



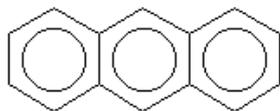
Aqueous Solubility of Binary and Multicomponent, Tarlike PAH Mixtures

James W. Rice, Ross J. Browne, Eric M. Suuberg

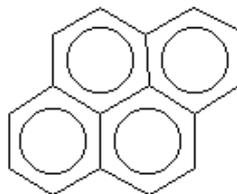
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Research Background & Motivation

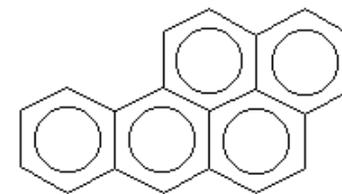
- PAHs are normally found in mixtures of similarly structured compounds.



anthracene



pyrene



benzo[a]pyrene

- Seven PAHs classified as probable human carcinogens by U.S. EPA, though it is commonly understood that many others belong on the list
- PAHs are common components of petroleum and byproducts of combustion and fuels conversion.
- Manufactured gas plant waste remains a concern.

Typical MGP Site

- Manufactured Gas Plants (1816 – 1960)
 - Provided lighting and heating gas
 - Byproduct tar contains high levels of PAHs that are likely carcinogenic.



Subsurface solid tar and non-aqueous phase liquids



Research Goals and Techniques

- Report, characterize, and predict the phase behavior and thermodynamics of PAH mixtures
 - Vapor pressure (Knudsen effusion technique)
 - Enthalpies of fusion (differential scanning calorimetry)
 - Melting point analysis
 - Microstructure (X-Ray diffraction)
 - Composition (gas chromatography – mass spectrometry)
 - **Aqueous solubility**
 - Sorption to Natural Particles
- Offer key data for design of remediation procedures



Some General Concepts & Comments

Mixtures and Model Tars Prepared by Quench-Cool Technique

- Components melted and agitated for 5 min
- Container is quench cooled in liquid nitrogen
- Intended to preserve disorder of well mixed liquid during crystallization

Vapor Pressure & Raoult's Law

-Equilibrium pressure of gas above condensed mixture phases

-For ideal mixture:
$$P = \sum_i x_i P_i^{sat}$$

What is an Azeotrope?

-Represents a non-ideal case

-Vaporization at constant vapor pressure and molar ratio

-Result of molecular interaction

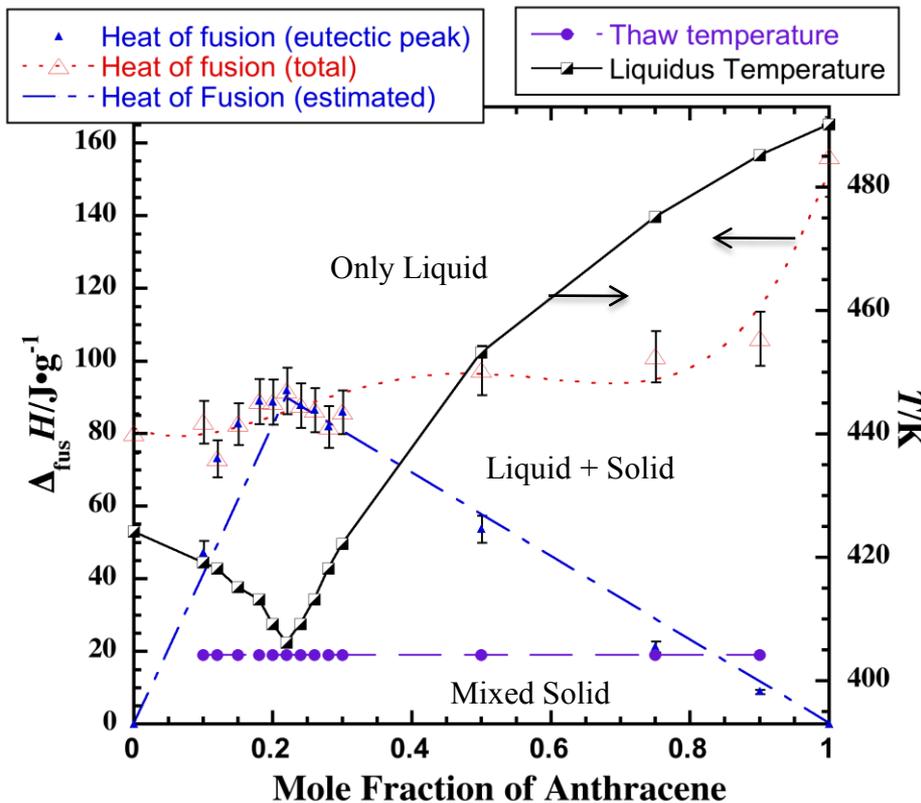
A Look Back:

Characterization of PAH Mixture Phase Behavior
In the Absence of Water

Solid-Liquid Phase Equilibrium

Binary Anthracene + Pyrene Mixture System

EUTECTIC PHASE DIAGRAM



- Eutectic point at 404 K and $x_A = 0.22$
- Coexistence of solid and liquid between thaw and liquidus curves
- Energetically, pyrene and eutectic mixture are very similar.
- Ability of anthracene to reach lower energy crystalline configuration is impeded by small amounts of pyrene
- “Estimated” heat of fusion (blue lines) represent stoichiometric model.

