Supercooled Liquid Vapor Pressures of the Polycyclic Aromatic Hydrocarbons

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The vapor pressure of the supercooled liquid (P_L) for 35 unsubstituted and alkylated polycyclic aromatic hydrocarbons (PAHs) was determined as a function of temperature using a gas chromatographic retention time technique. Pyrene and 1,2-benzanthracene, two compounds with well-established temperature-dependent vapor pressures, served as standard reference compounds. The method was calibrated with nine PAHs for which the vapor pressures at 25 °C are known from measurements relying on gas saturation and gas effusion techniques. Enthalpies of vaporization $\Delta_{vap}H$ were also determined. The P_L data were evaluated by comparison with several sets of published data and found to be reliable. For most of the investigated PAHs, a strong linear relationship between log P_L and molecular mass exists, ranging over more than 9 orders of magnitude. However, PAHs with bulky substituents, such as phenyl- and *tert*-butyl-groups, have a higher vapor pressure than would be expected on the basis of molecular mass, presumably because of the lack of molecular planarity.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important group of environmental contaminants. Many PAHs are semivolatile, that is, occur in the gas phase and sorbed to aerosol particles within the environmental temperature range. That partitioning process, which influences environmental fate and deposition in the lungs, is often described with an empirical relationship based on the supercooled liquid vapor pressure P_L.[1] Here we report the P_L for more than 30 unsubstituted and alkylated PAHs determined with a technique relying on gas chromatographic (GC) retention times.[2] Although many vapor pressure measurements for PAHs have been reported and high-quality data already exist for many substances, the study was motivated by the following reasons:

(1) For some PAHs, in particular many alkylated PAHs, no measured vapor pressure data exist. For many others, the temperature dependence of the vapor pressure has not been established.

(2) Most classical methods for measuring vapor pressure, such as gas saturation and effusion, yield the vapor pressure of the solid substance, whereas the GC retention time method directly gives the vapor pressure of the supercooled liquid.

(3) Most studies measure the vapor pressure for a select group of PAHs, yet for developing quantitative structure property relationships, a large and consistent data set is of utmost importance. The combination of data from various studies and laboratories is not always warranted.

The GC retention time method by Bidleman[2] was chosen, because it allows the relatively rapid determination of the temperature-dependent vapor pressures of a large number of compounds. Small quantities of the substances are sufficient, and a very high purity is not required. On the basis of a comprehensive review, Delle Site recently concluded that this method “can be recommended as one of the most suitable [methods] for the determination of the vapor pressure of low volatility compounds.”[3] The method’s success and reliability, however, are dependent on the availability of high-quality vapor pressure data for some related compounds to serve as standard reference and calibration compounds. Fortunately, no shortage of such data exist for the PAHs.

Experimental Section

Chemicals. PAHs with 99% or greater purity were obtained from Aldrich (Oakville, Ontario, Canada), Eastman Kodak (Rochester, NY), Fisher Scientific (Nepean, Ontario, Canada), and K&K Laboratories (Plainsview, NY). The solutions of PAHs were prepared by dissolving a small amount of chemical into HPLC grade hexane or isooctane (Caledon Laboratories, Ontario, Canada). The stock solutions were further diluted with hexane.

Instrumentation. A Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a DB-1 capillary column (0.32 mm i.d. × 1.0 m long, 0.25 μm film thickness, J & W Scientific, Folsom, CA) was used to determine isothermal retention times at six to seven temperatures within the range 50 to 200 °C. The injection port and detector were kept at 250 °C, the carrier gas (He) had a flow rate of approximately 4 mL·min^{-1}, and the split ratio was 10:1.

Data Analysis. Supercooled liquid vapor pressures P_L were obtained from the gas chromatographic retention times following the procedure described by Bidleman,[2] and Hinckley et al.[4] Specifically, for each analyte, a vapor pressure P_{GC} at 25 °C was calculated using

$$\ln(P_{GC}/\mathrm{Pa}) = (\Delta_{vap}H/\Delta_{vap}H_{ref})\ln(P_{Lref}/\mathrm{Pa}) + C \quad (1)$$

