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Phase Behavior and Vapor Pressures of the Pyrene + 9,10-Dibromoanthracene System

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Abstract

The present work concerns the thermochemical and vapor pressure behavior of the pyrene + 9,10-dibromoanthracene system. The phase diagram of the system has been studied using the thaw melt method and the results show the formation of non-eutectic multiphase mixtures. The temperatures of crystallization, and enthalpies of fusion and crystallization of the system were determined by differential scanning calorimetry. The system behavior can be divided into 5 regions. The X-ray diffraction results also indicated the existence of multiple phase characteristics. The solid-vapor equilibrium studies showed that for mixtures with high mole fractions of pyrene, two different preferred states exist that determine the vapor pressure. For those mixtures with moderate and low mole fractions of pyrene, only one preferred state exists that determines vapor pressure behavior. It was also demonstrated that the vapor pressure of the mixtures is independent of the mixture preparation technique.

Keywords

polycyclic aromatic compounds; pyrene; 9,10-dibromoanthracene; phase behavior; vapor pressure

1 Introduction

Although today much is known about the thermodynamic properties of polycyclic aromatic compounds (PAC)[1–4] and eutectic organic mixtures[5–14], there remains a paucity of thermodynamic data available on PAC mixtures. There is a need for more such data, considering the environmental importance of these chemicals[15,16].

This article presents the phase diagram, enthalpy of phase change, crystal structure and vapor pressure of the pyrene + 9,10-dibromoanthracene system. The interaction energies of mixtures with different compositions are also calculated using enthalpies of crystallization obtained via differential scanning calorimetry. Effects of different mixture preparation techniques were also examined.

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2 Materials and Methods

2.1 Materials

Pyrene (CAS Reg. No. 129-00-0, 97 % purity) and 9,10-dibromoanthracene (CAS Reg. No. 523-27-3, 98 % purity) were obtained from TCI America. Purity was verified by gas chromatography-mass spectrometry (GC-MS) analysis. The melting points of pyrene and 9,10-dibromoanthracene were found to be 424 ± 1 K (423 K), see also [6,7] and 498 ± 1 K (499 K), see also [17], respectively.

2.2 Mixture Preparation

Mixtures of pyrene and 9,10-dibromoanthracene were prepared at various compositions by using a melt and quench-cool technique. The desired quantities of pyrene and 9,10-dibromoanthracene were measured to ± 0.05 mg and sealed in a brass vessel. The vessel was heated to 503 ± 5 K in a fluidized bath and agitated for 5 min. Then the vessel was immediately placed into liquid nitrogen, which provided cooling at approximately $70 - 80$ K·s⁻¹ for the first 4 sec. The heating and cooling procedure was repeated 3 additional times.

2.3 Melting temperatures

Melting temperatures of pure samples and mixtures were measured using a Thermo Scientific 1001D MEL-TEMP® Capillary Melting Point Apparatus. 1 to 2 mg of each sample was placed in a capillary and heated at 1 ± 0.5 K·min⁻¹. The liquidus and thaw points were determined according to the method proposed by Pound and Masson [18]. The thaw temperature is the temperature at which the first droplet of liquid appears in the capillary. The liquidus temperature is the maximum temperature at which both solid crystals and liquid are observed coexisting.

2.4 Temperatures and enthalpies of fusion and crystallization

Temperatures and enthalpies of fusion and crystallization were measured using a DuPont 2910 differential scanning calorimeter (DSC). A 1 to 3 mg sample was placed into a hermetically sealed DSC pan and was scanned in heating and cooling modes. The rates of heating and cooling were 10 K·min⁻¹ and 2.5 K·min⁻¹, respectively. This procedure leads to crystallization enthalpy peaks that are more convenient to integrate than the fusion enthalpy peaks because the baseline of the cooling scan is stable, making it easy to distinguish the start and end points of phase transition peaks. Since the values of enthalpy and transition temperatures were generally insensitive to changes in heating and cooling rate in the range of $2.5 - 10$ K·min⁻¹, the enthalpy of crystallization was used to characterize the enthalpy of the phase transition. It was also determined that the cooling scan enthalpy of crystallization agreed to within ± 2 % of the total enthalpy of fusion, for all fusion peaks. Note that the crystallization typically occurs at a subcooled liquid condition in these experiments.