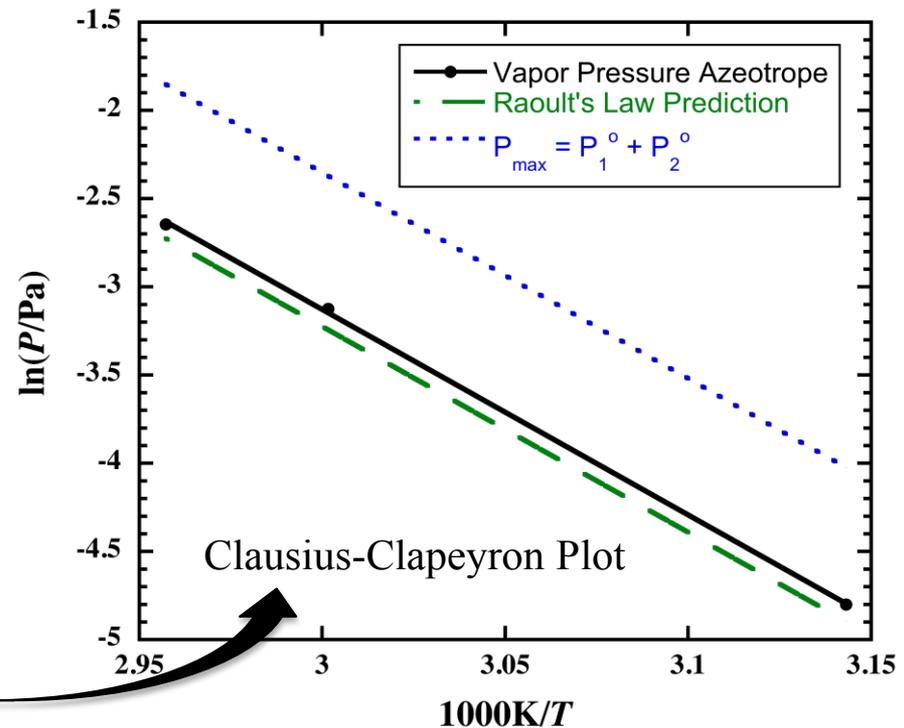
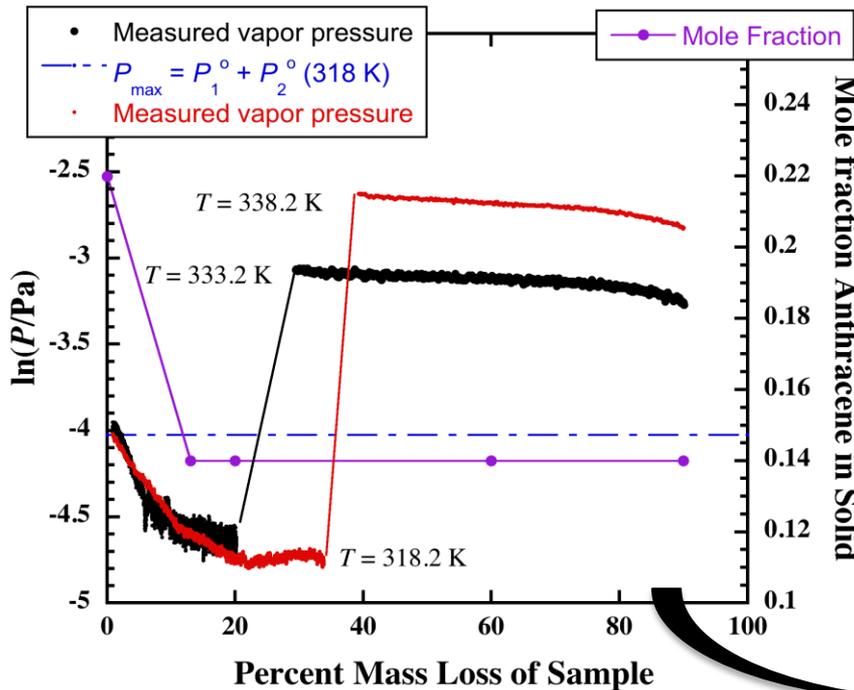
Experiments reveal complicated interaction between components.

$$\Delta_{fus} H_{peak} = x_{eut} \Delta_{fus} H_{eut}$$

Rice, I.W., Fu, J., Swoboda, E.M. *J. Chem. Eng. Data* 2010
 x_{eut} , linear function of $x_{anthracene}$

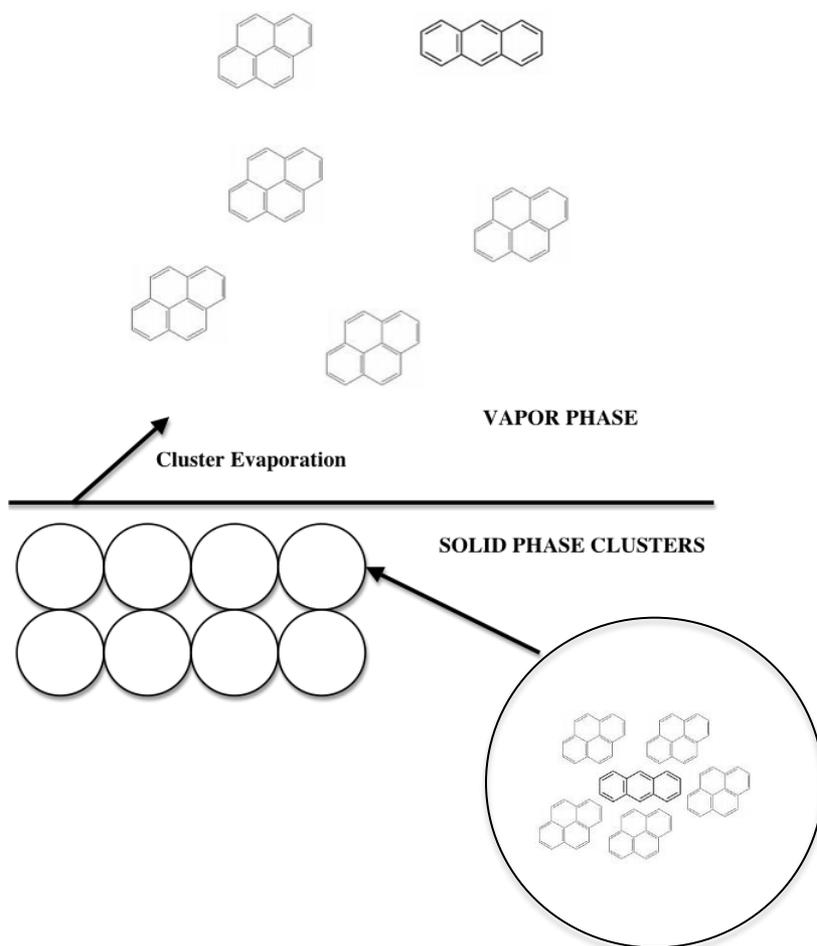
Solid-Vapor Phase Equilibrium

Binary Anthracene + Pyrene Mixture System



- Solid azeotrope formed at anthracene mole fraction of 0.14
- Vapor pressure of azeotrope near that predicted by Raoult's Law, but...
- Complicated & non-ideal interaction between components

