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Critical Review and Recommended Values for the Physical-Chemical Property Data of 15 Polycyclic Aromatic Hydrocarbons at 25 °C

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Accurate physical-chemical properties are of fundamental importance for interpreting and simulating the environmental fate and transport behavior of polycyclic aromatic hydrocarbons (PAHs). A complete set of thermodynamically consistent property data (vapor pressure, aqueous solubility, octanol solubility, octanol−water partition coefficient, octanol−air partition coefficient, and air−water partition coefficient) for 15 PAHs [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), chrysene (Chry), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), indeno[1,2,3-c,d]pyrene (IP), and benzo[g,h,i]perylene (BghiP)] is derived from measured data reported in the literature. First, literature-derived values (LDVs) at 25 °C for each property and compound are obtained by averaging, regression, and extrapolation. Then the LDVs for each compound are adjusted to conform to the thermodynamic relationships between them using a least-squares adjustment procedure. The influence of the mutual solubility of octanol and water on phase partitioning is taken into account in the adjustment of K_{OW}. Compared to other semivolatile organic compounds, the LDVs for the PAHs display a high degree of thermodynamic consistency and require only minor adjustments. The LDVs and the adjusted values for all properties show highly linear regressions with molar mass.

Introduction

The distribution of organic compounds among different phases and environmental media is an important factor in determining their fate and assessing their risk. Physical-chemical properties, such as vapor pressure (P), water solubility (S_W), octanol solubility (S_O), and the Henry's law constant (k_H) or the air−water partition coefficient (K_{AW}), the octanol-air partition coefficient (K_{OA}), and the octanol−water partition coefficient (K_{OW}), are usually required for predicting and understanding the distribution of organic pollutants in the environment. Accordingly, they are important input parameters for models simulating the fate and behavior of organic compounds.

Beyer et al.[1] presented a method for selecting values of chemical properties subject to thermodynamic constraints. Literature-derived values (LDVs) for the properties of a compound are adjusted on the basis of their perceived uncertainty to derive final adjusted values (FAVs) that fulfill all thermodynamic relationships between them. Li et al.[2] and Xiao et al.[3] improved this algorithm with a rigorous and transparent procedure for selecting LDVs using average value or linear regression equations based on experimental data selected from the literature. Later, Schenker et al.[4] introduced a least-squares-based method that minimizes the adjustment required for thermodynamic consistency, yet still allows for quantitative propagation of the uncertainty of the LDVs. Such procedures have been applied to derive thermodynamically consistent property data for 17 polychlorinated biphenyl (PCB) congeners,[2,4] α-, β-, and γ-hexachlorocyclohexane,[3] a group of 16 organochlorine pesticides,[5] and selected polychlorinated dibenzo-*p*-dioxins and furans.[6]

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds composed of at least two fused aromatic rings. They are primarily formed by incomplete combustion of carbon-containing materials such as wood, coal, diesel, fat, and tobacco and thus have both point (e.g., oil spill) and nonpoint sources (e.g., vehicle emissions). PAHs are widespread organic pollutants which have been found in various environmental media and regions. Sixteen PAHs are defined as priority pollutants by the United States Environmental Protection Agency:[7] naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), chrysene (Chry), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), indeno[1,2,3-c,d]pyrene (IP), and benzo[g,h,i]perylene (BghiP). The structures of these PAHs are shown in Figure 1. Some of them are confirmed carcinogens and mutagens, and others are probable human carcinogens.

For the last several decades, scientists investigated and studied the sources, the long-range transport behavior, the global fate, the partition relationships among particle, air, water, and organic materials, and the adsorption and desorption behavior of PAHs. Physical-chemical properties are key parameters for understanding these phenomena. Numerous experiments using different techniques and methods have been conducted to establish and verify these basic physical-chemical data and to discover the relationships among them. For some PAHs, such as Nap, many data exist, but some of them conflict with each other. For some

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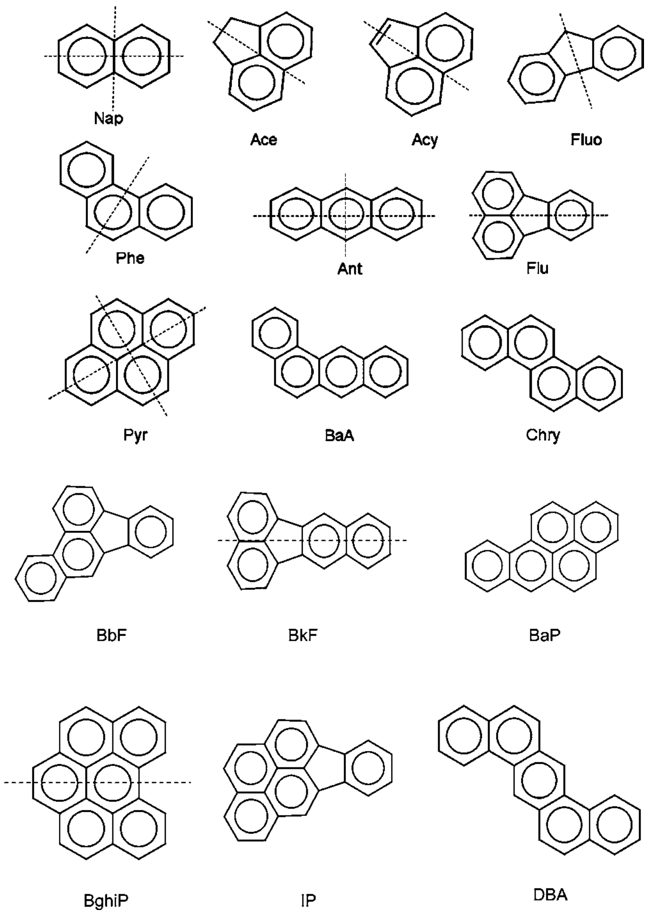

Figure 1. Structures of the polycyclic aromatic hydrocarbons considered in this study.

higher molar mass PAHs, such as BkF and IP, only few experimental data can be obtained from the literature. The aim of this study is to select, compile, and evaluate the experimental physical-chemical data for the priority PAHs, to adjust them so that they adhere to thermodynamic constraints using the least-squares algorithm by Schenker et al.,[4] and to establish regressions between these properties and molar mass.