2.5 Vapor pressure

The Knudsen effusion technique was used to measure the vapor pressure of pure pyrene, 9,10-dibromoanthracene and their mixtures. This is an indirect measurement technique based on the molecular effusion of a vapor through an orifice into a high vacuum chamber and is generally used to measure the vapor pressure of low volatility substances. The vapor pressure of a substance can be obtained from effusion data using

$$P = \frac{\omega}{tAW} \sqrt{\frac{2\pi RT}{M}}, \quad (1)$$

where ω is the weight loss during the effusion time interval, A is the orifice area, t is the effusion time, R is the universal gas constant, T is the sample temperature, M is the molecular weight, and W is the Clausing correction factor. W ranges from 0 to 1 and is an essential factor for the calculation of vapor pressure because it quantifies the probability of molecular escape from the effusion cell[19]. W is calculated by the empirical formula,

$$W = \frac{1}{1 + \frac{3l}{8r}}, \quad (2)$$

where l is the orifice effusion length and r is the orifice radius. In these experiments, W was always very close to unity, both by calculation using (2) and by experimental calibration.

Samples were placed inside effusion cells prepared from steel shim stock. The cells were sealed except for a single, circular orifice 0.60 ± 0.01 mm in diameter, and then placed on one arm of a continuously recording microbalance in a high vacuum chamber. The pressure inside of the chamber was reduced to 10^{-4} Pa in the experiments.

2.6 Other Characterization

Powder X-ray diffraction patterns were obtained using a Bruker AXS D8-Advanced diffractometer with $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned with 2θ angle $20^\circ - 60^\circ$ and a step-size 0.02° .

The composition of mixtures was determined by GC-MS. The samples were dissolved in dichloromethane to about $100 \mu\text{g} \cdot \text{ml}^{-1}$ and analyzed using a Varian CP3800 gas chromatograph and Saturn 2200 mass spectrometer. The analysis procedure followed the EPA Method 8270C[20].

2.7 Computational studies

The computer simulation studies on pure pyrene and 9,10-dibromoanthracene were carried out using Spartan'08 software[21]. The geometries of pyrene and 9,10-dibromoanthracene were optimized by density functional theory (DFT) using DFT (B3LYP/6-31 G*).

3 Result and Discussion

3.1 Phase diagram

The phase diagram of the pyrene (1) + 9,10-dibromoanthracene (2) system determined by thaw-melt method is given in Fig. 1. The phase diagram shows the non-ideality of the pyrene + 9,10-dibromoanthracene system, which is attributed to the difference in size and shape of the two components, see Table 1. The surface area and volume of 9,10-dibromoanthracene is larger than that of pyrene. The phase diagram can be crudely divided into 5 regions. The mixtures with relatively low mole fraction of 9,10-dibromoanthracene (< 0.30), in region A, form a pyrene like phase. When the mole fraction of 9,10-dibromoanthracene is between $0.30 - 0.41$, in region B, the mixtures transition from a pyrene-like phase to two phases that both have low melting temperatures. The divergence of the liquidus and thaw curve is $2 - 9 \text{ K}$. In region C, mixtures containing about $x_2 = 0.41 - 0.50$ also show two-phase character and start to transition to 9,10-dibromoanthracene behavior. Mixtures with $x_2 = 0.50 - 0.75$, in region D, also have two phases with 9,10-dibromoanthracene like behavior and high melting temperature. Only one of the phases evolves while the other gives a constant low melting temperature (corresponding to the thaw point). In region E, a 9,10-dibromoanthracene like phase is defined based upon the thermal behavior, shown below.

3.2 Temperature of crystallization and enthalpy of fusion and crystallization

The full heating, cooling and reheating scan of a pyrene + 9,10-dibromoanthracene mixture at $x_2 = 0.48$ (in region C) is shown in Fig. 2 where Φ is heat flow of the DSC. During the heating scan, two peaks appear at 428 K and 440 K, which indicates the two-phase character of the mixture. Two peaks are also observed in the cooling scan, in which the 9,10-dibromoanthracene like phase crystallizes first at 418 K, and then the pyrene like phase crystallizes at 410 K. The cooling scan also suggested two-phase behavior of the mixture just as did the melting behavior. When reheated, the phase transition enthalpies and associated temperatures matched those of the initial heating scan.