Explanation for this Non-Ideal Phase Behavior

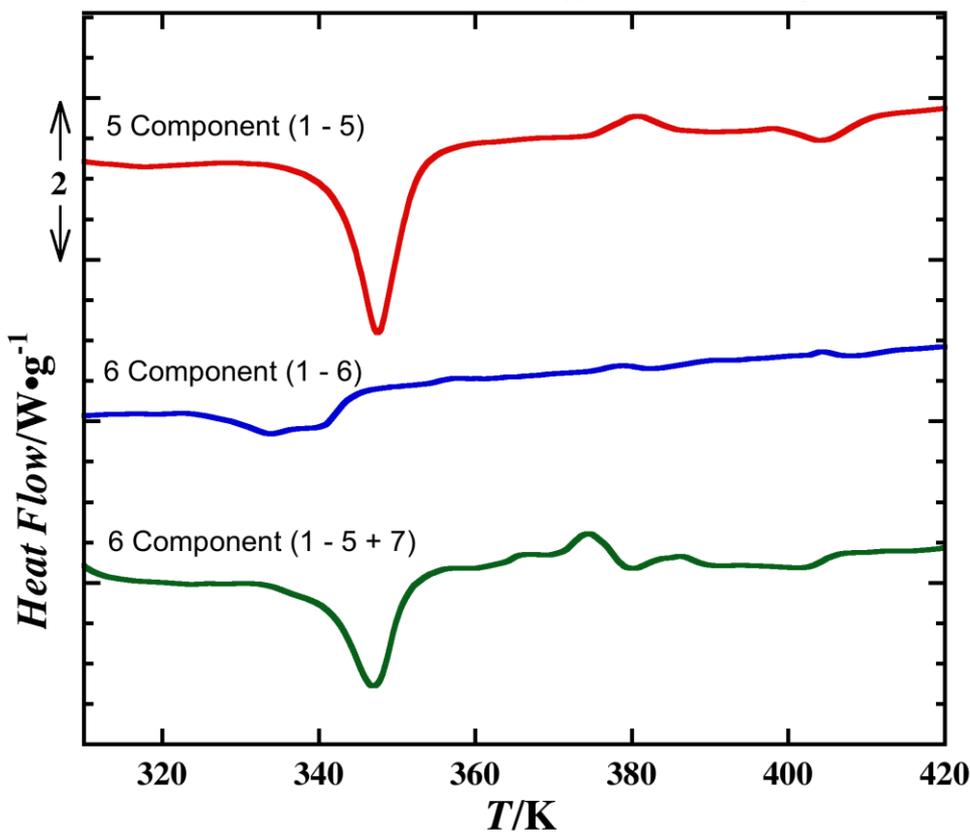


- Formation of cluster-like entities
- Cluster is the locus of local order
- Weak binding between clusters
 - Melt at low temperatures
 - Evaporate as packets