Methods

As the principles and procedures for evaluating, selecting, and adjusting the property data from the literature have been described in detail previously,[1,2,4] we only provide a brief summary here. First, as many directly measured data as possible are selected and compiled from the literature. Indirectly derived values such as those calculated from chromatographic retention times and calculated data are selected only if there are not enough directly measured values available. Then, all of the data are converted into standard units. As the liquid or subcooled liquid state is suitable for describing the environmental distribution of organic compounds, solid phase properties, such as vapor pressure (P_S in Pa) and water solubility (S_{WS} in $\text{mol}\cdot\text{m}^{-3}$), are converted into the liquid state (P_L and S_{WL}) using the fugacity ratio F.

$$P_L = P_S/F \tag{1}$$

$$S_{WL} = S_{WS}/F \tag{2}$$

The fugacity ratio F was estimated using an equation by van Noort:[8]

$$\log F = \log\{\exp[(\Delta_{fus}S/R)(1 - T_m/T)]\} - [(A + BT)(T_m - T)^2 + (C + DT)(T_m - T)] \tag{3}$$

where $\Delta_{fus}S$ is the entropy of fusion in $\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$, R is the ideal gas constant ($R = 8.3145$ J/(K·mol)), and T_m and T are the melting temperature and experimental temperature in K, respectively. The first part of eq 3 is the typical approach to estimating F from the entropy of fusion and the melting temperature. The second part of eq 3 is an empirical term that corrects for the fact that for high-melting rigid aromatic compounds the entropy of the solid-to-liquid transition is not independent of temperature. Empirical parameters A, B, C, and D applicable to PAHs were taken from Table 3 in van Noort.[8] For the smaller PAHs (Nap, Acy, Ace, Fluo, Phe) the correction term is negligible and was not applied. For high melting compounds such as Chry and BghiP, the correction is quite substantial. A limitation of the empirical part of eq 3 is that it only applies to the environmentally relevant temperature range of (260 to 320) K.[8] For the larger PAHs we therefore could only use and convert solid phase properties measured within that temperature range. Because no experimental entropy of fusion for BkF could be located, a generic default value of 56 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ had to be used for this compound. An uncertain entropy of fusion can lead to significant errors when calculating liquid state properties, especially for compounds with a high T_m such as BkF.

LDVs at 25 °C are obtained as the arithmetic mean of all reliable values at 25 °C or from linear regression equations between log property and $1/T$ when experiments had been carried out at different temperatures. FAVs are obtained by using the computer program with the least-squares adjustment algorithm by Schenker et al.[4,9] The relationship between the partition properties is given by four thermodynamic triangles.[3] The LDVs are adjusted as little as possible to conform to thermodynamic constraints. For example, the following equation relates the solubility in water S_{WL}, the vapor pressure P_L, and the Henry's law constant k_H, which equals $K_{AW}RT$:

$$\log S_{WL(LDV)} - \log P_{L(LDV)} + \log k_{H(LDV)} = \omega \tag{4}$$

where ω is the misclosure error.[4] The value of ω should be zero if the LDVs for S_{WL}, P_L, and k_H are internally consistent. The aim of the adjustment procedure is to reduce all misclosure errors ω to zero and thus obtain a consistent set of partitioning parameters.

Results

Data Compilation. All of the original data, experimental temperatures, experimental methods, and references are listed in a series of tables in the Supporting Information (Tables S1 to S16). In total, more than 200 original references were consulted which had been published in 17 different journals between 1923 and 2008. The LDVs for the physical-chemical properties of 15 PAHs are summarized in Table 1. This table does not include data for DBA, because the availability of data was judged too limited to derive reliable values; a detail justification for this exclusion is provided below. The LDVs in logarithmic form are plotted against the molar mass M of the PAHs in Figure 2 (red markers). All of the relationships, except those for $S_{OL(LDV)}$, are highly linear with r^2 values exceeding 0.98 (red lines in Figure 2, Table 2).

Three issues related to the application of the adjustment procedure require a more detailed discussion. These are the decision whether to use all LDVs in the adjustment procedure, the assignment of relative variances to the LDVs, and the

Table 1. Molar Mass M, Melting Temperature T_m, Entropy of Fusion $\Delta_{fus}S$, Fugacity Ratio F at 298.15 K, and the LDVs and FAVs for the Logarithm of the Water Solubility S_{WL}, the Vapor Pressure P_L, the Octanol−Water Partition Coefficient K_{OW}, the Ratio of the Solubilities in Pure Octanol and Pure Water S_O/S_W, the Octanol−Air Partition Coefficient K_{OA}, the Air−Water Partition Coefficient K_{AW}, and the Solubility in Octanol S_{OL} for 15 PAHs[a]