where P_{Lref} and $\Delta_{vap}H_{ref}$ refer to the well-established liquid-

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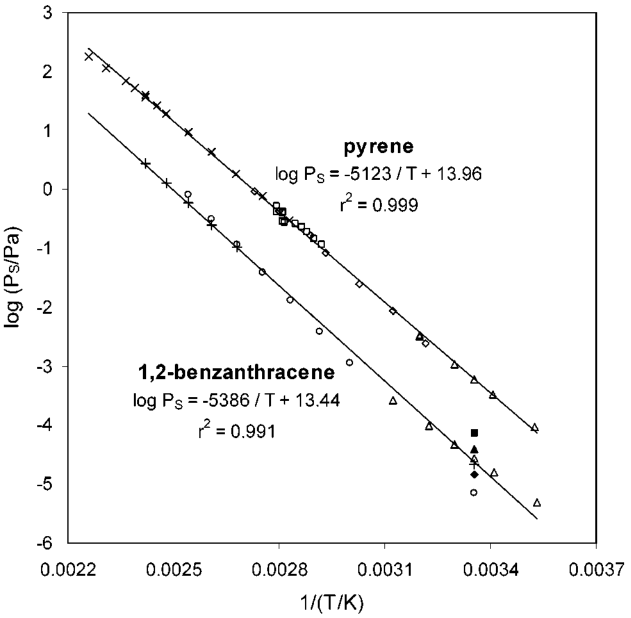

Figure 1. Temperature dependence of the solid vapor pressures P_S of the standard reference compounds pyrene and 1,2-benzanthracene based on data reported in ref 5, □; ref 6, △; ref 7, ×; ref 8, ◇; ref 9, ○; ref 10, +; ref 11, ▲; ref 12, ◆; and ref 13, ■.

phase vapor pressure at 25 °C and the enthalpy of vaporization of a standard reference compound. The enthalpies of vaporization are assumed to be constant over the temperature range from 25 °C to the temperatures of the GC retention time measurements. The enthalpy ratio $\Delta_{vap}H/\Delta_{vap}H_{ref}$ and the constant C in eq 1 were obtained by linearly regressing the logarithm of the ratios of the measured isothermal GC retention times t_R/t_{Rref} at each temperature against the logarithm of the vapor pressure of the reference compound at that temperature using the relation[2]

$$\ln(t_R/t_{Rref}) = [1 - (\Delta_{vap}H/\Delta_{vap}H_{ref})] \ln(P_{Lref}/\mathrm{Pa}) - C \quad (2)$$

Equation 2 assumes that the infinite dilution activity coefficients in the stationary phase are the same for both the analyte and the reference compound.[4] As this is an approximation, P_{GC} is not always identical to the vapor pressure of the (supercooled) liquid P_L, and a calibration of the method with closely related compounds is advisable.[2,4]

Vapor Pressure and Enthalpy of Vaporization for the Standard Reference Compounds. In the current study, pyrene and 1,2-benzanthracene served as standard reference compounds. Several determinations of the temperature-dependent vapor pressure have been reported for pyrene[5−8] and 1,2-benzanthracene.[6,9−13] All observed solid vapor pressure data P_S from these studies were regressed against reciprocal absolute temperature (Figure 1). The following equations were obtained

pyrene

$$\log(P_S/\mathrm{Pa}) = 13.96 - 5123(T/\mathrm{K})^{-1} \qquad r^2 = 0.999 \quad (3)$$

1,2-benzanthracene

$$\log(P_S/\mathrm{Pa}) = 13.44 - 5386(T/\mathrm{K})^{-1} \qquad r^2 = 0.991 \quad (4)$$

P_S was converted to P_L using the equation

$$P_L = P_S/\exp[(\Delta_{fus}S/R)(1 - T_{mp}/T)] \quad (5)$$

and values for the entropy of fusion[14] $\Delta_{fus}S$ of 43.36 and 49.23 J·K^{-1}·mol^{-1} and melting point temperature[14] T_{mp} of 423.8 and 434.3 K for pyrene and 1,2-benzanthracene, respectively.

pyrene

$$\log(P_L/\mathrm{Pa}) = 11.\ 70 - 4164(T/\mathrm{K})^{-1} \qquad r^2 = 0.999 \quad (6)$$

1,2-benzanthracene

$$\log(P_L/\mathrm{Pa}) = 10.87 - 4269(T/\mathrm{K})^{-1} \qquad r^2 = 0.991 \quad (7)$$

From the slopes of these relationships, we derive enthalpies of vaporization $\Delta_{vap}H$ of −79.7 for pyrene and −81.7 kJ·mol^{-1} for 1,2-benzanthracene.

