Gas/Solid and Gas/Liquid Partitioning of Organic Compounds: Critical Evaluation of the Interpretation of Equilibrium Constants

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Gas/solid and gas/liquid partition processes are pivotal for the transport and residence time of organic pollutants in the atmosphere. Commonly, experimentally determined partition constants (K) between air and condensed phases (i.e., aerosols, rain, fog, snow, soils, plants) of a series of compounds are evaluated as a function of their (subcooled) liquid saturation vapor pressure p_L°. Frequently, a linear free energy relationship of the form $\ln K = m \ln p_L^\circ + \text{constant}$ has been found for groups of structurally related compounds. In many cases, in the literature, deviations of the slope m from -1 have been considered to be in contradiction to theory and have thus been taken as indicative of nonequilibrium conditions or experimental artifacts. In this paper, it is shown by theoretical considerations as well as by experimental data from the literature that m may deviate significantly from -1 for equilibrium *ad*sorption and *ab*sorption and that such deviations do not necessarily indicate nonequilibrium effects. In fact, if true equilibrium partitioning data are available, the slope m is a characteristic parameter for the specific sorption process and can thus be helpful for obtaining information about unknown sorbents (e.g., from field data for gas/particle partitioning). Some examples demonstrate that earlier interpretations of experimental sorption constants may have to be revised. A review of slopes m for field data of gas/particle partitioning from the literature leads to the conclusion that aerosol particles sampled in different events at the same location may differ considerably in their chemical properties. Combining the information of the slopes m and the absolute sorption constants K, we further conclude that absorption rather than adsorption must have been the dominating sorption mechanism in many cases. Finally, it is shown that a linear free energy relationship directly relating the sorption coefficients for two sorbents ($\ln K_1$ vs $\ln K_2$) may provide more information with respect to the question of the chemical similarity of the investigated sorbents than a comparison of m values from plots of $\ln K_1$ and $\ln K_2$ vs $\ln p_L^\circ$.

Introduction

Transport and transformation in the atmosphere are important processes for the fate of volatile and semivolatile organic compounds in the environment. These processes are strongly influenced by the partitioning of a given compound between the gas phase and condensed (liquid or solid) phases including aerosols, rain, fog, snow, soils, and vegetation. The actual extent of the partitioning depends on the equilibrium partition constant and on the kinetics of the partitioning process. In this paper, we will focus on partitioning equilibrium.

For the low concentrations typically encountered under ambient conditions, the partitioning of organic compounds between air and condensed phases often follows a linear isotherm and can be characterized by a partition constant. While partitioning from air to bulk water and to a water surface is well understood (*1*−*3*), there is still a considerable lack of knowledge on the partitioning between the atmosphere and other, nonaqueous phases. In most cases it is not even clear whether adsorption (= partitioning to a surface/interface) or absorption (= partitioning into a bulk phase) is the dominating process. The knowledge of the type of sorption process is important since in the case of absorption the capacity of the sorbent depends on the bulk mass or volume of the sorbent (or one of its constituents) while in the case of adsorption the capacity depends on the surface area. Obviously, the performance of different sorbents can only be compared if the sorption process is the same and if the sorption constants are normalized to that property which appropriately describes the amount of sorbent, i.e., interfacial area or a bulk property. Some solids such as metals or minerals cannot be penetrated by organic molecules and can thus only act as *ad*sorbents. However, all media that can *ab*sorb organic vapors (some solids such as organic polymers as well as all liquids) may at the same time also adsorb these compounds, since every bulk phase has a surface.

When evaluating the partitioning of organic compounds between air and condensed phases, it is a common practice to plot partition constants versus the corresponding liquid (subcooled liquid where it applies) saturation vapor pressures, p_L°, of the studied compounds. For members i of certain compound classes, a linear correlation of the form

$$\ln K_i = m \ln p_{iL}^\circ + \text{constant} \qquad (1)$$

has been found (*4*−*11*). Pankow (*12*, *13*) has discussed the meaning of the slope m of such linear free energy relationships (eq 1) for true equilibrium partitioning and concluded that m should be near -1 regardless of whether absorption or adsorption takes place. The term ‘near -1’ was not further specified by Pankow (*12*), but it was noted by Pankow and Bidleman (*14*) that there is no a priori reason why m must equal -1. Nevertheless, in the literature, slopes deviating from -1 have mostly been attributed either to deviations from true equilibrium or to experimental problems (*6*−*8*,

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14–16). In this paper, we attempt to provide a theoretical framework for a critical evaluation of the gas/solid and gas/liquid partitioning of organic compounds. On the basis of these theoretical considerations and by using experimental data mostly from the literature, we will show that the slope *m* in linear free energy relationships as given by eq 1 may deviate significantly from −1 for true thermodynamic equilibrium adsorption and absorption. In fact, we will argue that *m* can be considered as a characteristic value for a sorption equilibrium that may help to evaluate and characterize sorption processes that are not yet understood very well (e.g., gas/particle partitioning). Since absorption and adsorption should be looked at as completely different processes, they will first be considered separately before common features are discussed.