The temperature and enthalpy of crystallization (subcooled), shown in Fig. 3, correspond to the results obtained from the phase diagram. Mixtures with a mole fraction of 9,10-dibromoanthracene 0.30 – 0.75, in regions B, C and D, have two-phase character, which is observed as two distinct phase-transition peaks during the cooling procedure. Region E showed two-phase melting behavior, but in the DSC experiments of Fig. 3, the low temperature crystallization peak was absent. Likewise, region B showed two distinct melting peaks, whereas in the DSC experiment only a single peak was observed.

Since the enthalpies of crystallization of the mixtures with 9,10-dibromoanthracene mole fractions of 0.55 and 0.75 are significantly lower than that of other mixtures, these are at higher energy state and are less stable than other mixtures with nearby compositions. Moreover, the mixture with 0.65 mole fraction of 9,10-dibromoanthracene is in a more stable state than those mixtures with 0.55 and 0.75 mole fraction of 9,10-dibromoanthracene meaning that around a 2:1 molar ratio of 9,10-dibromoanthracene to pyrene, there exists a particular lower energy configuration.

3.3 Interaction energy

The data of Fig. 3 may be used to calculate the interaction energy for the system. The results are shown in Fig. 4.

The interaction energy is defined by,

$$E_{inter} = (\Delta H_{fus})_{exp} - (\Delta H_{fus})_{cal}, \quad (3)$$

in which

$$(\Delta H_{fus})_{cal} = x_1(\Delta H_{fus})_1 + x_2(\Delta H_{fus})_2, \quad (4)$$

where E_{inter} is interaction energy, $(\Delta H_{fus})_1$ and $(\Delta H_{fus})_2$ are enthalpies of fusion of pyrene and 9,10-dibromoanthracene, respectively, $(\Delta H_{fus})_{cal}$ is the calculated enthalpy of fusion of the mixtures, $(\Delta H_{fus})_{exp}$ is enthalpy of fusion of the mixtures determined from the DSC measurements, x_1 and x_2 are the mole fractions of pyrene and 9,10-dibromoanthracene, respectively.

Since the enthalpy of crystallization agrees with the total enthalpy of fusion, the equations (3) and (4) can be written as

$$E_{inter} = (\Delta H_{cry})_{exp} - (\Delta H_{cry})_{cal}, \quad (5)$$

$$(\Delta H_{cry})_{exp} = x_1(\Delta H_{cry})_1 + x_2(\Delta H_{cry})_2, \quad (6)$$

where $(\Delta H_{cry})_1$ and $(\Delta H_{cry})_2$ are enthalpies of crystallization of pyrene and 9,10-dibromoanthracene, respectively, $(\Delta H_{cry})_{cal}$ is the calculated enthalpy of crystallization of the mixtures, $(\Delta H_{cry})_{exp}$ is enthalpy of crystallization of the mixtures determined from the DSC measurements.

This suggests that pyrene and 9,10-dibromoanthracene form mixtures with a higher energy state than that of the pure components, and that different kinds of interaction exist in the mixtures than in the pure compounds. There is weaker interaction between molecules in the mixtures with 0.55 and 0.75 mole fraction of 9,10-dibromoanthracene than that in the mixture with 0.65 mole fraction of 9,10-dibromoanthracene, which suggests that the latter mixture is in a lower energy state than others, as already noted above. The energy state of this 2:1 mixture is close to that of pure materials.

3.4 Powder XRD analysis

The powder X-ray diffraction method was used to study the crystal structures of pure pyrene, 9,10-dibromoanthracene and their mixtures (see Fig.5). The results are qualitative. For the 9,10-dibromoanthracene rich mixture at the region D–E boundary, at $x_2 = 0.75$ (curve E), the XRD data show a 9,10-dibromoanthracene like microstructure though there are distinct differences from 9,10-dibromoanthracene. The pyrene rich mixture in region A at $x_2 = 0.25$ (curve A) has the pyrene like microstructure. However, the mixture at $x_2 = 0.65$ (curve D) reflects neither pyrene nor 9,10-dibromoanthracene like microstructure, and in fact is amorphous.

3.5 Vapor pressure

The Knudsen effusion technique was used to measure the vapor pressure of pyrene and 9,10-dibromoanthracene mixtures in two different types of experiments. The experimentally measured vapor pressures are compared to those calculated by Raoult's law, an ideal weighted average of pure component vapor pressures.