Vapor Pressures of the Calibration Compounds. For the calibration, we employed nine PAHs with well-established vapor pressures at 25 °C. The selection of these nine PAHs was based on the following considerations: (a) the solid vapor pressure P_S at 25 °C had been determined by means other than the GC retention time technique, namely effusion and saturation column techniques, (b) the P_S values for these PAHs could be considered reliable, because several studies had obtained very similar results, (c) compound specific values for the entropy of fusion $\Delta_{fus}S$ and the melting point temperature T_{mp} are available,[14] so that a conversion from P_S to P_L using eq 5 is possible, (d) the vapor pressure of the calibration compounds covers a wide range. The literature data used in the construction of the calibration curve are listed in Table 1.

The P_{GC} values for these nine PAHs were determined as described above and regressed against the vapor pressure of the supercooled liquid P_L given in Table 1. The following relationship was obtained (Figure 2):

$$\log(P_L/\mathrm{Pa}) = (1.339 \pm 0.012) \log(P_{GC}/\mathrm{Pa}) + (0.674 \pm 0.017) \qquad r^2 = 0.9968 \quad (8)$$

Although the relationship between the GC derived vapor pressure P_{GC} and the P_L values calculated from P_S values taken from the literature is highly linear over 7 orders of magnitude, the slope is very different from 1 and the intercept different from 0. Whereas for the more volatile PAHs P_{GC} is lower than P_L, P_{GC} is higher than P_L for the very involatile PAHs. This strongly emphasizes the need for the calibration. The high r^2 on the other hand suggests that P_L values which are calculated from P_{GC} values using eq 8 are reliable.

Determination of Vapor Pressure for 26 PAHs. For 26 PAHs, P_{GC} was determined from gas chromatographic retention times using the procedure given above. The P_L values at 25 °C for these isomers were then calculated using eq 8.

Determination of the Enthalpy of Vaporization. For all investigated PAHs, the enthalpy of vaporization $\Delta_{vap}H$ of the analytes was derived from the enthalpy of vaporization of the reference compounds $\Delta_{vap}H_{ref}$ and the enthalpy ratios obtained in the regression of eq 2. To facilitate the calculation of vapor pressure at any temperature, the slope m_L and intercept b_L of the relationship

$$\log(P_L/\mathrm{Pa}) = m_L/(T/\mathrm{K}) + b_L \quad (9)$$

were also estimated.

Results

For the 35 investigated compounds, Table 2 lists the measured vapor pressures P_{GC} and P_L at 25 °C, the

Table 1. Solid Vapor Pressures P_S at 25 °C for Nine PAHs Measured by Various Methods, the Literature References for These Data, and the P_L Values at 25 °C Derived from These Using Eq 5 with Melting Point Temperatures T_{mp} and Entropies of Fusion $\Delta_{fus}S$ from ref 14

compd	T_{mp} / K	$\Delta_{fus}S$ / J·K^{-1}·mol^{-1}	P_L / Pa	P_S / Pa	ref
naphthalene	353.4	53.75	47.1	14.2	16
			35.8	10.8	5
			40.6	12.26	17
			36.1	10.9	18
			34.5	10.42	19
			35.5	10.7	20
			34.5	10.4	6
biphenyl	341.5	54.81	3.39	1.3	21
			3.32	1.273	5
			3.68	1.41	17
			3.10	1.19	22
			2.69	1.03	23
acenaphthene	366.6	58.55	1.88	0.373	24
			1.45	0.287	6
			1.45	0.287	25
			1.19	0.237	20
			1.61	0.319	20
fluorene	387.9	50.48	0.541	0.087	5
			0.790	0.127	24
			0.588	0.0946	26
			0.491	0.079	6
			0.498	0.08	25
			0.544	0.0875	20
			0.529	0.085	7
phenanthrene	372.4	44.83	0.0869	0.0227	5
			0.101	0.0263	27
			0.0689	0.018	13
			0.0609	0.0159	6
			0.0613	0.016	25
			0.0754	0.0197	8
anthracene	488.9	60.08	0.103	10.14×10^{-4}	16
			0.0846	8.31×10^{-4}	5
			0.0878	8.62×10^{-4}	10
			0.0921	9.04×10^{-4}	28
			0.0764	7.50×10^{-4}	13
			0.0803	7.89×10^{-4}	6
fluoranthene	383.4	48.89	3.58×10^{-3}	6.67×10^{-4}	9
			6.50×10^{-3}	1.21×10^{-3}	6
			6.66×10^{-3}	1.24×10^{-3}	25
chrysene	531.4	55.5	1.06×10^{-4}	5.70×10^{-7}	13
			1.56×10^{-4}	8.40×10^{-7}	9
perylene	551	57.87	6.74×10^{-6}	1.84×10^{-8}	8