Absorption from the Gas Phase into a Bulk Phase. The chemical potential of compound *i* in the gas phase $\mu_i(\mathrm{g})$ and in an absorbing phase $\mu_i(\mathrm{abs})$ can be expressed by the following equations (assuming an ideal gas phase):

$$\mu_i(\mathrm{g}) = \mu_i^\circ + RT \ln p_i / p_{i\mathrm{L}}^\circ \tag{2}$$

$$\mu_i(\mathrm{abs}) = \mu_i^\circ + RT \ln \gamma_i^{\mathrm{abs}} x_i^{\mathrm{abs}} \tag{3}$$

where μ_i° is the chemical potential of *i* in its pure liquid state, which serves as a reference state, p_i is the partial pressure of *i* in the gas phase, $p_{i\mathrm{L}}^\circ$ is the saturation vapor pressure over the (subcooled) liquid, γ_i^{abs} is the activity coefficient of *i* in the absorbing phase, and x_i^{abs} is the mole fraction of *i* in the absorbing phase. Assuming thermodynamic equilibrium between the absorbing phase and the gas phase, one can equate eqs 2 and 3:

$$\gamma_i^{\mathrm{abs}} x_i^{\mathrm{abs}} = p_i / p_{i\mathrm{L}}^\circ \tag{4}$$

Rearrangement yields

$$K_i'^{\mathrm{abs}} \equiv x_i^{\mathrm{abs}} / p_i = 1/(\gamma_i^{\mathrm{abs}} p_{i\mathrm{L}}^\circ) \tag{5}$$

If molar concentrations (*c*) are used instead of the mole fraction and partial pressure, the following expression is obtained:

$$K_i^{\mathrm{abs}} \equiv \frac{c_i^{\mathrm{abs}}}{c_i^{\mathrm{gas}}} = \frac{RT}{\gamma_i^{\mathrm{abs}} p_{i\mathrm{L}}^\circ V_\mathrm{m}} \tag{6}$$

where V_m is the molar volume of the absorbing phase. If only dilute concentrations of *i* in the absorbing phase are considered, then V_m is a constant (independent of *i*) for a given sorbing phase. In this case, eq 6 can be rewritten in its logarithmic form as:

$$\ln K_i^{\mathrm{abs}} = -\ln p_{i\mathrm{L}}^\circ - \ln \gamma_i^{\mathrm{abs}} + \ln \text{constant} \tag{7}$$

It can easily be seen from eq 7 that a plot of $\ln K_i^{\mathrm{abs}}$ vs $\ln p_{i\mathrm{L}}^\circ$ for different compounds *i* in a given absorbing phase yields a straight line with slope $m = -1$ only if the activity coefficients γ_i^{abs} of the compounds in the sorbing phase are constant. The same conclusion and a derivation similar to the one given here has already been presented by Pankow (*12*). Since then, it has often been stated that a slope of −1 is to be expected for equilibrium partitioning without acknowledging that the constancy of activity coefficients is a necessary prerequisite for this statement to be true. In fact, it is quite likely that activity coefficients in a given sorbent are not constant for a set of compounds (even within one compound class) so that a slope of −1 cannot principally be expected (see Figures 1 and 2). In the case of varying activity coefficients, the data in a $\ln K_i^{\mathrm{abs}}$ vs $\ln p_{i\mathrm{L}}^\circ$ plot are either scattered or they follow a straight line with a slope different from −1. The latter occurs if the change in $\ln \gamma_i^{\mathrm{abs}}$ between the compounds is proportional to the change in $\ln p_{i\mathrm{L}}^\circ$ (i.e., $\Delta \ln \gamma_i^{\mathrm{abs}} \propto \Delta \ln p_{i\mathrm{L}}^\circ$). Within a given compound class, this situation is actually quite likely since both $\ln p_{i\mathrm{L}}^\circ$ and the logarithm of the solubility (and thus $\ln \gamma_i^{\mathrm{abs}}$) are usually proportional to the size of the molecules. Figures 1 and 2 show plots of $\ln K_i^{\mathrm{abs}}$ vs $\ln p_{i\mathrm{L}}^\circ$ for different compounds in octanol and water, respectively, covering examples for all three cases: In octanol (Figure 1), alkanes, alkenes, and alkylbenzenes exhibit constant activity coefficients and thus exhibit a slope near −1 while the slope of the chlorobenzenes is −0.59. In case of absorption in water (Figure 2), no compound class exhibits constant activity coefficients, and thus all slopes deviate from −1. For some compound classes (chlorinated C1, C2-alkanes, and chlorobenzenes), the data are even too scattered to be correlated by a straight line (Figure 2).