	M	T_m (K)	$\Delta_{fus}S$ (J/mol·K)	F	$\log(S_{WL}/\text{mol}\cdot\text{m}^{-3})$		$\log(P_L/\text{Pa})$		$\log K_{OW}$		$\log(S_O/S_W)$		$\log K_{OA}$		$\log K_{AW}$		$\log(S_{OL}/\text{mol}\cdot\text{m}^{-3})$	
	(g·mol^{-1})	LDV	LDV	LDV	LDV	FAV	LDV	FAV	LDV	FAV	LDV	FAV	LDV	FAV	LDV	FAV	LDV	FAV
Nap	128.17	353.1	54.3	0.300	−0.09	−0.09	1.58	1.58	3.39	3.40	3.45	3.46	5.19	5.19	−1.72	−1.73	3.47	3.37
Acy	152.19	365.1	37.8	0.360	−0.53	−0.57	0.38	0.41	3.80	3.85	3.99	4.05	6.52	6.46	−2.31	−2.41	NA	3.48
Ace	154.21	366.3	58.5	0.200	−0.89	−0.91	0.22	0.24	3.97	3.95	4.21	4.19	6.42	6.44	−2.25	−2.24	3.31	3.28
Fluo	166.22	387.7	49.9	0.165	−1.17	−1.22	−0.32	−0.27	4.14	4.11	4.45	4.41	6.81	6.85	−2.42	−2.44	3.16	3.19
Phe	178.23	372.0	45.9	0.255	−1.57	−1.62	−1.04	−0.99	4.49	4.47	4.91	4.88	7.61	7.64	−2.75	−2.76	3.15	3.26
Ant	178.23	489.8	58.3	0.021	−1.87	−1.94	−1.30	−1.23	4.63	4.57	5.09	5.02	7.63	7.70	−2.69	−2.69	2.77	3.08
Pyr	202.25	423.4	38.2	0.183	−2.44	−2.51	−2.45	−2.38	5.06	5.01	5.66	5.59	8.79	8.86	−3.27	−3.27	2.83	3.09
Flu	202.25	382.0	49.5	0.203	−2.25	−2.29	−2.21	−2.17	4.98	4.97	5.56	5.55	8.80	8.81	−3.23	−3.27	2.93	3.25
Chry	228.29	530.0	49.2	0.026	−3.36	−3.44	−3.95	−3.87	5.67	5.67	6.47	6.47	10.30	10.30	−3.75	−3.82	2.42	3.03
BaA	228.29	431.8	50.6	0.086	−3.19	−3.22	−3.46	−3.42	5.83	5.83	6.68	6.68	10.28	10.28	−3.55	−3.59	NA	3.46
BbF	252.31	441.2	57.9	0.049	−3.82	−3.80	−4.96	−4.98	5.83	5.86	6.69	6.72	11.34	11.30	−4.57	−4.58	NA	2.93
BkF	252.31	485.4	56.0	0.026	−3.85	−3.87	−5.13	−5.11	5.85	5.86	6.71	6.72	11.37	11.36	−4.62	−4.64	NA	2.85
BaP	252.31	452.0	35.8	0.159	−4.24	−3.98	−4.85	−5.10	5.99	6.05	6.89	6.97	11.56	11.48	−4.69	−4.51	2.22	2.99
BghiP	276.33	547.7	31.7	0.127	−5.09	−4.96	−6.21	−6.34	6.60	6.63	7.71	7.74	12.55	12.55	−4.87	−4.77	NA	2.78
IP	276.33	436.0	49.4	0.086	−5.10	−4.88	−5.97	−6.18	6.53	6.57	7.60	7.67	12.43	12.43	−4.85	−4.70	3.47	2.78

[a] Solubilities and vapor pressure refer to the subcooled liquid. NA means there are no data available.

