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Recommended vapor pressures for acenaphthylene, fluoranthene, and fluorene

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ABSTRACT

Recommended vapor pressure data for three polycyclic aromatic hydrocarbons, acenaphthylene (CAS RN: 208-96-8), fluoranthene (CAS RN: 206-44-0), and fluorene (CAS RN: 86-73-7), were developed by the simultaneous correlation of vapor pressure and related thermal data (heat capacities of condensed phases, ideal-gas heat capacities and calorimetrically determined enthalpies of sublimation). For acenaphthylene, new experimental data on vapor pressure, enthalpy and temperature of fusion and solid and liquid heat capacity were obtained. New solid heat capacity data were measured also for fluorene. For fluoranthene, relevant thermodynamic data were taken from the literature. The thermodynamic properties in the ideal gaseous state were calculated using the methods of statistical thermodynamics based on experimental as well as calculated fundamental vibrational frequencies and molecular structure data. Supercooled vapor pressures were calculated using the relations suggested for polycyclic aromatic hydrocarbons in the literature. Comparisons with literature values are shown for all measured and derived properties.

1. Introduction

Compounds belonging into a class of organic compounds called polycyclic aromatic hydrocarbons (PAHs) are crystalline solids at room temperature and they are known for their persistence in the environment and toxicity for aquatic life. Some of them are confirmed carcinogens and mutagens, and others are probable human carcinogens. A significant amount of PAHs is contained in fossil fuels and they are also formed by incomplete combustion of carbon-containing materials [1,2]. Because of their negative influence on the environment and human health, PAHs are subject of regulation and monitoring by some governmental bodies. Well-known is e. g. an U. S. Environmental Protection Agency (EPA) list of 16 PAHs, which are called as priority pollutants (this list originated in the 1970s and nowadays it is a subject of discussion whether it should be revised [3–5]). For understanding and modeling the fate of pollutants in the environment, basic thermophysical properties of given compounds are needed. Vapor pressure, the property discussed in this work, controls the tendency of chemicals to partition into the atmosphere [6]. Besides the modeling of fate of pollutants in the environment, interest in the thermophysical properties of pure PAHs exists for thermodynamic property models for heavy oils and bitumen [7].

Though extensive reviews were published for PAHs vapor and sublimation pressures [8] and for enthalpies of phase transitions [9], the situation is not satisfactory for a number of individual polycyclic aromatic hydrocarbons. Interlaboratory agreement is often poor for both sublimation pressures and enthalpies, which is not surprising for compounds of such a low volatility. This work is a continuation of our effort to establish reliable vapor pressure data for PAHs [10,11]. All three compounds studied (acenaphthylene, fluoranthene and fluorene) belong to the abovementioned list of EPA priority pollutants.

In this work, we first assessed all available literature vapor pressure data and examined their consistency with calorimetrically determined sublimation or vaporization enthalpies and heat capacities of condensed phases and ideal gas. Literature review and consistency tests revealed that new vapor pressure data in the low pressure region for acenaphthylene and heat capacity for liquid acenaphthylene and solid fluorene were needed. These data were experimentally determined in this work. Also, thermodynamic properties in the ideal gaseous state for all the studied compounds were calculated using the methods of statistical thermodynamics. We employed both the experimental and calculated fundamental

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vibrational frequencies and structural parameters and compared the obtained results. Consequently, recommended vapor pressure data for acenaphthylene, fluoranthene, and fluorene were developed by the simultaneous correlation of selected vapor pressure and related thermal data. As vapor pressure of supercooled liquid $p_{\rm L}$ is required by models describing distribution of chemicals in the environment [6], this quantity was calculated using semiempiric relation suggested for polycyclic aromatic hydrocarbons in the literature (exact thermodynamic determination is not possible).

2. Simultaneous treatment of vapor pressures and related thermal data (SimCor method)

Vapor pressure p, enthalpy of sublimation/vaporization $\Delta_{\rm cd}^{\rm g}H_{\rm m}$ and the difference between ideal-gas heat capacity and heat capacity of condensed phase $\Delta_{\rm cd}^{\rm g}C_{p,\rm m}^0 = C_{p,\rm m}^{\rm g0} - C_{p,\rm m}^{\rm cd}$ are linked by exact thermodynamic relationships

$$RT^2(\mathrm{d}\ln p/\mathrm{d}T)_{\rm sat} = \Delta_{\rm cd}^{\rm g}H_{\rm m}\Big/\Delta_{\rm cd}^{\rm g}z = \Delta H' \qquad (1)$$

$$\begin{aligned}\left(\mathrm{d}\Delta H'\big/\mathrm{d}T\right)_{\rm sat} &= R\left\{\mathrm{d}\left[T^2(\mathrm{d}\ln p/\mathrm{d}T)\right]\big/\mathrm{d}T\right\}_{\rm sat} = \Delta C' \\ &= \Delta_{\rm cd}^{\rm g}C_{p,\rm m}^0 + [pVT\ \text{correction}]\end{aligned} \qquad (2)$$