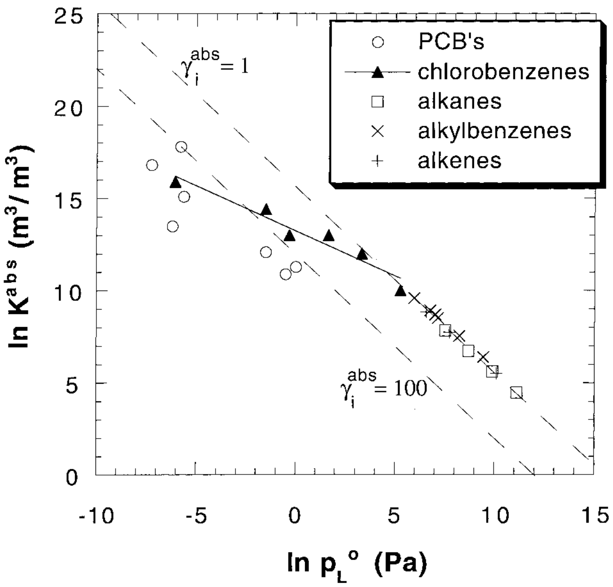

FIGURE 1. Absorption constants of various compounds from air into octanol plotted vs ln p_L° at 25 °C. Data referenced in Table 1.

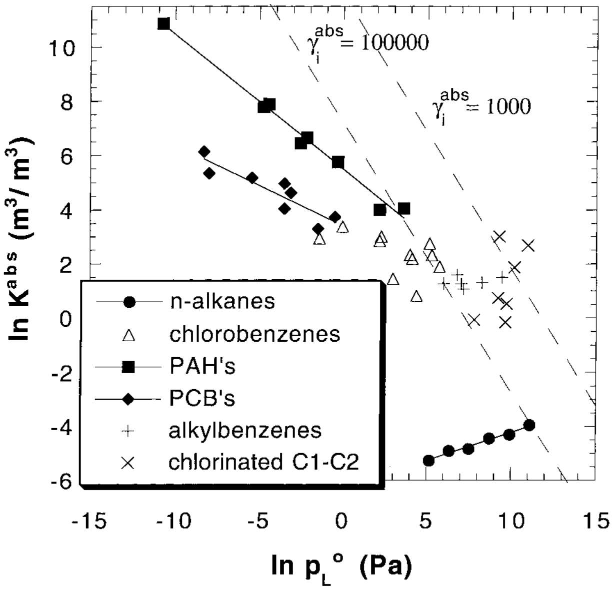

FIGURE 2. Absorption constants of various compounds from air into water plotted vs ln p_L° at 25 °C. Data referenced in Table 1.

It is instructive to take a closer look at the slope *m* in those cases where the $\ln K_i^{\mathrm{abs}}$ vs $\ln p_{i\mathrm{L}}^\circ$ plot does yield a straight line. As mentioned above, this will always be the case if the following linear relationship between the logarithms of the vapor pressure and the activity coefficient of the considered set of compounds in the absorbing phase exists:

$$\ln \gamma_i^{\mathrm{abs}} = s \ln p_{i\mathrm{L}}^{\circ} + c \qquad (8)$$

where s and c are constants. Substituting eq 8 into eq 7 yields

$$\ln K_i^{\mathrm{abs}} = -(1 + s) \ln p_{i\mathrm{L}}^{\circ} + c \qquad (9)$$

Some consideration about s ($= \Delta\ln \gamma_i^{\mathrm{abs}}/\Delta\ln p_{i\mathrm{L}}^{\circ}$) will help in understanding which values s and thus the slope $m = -(1 + s)$ may assume. The vapor pressure of a liquid compound is determined by the cohesive interactions between its molecules. For most organic compounds of environmental interest these interactions are almost entirely van der Waals interactions (small alcohols or carboxylic acids are exceptions due to their intermolecular H-bonds) and are thus related to the size of the molecules. As a consequence, there is approximately an inverse linear relationship between the size of these molecules and their $\ln p_{i\mathrm{L}}^{\circ}$ so that $\Delta\ln p_{i\mathrm{L}}^{\circ}$ is negative for molecules increasing in size. The change in the activity coefficients, $\Delta\ln \gamma_i^{\mathrm{abs}}$, depends on the molecular entities by which the compounds under consideration differ. In many cases, compounds within a class differ by entities that can only engage in van der Waals interactions (e.g., CH_2 units in any homologous series). Due to the principles of van der Waals interactions, the affinity of such molecular entities to any other liquid phase should be equal to or smaller than their own liquid phase (ref *17*, p 104) so that the change in the activity coefficient $\Delta\ln \gamma_i^{\mathrm{abs}}$ that is caused by adding such an entity to the molecule is ≥ 0. Thus, in general, s is smaller or equal to zero, and consequently the slope $m = -(1 + s)$ in eq 9 will be equal or shallower (less negative) than -1. The more the slope deviates from -1 the smaller is the affinity of the molecular entities to the absorbing phase as compared to their pure liquid phase. One extreme example is the air/water partitioning of the *n*-alkanes (see Figure 2) where a slope of $+0.21$ is obtained. Table 1 lists a number of slopes calculated from literature data on gas/liquid partitioning.