enthalpies of vaporization $\Delta_{vap}H$, and the intercepts b_L and slopes m_L for eq 9. The retention time measurements were very reproducible, as seen from the small standard deviation of P_{GC}, resulting from two to three replicate injections. The standard deviation of the P_L values, which is less than 0.1 log units in all cases, was estimated by error propagation from the standard deviation of P_{GC} and the standard error of the slope and intercept of eq 9. The relative standard deviation of P_L is around 10%, being lower (around 5%) for compounds with a P_L in the middle of the investigated vapor pressure range and higher (up to 18%) for compounds at the upper and lower extremes of that range. The error in P_L is dominated by the error in the parameters of the calibration equation rather than the error in the retention time measurement.

Discussion

Evaluation of the Vapor Pressure Data at 25 °C. Evaluation of the data obtained with this method was complicated by the fact that many of the PAHs for which high-quality vapor pressure data exist were employed either as a standard reference compound or a calibration compound. Nevertheless, we sought to evaluate the new data by comparison with previously reported measurements.

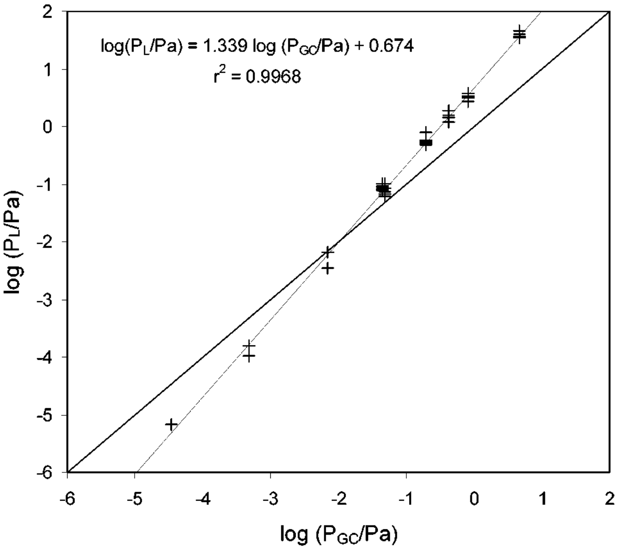

Figure 2. Relationship between the GC determined vapor pressure P_{GC} at 25 °C and the vapor pressure of the supercooled liquid P_L at 25 °C derived from data reported in the literature for nine PAHs (data given in Table 1). The solid line represents the 1:1 relationship.

The first comparison was with data that had been obtained with the classical techniques of gas saturation and effusion but had not been used in the calibration. The respective literature data for nine compounds are listed in Table 3. Again, the values for the solid reported in the literature were converted to P_L using eq 5. Our P_L data (Table 2) and those in Table 3 are typically within 0.2 log units of each other. The largest disagreement (2,3-benzofluorene) is half a log unit. At least partially, the observed discrepancies may be due to uncertain entropy of fusion values, which can result in large uncertainties of calculated P_L values for compounds with high melting points. Overall, the agreement for the 11 data points is good, indicated by a high r^2, a slope close to 1, and an intercept close to 0 of the regression between our values and those in Table 3:

$$\log(P_L/\mathrm{Pa})_{\mathrm{Table3}} = 1.0316 \log(P_L/\mathrm{Pa})_{\mathrm{this\ study}} + 0.0078 \qquad r^2 = 0.9955 \quad (10)$$

The second comparison was with vapor pressure data reported by Yamasaki et al.[15] Those data had been obtained using the same GC retention time method used in this study. However, no calibration had been performed, so the reported vapor pressures are P_{GC} values. A direct comparison of the P_{GC} values by Yamasaki et al.[15] with those from this study is not possible, because P_{GC} values are dependent on the standard reference compound[4] and the previous study had used nonadecane rather than a PAH for that purpose. For that reason, we first calibrated the P_{GC} data by Yamasaki et al.[15] using the same procedure as described above and then compared the resulting P_L values with those from this study. Details of the calibration are given in the Supporting Information. The agreement between the P_L values for the 14 PAHs measured in both studies was excellent. The log P_L values differ by usually less than 0.1 log units; the highest discrepancy is 0.23 log units for 2,3-benzofluoranthene. The high r^2, the slope close to 1, and the intercept close to 0 in the following regression

