

Raoult's Law and Its Application to Sublimation Vapor Pressures of Mixtures of Polycyclic Aromatic Hydrocarbons

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Abstract

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous pollutants resulting from incomplete combustion and many fuel processing and storage operations. They are encountered in the environment in many forms, ranging from non-aqueous phase liquid and/or solid mixtures (i.e., NAPL and NAPS materials), to dissolved aqueous phase components, to adsorbed species on solid surfaces. The present work concerns the vapor pressure behavior of non-aqueous phase mixtures of PAH, as may characterize tars or solid PAH phase contaminants. In particular, model mixtures of anthracene, perylene, and fluoranthene are examined herein. Mixture vapor pressure data are important to understanding and modeling exposure opportunities. There exist few data in the literature concerning the vapor-liquid and vapor-solid equilibrium behavior of mixtures of high molecular weight organic compounds as they tend to degrade at the high temperatures required to conveniently perform such measurements. This degradation issue is overcome by implementing the Knudsen effusion technique, an indirect method of vapor pressure measurement at temperatures sufficiently low to ensure thermal stability of the PAH studied. Our results indicate that commonly employed Raoult's law assumptions may represent an over-simplification of some actual near-ambient PAH mixture behavior for the compounds studied, yet there are many instances in which this law is closely followed.

Key words: polycyclic aromatic hydrocarbons; PAH; perylene; fluoranthene; anthracene; vapor pressure; mixture; Knudsen effusion; Raoult's law

Introduction

VAPOR PRESSURE is a fundamental property key to predicting and modeling the fate and transport of a compound or mixture within the environment. There are many common environmental pollutants, such as polycyclic aromatic hydrocarbons (PAH), for which there exist few, if any, literature data on their vapor pressures. In recent years, several laboratories have presented new pure PAH vapor pressure data (Chickos *et al.*, 1998; Goldfarb and Suuberg, 2008; Ribeiro da Silva *et al.*, 2006; Ruzicka *et al.*, 2005; Verevkin, 2003). Vapor pressure is highly dependent on the intra- and intermolecular interactions of the chemical species of interest. As such, vapor pressures may vary by many orders of magnitude for organic compounds of comparable molecular size. Reported vapor pressures of common PAH range from 10^{-2} to 10^{-12} atmospheres at ambient conditions. Despite the fact that the vapor pressures of some PAH are 12 orders of

magnitude less than atmospheric pressure, vapor pressures may still play a pivotal role in environmental transport (Schwarzenbach *et al.*, 1993).

Measurements on pure compound vapor pressures represent only part of the necessary data for understanding fate and transport. More often than not, PAH are present as mixtures within the environment, often in contact with other phases. At former manufactured gas plants (MGPs), soils may contain tars—dense nonaqueous phase liquids (DNAPLs) or nonaqueous phase solids (NAPS) that are mixtures of hundreds, even thousands of different PAH. A dearth of mixture thermodynamic data, including vapor pressure, can hinder the modeling of volatilization and the fate and transport of mixtures within the environment (Voutsas *et al.*, 2005; Weschler, 2003).

There are many relationships that describe the thermodynamic behavior of multi-phase and multi-component mixtures. One of the simplest and most widely applied for non-aqueous mixtures is Raoult's law. It is used to estimate the contribution of individual components of a liquid or solid mixture to the total pressure exerted by the system, especially for discrete mixtures where the quantity of each component is known.

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Ideal solutions are mixtures that obey Raoult's law through the entire range of compositions of the mixture.

$$P^{vap} = \sum_i x_i P_i^\circ \quad (1)$$

The vapor pressure of the mixture, P^{vap} , is equal to the sum of x_i , the components' mole fractions, times P_i° , their respective pure component vapor pressures. While commonly applied to liquid mixtures, Raoult's law is also applied to solid mixtures undergoing sublimation.

Some mixtures, especially those of chemically similar components (i.e., similar polarity, structure, aromatic nature, and hetero-atoms present), obey Raoult's law quite well. Substances with uniform intermolecular forces are most able to fully obey Raoult's law. Woodrow (2003) reported that the fuel vapor of a jet fuel mixture behaved according to Raoult's law predictions. Despite this being a mixture of heavy hydrocarbons, the generally uniform chemical nature of the jet fuel components contributes to the observed ideal behavior (Woodrow, 2003).

On the other hand, as early as 1934, Beatty and Calingaert (1934) observed that hydrocarbon systems could experience non-ideality when aromatic hydrocarbons are present. Likewise, Djordjevic (1991) found that mixtures of several polycyclic aromatic hydrocarbons in n-octadecane are slightly non-ideal, attributed to the compensation between enthalpic and entropic effects. Activity coefficients determined by Aoulmi *et al.* (1995) for mixtures of PAH in long-chain alkanes ranged from 0.37 for naphthalene in squalane to 3.86 for anthracene in n-C₃₆, with many of the mixtures having activity coefficients close to one, indicating only mildly non-ideal behavior. Along similar lines, several groups have studied the partitioning behavior of PAH components between aqueous phases and nonaqueous phases, including Mukherji *et al.* (1997). Their work concluded that Raoult's law is a good approximation for non-aqueous phase behavior.