Multi-Component PAH Mixture Behavior

Melting Temperatures and Enthalpies of Fusion

Differential Scanning Calorimetry

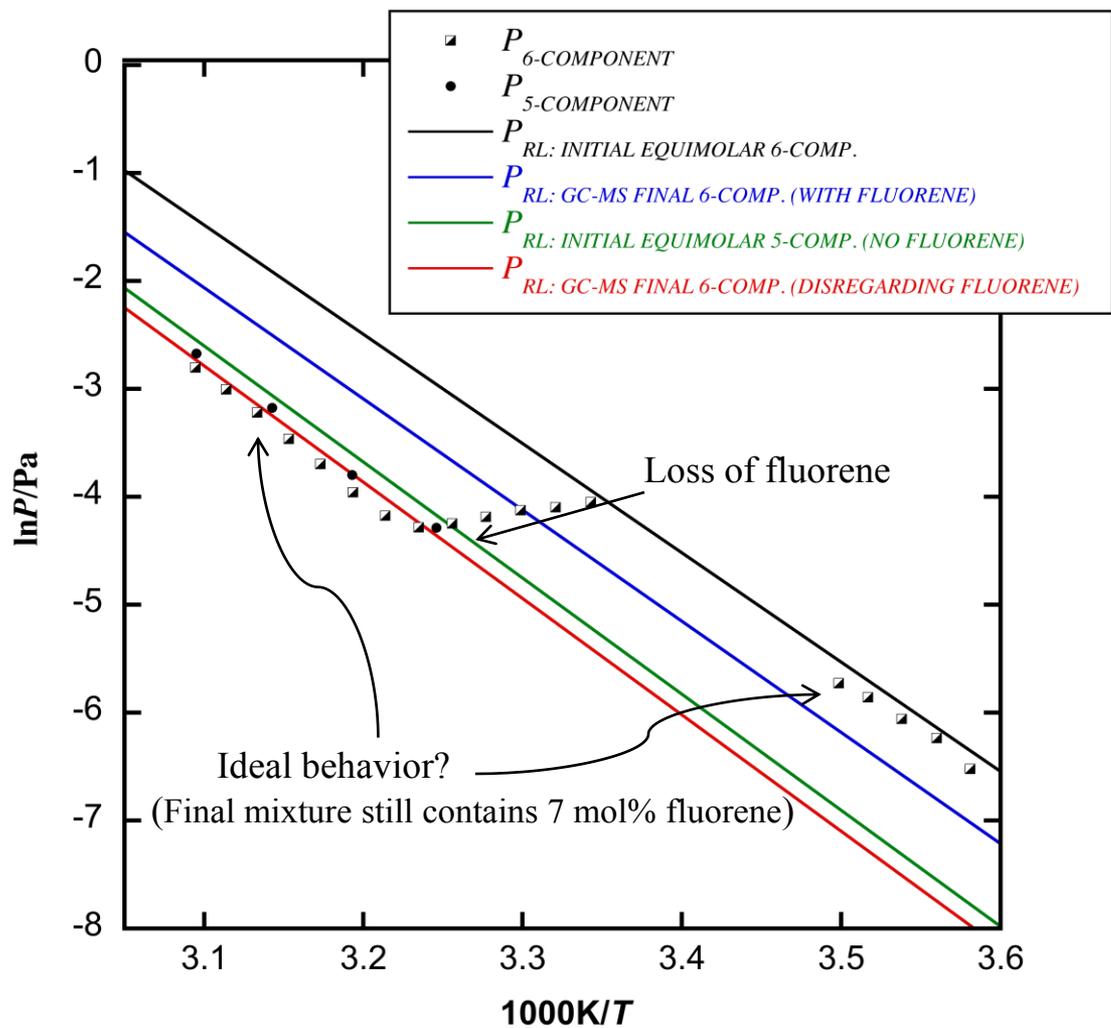


Description	T_{THAW} (K)	T_{LIQ} (K)	$\Delta_{fus}H$ (kJ·mol ⁻¹)
Anthracene(1)	487	489	27.8 ± 1.9
Pyrene(2)	422	423	16.2 ± 1.1
Fluoranthene(3)	382.5	384	18.2 ± 1.3
Benzo[<i>a</i>]pyrene (4)	449	419	11.3 ± 0.3
Phenanthrene (5)	371	372	16.3 ± 1.1
Fluorene (6)	387	388	19.4 ± 1.4
Chrysene (7)	525	526	23.3 ± 1.6
1 + 2 (equimolar)	404	453	18.6 ± 1.3
1 + 4 (equimolar)	414	440	14.6 ± 1.0
1 + 2 + 3 (equimolar)	377	433	14.6 ± 1.0
1 - 4 (equimolar)	353	369	6.9 ± 0.5
1 - 5 (equimolar)		358	
1 - 6 (equimolar)	321	348	4.5 ± 0.3
1 - 5 + 7 (equimolar)	333	353	5.8 ± 0.4

Fusion enthalpies approaching liquid limit of $\Delta_{fus}H = 0$

Multi-Component PAH Mixture Behavior

Vapor Pressure Measurements



PAH Mixture Phase Behavior

Conclusions to Keep in Mind

- Tarlike visual appearance begins to manifest itself with 5-6 components.
 - Mixtures black in color (Binaries and ternaries are white or yellow.)
 - Mixtures inhomogeneous in texture
- Gradual transition from distinct solid melting behavior to a more ill-defined “melting.”
 - DSC peaks lose definition
 - Fusion enthalpies approach liquid limit of $\Delta_{\text{fus}}H=0$
 - Melting temp analysis can no longer discern thaw or liquidus point
- Non-ideal vapor pressure of fewer component mixtures gives way to commonly assumed ideal mixture behavior, i.e., Raoult’s law

Moving Forward:

Characterization of PAH Mixture Phase Behavior
In the Presence of Water

Aqueous Solubility of PAH Mixtures

- Environmentally significant for aquatic environments, sediment, and saturated soil
- Aqueous solubility behavior of PAH mixtures not fully understood
 - Especially true for weathered mixtures that have a reduced number of components
- Data exist for non-aqueous phase liquids (Peters and coworkers, 1993; 1997; 1999; 2000):

- NAPL Model:
$$C_i^{water} = x_i S_i^{pure} \left(\frac{f^L}{f^S} \right)_i$$

C_i^{water} = solubility of species i in water

x_i = mole fraction of i in mixture

S_i^{pure} = pure species i solubility

- Solid Solution Model:
$$C_i^{water} = x_i S_i^{pure}$$

$(f^S/f^L)_i$ = ratio of solid-liquid reference fugacities of pure i



- Solid and liquid system of PAHs described by: $x_i^N \gamma_i^N f_i^L = x_i^S \gamma_i^S f_i^S$

- Definition of the mole fraction of species i in the NAPL phase and subsequent simplification assuming that

$$x_i^N = \frac{x_i^S \gamma_i^S f_i^S}{\gamma_i^N f_i^L} = \frac{x_i^S \gamma_i^S}{\gamma_i^N} \left(\frac{f^S}{f^L} \right)_i$$


- ✓ NAPL is an ideal solution.
- ✓ if solid phase precipitates from liquid solution, it does so as a pure species.

- If system above is in equilibrium with water, and the aqueous phase is dilute so the total volume is unaffected by presence of dissolved PAHs:

$$x_i^A \gamma_i^A f_i^L = x_i^N \gamma_i^N f_i^L \quad \Rightarrow \quad x_i^A = x_i^N \gamma_i^N x_i^{A*} \left(\frac{f^L}{f^S} \right)_i \quad \Rightarrow \quad C_i^A = x_i^N \gamma_i^N S_i^S \left(\frac{f^L}{f^S} \right)_i$$

- If the components in the NAPL were to exist as solids (as might be the case in a dense NAPL or tar), the species-specific fugacity ratios would be unity:

$$C_i^A = x_i^N \gamma_i^N S_i^S$$

NOTE: Superscripts are Solid S , NAPL N , Liquid L , Aqueous A ; and x_i^{A*} is the aqueous solubility of pure species i .