Table 2. GC Determined Vapor Pressure P_{GC} at 25 °C with Standard Deviation, Super-Cooled Liquid Vapor Pressure P_L at 25 °C, and Slope m_L and Intercept b_L of Eq 9 for 35 PAHs[a]

compound	n	ref	P_{GC}/Pa	P_L/Pa	m_L	b_L	$\Delta_{vap}H$/kJ·mol^{-1}
calibration compounds							
naphthalene	3	P	4.65 ± 0.30	37.0 ± 3.6	−2930	11.39	−56.1
biphenyl	2	P	0.822 ± 0.064	3.63 ± 0.41	−3265	11.51	−62.5
acenaphthene	3	P	0.428 ± 0.013	1.52 ± 0.09	−3337	11.37	−63.9
fluorene	2	P	0.194 ± 0.004	0.526 ± 0.027	−3492	11.43	−66.9
phenanthrene	3	P	0.0475 ± 0.0002	0.0799 ± 0.0043	−3768	11.54	−72.2
anthracene	2	P	0.0442 ± 0.0003	0.0724 ± 0.0039	−3780	11.54	−72.4
fluoranthene	3	P	$(6.87 \pm 0.14) \times 10^{-3}$	$(5.98 \pm 0.45) \times 10^{-3}$	−4141	11.66	−79.3
chrysene	2	P	$(4.81 \pm 0.02) \times 10^{-4}$	$(1.70 \pm 0.17) \times 10^{-4}$	−4679	11.92	−89.6
perylene	3	B	$(3.39 \pm 0.03) \times 10^{-5}$	$(4.88 \pm 0.63) \times 10^{-6}$	−4694	10.43	−89.9
remaining compounds							
1-methylnaphthalene	2	P	1.28 ± 0.10	6.55 ± 0.75	−3258	11.74	−62.4
2-ethylnaphthalene	2	P	0.633 ± 0.013	2.56 ± 0.12	−3381	11.75	−64.7
1,6-dimethylnaphthalene	2	P	0.604 ± 0.010	2.40 ± 0.11	−3319	11.51	−63.6
1,5-dimethylnaphthalene	3	P	0.513 ± 0.020	1.93 ± 0.12	−3346	11.51	−64.1
dibenzofuran	2	P	0.302 ± 0.005	0.952 ± 0.045	−3456	11.57	−66.2
bibenzyl	3	P	0.249 ± 0.003	0.734 ± 0.033	−3522	11.68	−67.4
2,3,5-trimethylnaphthalene	2	P	0.176 ± 0.004	0.460 ± 0.025	−3581	11.67	−68.6
1-methylfluorene	3	P	0.0708 ± 0.0010	0.136 ± 0.007	−3711	11.58	−71.1
2-methylanthracene	3	P	0.0173 ± 0.0001	0.0207 ± 0.0013	−3976	11.65	−76.1
1-methylphenanthrene	2	P	0.0160 ± 0.0002	0.0186 ± 0.0012	−3987	11.64	−76.3
2-(*tert*-butyl)anthracene	3	P	$(2.31 \pm 0.11) \times 10^{-3}$	$(1.39 \pm 0.14) \times 10^{-3}$	−4411	11.94	−84.5
1,2-benzofluorene	3	P	$(2.27 \pm 0.01) \times 10^{-3}$	$(1.36 \pm 0.11) \times 10^{-3}$	−4373	11.80	−83.7
2,3-benzofluorene	2	P	$(1.90 \pm 0.01) \times 10^{-3}$	$(1.07 \pm 0.09) \times 10^{-3}$	−4423	11.86	−84.7
p-terphenyl	2	P	$(1.14 \pm 0.01) \times 10^{-3}$	$(5.40 \pm 0.49) \times 10^{-4}$	−4135	10.60	−79.2
triphenylene	1	B	6.20×10^{-4}	2.39×10^{-4}	−4624	11.89	−88.5
9-phenylanthrancene	3	P	$(3.97 \pm 0.02) \times 10^{-4}$	$(1.31 \pm 0.13) \times 10^{-4}$	−4785	12.17	−91.6
8,9-benzofluoranthene	3	B	$(5.34 \pm 0.02) \times 10^{-5}$	$(8.96 \pm 1.11) \times 10^{-6}$	−4623	10.46	−88.5
2,3-benzofluoranthene	2	B	$(4.70 \pm 0.11) \times 10^{-5}$	$(7.55 \pm 0.97) \times 10^{-6}$	−4682	10.58	−89.7
7,12-dimethyl-1,2-benzanthracene	3	B	$(4.15 \pm 0.09) \times 10^{-5}$	$(6.38 \pm 0.83) \times 10^{-6}$	−4643	10.38	−88.9
3,4-benzopyrene	3	B	$(3.91 \pm 0.03) \times 10^{-5}$	$(5.90 \pm 0.75) \times 10^{-6}$	−4755	10.72	−91.0
3-methylcholanthrene	3	B	$(1.39 \pm 0.01) \times 10^{-5}$	$(1.48 \pm 0.21) \times 10^{-6}$	−4901	10.61	−93.8
1,12-benzoperylene	3	B	$(5.52 \pm 0.10) \times 10^{-6}$	$(4.28 \pm 0.65) \times 10^{-7}$	−5018	10.46	−96.1
1,2,3,4-dibenzanthracene	3	B	$(4.69 \pm 0.04) \times 10^{-6}$	$(3.44 \pm 0.52) \times 10^{-7}$	−5094	10.62	−97.5
1,2,5,6-dibenzanthracene	2	B	$(3.70 \pm 0.22) \times 10^{-6}$	$(2.51 \pm 0.44) \times 10^{-7}$	−5193	10.82	−99.4
9,10-diphenylanthracene	2	B	$(2.86 \pm 0.09) \times 10^{-6}$	$(1.78 \pm 0.29) \times 10^{-7}$	−5365	11.24	−102.7
coronene	2	B	$(6.71 \pm 0.18) \times 10^{-7}$	$(2.55 \pm 0.45) \times 10^{-8}$	−5446	10.67	−104.2