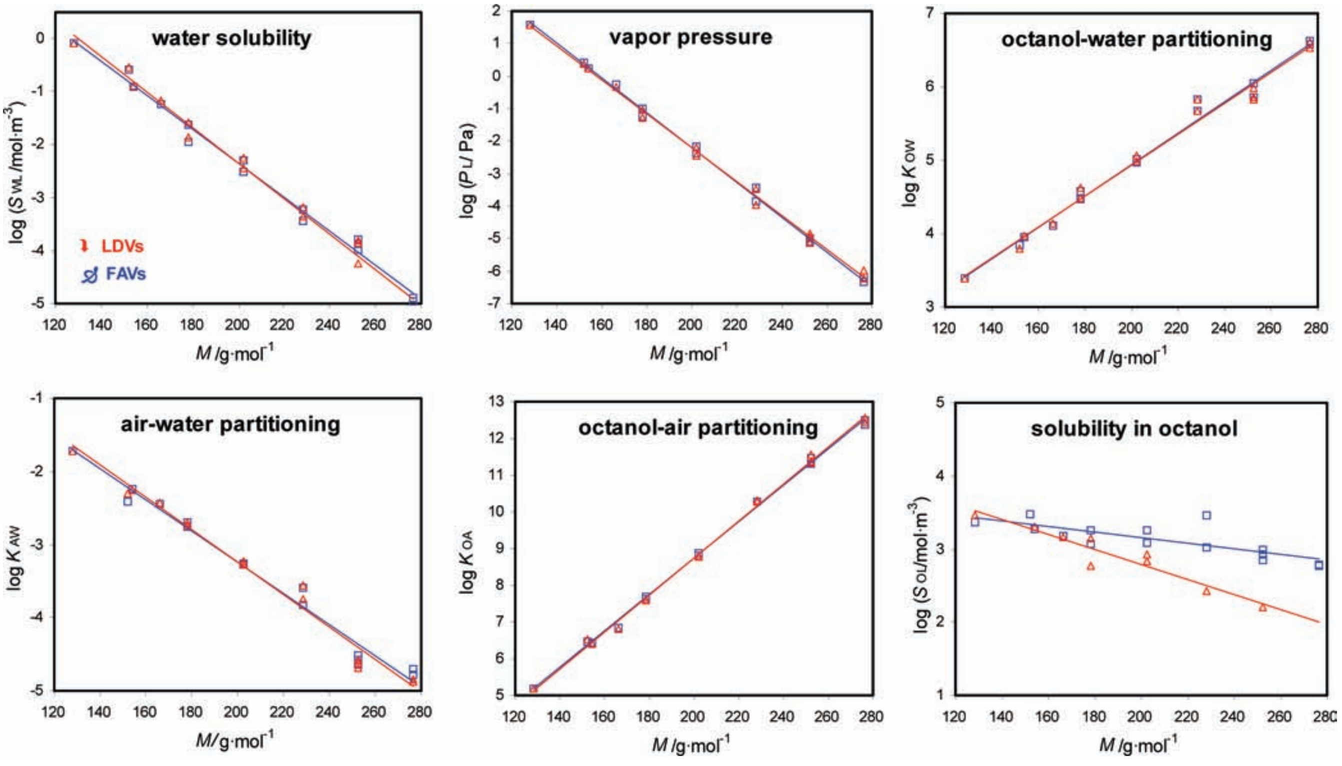

Figure 2. LDVs (red triangles) and FAVs (blue squares) of the solubility in water S_{WL} and octanol S_{OL}, the vapor pressure P_L, and the partition coefficients between air, water, and octanol, K_{AW}, K_{OA}, and K_{OW}, for 15 PAHs plotted as a function of the molar mass M.

Table 2. Linear Regression between the Logarithm of the LDVs and FAVs for Various Physical-Chemical Parameters at 25 °C and the Molar Mass M for 15 PAHs

$\log(S_{WL(LDV)}/\text{mol}\cdot\text{m}^{-3})$	$= -0.034 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+4.36 \pm 0.21$	$n = 15$, $r^2 = 0.988$
$\log(S_{WL(FAV)}/\text{mol}\cdot\text{m}^{-3})$	$= -0.032 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+4.09 \pm 0.19$	$n = 15$, $r^2 = 0.990$
$\log(P_{L(LDV)}/\text{Pa})$	$= -0.052 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+8.25 \pm 0.19$	$n = 15$, $r^2 = 0.996$
$\log(P_{L(FAV)}/\text{Pa})$	$= -0.054 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+8.52 \pm 0.16$	$n = 15$, $r^2 = 0.997$
$\log K_{AW(LDV)}$	$= -0.022 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+1.20 \pm 0.19$	$n = 15$, $r^2 = 0.980$
$\log K_{AW(FAV)}$	$= -0.021 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+1.03 \pm 0.18$	$n = 15$, $r^2 = 0.979$
$\log K_{OA(LDV)}$	$= 0.050 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	-1.30 ± 0.14	$n = 15$, $r^2 = 0.998$
$\log K_{OA(FAV)}$	$= 0.050 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	-1.20 ± 0.13	$n = 15$, $r^2 = 0.998$
$\log K_{OW(LDV)}$	$= 0.021 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+0.72 \pm 0.16$	$n = 15$, $r^2 = 0.983$
$\log K_{OW(FAV)}$	$= 0.021 \pm 0.001\cdot M/\text{g}\cdot\text{mol}^{-1}$	$+0.65 \pm 0.15$	$n = 15$, $r^2 = 0.986$

correction for bias in the misclosure error resulting from the effect of the mutual solubility of water and octanol.

Selection of LDVs for Adjustment. After careful consideration, the LDVs for the solubilities of the PAHs in octanol, $S_{OL(LDV)}$, were not used in the adjustment procedure. S_{OL} have only been reported for 9 of the 15 investigated PAHs (Table S17 of Supporting Information). Whereas the LDVs for the remaining five properties are highly consistent and yield only minor misclosure errors (see below), the inclusion of $S_{OL(LDV)}$ in the procedure results in larger adjustments (Table S18 of Supporting Information). Furthermore, because of the lack of $S_{OL(LDV)}$ for some PAHs, such larger adjustments would apply to some PAHs but not to others; that is, the data set of FAVs would not be consistent between different PAHs, even though it is consistent for each individual PAH.

Assignment of Relative Variances to the LDVs. If LDVs are judged to be of variable reliability, relative variance values can ensure that more reliable LDVs are not unduly adjusted to conform with less reliable LDVs. Typically, and somewhat subjectively, each LDV is assigned a variance value between 1 and 5, indicative of the certainty with which this value is known (e.g., ref 5). Because the LDVs for P_L, S_{WL}, log K_{OW}, log K_{OA}, and log K_{AW} displayed a high degree of thermodynamic consistency (see below), they were assigned a uniform relative variance value of 1 in the adjustment procedure; that is, it was not considered necessary to allow for differences in the reliability of the LDVs for different properties.

Accounting for the Effect of the Mutual Solubility of Water and Octanol. Previous efforts seeking to obtain thermodynamically consistent partitioning properties for groups of related substances noted that inconsistencies among the LDVs of K_{OW}, K_{OA}, and K_{AW} are substantial and nonrandom; that is, they tended to increase with increasing size of the molecule.[1,2] In other words, in eq 5:

$$\log K_{AW(LDV)} - \log K_{OW(LDV)} + \log K_{OA(LDV)} = \omega \qquad (5)$$

the misclosure error is nonrandom and therefore should not be forced to assume zero values. If it is done anyway, the adjustments to the LDVs show a systematic bias. Such bias was also apparent for the PAHs, when the LDVs for K_{OW}, K_{OA}, and K_{AW} were fed directly into the adjustment procedure. Table S19 in the Supporting Information shows the extent of adjustment that would have been required to achieve FAVs that adhere to the thermodynamic constraints. Very large adjustments to the log $K_{OW(LDV)}$ of up to 195 % would be required, and importantly, the required adjustment to the K_{OW} increases with increasing molecular size of the PAH. Also, the adjustments to the other properties are biased as a result.