where subscript ‘sat’ denotes a derivative along the saturation line, R is the molar gas constant ($R = 8.3144598$ J K^{-1} mol^{-1} [12]). $\Delta_{\rm cd}^{\rm g}z$ stands for the difference between the compressibility factors of the coexisting phases. $\Delta H'$ and $\Delta C'$ are auxiliary quantities which can be calculated using Eq. (1) and Eq. (2) either from the vapor pressure correlating equation (by substituting the derivative $\mathrm{d}\ln p/\mathrm{d}T$ into Eqs. (1) and (2)) or from experimental values of enthalpy of sublimation/vaporization $\Delta_{\rm cd}^{\rm g}H_{\rm m}$ and $\Delta_{\rm cd}^{\rm g}C_{p,\rm m}^0$ calculated from experimental data by combining heat capacity of ideal gas $C_{p,\rm m}^{\rm g0}$ and calorimetric values of heat capacity of condensed phase $C_{p,\rm m}^{\rm cd}$. The possibility to calculate $\Delta H'$ and $\Delta C'$ both from the experimental thermal data and vapor pressure data and from a vapor pressure correlating equation means that after selecting a suitable relationship describing p vs. T it is possible to correlate simultaneously experimental vapor pressures p, enthalpies of sublimation/vaporization $\Delta_{\rm cd}^{\rm g}H_{\rm m}$ and heat capacity difference $\Delta_{\rm cd}^{\rm g}C_{p,\rm m}^0$ as a function of temperature. A detailed description of the SimCor procedure can be found in Ref. [13] and also in the Supplementary Information (SI). The Cox equation was found to be the most adequate for describing simultaneously vapor pressure and related thermal data as a function of temperature down to the triple point [14]. The Cox equation has the form [15]

$$\ln\frac{p}{p^0} = \left(1 - \frac{T^0/\mathrm{K}}{T/\mathrm{K}}\right)\exp\left(\sum_{i=0}^{n}A_i(T/\mathrm{K})^i\right) \qquad (3)$$

where p is the vapor pressure, T is the temperature, T^0 and p^0 is the temperature and pressure of an arbitrarily chosen reference point and A_i are correlation parameters.

The SimCor method was thoroughly tested in our laboratory [14] and used to obtain recommended vapor pressure for several crystalline and liquid compounds (see SI and references therein).

3. Experimental section

3.1. Materials

Commercially available acenaphthylene and fluorene were used; the sample characteristics are summarized in Table 1. The compounds were used as received without further purification.

Table 1
Sample description table.

Compound	CAS number	Supplier	Mole fraction purity[a]
Acenaphthylene	208-96-8	Supelco	0.9952
Fluorene	86-73-7	Aldrich	0.9925

[a] Gas-liquid chromatography analysis by Hewlett-Packard 6890 gas chromatograph equipped with column HP5 cross-linked 5% PHME siloxane, length 30 m, film thickness 0.25 μm, i.d. 0.32 mm, and FID detector.

3.2. Vapor pressure measurements

The vapor pressure measurements were performed using the static method with an apparatus internally denoted as STAT8, which was previously described in detail [16]. The pressure was measured by absolute capacitance diaphragm gauge (CDG) Barocel 659 (Edwards, UK) with the measuring upper limit of 1333 Pa, which was kept at 396 K by an internal temperature controller. The sample temperature was measured by a secondary reference thermistor silicon-bead probe Hart 5611A (Fluke, USA) in a four-wire connection. The resulting standard uncertainty of the pressure measurements by the CDGs was $u(p_{\rm CDG}) = 0.001p_{\rm CDG}$ and that of the sample temperature was $u(T) = 0.01$ K, which is insignificant in the pressure range investigated in this work. The combined expanded uncertainty of vapor pressure measurements $U_{\rm c}(p)$ (0.95 level of confidence, $k = 2$) using the STAT8 apparatus was estimated based on the deviations of experimental data points from the recommended vapor pressure data for naphthalene [11], ferrocene [17], and n-decane [13]. $U_{\rm c}(p)$ can be described as a function of the measured pressure as $U_{\rm c}(p/\mathrm{Pa}) = 0.01(p/\mathrm{Pa}) + 0.05$.

3.3. Heat capacity measurements

The Tian-Calvet calorimeter (SETARAM μDSC IIIa, France) was used for the heat capacity determination of solid fluorene in the temperature range 263 K–358 K. A detailed description of the calorimeter and its calibration was published previously [7,18]. The power-compensated differential scanning calorimeter (Perkin-Elmer 8500, USA) was used for the heat capacity determination of solid and liquid acenaphthylene in the temperature range 304 K–332 K and 368 K–387 K, respectively. StepScan method with a step of 2 K and heating rate 2 K min^{-1} was employed. The data were evaluated in a standard three-run procedure (sample, blank, and sapphire, see Ref. [19]) using our own code as the software Pyris 11 provided by PerkinElmer does not offer this option. The combined expanded uncertainty (0.95 level of confidence) of the heat capacity measurements is estimated to be $U_{\rm c}(C_{p,\rm m}) = 0.01\ C_{p,\rm m}$ and $U_{\rm c}(C_{p,\rm m}) = 0.03\ C_{p,\rm m}$ for SETARAM μDSC IIIa and PerkinElmer 8500, respectively.

The saturated molar heat capacities $C_{\rm sat,m}$ obtained in this work are identical to isobaric molar phase heat capacities $C_{p,\rm m}$ in the temperature range studied as it is not necessary to make a clear distinction between $C_{p,\rm m}$ along the saturation curve and $C_{\rm sat,m}$ below 0.9 $T_{\rm b}$, where $T_{\rm b}$ is the normal boiling temperature [20].

3.4. Enthalpy and temperature of fusion measurements

For determination of temperature and enthalpy of fusion of acenaphthylene, the power-compensation differential scanning calorimeter PerkinElmer 8500 (PerkinElmer, USA) and heat-flux differential scanning calorimeter TA Q1000 (Thermal Analysis, USA) were used. The enthalpy and temperature calibration of calorimeters was performed using water, gallium, indium, naphthalene, and tin. The combined expanded uncertainty (0.95 level of confidence) of temperature and enthalpy determination was