[a] Also given are the enthalpies of vaporization $\Delta_{vap}H$, the number of replicate retention time measurements n, and the reference compound (P = pyrene, B = 1,2-benzanthracene).

Table 3. Melting Point Temperatures T_{mp}, Entropies of Fusion $\Delta_{fus}S$, Solid and Liquid Phase Vapor Pressures P_S and P_L at 25 °C for Selected PAHs, and the Literature References for These Data[a]

compound	T_{mp}/K	ref	$\Delta_{fus}S$/J·K^{-1}·mol^{-1}	ref	P_S/Pa	ref	P_L/Pa	ref
1-methylnaphthalene	242.7	14					8.82	27
							8.93	7
2-ethylnaphthalene	242.7	14					3.71	7
dibenzofuran	359.7	14	54.0	29	0.35	29	1.34	*
bibenzyl	325.4	14	94.2	30	0.198	21	0.557	*
2,3-benzofluorene	489.7	14	47.78	14	7.37×10^{-6}	8	2.96×10^{-4}	*
triphenylene	471	14	52.53	14	2.30×10^{-6}	13	8.96×10^{-5}	*
3,4-benzopyrene	454.2	14	38.13	14	7.32×10^{-7}	12	8.07×10^{-6}	*
1,2,5,6-dibenzanthracene	544.2	14	57.26	14	3.70×10^{-10}	13	1.09×10^{-7}	*
coronene	710.5	14	27.02	14	1.95×10^{-10}	12	1.75×10^{-8}	*
					2.89×10^{-10}	8	2.59×10^{-8}	*

[a] The data marked * were derived using eq 5.

equation further suggest a good agreement, as given by

$$\log(P_L/\mathrm{Pa})_{\text{Yamasaki et al.}} = 0.9903 \log(P_L/\mathrm{Pa})_{\text{this study}} + 0.0018 \qquad r^2 = 0.9989 \quad (11)$$

The third comparison was with supercooled liquid vapor pressure values reported by Hinckley et al.[4] This study had also used the GC retention time method, relying on eicosane and *p,p′*-DDT as standard reference compounds and calibrating the P_{GC} data with a large and diverse set of semivolatile compounds. Different log P_L versus log P_{GC} calibration equations, and therefore P_L values, were presented in this paper depending on (a) the choice of standard reference compound and (b) whether the literature P_S values were converted to P_L values using measured or default values for $\Delta_{fus}S$ (see Table 4 in ref 4). We chose to compare our data with the average of the P_L values derived using eicosane and *p,p′*-DDT as reference compounds and the measured entropies of fusion. A large discrepancy was found for the P_L of 3,4-benzopyrene ($\log(P_L/\mathrm{Pa})_{\text{this study}} = -5.23$ vs $\log(P_L/\mathrm{Pa})_{\text{Hinckley}} = -4.34$). However, Hinckley et al.[4] had listed a literature value for 3,4-benzopyrene of $\log(P_L/\mathrm{Pa}) = -5.14$, which agrees very well with our value of −5.23, suggesting that it is more reliable than the value of −4.34 measured by Hinckley et al.[4] When this outlier is eliminated, the agreement between the remaining nine P_L values from both studies is better, although we note that the P_L values by Hinckley et al.[4] are consistently higher