In contrast to CH_2 units, Cl substituents in some cases can affect the compound's ability to engage in H-bond interactions (e.g., C_1, C_2-alkanes, and chlorobenzenes (*18*)). This effect is not necessarily proportional to the number of Cl substituents and thus explains why experimental partitioning data scatter within a compound class rather than lying on a straight line in cases where H-bond interactions are important for the partitioning process (e.g., partitioning into water, Figure 2).

The considerations and experimental data discussed above allow the following conclusions for absorption from the gas phase: The slopes m for equilibrium absorption may fall in the range between about $+0.2$ and -1. These slopes are characteristic for the equilibrium conditions and may provide information about unknown absorbents. Different slopes for two absorbents—one or both of which are unknown—unambiguously indicate different absorbents if all other conditions (set of compounds, temperature, relative humidity) are the same. Furthermore, differences in the slopes are indicative of differences in the cohesive energy of the absorbent if alkanes are used as sorbates. In this case, the slope m becomes more positive with increasing cohesive energy of the absorbent (see Table 1). Thus, an unknown absorbent can be ranked with respect to its cohesive energy by comparing the slope m with the values reported in Table 1 for different absorbents. It must be noted that similar slopes for a given set of compounds and two absorbents is a necessary but not a sufficient condition for the absorbents to be the same (see heptane and dibutyl ether in Table 1). Thus, similar slopes do not allow a clear conclusion.

TABLE 1. Values of *m* (see eq 1) for Compounds *Ab*sorbing at Infinite Dilution in Different Liquids[a]

	$m \pm$ se	temp (°C)	ref	δ[b] (kJ mol cm^{-3})
alkanes in				
n-heptane	-1.00	20	*32*	0.48
dibutyl ether	-1.00 ± 0.00[c]	20	*32*	0.50
dioctyl phthalate	-0.98 ± 0.07	36	*25*	na[d]
1-octanol	-0.92 ± 0.00[c]	25	*32*	0.66
phthalic acid dibutyl ester	-0.89 ± 0.00[c]	25	*32*	na
o-cresol	-0.87 ± 0.00[c]	25	*32*	na
aniline	-0.79 ± 0.01[c]	25	*32*	0.77
glycerol	-0.77 ± 0.04	20	*33*	na
1,3-propanediol	-0.75 ± 0.01[c]	25	*32*	~0.85
triethylene glycol	-0.69 ± 0.01[c]	25	*32*	na
diethylene glycol	-0.64 ± 0.01[c]	20	*32*	na
ethylene glycol	-0.55 ± 0.03[c]	20	*32*	1.11
water	0.21 ± 0.05[c]	25	*34*	1.52
PAHs in water	-0.50 ± 0.02[c]	25	*34*	
chlorobenzenes in water	not linear[e]	25	*34*	
PCB's in water	-0.30 ± 0.06[e]	25	*34*	
chlorobenzenes in octanol	-0.59 ± 0.13	25	*35*	
PCB's in octanol	-0.67 ± 0.14	25	*36*	

[a] For the absorption of alkanes, the slopes become less negative with increasing cohesive energy of the solvent (expressed by the Hildebrand parameter $\delta = (\Delta U_{\mathrm{evap}}/\text{molar volume})^{0.5}$). [b] Reference 37. [c] The gas/liquid absorption coefficients used for the determination of m were backcalculated from activity coefficients compiled in ref *32*. [d] na, not available. [e] Gas/liquid absorption coefficients were calculated from solubility and saturated vapor pressure.

Adsorption from the Gas Phase to a Surface. An equation analogous to eq 7 for absorption could, in principle, also be derived for the adsorption process. However, adsorption at a two-dimensional surface is principally different from absorption into a three-dimensional phase. The adsorption equilibrium is determined only by the interactions between the adsorbed molecules and the surface while an absorption equilibrium not only depends on the interactions between the absorbing phase and the absorbed molecules but also on the cohesive interactions between the molecules of the absorbing phase that must be overcome in order to create a cavity. Thus, activity coefficients for the adsorbed state that are related to the activity in the pure liquid compound (i.e., a three-dimensional phase) as a reference are not suitable for a direct interpretation with respect to intermolecular interactions. It is advantageous to take a different approach to elucidate the relationship between adsorption constants and vapor pressure. For uncharged organic molecules, the interactions between the surface and the adsorbed molecules comprise van der Waals interactions and—in some cases—Lewis acid−base interactions (= electron donor−acceptor interactions, a subclass of which are H-bonds). It has been shown elsewhere that adsorption coefficients at 20 °C can be expressed based on these interactions by the following equation (eq 10 is obtained by combining eqs 2 and 12 from ref *3*)