Fig. 6 shows the vapor pressure and the change in concentration of pyrene with sample mass loss in an experiment that begins with a mixture at $x_1 = 0.75$ and 333.3 K. The temperature was changed to 358.7 K, after about 20 % of the original mass was lost. Compositions were determined by interruption of the experiment, and removal of some of the sample for analysis. At the beginning, the vapor pressure of mixture with $x_1 = 0.75$ closely follows a Raoult's law prediction corresponding to roughly 0.70 mole fraction of pyrene. After the mixture in the cell loses about 35% mass, the vapor pressure of the mixture falls to another stable state which is at Raoult's law prediction for a 0.35 mole fraction of pyrene. This further suggests that the pyrene and 9,10-dibromoanthracene prefer to form a mixture at $x_1 = 0.35$, even though the initial mole fraction of pyrene before melting is different. These results strongly indicate that the system has a preferred composition.

Fig. 7 shows the vapor pressures of pure pyrene, consistent with [2], and 9,10-dibromoanthracene, consistent with [4]. The vapor pressure of pyrene is about 2 orders of magnitude higher than that of 9,10-dibromoanthracene. From linear regression of the data, the enthalpy of sublimation can be obtained. The enthalpies of sublimation of pyrene and 9,10-dibromoanthracene are $93.1 \text{ kJ}\cdot\text{mole}^{-1}$ in a temperature range of 324 – 359 K and $110.1 \text{ kJ}\cdot\text{mole}^{-1}$ in a temperature range of 359 – 392 K, respectively. Roux et al.[1] remark

that most sublimation enthalpy of pyrene published over the past 50 years range from 93 to 101 kJ·mole⁻¹ in a temperature range of 322 – 423 K. Our value fits well within this range.

$P_{\max}$ is the maximum vapor pressure that can be achieved in the Knudsen effusion cell containing pyrene + 9,10-dibromoanthracene mixtures. By assuming that these components are present as two separate phases,

$$P_{\max} = P_1^0 + P_2^0, \quad (7)$$

where P_1^0 and P_2^0 are the vapor pressure of pure pyrene and 9,10-dibromoanthracene, respectively.

For the pyrene rich mixtures not allowed to lose significant mass (see Fig.8), the vapor pressure follows the Raoult's law prediction at $x_1 = 0.70$, which suggests that a preferred state for pyrene rich mixture systems exists at $x_1 = 0.70$. This state exists at the boundary between region A and B and is the limit of a single phase system.

After mixtures initially at $x_1 = 0.70, 0.75$ and 0.90 lose about 19 %, 35 % and 69 % mass, respectively, the vapor pressure transitions to the Raoult's law prediction curve for $x_1 = 0.35$ (see Fig. 9). The vapor pressure stays at this value for a significant degree of mass loss, which suggests that mixtures of pyrene and 9,10-dibromoanthracene form a stable state at $x_1 = 0.35$ that behaves like an azeotrope. This is consistent with the DSC measurements (Fig. 3) showing that this mixture composition is a stable state. Thereafter the vapor pressure falls to the vapor pressure of 9,10-dibromoanthracene, even though there is 14 ± 1 % pyrene still left in the mixture in region E. Hence, the observed behavior is not that of a true azeotrope.

The vapor pressure behavior of mixtures with moderate initial mole fraction of pyrene is shown in Fig. 10. Mixtures at $x_1 = 0.50$ and 0.60 are in an unstable state. The vapor pressures of these mixtures transition to the Raoult's law prediction value at $x_1 = 0.35$ after they lose about 3 % and 5 % mass, respectively. This again reflects that the mixture with pyrene mole fraction of 0.35 is a stable mixture, whose behavior dominates the solid-vapor equilibrium.

Fig. 11 further demonstrates that a stable state of pyrene and 9,10-dibromoanthracene mixtures exists at $x_1 = 0.35$. Even if the initial pyrene mole fraction in the mixture is lower than 0.35 in region D and E, the stable state 2:1 mixture is formed.

3.6 Sensitivity to mixture preparation condition

Other methods were used to prepare the pyrene + 9,10-dibromoanthracene mixtures, such as slow cooling the melts and ball milling the components together at room temperature. The vapor pressures of pyrene and 9,10-dibromoanthracene mixtures did not depend on the mixture preparation techniques.