A study by Burks and Harmon (2001) examined vapor phase concentrations of PAH in equilibrium with the solid state of pure PAH binary mixtures and with two lampblack-contaminated soils from former MGP sites (examples of NAPS). Two binary mixtures were investigated: fluorene-naphthalene (two compounds of widely different crystalline structures) and anthracene-naphthalene (of similar crystal

class with cell dimensions within 10% of each other). The authors found that the vapor pressures of both of these mixtures were closer to the more volatile component present, as opposed to following a Raoult's law prediction. In addition, PAH behavior in the presence of soil core samples from two different former MGP sites (one a moist, fine to medium grain sand, and the other a wet, silt-clay) was studied. The authors concluded that independent PAH behavior occurs in some contaminated soil as they noted that the vapor pressures above the organic material-contaminated soils mimicked the results of the model PAH mixtures relative to their solid-phase concentrations. In these contaminated soils, the PAH achieved high partial pressures relative to their measured solid-phase concentrations, despite the presence of other organics in the soil. This again calls into question the ability to describe such behavior using an ideal mixing model (though Burks and Harmon did not quantify the other organics present, so a more formal analysis of the results is not possible).

Another study by Oja and Suuberg (2005) reported the vapor pressures of model mixtures of solid PAH. For an equimolar mixture of anthracene and perylene, they noted no significant deviations from ideality. However, for a mixture of 25 mol% anthracene, balance benzofluorene, significant deviations from ideality occurred; at low temperatures the mixture vapor pressure behavior was that of two separate solid phases, but approached ideal behavior at high temperatures (but still well below the melting point of the mixture). This trend was noted for several other mixtures, suggesting, "that as the systems approach melting they begin to behave as more nearly ideal single phases" (Oja and Suuberg, 2005). When two components in two phases act independently, the vapor pressure of that mixture is the summation of the vapor pressure of the components at a given temperature, very different behavior than that predicted by Equation (1).

Oja and Suuberg saw very different behavior when the compounds comprising the mixture were chosen to promote interactions with one another. 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 phe-

TABLE 1. MIXTURES OF PURE PAH PREPARED USING QUENCH-COOL METHOD

Mixture	Compound	Formula	CAS Reg. No.	Molecular Weight g/mol	Melt Point C	Supplier	Min. Purity %	Mole Fraction
1	Anthracene	C ₁₄ H ₁₀	120-12-7	178.23	217	Aldrich	99	0.50
	Perylene	C ₂₀ H ₁₂	198-55-0	252.31	274	Aldrich	99	0.50
2	Anthracene	C ₁₄ H ₁₀	120-12-7	178.23	217	Aldrich	99	0.51
	Fluoranthene	C ₁₆ H ₁₀	206-44-0	202.26	110	TCI America	98	0.49
3	Anthracene	C ₁₄ H ₁₀	120-12-7	178.23	217	Aldrich	99	0.50
	Phenanthrene	C ₁₄ H ₁₀	85-01-8	178.23	100	Kodak, Inc	99	0.50
4	Phenanthrene	C ₁₄ H ₁₀	85-01-8	178.23	100	Kodak, Inc	99	0.33
	Anthracene	C ₁₄ H ₁₀	120-12-7	178.23	217	Aldrich	99	0.33
	Fluoranthene	C ₁₆ H ₁₀	206-44-0	202.26	110	TCI America	98	0.33
5	Perylene	C ₂₀ H ₁₂	198-55-0	252.31	274	Aldrich	99	0.33
	Anthracene	C ₁₄ H ₁₀	120-12-7	178.23	217	Aldrich	99	0.33
	Fluoranthene	C ₁₆ H ₁₀	206-44-0	202.26	110	TCI America	98	0.33

TABLE 2. SUMMARY OF RESULTS OF PAH MIXTURES; CLAUZIUS-CLAPEYRON EQUATION CONSTANTS WITH 95% CONFIDENCE INTERVAL AND VAPOR PRESSURE EXTRAPOLATION AT 298 K