$$\ln K_i^{ads} = \underbrace{-0.133\sqrt{\gamma^{\mathrm{vdw}}}\ln p_{i\mathrm{L}}^{\circ} + 2.09\sqrt{\gamma^{\mathrm{vdw}}}}_{\text{van-der-Waals interactions}} + \underbrace{2.08\beta_i\sqrt{\gamma^{+}} + 1.37\alpha_i\sqrt{\gamma^{-}} - 19.5}_{\text{acid-base interactions}} \qquad (10)$$

where γ^{vdW}, γ^+, and γ^- (all in mJ/m^2) are the van der Waals, the electron acceptor, and the electron donor parameter of the surface, respectively. For the adsorbates, the van der Waals properties are represented by ln p°_{iL} (Pa) while α_i and β_i (both dimensionless) describe the electron acceptor and donor properties, respectively. K_i^{ads} is defined as adsorbed concentration (mg/m^2) over concentration in the gas phase (mg/m^3). Note that eq 10 is valid only for organic molecules that do not have a considerable degree of self-association, i.e., compounds that do not exhibit both donor and acceptor properties such as small alcohols or carboxylic acids. For a detailed discussion of eq 10, the reader is referred to ref *3*. Here we are only interested in using this equation to evaluate plots of ln K_i^{abs} vs ln p°_{iL} for different series of structurally related compounds for different surfaces. According to eq 10, a linear plot of ln K_i^{ads} vs ln p°_{iL} for a given set of compounds *i* and a given surface (i.e., constant surface parameters) can be expected if the following applies:

(a) The acid–base interactions between the compounds *i* and the surface are 0, i.e., only van der Waals interactions are important

(b) The acid–base interactions with the surface are constant for all compounds *i*

(c) The acid–base interactions of the compounds with the surface change proportionally to their corresponding ln p°_L

Case a applies to surfaces that cannot undergo Lewis acid–base interactions (i.e., $\gamma^+ = \gamma^- = 0$; e.g., surfaces of Teflon, paraffin, polyethylene) with any adsorbate as well as adsorbates that cannot undergo Lewis acid–base interactions (i.e., $\alpha_i = \beta_i = 0$; e.g., alkanes, chlorobenzenes) with any surface. Note that in both cases eq 10 simplifies to

$$\ln K_i^{ads} = -0.133\sqrt{\gamma^{vdW}}\ \ln p^\circ_{iL} + \text{constant} \qquad (11)$$

where constant = $2.09(\gamma^{vdW})^{1/2} - 19.5$. Hence, on one hand, when plotting ln K_i^{ads} versus ln p°_{iL} for a given surface with $\gamma^+ = \gamma^- = 0$, all compounds, irrespective of their Lewis acid–base properties, will fit the same straight line (eq 11). This is illustrated in Figure 3 for the adsorption of a series of very different compounds on Teflon. On the other hand, irrespective of the properties of a given surface, one regression line is expected for all compounds with $\alpha_i = \beta_i = 0$ (see adsorption of alkanes and chlorobenzenes on quartz in Figure 3). Hence, both examples demonstrate that linear ln K_i^{ads} vs ln p°_{iL} plots are not necessarily restricted to compounds belonging to one compound class.

Case b applies to compounds that exhibit functional groups that can interact by Lewis acid–base interactions (e.g., groups containing O or N or aromatic rings) with a given surface, but which differ by molecular entities that interact by van der Waals forces only (typically alkyl groups). In these cases, an additional constant term (i.e., $2.08\beta_i(\gamma^+)^{1/2}$ or $1.37\alpha_i(\gamma^-)^{1/2}$, respectively) is added to eq 11, which leads to a parallel shift of the regression lines as compared to those in case a. The extent of this shift is a measure of the strength of the Lewis acid–base interactions. The slope *m* in both cases a and b equals $-0.133(\gamma^{vdW})^{1/2}$ and is independent of the studied compounds. Examples for case b are the adsorption of alkylbenzenes (weak Lewis acid–base interactions) and alkyl ethers (strong Lewis acid–base interactions) on quartz (see Figure 3).

Case c finally applies to compounds that differ by molecular entities that can interact by Lewis acid–base interactions with the surface (e.g., aromatic rings of the PAHs). For the PAHs, the electron donor parameter β_i is proportional to their ln p°_{iL}. Thus, the term $2.08\beta_i(\gamma^+)^{1/2}$ in eq 10 rises proportional to ln p°_{iL} for PAHs adsorbing on electron-accepting surfaces (i.e., $\gamma^+ > 0$). In this case, a plot of ln K_i^{abs} vs ln p°_{iL} still yields a straight line but with a slope that is steeper than in cases a and b. Indeed, there is a general trend in many experimental data that PAHs exhibit a steeper slope than alkanes (e.g., refs *16* and *17*). However, this difference is often not statistically significant due to rather large standard errors of the slopes.