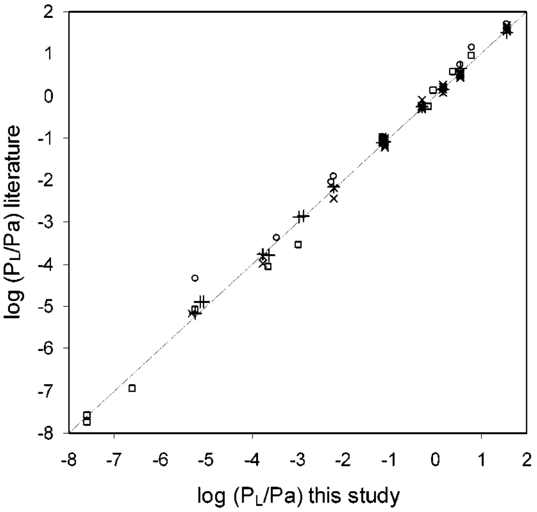

Figure 3. Comparison of the vapor pressure P_L at 25 °C determined in this study with various sets of published values (literature data from Table 1, used in the calibration (×); literature data from Table 3, not used in the calibration (□); data from ref 15, calibrated (+); data from ref 4 (○)). The line represents the 1:1 relationship.

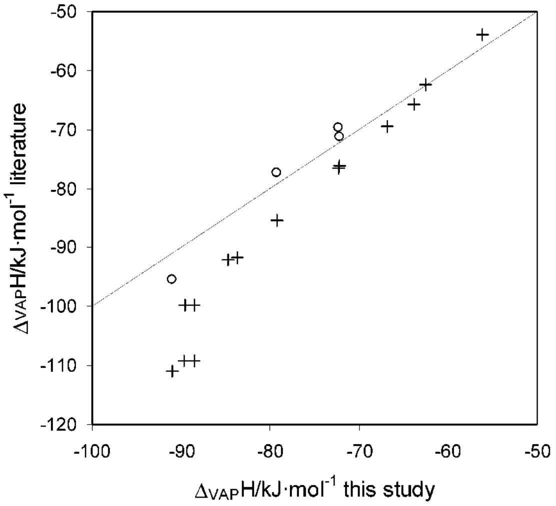

Figure 4. Comparison of the enthalpies of vaporization $\Delta_{vap}H$ determined in this study with those reported in ref 15 (+) and ref 4 (○). The line represents the 1:1 relationship.

by about 0.17 log units than our values.

$$\log(P_L/\mathrm{Pa})_{\text{Hinckley et al.}} = 1.0057 \log(P_L/\mathrm{Pa})_{\text{this study}} + 0.1726 \qquad r^2 = 0.9966 \quad (12)$$

The comparison with the three sets of data is summarized in Figure 3, which plots the log P_L from this study against the log P_L from the literature. Also included in this graphical comparison are the P_L values used in the calibration (Table 1). Most of the points on this graph fall onto or very close to the 1:1 line, suggesting that the P_L values from this study are comparable to those reported previously.

Evaluation of the Enthalpy of Vaporization Data. The enthalpy of vaporization values from this study were compared with those reported by Yamasaki et al.[15] and Hinckley et al.[4] in Figure 4. The latter study did not report $\Delta_{vap}H$ values, but they can be estimated from the slopes given for relationships defined as in eq 9 (Table 7 in ref 4). Whereas there is reasonably good agreement for the $\Delta_{vap}H$ values of the smaller PAHs, Yamasaki et al.[15]'s $\Delta_{vap}H$ values for the heavier PAHs are lower than those in our study or those that can be derived from the slopes by Hinckley et al.[4] (not shown). In the GC retention time technique the values obtained for $\Delta_{vap}H$ are dependent on the $\Delta_{vap}H$ of the reference compound. Our study used PAHs; the other studies used *p,p′*-DDT or a long chain alkane for that purpose.