Mix	Compound	Mole Frac.	Melt Point, K	Temp Range, K	$\ln(P^{\text{vap}}/\text{Pa}) = a - b \cdot 10^3(\text{K}/T)$		$\Delta_{\text{sub}}H$ kJ/mol	$\Delta_{\text{sub}}H$ % Error	p^{vap} 298K, Pa	% Error p^{vap} 298K
1	Anthracene	0.50	490	322–348	32.59 ± 1.1	11.85 ± 0.40	98.5 ± 3.3		7.65E-04	
	Perylene	0.50	547	390–432	34.66 ± 0.03	15.16 ± 0.012	126.0 ± 0.10		8.65E-08	
	MIXTURE RAOULT'S		474.9 ± 1.2	293–332	27.55 ± 1.0 31.90	10.44 ± 0.38 11.85	86.8 ± 3.2 98.5	11.9%	5.70E-04 3.85E-04	–48.1%
2	Anthracene	0.51	490	322–348	32.59 ± 1.1	11.85 ± 0.40	98.5 ± 3.3		7.65E-04	
	Fluoranthene	0.49	383	327–359	32.49 ± 0.90	11.66 ± 0.32	96.9 ± 2.7		1.32E-03	
	MIXTURE RAOULT'S		377.7 ± 0.3	309–333	30.10 ± 1.3 32.4	10.96 ± 0.48 11.72	91.1 ± 4.0 97.4	6.5%	1.26E-03 9.79E-04	–28.7%
3	Anthracene	0.50	490	322–348	32.59 ± 1.1	11.85 ± 0.40	98.5 ± 3.3		7.65E-04	
	Phenanthrene*	0.50	373	303–333	34.39 ± 1.6	11.42 ± 0.53	95.0 ± 4.4		1.94E-02	
	MIXTURE RAOULT'S		366.3 ± 0.2	302–335	31.01 ± 1.6 33.73	10.54 ± 0.53 11.42	87.6 ± 4.4 94.9	7.7%	1.28E-02 1.01E-02	–26.2%
4	Phenanthrene*	0.33	373	303–333	34.39 ± 1.6	11.42 ± 0.53	95.0 ± 4.4		1.94E-02	
	Anthracene	0.33	490	322–348	32.59 ± 1.1	11.85 ± 0.40	98.5 ± 3.3		7.65E-04	
	Fluoranthene	0.33	383	327–359	32.49 ± 0.90	11.66 ± 0.32	96.9 ± 2.7		1.32E-03	
	MIXTURE RAOULT'S		353.4 ± 0.5	305–330	28.67 ± 2.70 32.07	9.90 ± 0.99 11.02	82.3 ± 8.2 91.6	10.2%	1.06E-02 7.37E-03	–43.1%
5	Perylene	0.33	547	390–432	34.66 ± 0.03	15.16 ± 0.012	126.0 ± 0.10		8.65E-08	
	Anthracene	0.33	490	322–348	32.59 ± 1.1	11.85 ± 0.40	98.5 ± 3.3		7.65E-04	
	Fluoranthene	0.33	383	327–359	32.49 ± 0.90	11.66 ± 0.32	96.9 ± 2.7		1.32E-03	
	MIXTURE		375.8 ± 0.8	305–351	30.09 ± 0.76	11.06 ± 0.28	92.0 ± 2.3		8.90E-04	
	RAOULT'S				31.99	11.72	97.4	5.5%	6.50E-04	–37.0%

*(Oja and Suuberg, 1998)

nolic 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. On the other hand, the mere existence of heteroatoms does not automatically dictate a reduction in vapor pressure. The same study reported that other mixtures could approach ideal behavior even if the molecular components contained a number of heteroatoms. Overall, these polycyclic aromatic compounds that contained heteroatom showed the highest degree of non-ideality due to their strong intermolecular interactions (Oja and Suuberg, 2005).

Recent studies on PAH-containing tars support the above conclusions. While measuring the vapor pressures of tobacco tar, Shim *et al.* (2003) noted that although a mixture's average molecular weight was a decisive factor in determining its vapor pressure, variations in the chemical nature of the mixture's components, including any heteroatom present and the chemical structure of the compounds were also important factors.

Materials and Methods

Mixtures of high-molecular-weight organics are problematic to measure due to the tendency of their constituents to chemically decompose at the high temperatures usually required for such measurements. This difficulty is overcome via implementation of the Knudsen effusion technique, an indirect measurement technique based on the molecular effusion of a vapor through an orifice into a high vacuum. The method is widely applied for the measurement of vapor pressures of many materials.

Briefly, the application of the Knudsen theory requires that the interior of a sample cell be subject to both chemical and

thermal equilibrium. It is assumed that the rate of molecular effusion of a species contained in the cell through a pinhole leak in the cell cover equals the rate at which its molecules would strike an area of wall equal to the area of the hole if the hole were not present. This is justified when the mean free path of the vapor molecules exiting the hole is long as compared to the radius of the hole. The use of high vacuum ($< 10^{-7}$ torr) and proper pinhole size ensures that these conditions are met, and enables measurements of vapor pressures as low as 10^{-6} torr. This means that experimental temperatures are maintained sufficiently low as to prevent thermal degradation of the sample. The molecular escape rate is the measured mass loss rate of the sample from the cell.