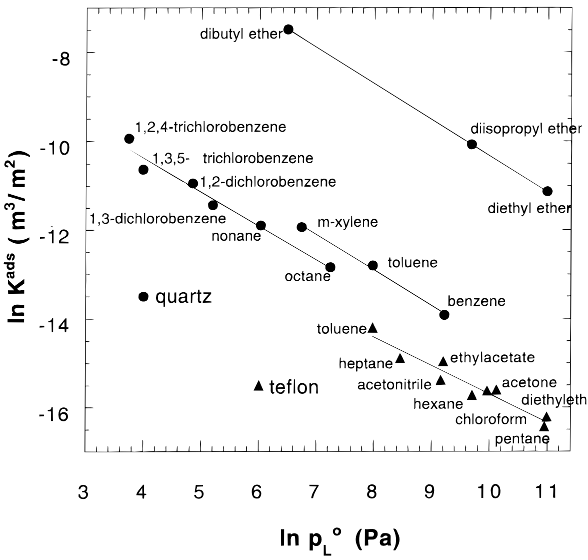

FIGURE 3. Adsorption constants for various compounds on quartz and Teflon extrapolated from different experimental temperatures to 20 °C (*30*, *31*). Some of the data (all adsorption data on Teflon as well as ethers on quartz) have been produced for this work. The experimental procedure was according to the one described in ref *30*. The slopes of the regression lines are −0.77 ± 0.06 for alkanes and chlorobenzenes on quartz; −0.80 ± 0.06 for alkylbenzenes on quartz; −0.81 ± 0.01 for ethers on quartz; and −0.64 ± 0.07 for all compounds on Teflon.

Table 2 summarizes *m* values for a number of surfaces for those cases for which eq 11 applies, i.e., for which *m* depends on the surface property γ^{vdW} only (cases a and b). From these values, some general conclusions can be drawn. Since water has the lowest γ^{vdW} among environmental surfaces, the slope $m_{H_2O} = -0.64$ can be taken as the shallowest slope that may possibly be encountered for *ad*sorption coefficients on ambient surfaces. The values for graphite show that the slope may also be significantly steeper than −1. However, judging from those values listed in Table 2 one may expect most slopes for the *ad*sorption on ambient surfaces to be in the range between −0.6 and −1.1. Hence, also in the case of adsorption, there is no a priori reason that *m* should be equal to −1. Like in the case of absorption, different slopes (*m*) for a given set of compounds on two adsorbents unambiguously indicate different adsorbents. In fact, experimental adsorption coefficients may provide much more information about unknown adsorbent surfaces if suitable adsorbates are chosen. If the adsorbates cover all three possible modes of interaction (van der Waals, electron donating, and electron accepting), then a complete characterization of the van der Waals and Lewis acid–base properties of the surface (γ^{vdW}, γ^+, and γ^-) is possible by using eq 10 or similar approaches. This procedure is known under the name 'inverse gas chromatography (IGC)' and has become a standard procedure for characterizing surfaces in material sciences (*19*–*21*). Although the similarity of two sorbents in all three surface parameters (γ^{vdW}, γ^+, γ^-) is still no proof that both sorbents are the same, it does indicate a high chemical similarity.

General Implications from ln K_i^{abs} vs ln p°_{iL} Plots. The data discussed above clearly show that slopes (*m*) differing from −1 can occur for equilibrium adsorption and absorption

TABLE 2. Values of the Slope m in $\ln K^{\mathrm{ads}} = m \ln p^{\circ}_{L} +$ Constant at 20 °C for *Ad*sorbing Compounds That Have No or Constant Lewis Acid−Base Interactions with the Surface[a]

surface	$m \pm$ se from ads expt	ref	m calcd from γ^{vdW}	ref
water	−0.64 ± 0.03	*38*	−0.62	*39*
octanol			−0.70	*40*
paraffin wax			−0.67	*39*
glycerol	−0.76 ± 0.04	*33*	−0.77	*40*
diethylene glycol	−0.82 ± 0.01	*41*	−0.76	*42*
polyethylene			−0.76	*40*
poly(vinyl chloride)			−0.87	*40*
graphite			−1.42/−1.53	*39*
most biological and other organic materials			∼−0.84	*40*, p 29
$(NH_4)_2SO_4$ 10% RH (32 °C)	−1.04 ± 0.08	*25*		
soot 70% RH	−1.06 ± 0.02	*26*		
soot 55% RH	−1.10 ± 0.02	*26*		
silica 88% RH (15 °C)	−0.68 ± 0.00	*28*		
silica 62% RH (15 °C)	−0.74 ± 0.00	*28*		
silica 26% RH (15 °C)	−0.82 ± 0.00	*28*		
Ca-kaolinite 70% RH	−0.73 ± 0.02	*43*		
Ca-kaolinite 50% RH	−0.81 ± 0.02	*43*		
Ca-kaolinite 30% RH	−0.93 ± 0.02	*43*		
α-Fe_2O_3 70% RH	−0.69 ± 0.02	*44*		
α-Fe_2O_3 50% RH	−0.76 ± 0.02	*44*		
α-Al_2O_3 70% RH	−0.66 ± 0.02	*44*		