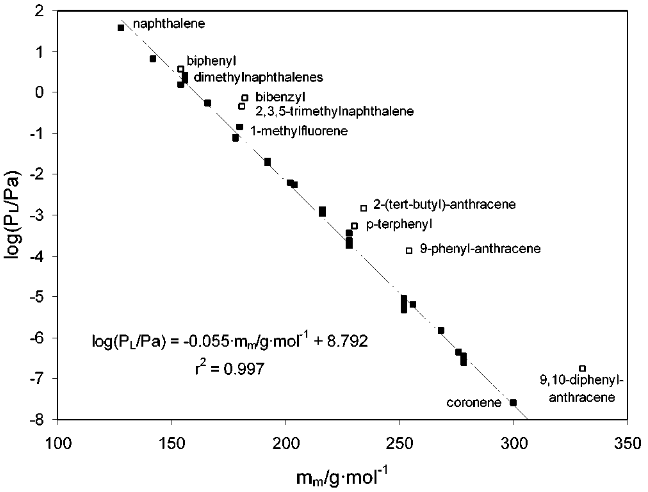

Figure 5. Relationship between the vapor pressure P_L at 25 °C determined in this study and molecular mass m_m. The regression curve only refers to the filled squares.

Vapor Pressure and Molecular Structure. In Figure 5 the logarithm of the vapor pressure value of a PAH at 25 °C is plotted against its molecular mass m_m. A linear relationship ranging over 9 orders of magnitude is apparent, suggesting that molecular size is the most important structural factor controlling the vapor pressures of these nonpolar substances. When outliers are eliminated (Figure 5), the following relationship can be obtained for the remaining 29 compounds:

$$\log(P_L/\mathrm{Pa}) = -0.055 m_m/\mathrm{g{\cdot}mol^{-1}} + 8.79 \qquad r^2 = 0.997 \quad (13)$$

The slope of this equation suggests that, with each mass unit increase in molecular mass, the vapor pressure decreases by about 0.055 log units.

It is illuminating to note which substances deviate from this linear relationship. Vapor pressures that are higher than expected are more common and occur for molecules with two or three nonfused aromatic systems (biphenyl, bibenzyl, *p*-terphenyl. 9-phenylanthracene, 9,10-diphenylanthracene) and molecules with large alkyl-substituents (2-(*tert*-butyl)anthracene) or with three methyl-substituents (2,3,5-trimethylnaphthalene). The effect can be quite significant: the P_L values of the *tert*-butylated and the phenylated anthracenes are higher by 1 to 2 orders of magnitude than would be expected from the linear relationship between log P_L and m_m. This deviation is likely caused by the nonplanar configurations of these molecules, which limit their intermolecular interactions and thus increase vapor pressure.

A methyl-group lowers the vapor pressure of a PAH by an average of 0.66 log units (range 0.54 to 0.87 units) or 0.047 log units per additional mass unit. This is somewhat lower than the overall rate of decrease with increasing mass of 0.055 log units per additional mass unit, suggesting that a methyl-substituent lowers the vapor pressure less than would a similar mass increase within the aromatic system. Accordingly, methylated PAHs tend to lie above the regression curve displayed in Figure 5.

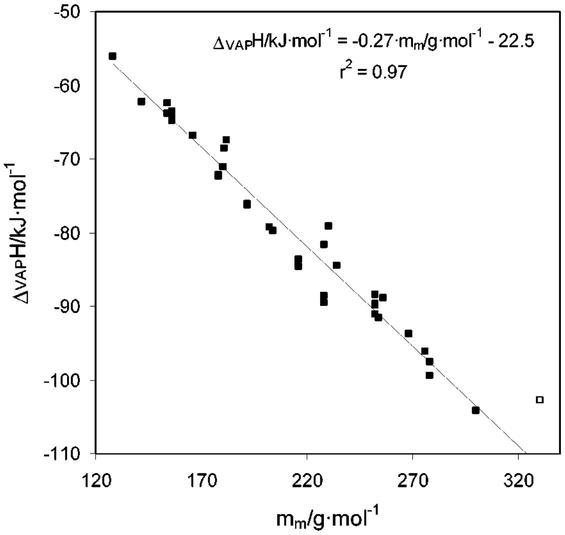

Figure 6. Relationship between the enthalpies of vaporization $\Delta_{vap}H$ determined in this study and molecular mass m_m. The regression curve only refers to the filled squares.

Small deviations in the other directions, that is, vapor pressures that are lower than expected from eq 13, are apparent for the smallest PAHs, namely naphthalene and acenaphthene, suggesting that other factors than molecular mass contribute to controlling the vapor pressure of these substances.

Enthalpy of Vaporization and Molecular Structure. There is also a fairly strong linear relationship between the enthalpies of vaporization of the PAHs and molecular mass m_m (Figure 6). This relationship displays more scatter than that between log P_L and m_m, and only one substance (9,10-diphenylanthracene) stands out as an obvious outlier.

Supporting Information Available:

Two pages with a detailed description of the calibration of the P_{GC} data given in ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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