4 Conclusion

The pyrene (1) + 9,10-dibromoanthracene (2) system is complicated and non-ideal. It is not a eutectic system. The melting and crystallization studies show that the phase character depends on the composition of the mixture and that a stable state of 9,10-dibromoanthracene + pyrene mixture is formed at a 2:1 molar ratio. Interaction energies calculated from enthalpies of crystallization and XRD data also indicate that the phase behavior depends on mixture composition. The vapor pressure measurements further indicate the existence of the stable 2:1 mixture state. Mixtures with high mole fraction of pyrene also have another stable

state at $x_1 = 0.70$. Additionally, mixtures with $x_1 < 0.35$ can also form the stable 2:1 mixture. The vapor pressure of mixtures with near equimolar composition quickly transitions to that of the Raoult's law prediction curve for a 2:1 mixture.

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Biographies

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Eric Suuberg, Professor of Engineering at Brown University, is co-Director of Brown's Superfund Research Program, and leads its Research Translation Core. He is also a principal editor of the journal *Fuel*. Dr. Suuberg's research interests are in the areas of energy and the environment, including fuels chemistry, coal tars, chars, ash, and on the heterogeneous reduction of NO on carbons. Recently, he has been interested in the thermodynamics of semi-volatile organics (particularly vapor pressures), and leads a new effort at understanding vapor intrusion, in which contaminant vapors move through soil and enter structures built atop or near contaminated sites.

References

- [1]. Roux MV, Temprado M, Chickos JS, Nagano Y. *J Phys Chem Ref Data* 2008;37:1855–1996.
- [2]. Goldfarb JL, Suuberg EM. *J Chem Eng Data* 2008;53:670–676.
- [3]. Goldfarb JL, Suuberg EM. *Environ Toxicol Chem* 2008;27:1244–1249. [PubMed: 18220445]
- [4]. Goldfarb JL, Suuberg EM. *J Chem Thermodyn* 2008;40:460–466. [PubMed: 20376299]
- [5]. Das SS, Singh NP, Agrawal T, Gupta P, Tiwari SN, Singh NB. *Molecular Crystals and Liquid Crystals* 2009;501:107–124.
- [6]. Szczepanik R, Skalmowski W, Bitumen T. *Asphalte, Peché* 1963;14:506, 508–512.
- [7]. Szczepanik R. *Chem. Stosowana Ser. A* 1963;7:621–660.
- [8]. Rastogi RP, Bassi PS. *The Journal of Physical Chemistry* 1964;68:2398–2406.
- [9]. Singh NB, Giri DP, Singh NP. *J Chem Eng Data* 1999;44:605–607.
- [10]. Rai RN, Varma KBR. *Materials Letters* 2000;44:284–293.
- [11]. Singh NB, Srivastava MA, Singh NP. *J Chem Eng Data* 2001;46:47–50.
- [12]. Gupta RK, Singh RA. *Journal of Crystal Growth* 2004;267:340–347.
- [13]. Singh NB, Das SS, Singh NP, Agrawal T. *Journal of Crystal Growth* 2008;310:2878–2884.
- [14]. Aoulmi A, Bouroukba M, Solimando R, Rogalski M. *Fluid Phase Equilib* 1995;110:283–297.
- [15]. Van Metre PC, Mahler BJ. *Environ Sci Technol* 2005;39:5567–5574. [PubMed: 16124288]
- [16]. Paumen ML, Borgman E, Kraak MHS, van Gestel CAM, Admiraal W. *Environ Pollut* 2008;152:225–232. [PubMed: 17644226]
- [17]. Lide, DR.; Baysinger, G.; Kehiaian, HV.; Berger, LI.; Kuchitsu, K. *Handbook of Chemistry and Physics*. 90 ed.. CRC Press; 2010.
- [18]. Pounder FE, Masson I. *J. Chem. Soc* 1934:1357–1360.
- [19]. Oja V, Suuberg EM. *Anal Chem* 1997;69:4619–4626.
- [20]. *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry(GC/MS)*. Varian Inc.; 2001–2004.
- [21]. Spartan' 08. Wavefunction, Inc.; Irvine, CA:

Fig. 1. Phase diagram of pyrene (1) + 9,10-dibromoanthracene (2) mixtures, x_2 is the mole fraction of 9,10-dibromoanthracene in the mixture: —●—, liquidus curve, T; —▲—thaw curve, T.