[a] m values obtained from adsorption experiments and/or calculated from $m = -0.133(\gamma^{\mathrm{vdW}})^{1/2}$ are shown.

and thus cannot be taken as indicative for nonequilibrium conditions. This conclusion has also been drawn in a very recent paper by Simcick et al. (*22*), who found slopes shallower than −1 for the gas/particle partitioning of PCBs and PAHs in field experiments that were assumed to be free of artifacts and to represent equilibrium partitioning.

If it can be assumed that measured K values represent a true thermodynamic equilibrium, then m contains information about the important factors that determine the sorption process, e.g., type of adsorbates, adsorbent, temperature, relative humidity (RH). If the type of sorption process is known (absorption or adsorption), the slopes may be used to characterize unknown sorbents as discussed above. If the type of sorption process is unknown, the slopes are less informative. However, one conclusion is generally valid: slopes that differ significantly from each other for a given set of compounds unambiguously indicate differences in the sorbents if all other conditions (temperature, RH) were kept identical. This information is helpful in comparing different sets of field data where the sorbents are not known or in comparing an unknown sorbent (e.g., field data on gas/particle partitioning) to a known sorbent (lab data). Extreme values of m even provide direct hints on the type of the sorption process. Slopes significantly steeper than −1 indicate adsorption (on a rather strong adsorbent) while slopes shallower than −0.6 point to absorption (into an absorbent with high cohesive energy). Slopes in the range between −0.6 and −1, which are more commonly encountered, can occur for absorption as well as for adsorption and do therefore not allow such a distinction.

The interpretation of m values is advantageous over the comparison of absolute K values of single compounds. Regardless of the type of sorption process, m values are independent of the units of the sorption coefficients and vapor pressures used in the $\ln K_i^{\mathrm{abs}}$ vs $\ln p^{\circ}_{iL}$ plots. For example, if an adsorption equilibrium has been measured but the sorption constants were normalized to the bulk mass of the sorbent because the type of sorption process or the specific surface area of the sorbent was unknown, the slope m will still allow a meaningful comparison with other slopes since it is not effected by the units of K. Conversely, the comparison of absolute values of K is meaningless if the K values do not have units that are appropriate for the sorption process. A simple hypothetical example may demonstrate this: the sorption of a compound is determined for two sorbents that have a chemically identical surface but different surface area to volume ratios. If the sorption process is *ad*sorption, but the sorption coefficients are normalized to the volume of the sorbents, then different sorption coefficients for the two sorbents will be obtained although thermodynamically the sorption equilibrium in both cases is exactly the same. Only if the sorption constants are related to the surface area of the sorbents will they indicate (correctly) a similarity of both sorbents. It may also happen that similar sorption constants K are obtained for a given compound on two completely different sorbents if the sorption constants are not normalized to the correct sorbent properties. These problems become even more pronounced if the sorbents are not homogeneous. Thus, an unambiguous interpretation of absolute sorption constants K is only possible if the type of sorption process and the appropriate measure of the amount of sorbent are known beforehand. For field data this information is often not available.

In the following, some experimental data from lab and field experiments will be reviewed in the light of the previous discussion of m.

Evaluation of Experimental m Values for Gas/Particle Partitioning. Plots of $\ln K$ vs $\ln p^{\circ}_{L}$ have mostly been used for evaluation of experimental gas/particle partitioning data. As discussed in detail by Pankow and Bidleman (*14*), experimental field data on gas/particle partitioning may often not represent a true partitioning equilibrium. Therefore, the experimental data are assigned symbols [$(F/\mathrm{TSP})/A$ and m_r, where F and A are the particle- and gas-phase concentrations (ng/m^3) of the compounds, respectively; and TSP (μg/m^3) is the total suspended particle concentration] that are different from the symbols used for true thermodynamic partitioning (K_p and m) (*14*). In Table 3, slopes m_r from experimental $(F/\mathrm{TSP})/A$ data compiled from the literature are summarized.