The same basic apparatus used by Oja and Suuberg (1998) was utilized for the experiments in this investigation. The sample cell with a pre-drilled pinhole leak was suspended on one arm of the Cahn 2000 microbalance (sensitivity of $0.5 \mu\text{g}$) inside a blackened copper capsule approximately 2.5 cm in diameter and 15 cm in length. Within this capsule sat an Omega Type K thermocouple (calibrated against a precision thermometer to $\pm 0.1\text{K}$) positioned directly above the cell opening. The capsule served to ensure a uniform temperature environment around the sample cell, blackened to promote radiative heat transfer. It is the mass loss rate from the cell, at a particular temperature, that permits calculation of the vapor pressure within the cell using Knudsen effusion equation (see, for example, Oja and Suuberg, 1998).

The stainless steel cell (prepared in this laboratory with pre-measured cell orifice diameters) was heated in a propane flame to remove surface impurities and blacken the exterior to improve heat transfer prior to use. The cell is indirectly heated via radiation from an aluminum block oven sur-

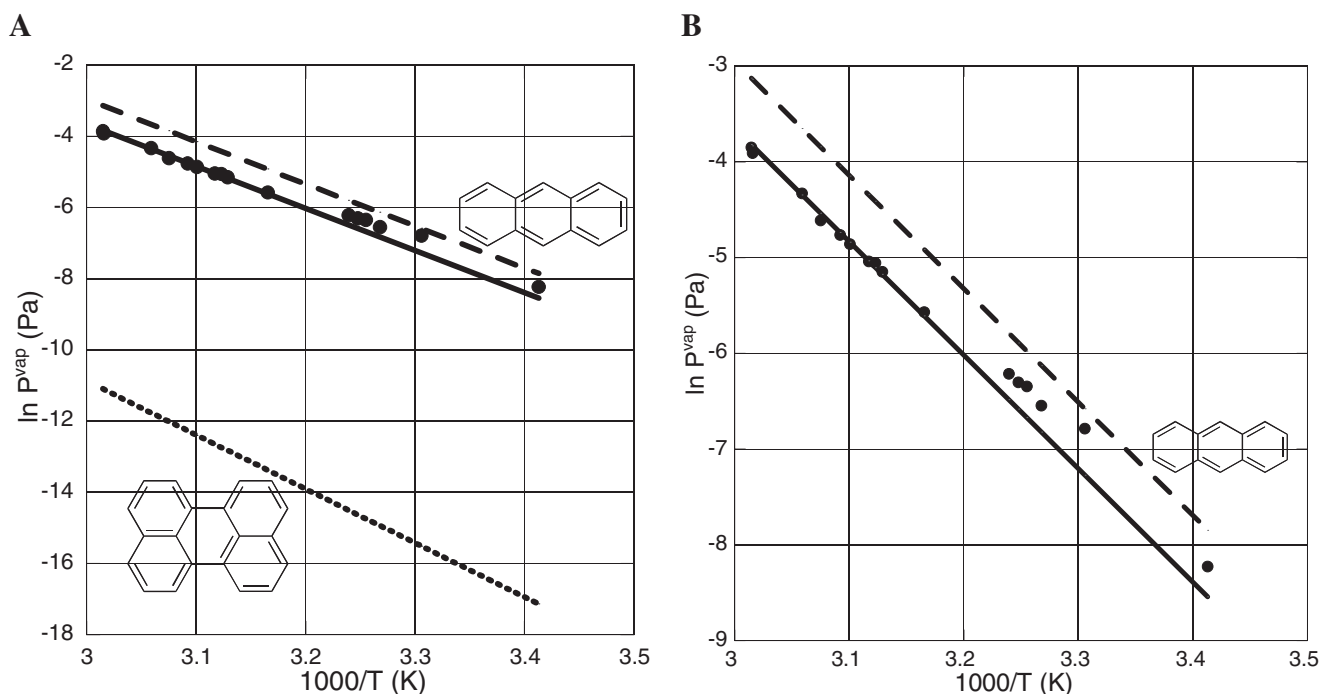


FIG. 1(A). Clausius-Clapeyron plot of vapor pressure as a function temperature for an equimolar mixture of anthracene and perylene compared to Raoult's law prediction and pure component vapor pressures; • experimental data; _ _ _ Raoult's law prediction; . . . perylene (This Laboratory); _ _ _ anthracene (This Laboratory). **(B).** Clausius-Clapeyron plot of vapor pressure as a function temperature for an equimolar mixture of anthracene and perylene compared to Raoult's law prediction and pure anthracene; • experimental data; _ _ _ Raoult's law prediction; . . . anthracene (This Laboratory).

rounding the glass vacuum enclosure that surrounds the copper capsule enclosing the sample cell. The block is heated using a Watlow cartridge heater, controlled via an Omega CN8202 temperature controller, enabling the temperature of the capsule to be raised at a nearly constant rate, comparable to the rate of temperature change in the aluminum block. A BOC Edwards turbomolecular pump maintains the back-pressure in a glass enclosure and is assisted by a downstream condenser that removes species that effuse out from the cell, preventing them from contaminating the pump. The implementation of this technique is described in considerable detail elsewhere (Oja and Suuberg, 1998).