It is generally accepted that this nonrandom misclosure error in eq 5 is the result of the mutual solubility of water and octanol.[1] Whereas K_{AW} refers to the pure aqueous phase and K_{OA} the pure octanol phase, the K_{OW} is the partition coefficient between water-saturated octanol and octanol-saturated water. The extent of this effect is often illustrated by displaying the logarithm of the partition coefficient between pure octanol and pure water (S_O/S_W), which can be estimated as the sum of the LDVs of log K_{AW} and log K_{OA}, as a function of the LDV of log K_{OW}. Figure 3 shows this relationship for the LDVs for 15 PAHs.

The respective linear regression is:

$$\log(K_{OA(LDV)} \cdot K_{AW(LDV)}) = 1.324 \log K_{OW(LDV)} - 1.038 \quad r^2 = 0.995 \text{ (15 PAHs)} \qquad (6)$$

The log $K_{OW(LDV)}$ for the 15 PAHs is lower than $\log(K_{OA(LDV)} \cdot K_{AW(LDV)})$ by an average of 0.62 log unit (from (−0.07 to −1.08) log units). For the least hydrophobic of the PAHs, Nap, the three partitioning coefficients display good thermodynamic consistency (discrepancy of −0.07), suggesting that the mutual solubility of octanol and water has no significant effect on its partitioning behavior. However, with the increasing molecular size of the PAHs, the thermodynamic inconsistency among the three partitioning coefficients increases, until it reaches an order of magnitude for the most hydrophobic PAHs included in this study. For example, whereas IP has log $K_{OW(LDV)}$ of around 6.5, the log of the product of $K_{OW(LDV)}$ and $K_{AW(LDV)}$ is higher than 7.5. This implies that either IP is 1 order of magnitude more soluble in octanol-saturated water than in pure water or 1 order of magnitude less soluble in water saturated octanol than in pure octanol. Of course, any combination of these two effects could also be responsible.

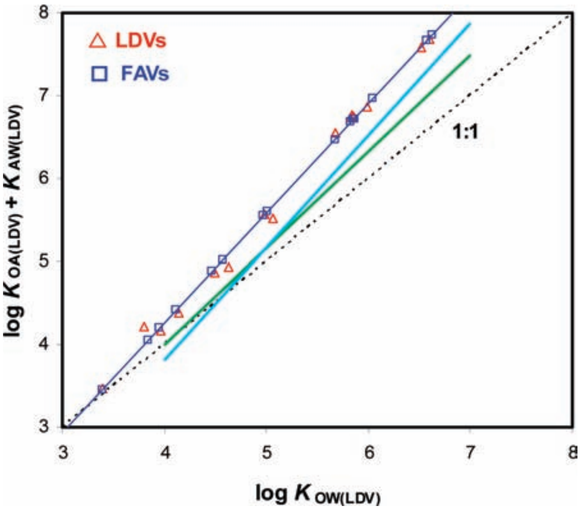

Figure 3. Relationship between the ratio of the solubilities in pure octanol and pure water log(S_O/S_W), estimated from the sum of the LDV for log K_{OA} and log K_{AW}, and the LDV of the log K_{OW} for 15 PAHs (red triangles). For comparison, similar relationships obtained for 40 organic compounds by Beyer et al.[1] and for 21 PCBs by Li et al.[2] are indicated by light blue and green lines, respectively. After adjustment, the FAVs (blue squares) fall onto the regression line.

Figure 3 compares the relationship of eq 6 with equivalent relationships derived for a group of 16 PCBs (eq 3 and Figure 1 in ref 2) and for a group of 40 diverse organic compounds (eq 10b and Figure A1 in ref 1), which included 11 PAHs. The respective linear regressions reported in those references are:

$$\log(K_{OA(LDV)} \cdot K_{AW(LDV)}) = 1.16 \log K_{OW(LDV)} - 0.64 \quad r^2 = 0.914 \quad n = 21 \text{ (PCB congeners)} \qquad (7)$$

$$\log(K_{OA(LDV)} \cdot K_{AW(LDV)}) = 1.35 \log K_{OW(LDV)} - 1.58 \quad r^2 = 0.953 \quad n = 40 \text{ (diverse organics with } \log K_{OW} > 4) \qquad (8)$$

The relationship observed in this study is quite similar to those in Beyer et al.[1] and Li et al.[2] In particular, all three relationships indicate a deviation (i) in the same direction, (ii) of the same general magnitude, and (iii) with a similar increasing trend with increasing molecular size (Figure 3). In particular, the slope of the relationship by Beyer et al.[1] is essentially the same as the one deduced here. However, they also have notable differences. In particular, it appears that the apparent thermodynamic discrepancies are quite a bit larger for the PAHs than for the PCBs (Figure 3). In other words, the effect of the mutual solubility of octanol and water is considerably larger for the partitioning behavior of the PAHs than that of the PCBs. The group of 50 organic substances used by Beyer et al.[1] included 11 PAHs, and this may be the reason for the larger similarity in the slopes of eqs 6 and 8.