Renewed Interest and Deviation from Models

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The Open Thermodynamics Journal, 2011, 5, (Suppl 1-M4) 40-47

Open Access

Analysis of Predictive Thermodynamic Models for Estimation of Polycyclic Aromatic Solid Solubility in Hot Pressurized Water

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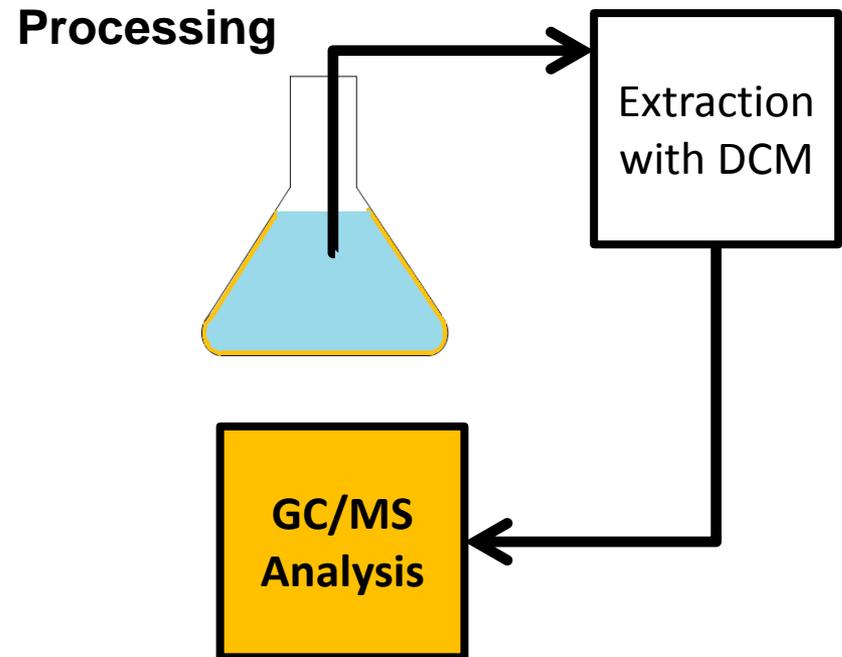
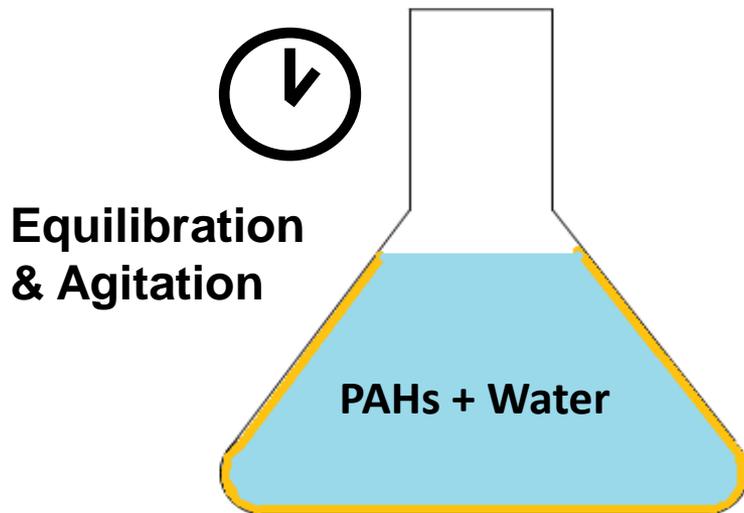
Environmental Chemistry

PARTITION BEHAVIOR OF POLYCYCLIC AROMATIC HYDROCARBONS BETWEEN AGED COAL TAR AND WATER

LIHUA LIU, SATOSHI ENDO, CHRISTINA EBERHARDT, PETER GRATHWOHL, and TORSTEN C. SCHMIDT*
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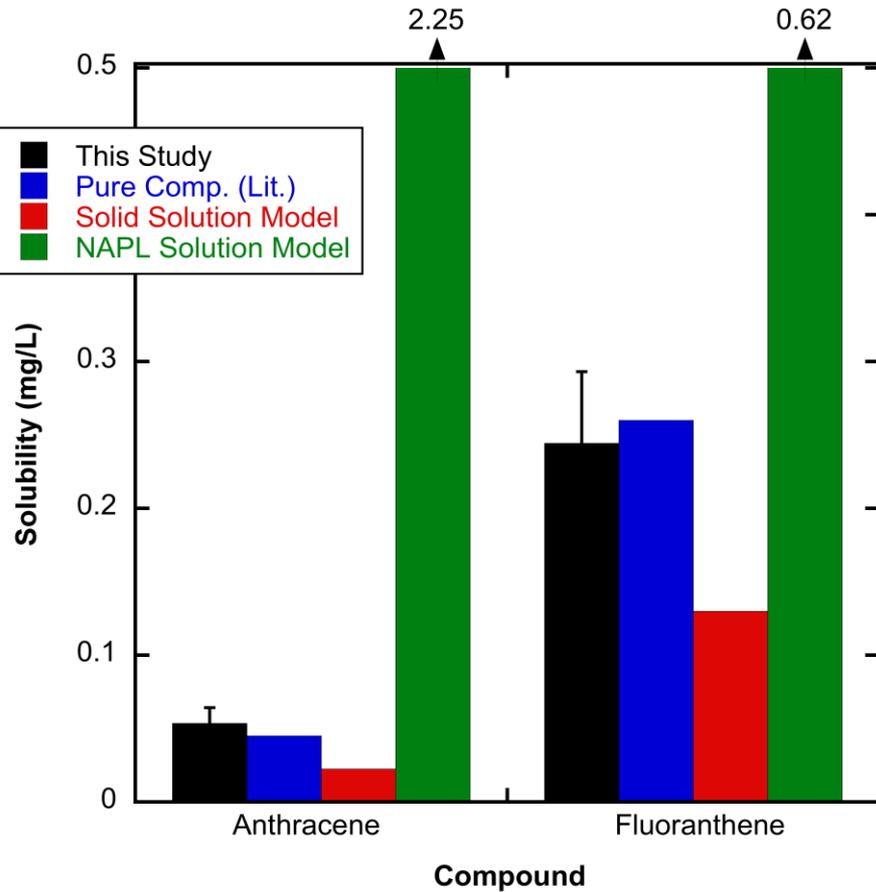
(Received 16 June 2008; Accepted 3 February 2009)

- The composition of a coal tar aged for five-years in an artificial aquifer changed due to depletion of relatively soluble compounds.
- Aqueous phase concentrations of PAHs from aged, solidified coal tar “were much smaller than those from fresh coal tar and also those from Raoult’s law calculations using subcooled liquid solubilities.”
- “If solid solubilities are used as a reference state, Raoult’s Law can give better approximations of aqueous-phase equilibrium concentrations.”