Mixtures of pure, solid, polycyclic aromatic hydrocarbons

were prepared using a quench cooling method. Known amounts of these organic compounds, at purities of greater than 98%, were measured into a stainless steel vessel, manually agitated, and heated to the melting point of the lower melting compound. Upon achieving this melting temperature, the samples were then quench-cooled in liquid nitrogen (Oja and Suuberg, 2005). Entering the liquid state assures that the compounds are well mixed, and the quench-cooling method is assumed to retain the molecular-level mixing of the components, as the time for phase separation to occur is minimized. Indeed, no physical separation of the mixture was observed, nor was there evidence of such from differential scanning calorimetry of the mixtures (see below).

TABLE 3. EXPERIMENTAL VAPOR PRESSURE DATA OBTAINED VIA KNUDSEN EFFUSION ON MIXTURES 1–5

<i>Mixture 1</i>			<i>Mixture 4</i>		
<i>Temp, K</i>	<i>P^{vap}, Pa</i>	<i>P^{vap,Raoult}, Pa</i>	<i>Temp, K</i>	<i>P^{vap}, Pa</i>	<i>P^{vap,Raoult}, Pa</i>
293.0	0.00027	0.00020	305.2	0.0246	0.0175
302.5	0.00113	0.00070	308.9	0.0357	0.0275
306.0	0.00143	0.00109	312.6	0.0487	0.0426
307.2	0.00175	0.00127	316.0	0.0659	0.00632
307.9	0.00183	0.00138	319.8	0.0892	0.0972
308.7	0.00201	0.00153	324.6	0.164	0.119
315.9	0.00381	0.00367	326.1	0.215	0.194
319.6	0.00581	0.00566	329.7	0.255	0.284
320.2	0.00638	0.00607			
320.8	0.00648	0.00650			
322.5	0.00777	0.00790			
323.4	0.00852	0.00875			
325.2	0.00992	0.0107			
326.9	0.0132	0.01295			
331.6	0.0200	0.0217			
331.7	0.0213	0.0219			
<i>Mixture 2</i>			<i>Mixture 5</i>		
<i>Temp, K</i>	<i>P^{vap}, Pa</i>	<i>P^{vap,Raoult}, Pa</i>	<i>Temp, K</i>	<i>P^{vap}, Pa</i>	<i>P^{vap,Raoult}, Pa</i>
308.9	0.00488	0.00388	304.5	0.00203	0.00149
312.5	0.00651	0.00601	307.7	0.00292	0.00222
315.8	0.00961	0.00889	311.4	0.00405	0.00350
319.6	0.0149	0.0138	314.9	0.00706	0.00531
321.5	0.0196	0.0172	319.3	0.0991	0.00887
323.3	0.0228	0.0210	321.8	0.0140	0.0118
324.8	0.0274	0.0249	323.2	0.0173	0.0138
327.2	0.0327	0.0324	325.6	0.0197	0.0181
328.8	0.0394	0.0386	329.9	0.0318	0.0289
332.5	0.0564	0.0574	331.9	0.0363	0.0358
			335.0	0.0549	0.0496
			338.8	0.0822	0.0734
			345.3	0.154	0.141
			351.4	0.238	0.254
<i>Mixture 3</i>					
<i>Temp, K</i>	<i>P^{vap}, Pa</i>	<i>P^{vap,Raoult}, Pa</i>			
301.6	0.0212	0.0158			
306.0	0.0326	0.0273			
309.7	0.0548	0.0426			
313.6	0.0715	0.0674			
316.7	0.0945	0.0963			
320.2	0.1385	0.1429			
320.5	0.1493	0.1478			
329.0	0.3689	0.3711			
331.9	0.5038	0.026			
335.0	0.6918	0.6912			

Small quantities (approximately 20 mg) of each mixture were loaded into each effusion cell for vapor pressure measurement. Table 1 details the mixtures prepared for experiments reported herein. Each mixture was run in at least three different effusion cells in three different experiments following different temperature profiles. 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 reheated as data were taken. This was done to ensure reproducibility and further rule out possible phase separation as an experimental artifact.

To ensure that mixtures were homogeneous, we measured the melting points of each using a DuPont 2910 Differential Scanning Calorimeter (DSC) with a heating rate of 5°C per minute. The DSC was calibrated with indium. We were able to replicate what appeared to be single melting points (within 2°C) at least three times per mixture, indicating the existence of a homogeneous mixture. The average melting point of each mixture is given in Table 2, along with the vapor pressure summary results of each mixture. The melting points of the pure PAH compounds themselves were also examined using this technique and agreed well with published values.