No matter what the origin of this apparent thermodynamic inconsistency is, it has to be accounted for in the adjustment

Table 3. Adjustments to the LDVs of the Water Solubility S_{WL}, the Vapor Pressure P_L, the Ratio of the Solubilities in Pure Octanol and Pure Water S_O/S_W, the Octanol−Air Partition Coefficient K_{OA}, and the Air−Water Partition Coefficient K_{AW} that Were Required to Achieve Thermodynamically Consistent FAVs for Those Properties[a]

	$S_{WL}/\text{mol}\cdot\text{m}^{-3}$	P_L/Pa	$\log(S_O/S_W)$	$\log K_{OA}$	$\log K_{AW}$
Nap	0 %	**0 %**	1 %	**−1 %**	**−1 %**
Acy	10 %	**−9 %**	15 %	**−13 %**	**−20 %**
Ace	4 %	**−4 %**	**−5 %**	5 %	1 %
Fluo	12 %	**−11 %**	**−8 %**	9 %	**−3 %**
Phe	12 %	**−11 %**	**−7 %**	8 %	**−4 %**
Ant	17 %	**−14 %**	**−15 %**	18 %	1 %
Pyr	17 %	**−14 %**	**−14 %**	17 %	0 %
Flu	10 %	**−9 %**	**−2 %**	2 %	**−7 %**
Chry	19 %	**−16 %**	1 %	**−1 %**	**−17 %**
BaA	9 %	**−8 %**	1 %	**−1 %**	**−9 %**
BbF	**−5 %**	6 %	8 %	**−8 %**	**−3 %**
BkF	3 %	**−3 %**	2 %	**−2 %**	**−5 %**
BaP	**−44 %**	80 %	19 %	**−16 %**	51 %
BghiP	**−26 %**	35 %	8 %	**−8 %**	24 %
IP	**−39 %**	64 %	16 %	**−14 %**	41 %

[a] Bold text means negative adjustments, while normal text means positive adjustments.

procedure, to prevent the introduction of bias into unbiased experimental data. We therefore did not feed the LDV for the K_{OW} into the adjustment algorithm by Schenker et al.[9] but calculated LDVs for the ratio of the solubility in pure octanol and solubility in pure water $(S_O/S_W)_{(LDV)}$ and used those in the adjustment procedure instead. $(S_O/S_W)_{(LDV)}$ was calculated using:

$$\log(S_O/S_W)_{(LDV)} = 1.324 \log K_{OW(LDV)} - 1.038 \quad (9)$$

that is, by plugging the LDV values for K_{OW} into eq 6.

The adjustment procedure then yields thermodynamically consistent values for P_L, S_W, S_O, K_{OA}, K_{AW}, and S_O/S_W, which are referred to as the FAVs for those properties. The latter FAV finally has to be converted back into a K_{OW} value, that is, a partition coefficient between water-saturated octanol and octanol-saturated with water. This is achieved using:

$$\log K_{OW(FAV)} = (1/1.324) \log(S_O/S_W)_{(FAV)} + (1.038/1.324) = 0.76 \log(S_O/S_W)_{(FAV)} + 0.78 \quad (10)$$

FAVs and Misclosure Errors. The FAVs are included in Table 1 and Figure 2 (blue markers). The regression of the log property versus M regressions using FAVs are included in Table 2. The slopes, intercepts, and r^2 values of the regression equations are very similar for LDVs and FAVs. While the linearity of the regression increases after adjustment for K_{OW}, it ever so slightly deteriorates for S_{WL}.

Table 3 lists the percentage adjustments that were required to achieve consistency with the thermodynamic constraints. The average misclosure error for all properties and all PAHs was 12.6 %. When compared with the misclosure errors reported for the properties of the PCBs,[2] PCDD/Fs,[6] and organochlorine pesticides,[5] these are exceptionally small. In the case of Nap, no adjustments were required at all. There is a tendency for the lower molar mass PAHs to require less adjustment than higher ones (BaP, BghiP, IP), which is likely related to the much greater difficulty of reliably measuring properties for substances with very low aqueous solubility and volatility. There is slight indication of bias in the properties of the three- and four-ring PAHs (Acy to BaA), in that they all require a slight increase in the P_L and an equally slight decrease in the S_L (Table 3) to achieve consistency. As will be discussed in detail below, we believe that this is due to $K_{AW(LDV)}$ values for these PAHs that are slightly too high. Otherwise, the misclosure errors are generally random and show no major bias, suggesting that they indeed are due to experimental uncertainty in the LDVs and not an indication of a real thermodynamic phenomenon. For example, it confirms that it is valid to relate properties of PAHs measured at saturation (such as vapor pressure and water solubility) to properties measured generally at high dilution (such as the partition coefficients). Overall, this high thermodynamic consistency of the LDVs attests both to the high quality of the physical chemical property data reported for the PAHs and to the success of the data selection procedure leading to the LDVs.

Originally, we had included dibenzoanthracene (DBA) in the data compilation (Table S16 in the Supporting Information). However, no measured K_{AW} for DBA was found. Furthermore, the $S_{WL(LDV)}$ value for DBA deviates very strongly from the tight linear relationship between $\log S_{WL}$ and molar mass M that was observed for the remaining 15 PAHs. According to the LDVs, DBA is 1.5 orders of magnitude more water-soluble than BghiP and IP, which have identical M values. A closer look at the data underlying the LDVs for the three heaviest PAHs shows that the deviations in the actually measured water solubilities of the solid substances, S_{WS}, are much smaller. This indicates that the unusually high $S_{WL(LDV)}$ for DBA is at least partially due to its $\Delta_{fus}S$ value (57 $\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$), which is much higher than for IP (49 $\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$) and BghiP (31 $\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$). Also, because of its very high T_m, even a slightly incorrect F could yield highly inaccurate LDVs for S_{WL} and P_L of DBA. Even after downward adjustment by half an order of magnitude, the $S_{WL(FAV)}$ for DBA continues to be much higher than the corresponding value for IP and BghiP. However, because no $K_{AW(LDV)}$ for DBA exists, the thermodynamic triangle involving P_L, S_L, and K_{AW} cannot be used in the adjustment procedure. Eventually, we decided that the availability and reliability of the experimental data for DBA is too limited to report a thermodynamically consistent set of partitioning properties.

