared to Raoult's law prediction (solid line).

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 likely precipitated by the need to accommodate the functional groups on the PAC, which leads to the lower vapor pressures measured than predicted.

3.6. Equimolar phenanthridine and 9-fluorenone

Again, we see an inverse trend than that encountered for unsubstituted PAH mixtures with an equimolar mixture of (phenanthridine + 9-fluorenone) (figure 6). At lower temperatures, the vapor pressure of the mixture is very close to Raoult's law. However, from T = (310 to 340) K the vapor pressure continues to decrease from Raoult's law. At T = 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. In addition, the pure compound vapor pressures for this mixture are reasonably similar, and thus we would not expect to see very large deviations from Raoult's law, in terms of absolute differences, given the similar pure compound vapor pressures, unless these two compounds were highly interactive with each other.

As seen in table 3, the enthalpy and entropy of mixture sublimation in this case are actually less than would be predicted for 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, which encouraged it to remain in the solid phase.

3.7. Equimolar phenanthridine and phenoxathiin

Finally, strong non-ideality was noted for an equimolar mixture of (phenanthridine + phenoxathiin), as seen in figure 7. In this case, the measured vapor pressures of the mixture were all much lower than 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 ± 6.9) kJ·mol⁻¹ compared to that predicted by Raoult's law at 65.7 kJ·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 ± 0.021) kJ·K⁻¹·mol⁻¹ and predicted at 0.203 kJ·K⁻¹·mol⁻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 ture line than would be the case given the strength of the specific interactions.



FIGURE 6. Plot of vapor pressure against reciprocal temperature for pure 9-fluorenone (long dash [21]) and phenanthridine (dotted [14]) and experimental equimolar mixture (\bullet) compared to Raoult's law prediction (solid line).



FIGURE 7. Plot of vapor pressure against reciprocal temperature for of pure phenoxathiin (long dash [21]) and phenanthridine (dotted [14]) and experimental equimolar mixture (•) compared to Raoult's law prediction (solid line).

3.8. Deviations from ideality of PAC mixtures

In these experiments we tend to see negative deviations from Raoult's law for these equimolar mixtures of polycyclic aromatic compounds with interacting heteroatoms. Oja and Suuberg [4] note similar trends with other mixtures. The vapor pressure of a nearly equimolar mixture of (1-hydroxypyrene + 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.

The deviations from ideality depend on the mixture at hand. 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 decrease in enthalpy as mixtures tend further from ideal behavior especially at lower temperatures. Some mixtures experience higher enthalpy and entropy of sublimation than predicted by Raoult's law, which illustrates a 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-fluorenecarboxaldehyde) are all pairs with potential intermolecular interactions. There is nitrogen in phenanthridine which gives these mixtures a lone pair of electrons [20]. The 9-fluorenone and 2-fluorenecarboxaldehyde each contain a single double-bonded oxygen atom, 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-fluorenecarboxaldehyde) 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 non-ideal mixtures investigated as it is the only one to cross the Raoult's line on the Clausius-Clapeyron plot.

4. Conclusions

One trend noted throughout almost all of the non-ideal 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 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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