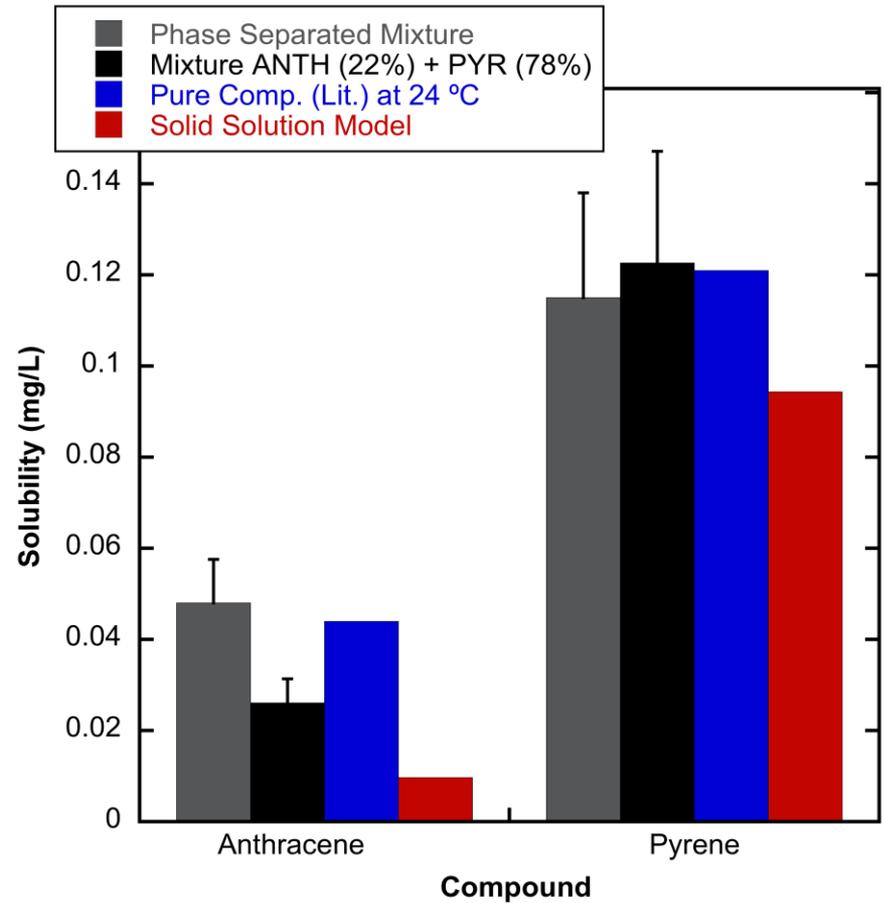


Aqueous Solubility of Binary Quench-Cooled PAH Mixtures

Anthracene + Fluoranthene Mixtures



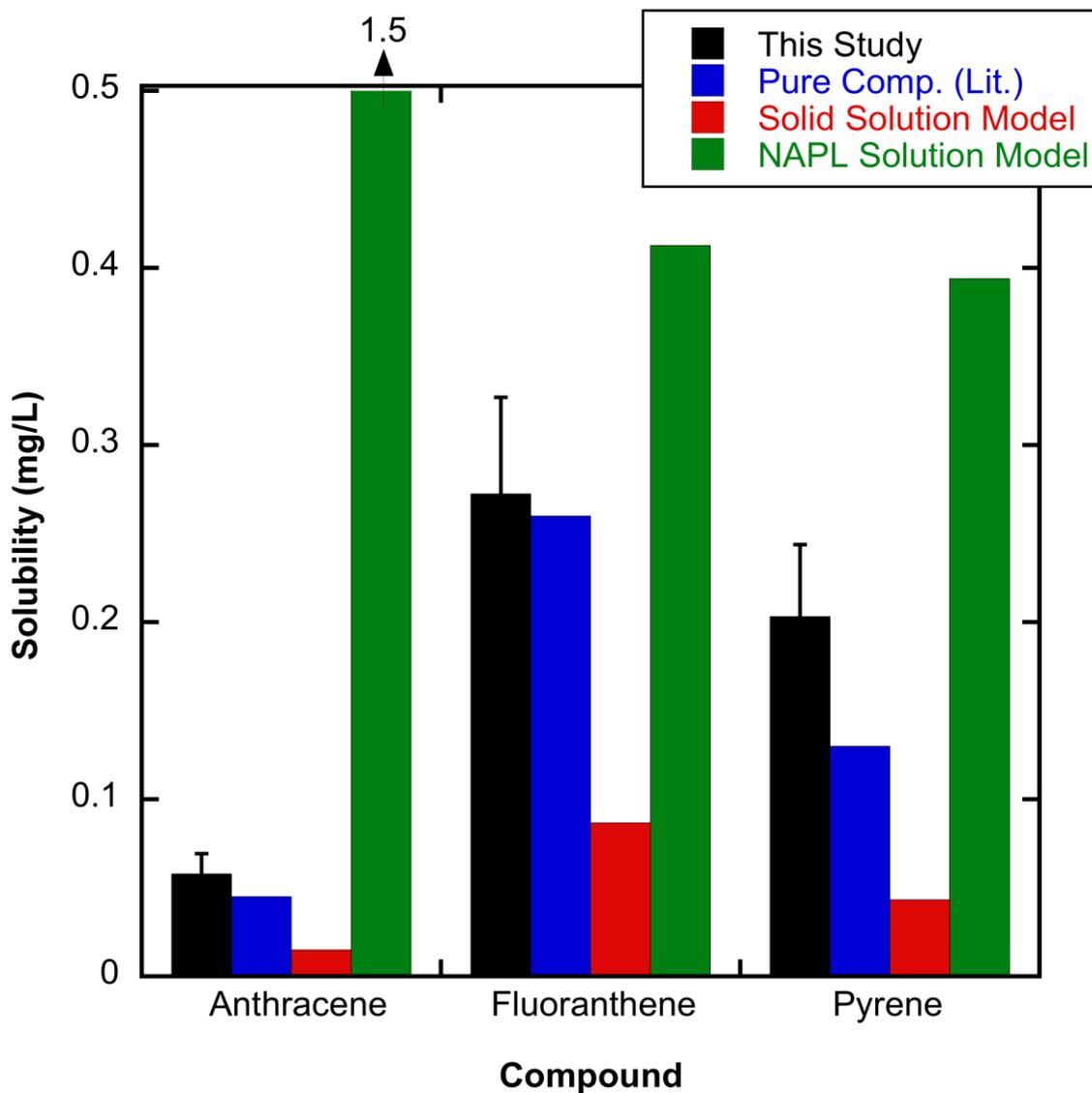
Anthracene + Pyrene Eutectic Mixtures