Fig. 2.
Full DSC scan of a pyrene (1) + 9,10-dibromoanthracene (2) mixture at $x_2 = 0.48$.

Fig. 3. Crystallization temperature and ΔH_{cry} of pyrene (1) + 9,10-dibromoanthracene (2) mixtures, x_2 is the mole fraction of 9,10-dibromoanthracene in the mixture: —•—, ΔH_{cry} ; —▲—, low crystallization temperature, which is the lower temperature peak in the DSC cooling scan, T; - - o - -, high crystallization temperature, which is the higher temperature peak in the DSC cooling scan, T.

Fig. 4. Interaction energy of pyrene (1) and 9,10-dibromoanthracene (2) mixtures, x_2 is the mole fraction of 9,10-dibromoanthracene in the mixture: —▲—, interaction energy, E_{inter} .

Fig. 5.

X-ray diffraction patterns of pure components and mixtures, x_2 is the mole fraction of 9,10-dibromoanthracene in the mixture: 1, pure pyrene (1); 2, pure 9,10-dibromoanthracene (2); E, mixture at edge of region E at $x_2 = 0.75$; D, mixture in region D at $x_2 = 0.65$; A, mixture in region A at $x_2 = 0.25$.

Fig. 6.

Vapor pressure and composition change of a mixture initially at $x_1 = 0.75$ versus sample mass loss, x_1 is the mole fraction of pyrene in the mixture: —, P_{measured} ; —•—, measured x_1 of solid mixture; - - - - -, Raoult's law prediction P at $x_1 = 0.35$ and 333.3K; ———, Raoult's law prediction P at $x_1 = 0.35$ and 358.7K; — - —, Raoult's law prediction P at $x_1 = 0.70$ and 333.3K; — — —, Raoult's law prediction P at $x_1 = 0.70$ and 358.7K.

Fig. 7.

Vapor pressures of pyrene (1), P_1^0 , and 9,10-dibromoanthracene (2), P_2^0 , where $\ln(P_1^0/\text{Pa}) = 30.485 - 11197/T$ and $\ln(P_2^0/\text{Pa}) = 32.125 - 13247/T$: ●, pyrene; ▲, 9,10-dibromanthracene.

Fig. 8.

Vapor pressure measurements of pyrene (1) + 9,10-dibromoanthracene (2) mixtures with high initial mole fraction of pyrene: ----, $P_{\max}$; —, Raoult's law prediction P at $x_1 = 0.70$; ◆, $P_{(1)+(2)}$ at $x_1 = 0.70$; ●, $P_{(1)+(2)}$ at $x_1 = 0.75$; △, $P_{(1)+(2)}$ at $x_1 = 0.90$

Fig. 9.

Vapor pressure measurements of pyrene (1) + 9,10-dibromoanthracene (2) mixtures with high initial mole fraction of pyrene that have reached a stable state: —, Raoult's law prediction P at $x_1 = 0.35$; ◆, $P_{(1)+(2)}$ at $x_1 = 0.70$; ●, $P_{(1)+(2)}$ at $x_1 = 0.75$; △, $P_{(1)+(2)}$ at $x_1 = 0.90$.

Fig. 10.

Vapor pressure measurements of pyrene (1) + 9,10-dibromoanthracene (2) mixtures with moderate initial mole fraction of pyrene: ----, Raoult's law prediction P at $x_1 = 0.70$; —, Raoult's law prediction P at $x_1 = 0.35$; ●, $P_{(1)+(2)}$ at $x_1 = 0.50$; ◆, $P_{(1)+(2)}$ at $x_1 = 0.60$.

Fig. 11.

Vapor pressure measurements of pyrene (1) + 9,10-dibromoanthracene (2) mixtures with low initial mole fraction of pyrene:—, Raoult's law prediction P at $x_1 = 0.35$; ●, $P_{(1)+(2)}$ at $x_1 = 0.25$; ◆, $P_{(1)+(2)}$ at $x_1 = 0.35$.

Table 1

Molecular surface area, volume calculated by space filling model (CPK)

Compound	CPK Area($\text{\AA}^2$)	CPK Volume($\text{\AA}^3$)
pyrene	220.51	220.78
9,10-dibromoanthracene	241.28	237.44