Results and Discussion

Data are interpreted using the Clausius-Clapeyron equation,

$$\frac{d[\ln P^\circ]}{d[1/T]} = \frac{-\Delta_{sub}H}{R} \quad (2)$$

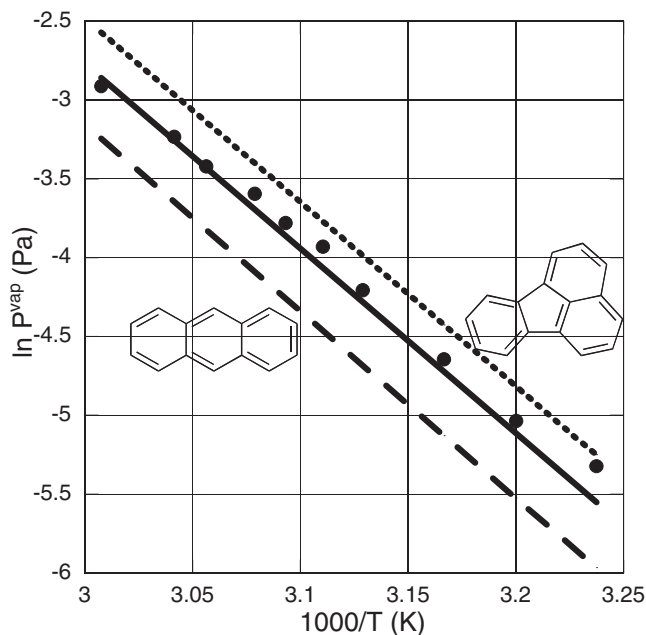


FIG. 2. Clausius-Clapeyron plot of vapor pressure as a function of temperature for mixture of 51 mol% anthracene, balance fluoranthene compared to Raoult's law predictions and pure component vapor pressures; • experimental data; _ Raoult's law prediction; . . . fluoranthene (This Laboratory); _ _ _ anthracene (This Laboratory).

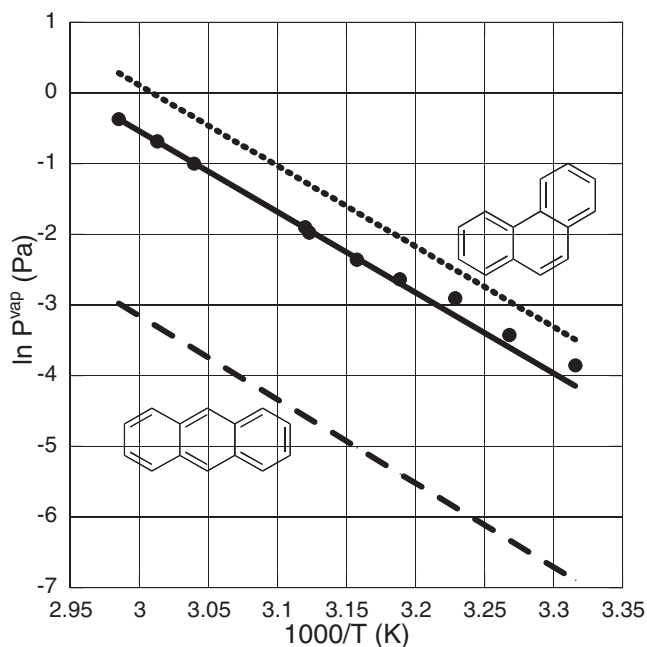


FIG. 3. Clausius-Clapeyron plot of vapor pressure as a function of temperature for an equimolar mixture of anthracene and phenanthrene compared to Raoult's law predictions and pure component vapor pressures; • experimental data; _ Raoult's law prediction; . . . phenanthrene (Oja and Suuberg, 1998); _ _ _ anthracene (This Laboratory).

where P° is the saturation vapor pressure; $\Delta_{sub}H$ is the sublimation enthalpy; T is the absolute temperature; and R is the universal gas constant. This presentation is commonly used for pure compounds, where the sublimation enthalpy is not normally a strong function of temperature over the range examined and plots of $\ln P^\circ$ vs. $1/T$ are normally straight lines. There is no particular reason to expect that the same should be true for any mixture. Even if each component of the mixture were to follow the constant enthalpy behavior, if there is a different sublimation enthalpy for each component, there could be curvature in the Clausius-Clapeyron plot. Still, it is expected that since the temperature dependence of each component's contribution would follow the general Clausius-Clapeyron form, this method of plotting the data is likely the best way to capture the actual behavior.

After establishing the performance of the apparatus using pure compounds such as anthracene, perylene, and fluoranthene (Goldfarb and Suuberg, 2008), we reexamined an equimolar anthracene and perylene mixture reported by Oja and Suuberg. We reproduced the observed mixture behavior, whereby the mixture vapor pressure approached that of the more volatile component, anthracene, at lower temperatures, and more closely followed the behavior predicted by Raoult's law at higher temperatures; this behavior is observed in Figs. 1a and 1b. (Figure 1b makes the comparison with anthracene a bit easier because of its expanded scale.) This mixture is below referred to as Mixture 1, and its melting point data are shown in Table 2.