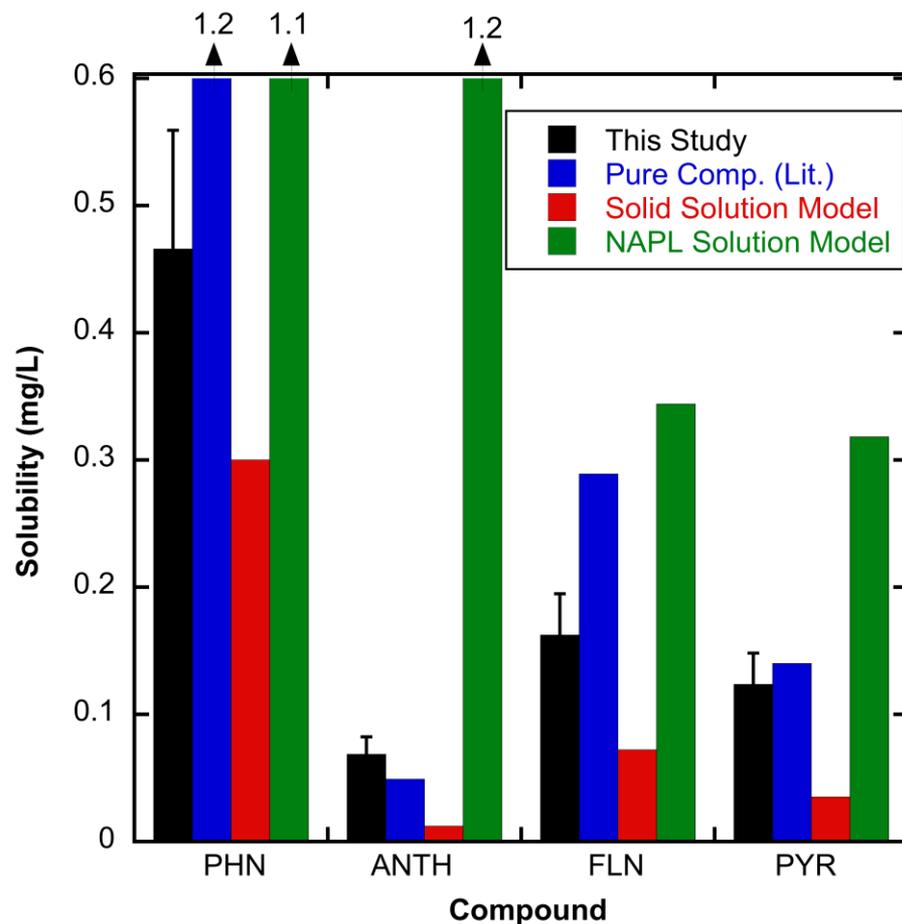
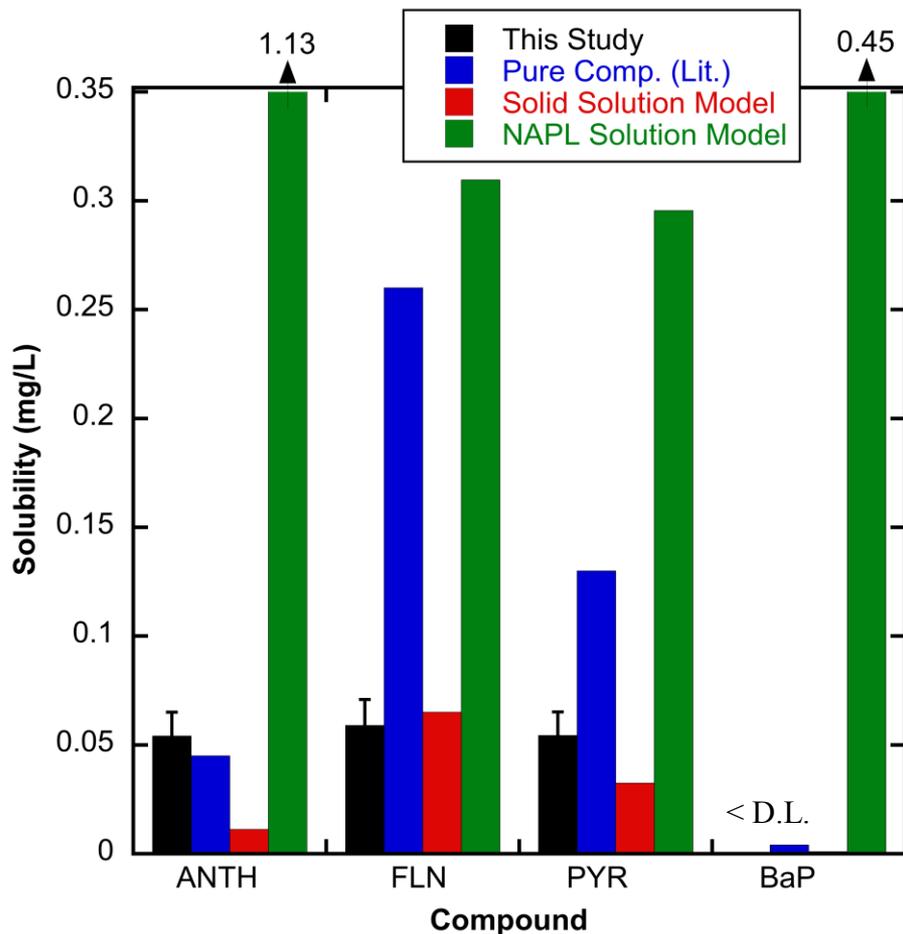


- Apparent phase separation behavior for the equimolar binary mixture components
- More complicated behavior might exist for the A:P eutectic.