Discussion

Melting Temperature. All 15 PAHs are solids at environmental temperatures, with melting temperatures T_m ranging from (80 to 280) °C. Although there is a tendency for larger PAHs to melt at higher temperatures, T_m does not increase linearly with increasing molar mass. T_m appears to be related to molecular symmetry. If two PAHs have the same molar mass, the one with the higher rotational symmetry number σ has the higher melting temperature.[10] For example, the T_m of Ant, with a σ of 4, is 118 K higher than the T_m of Phe, with a σ of 2. Almost as large is the difference in T_m (112 K) between BghiP ($\sigma = 2$) and IP ($\sigma = 1$) and the one (97 K) between Chry ($\sigma = 2$) and BaA ($\sigma = 1$). The T_m differences between Pyr ($\sigma = 4$) and Flu ($\sigma = 2$) and between BkF ($\sigma = 2$) and BbF ($\sigma = 1$) are considerably smaller [(43 and 44) K, respectively].

Vapor Pressure. The subcooled liquid vapor pressure of the 15 PAHs spans almost 8 orders of magnitude, from Nap with a $\log(P_{L(FAV)}/\text{Pa})$ of 1.58 to BghiP with a $\log(P_{L(FAV)}/\text{Pa})$ of −6.34. The relationship between $\log(P_{L(FAV)}/\text{Pa})$ and molar mass M is exceptionally tight ($r^2 = 0.997$), indicating that the vapor pressure decreases by half a log unit (−0.54) with every additional 10 $\text{g}\cdot\text{mol}^{-1}$.

Water Solubility. The water solubility of the subcooled liquid ranges from a $\log(S_{WL(FAV)}/\text{mol}\cdot\text{m}^{-3})$ of −0.09 for Nap to a $\log(S_{WL(FAV)}/\text{mol}\cdot\text{m}^{-3})$ of −4.96 for BghiP and is thus only about half as dependent on molar mass as vapor pressure; the $S_{WL(FAV)}/\text{mol}\cdot\text{m}^{-3}$ decreases by approximately 0.32 log units for each additional 10 $\text{g}\cdot\text{mol}^{-1}$. The $\log(S_{WL(LDV)}/\text{mol}\cdot\text{m}^{-3})$ shows a remarkably good linear relationship with M ($r^2 = 0.988$),

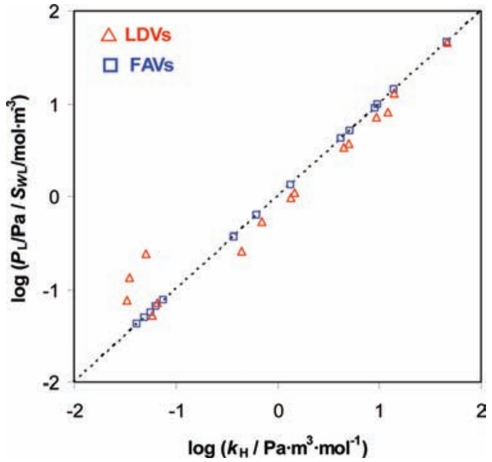

Figure 4. Relationship between the logarithm of the ratio of the LDVs for vapor pressure ($P_{L(LDV)}$) and water solubility ($S_{WL(LDV)}$) and the logarithm of the LDV of the Henry's law constant ($k_{H(LDV)}$) for 15 PAHs. Small discrepancies from the dashed 1:1 line indicate good thermodynamic consistency.

especially in light of the considerable uncertainty of the $S_{WL(LDV)}$ values for the larger PAHs. This uncertainty is due to experimental difficulties in measuring such low solubilities and to high melting temperatures, which result in very small fugacity ratios and thus introduce a high uncertainty in the S_{WS} to S_{WL} conversion.

Air−Water Partition Coefficient and the Thermodynamic Triangle among P_L, S_{WL}, and K_{AW}. The log $K_{AW(FAV)}$ for 15 PAHs spans a little more than 3 orders of magnitude, from −1.73 for Nap to −4.77 for BghiP. Because P_L decreases much faster (0.54 log units per 10 g·mol^{-1}) than S_{WL} (0.32 log units per 10 g·mol^{-1}) with increasing molar mass, the heavier PAHs partition much more strongly to the aqueous phase from the gas phase than the lighter PAHs; K_{AW} decreases by about 0.21 log units for each additional 10 g·mol^{-1}. The relationship between log K_{AW} and M is tight for both LDVs ($r^2 = 0.980$) and FAVs ($r^2 = 0.979$). The $K_{AW(LDV)}$ for Chry and BaA are somewhat higher, whereas those for BkF, BbF, and BaP are somewhat lower than the log K_{AW} versus M relationship suggests. For the $K_{AW(FAV)}$ these deviations are reduced and appear more random.

The extent of thermodynamic consistency between the LDVs of P_L, S_{WL}, and K_{AW} can be tested by plotting log($P_{L(LDV)}$/Pa/$S_{WL(LDV)}$/(mol·m^{-3})) against log($K_{AW(LDV)}RT$) = log(k_H/Pa·m^3·mol^{-1}), which has been done in Figure 4. Data points lying close to the 1:1 line indicate good thermodynamic consistency. Interestingly, the LDVs of the three- and four-ring PAHs are all falling slightly below this line, suggesting that the $K_{AW(LDV)}$ values for these substances are slightly higher than would be expected from the thermodynamic triangle. This is what led to the bias apparent in the percentage adjustment values in Table 3 mentioned above. In the derivation of the $K_{AW(LDV)}$ for these PAHs we used data measured by Bamford et al.[11] and others with the inert gas stripping technique. We had earlier shown that these data can be biased highly because of a surface adsorption artifact in the inert gas stripping technique.[12] A detailed look at the reported K_{AW} data for the three- and four-ring PAHs (Tables S2 to S10, Supporting Information) confirms that the data by Bamford et al.[11] are consistently at the higher end of the range of reported values. Especially for the four-ring PAHs, this results in higher $K_{AW(LDV)}$ values than would have been obtained if we had not considered the data by Bamford et al.[11] We nevertheless decided to use them in the derivation of the $K_{AW(LDV)}$ because of the dearth of measured K_{AW} for four-ring PAHs and because of the small size of the adjustments required for thermodynamic consistency (less than 20 %).