It is also easy to show that in a case in which the vapor pressures of the mixture components are so vastly different

from one another as in Fig. 1a, that the temperature dependence of such an equimolar mixture should closely follow that of the more volatile component if Raoult's law is followed (the less volatile component contributes practically nothing in Equation (1), (particularly at low temperatures). Hence, the observed temperature dependence is not predicted from Raoult's law.

The observed deviations from Raoult's law were noted regardless of the temperature history of a particular experiment. In other words, a sample that saw a higher temperature still exhibited the same deviations from Raoult's law when it returned to lower temperatures.

Several other mixtures containing commonly encountered PAH in coal tar were examined in this study. Table 3 represents the individual data points of vapor pressure and temperature for each of the mixtures compared to Raoult's law predictions.

Mixture 2, composed of 51 mol% anthracene and 49 mol% fluoranthene, showed similar behavior to Mixture 1. It displayed a tendency to follow Raoult's law at all but the lowest temperatures, as seen in Fig. 2 and from the raw data in Table 3. All of the mixture plots of $\ln P^\circ$ vs. $1/T$ showed more curvature than did any of the pure component data, so the curvature is real and significant. Again, the deviations from Raoult's law are not a result of taking points in a direction of increasing temperature, as the order of interrogation of the different temperature points is of no consequence. We successfully measured the lowest three temperature points for Mixture 2 as the first, middle, and last points of an experiment.

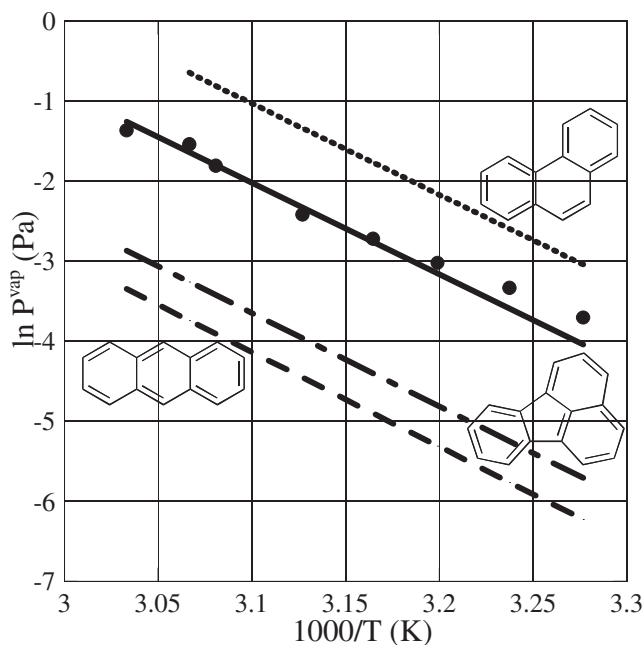


FIG. 4. Clausius-Clapeyron plot of vapor pressure as a function of temperature for an equimolar mixture of anthracene, phenanthrene, and fluoranthene compared to Raoult's law predictions and pure component vapor pressures; • experimental data; _ Raoult's law prediction; . . . phenanthrene (Oja and Suuberg, 1998); _ _ _ anthracene (This Laboratory); _ . _ fluoranthene (This Laboratory).

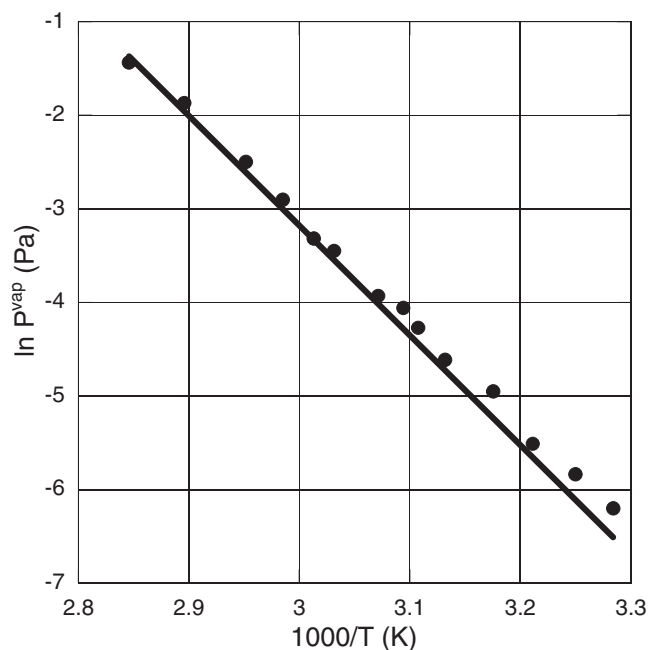


FIG. 5. Clausius-Clapeyron plot of vapor pressure as a function of temperature for an equimolar mixture of perylene, phenanthrene, and fluoranthene; • experimental data; _ Raoult's law prediction.