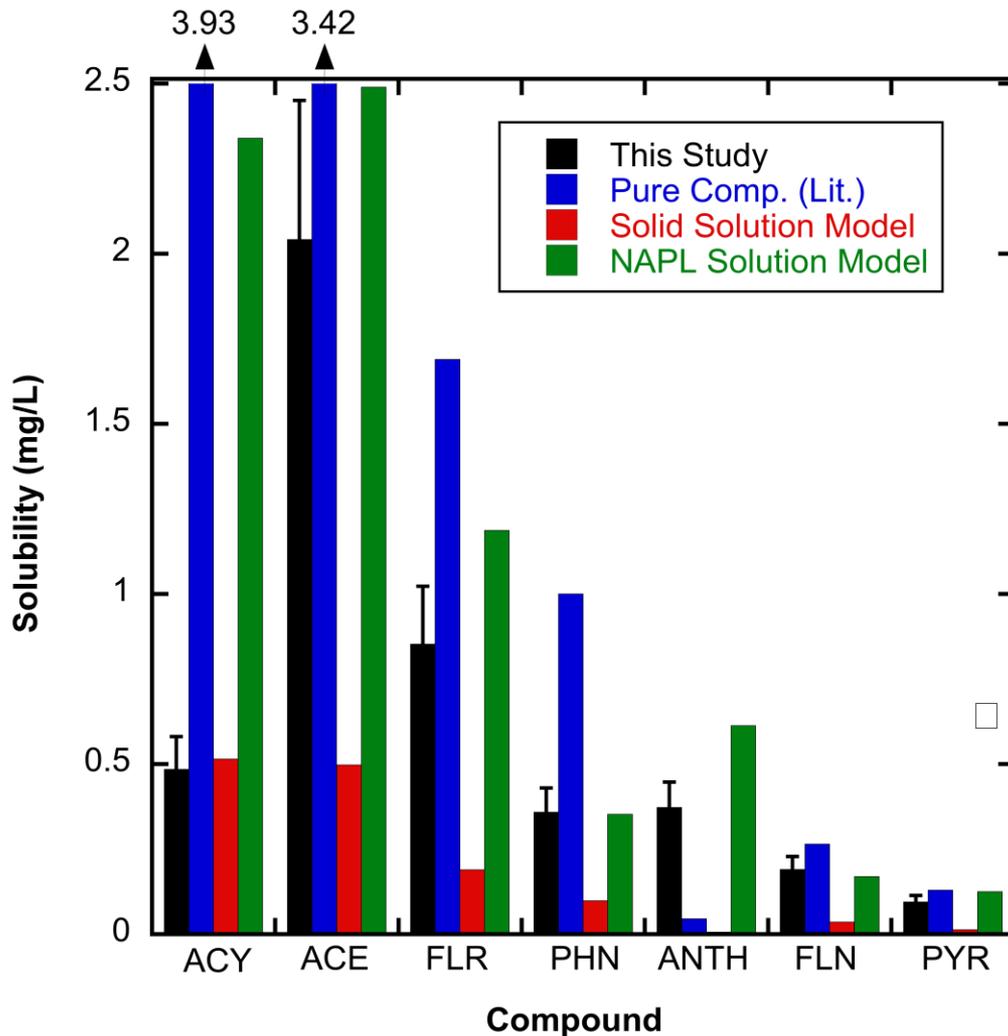
Ternary Anthracene + Fluoranthene + Pyrene Mixtures More Apparent Phase Separation Behavior





$$\text{Solid Model: } C_i^{\text{water}} = \bar{x}_i S_i^{\text{pure}}$$

The compounds that loosely follow the solid solution model (FLN, PYR, PHN) exist at mole fractions ($x_i^{\text{mixture}} = 0.25$) that approaches the predicted NAPL solubilities (x_i^N).



- Concentrations of both benzo(a)pyrene and chrysene
 - below detectable limits

- Acenaphthylene behaving as mixed solid
- $x_i^N > x_i^{\text{mixture}}$

$$C_i^{\text{water}} = x_i S_i^{\text{pure}}$$

- Acenaphthene, Fluorene, Fluoranthene, Phenanthrene, Anthracene, and Pyrene have begun to follow the NAPL model
- x_i^N near or $> x_i^{\text{mixture}}$

$$C_i^{\text{water}} = x_i S_i^{\text{pure}} \left(\frac{f^L}{f^S} \right)_i$$

Summary & Conclusions

- PAH mixtures (and potentially other systems of large, organic compounds) with a finite number of agents may be surprisingly non-ideal.
 - Melting temperature depression and azeotropy
 - Aqueous dissolution that is not easily predicted by common solution models
- As PAH mixtures become enriched in components to a point at which only a discrete number of compounds exist in the mixture, solubility might be roughly predicted by ideal solid-solution theory or by pure component values.
- “Tars” tend to form as the number of mixture components increases.
- As more PAHs are added to create tarlike mixtures, the aqueous solubilities of these higher-component mixtures seem to better fit the values predicted by ideal solid and NAPL solution theory, though there is still failure to predict actual values.
- Prediction of aqueous solubility by ideal NAPL models may not be appropriate for weathered tars or NAPLs in the environment.

Thank You

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- Dr. Indrek Külaots
- Jinxia Fu, Rui Shen, Yijun Yao