Deviations from the 1:1 line in Figure 4 are larger for the three heaviest PAHs (BaP, BghiP, IP), and they indicate that the $K_{AW(LDV)}$ values are too low. These $K_{AW(LDV)}$ values rely largely on the inert gas stripping experiments by ten Hulscher et al.,[13] which are believed to be less subject to the surface sorption artifact[12] than those by Bamford et al.[11] These deviations are not surprising considering the considerable difficulty in measuring P_L, S_{WL}, and K_{AW} for compounds as sparingly water-soluble and as involatile as the heavy PAHs. The FAVs for P_L, S_{WL}, and K_{AW} show perfect consistency (blue markers in Figure 4), as they should.

Octanol−Air Partition Coefficient. The log $K_{OA(FAV)}$ of the PAHs ranges over almost 8 orders of magnitude from 5.2 for Nap to 12.5 for BghiP. Whereas multiple measured K_{OA} values are available for some of the smaller PAHs, for many PAHs (Acy, Chry, BaA, BbF, BkF, BaP, BghiP, DBA, and IP) only one experimentally determined value exists.[14] The K_{OA} values reported by Harner and Bidleman,[15] Abraham et al.,[16] and Odabasi et al.[14] are generally in good agreement with each other. As a result, the $K_{OA(LDV)}$ data set for the PAHs appears to be very consistent, which is reflected in a very tight linear correlation between log $K_{OA(LDV)}$ and M ($r^2 = 0.998$) and $K_{OA(FAV)}$ values that are only marginally different from the $K_{OA(LDV)}$. The dependence of log K_{OA} on M is very similar to that for vapor pressure; that is, K_{OA} increases by half a log unit with each additional 10 g·mol^{-1}. This suggests that the octanol solubility of the PAHs does not change notably with molar mass.[17]

Octanol−Water Partition Coefficient. The log K_{OW} ranges over 3 orders of magnitude from 3.4 for Nap to 6.6 for the six-ring PAHs. The regression equation between log K_{OW} and M is virtually identical for LDVs and FAVs (Table 2), but the deviation from the regression line is quite a bit smaller after adjustment, reflected in an increase in r^2 from 0.983 to 0.986. The slope of these regressions suggests that the log K_{OW} of the PAHs increases by 0.21 log units for each additional 10 g·mol^{-1}.

Octanol Solubility. Although the S_{OL} values were not used in the adjustment procedure, that procedure still yields $S_{OL(FAV)}$, which can be compared with the $S_{OL(LDV)}$. All of the log $S_{OL(FAV)}$ (mol·m^{-3}) values are scattered in a narrow zone ranging from 2.8 to 3.5 (Figure 2, Table 1). This is in agreement with S_{OL} values reported for other hydrophobic chemicals of comparable size (e.g., refs 2, 6, and 17). It is also in line with theoretical expectations, which states that liquid substances miscible with octanol have a constant log (S_{OL}/mol·m^{-3}) of 3.5.[18] The measured $S_{OL(LDV)}$ values are somewhat lower than the $S_{OL(FAV)}$, especially for Chry and BaP (Figure 2). The latter two compounds have very high T_m, and even minor uncertainties in their F values could affect the conversion from the measured S_{OS} to the S_{OL}.

Trends of solubilities in octanol with M tend to be highly variable. Xiao and Wania[17] showed that they often depend on the data sets selected in the derivation of S_{OL}. Åberg et al.[6] obtained a slightly increasing trend for the S_{OL} of PCDDs but a decreasing trend in the S_{OL} of the closely related PCDFs, which they attributed "to a small bias in values of the sets of property data selected as LDVs". The lack of a strong trend in the $S_{OL(FAV)}$ with M can thus be seen as another indication of the absence of bias in our LDVs.

Conclusions

Although the LDVs for the 15 PAHs already display an exceptionally high degree of thermodynamic consistency, we suggest that the FAVs in Table 1 be used when the distribution behavior of PAHs is investigated quantitatively. Although the adjustment procedure does not explicitly take into account consistency between different PAHs, the high linearity of the log property versus molar mass regressions shows that such consistency is nevertheless achieved, in particular if $S_{\mathrm{OL(LDV)}}$ is not used in the adjustment procedure. Consistency between the properties of several PAHs is particularly important when seeking to interpret and understand divergent behavior of the constituents of PAH mixtures. We further suggest that the regression equations for the FAVs in Table 2 be used to estimate properties of other nonsubstituted PAHs.

The partitioning property data for the PAHs presented here are the clearest indication yet that the K_{OW} can deviate significantly from the ratio of the solubility in pure water and pure octanol, especially for high K_{OW} compounds. This also suggests that the estimation of K_{OA} from K_{OW} and K_{AW}[19] is not valid for highly hydrophobic substances, as it could easily result in systematic errors of 1 order of magnitude and higher. So far, it is unresolved whether highly hydrophobic substances are more soluble in octanol-saturated water than in pure water or less soluble in water-saturated octanol than in pure octanol. Further experiments need to be carried out on the partitioning to solvents that are saturated with other solvents.[20−22] Theoretical approaches may eventually also shed light on this issue.[23] Important other data gaps that were identified in this study are the entropy of fusion for BkF and additional reliable data of the physical-chemical properties for DBA, including a confirmation of the single available $\Delta_{\mathrm{fus}}S$ value by Casellato et al.[24]

Supporting Information Available:

Original data, experimental temperatures, experimental methods, and references listed in a series of tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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