The same trend is again observed in an equimolar mixture of anthracene and phenanthrene, as shown in Fig. 3. From Table 3 the convergence with Raoult's law behavior for Mixture 3 occurs between 313 and 317 K, as compared to Mixture 1 where the convergence occurred around 321 K and for Mixture 2 between 325 and 327 K. This indicates that the transition to Raoult's law behavior for a binary mixture of PAH is dependent on the particular mixture composition. All three mixtures contained anthracene, which has a melting point of 490 K, and none of them had a component with a melting point as low as the observed convergence temperature, nor did any of the mixtures exhibit a DSC melting point as low as the observed convergence temperature.

A ternary mixture of anthracene, fluoranthene, and phenanthrene of equimolar composition was also examined. Figure 4 shows, similar to Mixtures 1, 2, and 3, that the vapor pressure of this mixture tends towards the vapor pressure of the more volatile component at lower temperatures, and then towards Raoult's law at higher temperatures; the transition to Raoult's law behavior occurs between 316 and 319 K, close to that of the three binary mixtures.

Finally, we examined an equimolar mixture of perylene, anthracene, and fluoranthene in the temperature range of 305 to 351 K. The results of this study are represented in Fig. 5, showing only the experimental vapor pressure points and Raoult's law prediction; the Raoult's law prediction curve is quite close to the anthracene vapor pressure curve and only the former is shown in this figure for clarity. As seen here, the transition or convergence to Raoult's law behavior occurs around 319 K, still well below the melting point of the mixture, as seen in Table 2.

From Table 2, we note that at 298 K, the measured vapor pressures of these five mixtures are higher than those predicted by Raoult's law. This is not surprising, since 298 K is below the convergence temperature for all of the mixtures. Also, the calculated enthalpies of sublimation for Mixtures 1, 2, 3, and 5 are considerably lower than those predicted by Raoult's law, within 95% confidence intervals (calculated via linear regression in STATA version 9 SE) and they are just outside the interval for Mixture 4. Of course, this is also not surprising, given the observed trends in every case. Forcing a fit to a curve that starts out high at low temperatures and then converges to the Raoult's law result at high temperature inevitably must lead to an apparent enthalpy value lower than that predicted by Raoult's law.

The results of Table 2 make clear that the deviations from Raoult's law vapor pressure predictions at 298 K are modest, across all mixtures. This is consistent with some of the literature cited above reporting near-ideal mixture behavior based upon other types of measurements relating to Raoult's law (Mukherji *et al.*, 1997).

The largest deviation in mixture vapor pressures at 298 K occurred for Mixture 1, the equimolar anthracene and perylene mixture—the actual vapor pressure is 48% higher than the predicted ideal mixture vapor pressure. Thus, the mixture sublimates much more readily at ambient temperatures than predicted through Raoult's law. The smallest deviations from ideality in terms of vapor pressure occurred with Mixture 3, the equimolar anthracene and phenanthrene mixture. Both of these compounds contain three fused benzene rings. There is no obvious tie between the observed deviation from Raoult's law and the comparative structures of the mixture constituents.

It is worth noting that the deviations from ideality reported by Mukherji *et al.* (1997) for the activity phase coefficients of dense non-aqueous phase liquid (DNAPL) mixtures were in the opposite direction from those reported here. In that study, PAH were reported to have negative deviations from Raoult's law (with activity coefficients less than one), indicating stronger interactions between compounds than predicted and an affinity for the solution state. However, for our mixtures, we see all positive deviations from Raoult's law, in that the vapor pressures of the mixtures at ambient temperature are larger than the sum of the individual vapor pressures as predicted by Raoult's law, requiring activity coefficients greater than unity. Care must be exercised in comparing the results; the common choice of a subcooled liquid reference state (Schwarzenbach *et al.*, 2003) will influence the value of activity coefficient calculated from such data. The choice of reference state is not relevant here, where we are simply comparing the direction of deviation of vapor pressure from the ideal state.

For each mixture studied, at low temperature the vapor pressure behavior is strongly influenced by the more volatile component; for every mixture there is a transition from this behavior towards ideality at temperatures slightly above ambient. As this transition occurs well below the melting points of each mixture, it cannot involve a solid-liquid phase transition phenomenon, yet at the lower temperatures the mixtures appear to behave as two separate solid phases, and at the so-called transition temperature they assume a single-phase behavior. Further studies are underway to elucidate the origin of this transition behavior.

Summary

From measurements of model mixtures of polycyclic aromatic hydrocarbons we observed a clear trend in the deviations from ideality. At low temperatures (near ambient), Raoult's law appears to slightly underestimate the vapor pressures of these mixtures. As temperature increases above the range of 316 to 327 K, each mixture exhibits a transition in behavior, wherein the vapor pressure becomes well predicted by Raoult's law, and this appears to continue throughout the measurable (higher) temperature range. Raoult's law is acknowledged as a fair approximation to real mixture behavior in all of these cases, though caution should be exercised because of the apparent tendency to under-predict vapor pressures of solid PAH mixtures at ambient temperature.

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Author Disclosure Statement

The authors declare that no competing financial interests exist.

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