From the above discussion, it follows that the slopes m_r are only comparable if the following requirements are fulfilled: (a) m_r values represent true equilibrium partitioning ($m_r \cong m$), (b) the conditions (i.e., sorbates, temperature and relative humidity (where it plays a role)) of the considered sampling events have been the same, (c) the slopes are based

TABLE 3. Literature Values of m_r in $\ln(F/\mathrm{TSP})/A = m_r \ln p^\circ_L +$ Constant for Gas/Particle Partitioning at Urban Sites

sorbates	av temp (°C)	av RH (%)	$m_r \pm$ se	site	ref
alkanes	na	~65	−0.70 to −1.06	Portland	Hart (1989) cited in *14*
alkanes	5	na	-0.73, $n = 6$, $r^2 = 0.99$	Denver	*6*
alkanes	37	42	-1.03 ± 0.12, $n = 5$	Los Angeles	*25*
PAHs	na	~65	−0.69 to −1.06	Portland	Hart (1989) cited in *14*
PAHs	5	na	-0.76, $n = 4$, $r^2 = 0.96$	Denver	*6*
PAHs	6	na	−0.57 to −0.73	Baltimore Tunnel	*10* cited in *14*
PAHs	25	na	-0.81, $n = 12$, $r^2 = 0.96$	Brazzaville	*11*
PAHs	3.1	84	-0.71, $n = 13$	Chicago	*15*
PAHs	−0.2	85	-0.90, $n = 13$	Chicago	*15*
PAHs	3.7	66	-1.04, $n = 13$	Chicago	*15*
PAHs	0.9	89	-0.76, $n = 13$	Chicago	*15*
PAHs	2.3	78	-0.71, $n = 13$	Chicago	*15*
PAHs	2.4	86	-0.77, $n = 13$	Chicago	*15*
PAHs	−4.2	59	-0.38, $n = 12$	Chicago	*15*
PAHs	−10	60	-0.44, $n = 13$	Chicago	*15*
PAHs	−5.3	58	-0.67, $n = 12$	Chicago	*15*
PAHs	1.6	72	-0.76, $n = 12$	Chicago	*15*
PAHs	5−30	~73	−0.83 to −1.17	Osaka	*4* cited in *14*
PAHs	7	na	-0.84 ± 0.07	Portland	*5*
PAHs	7	na	-0.80 ± 0.09	Portland	*5*
PAHs	0−30	na	-1.04 ± 0.17	Chesapeake Bay	*8*, industrialized site
	0−30	na	-0.97 ± 0.14	Chesapeake Bay	*8*, semi-urban site
	0−30	na	-1.03 ± 0.19	Chesapeake Bay	*8*, urban site
PCBs	5	na	-0.95, $n = 16$	Denver	*6*
PCBs	25	10−25	-0.97, $n = 10$, $r^2 = 0.93$	Chicago	*7*, lab studies
	25	10−25	-0.86, $n = 32$, $r^2 = 0.94$	Chicago	*7*, lab studies
PCBs	3.1	84	-0.90, $n = 18$	Chicago	*15*
PCBs	1.8	69	-0.76, $n = 18$	Chicago	*15*
PCBs	−0.2	85	-0.61, $n = 18$	Chicago	*15*
PCBs	3.7	66	-0.59, $n = 18$	Chicago	*15*
PCBs	0.9	89	-0.82, $n = 18$	Chicago	*15*
PCBs	2.3	78	-0.83, $n = 18$	Chicago	*15*
PCBs	2.4	86	-0.59, $n = 18$	Chicago	*15*

on consistent vapor pressure data p°_L. In many cases, either field data from the literature do not comply with all three conditions or necessary information (including standard errors of the slopes) is missing. Among the various field data sets reported in the literature, the one by Cotham and Bidleman (*15*) is an example of a set that meets all requirements for a comparison of the slopes because (i) the experimental data were corrected for adsorption of gaseous compounds to the filter used for sampling particles; (ii) temperature variations during the sampling event were kept to a minimum by sampling during night with short sampling times; (iii) the average temperatures of the sampling events are similar, and the existing differences may be expected to have little influence on the variability in m_r because the heats of sorption and condensation are usually quite similar; and (iv) the relative humidity was found to have little effect on the partitioning. The event-to-event variations in m_r for Chicago ranged from −0.59 to −0.90 for PCBs and from −0.38 to −1.04 for PAHs. From these data, one can conclude that the particles sampled in the different events exhibited very different molecular interactions with the compounds investigated and, therefore, must have had quite different chemical properties (assuming that $m_r \cong m$). Thus, these data suggest that a 'typical' urban aerosol with respect to the sorption of organic vapors does not exist. Earlier conclusions that suggested a rather high similarity of urban aerosol from a variety of sampling locations had been based on the similarity of absolute sorption constants (*23*). However, as discussed above, comparison of absolute sorption in general does not allow unambiguous conclusions. Therefore, the information obtained from the slopes must be regarded as more reliable.

As pointed out above, from slopes alone, it is not possible to conclude whether *ad*sorption or *ab*sorption dominates the gas/particle partitioning in a given case, unless m assumes rather extreme values. However, for compound classes for which sorption is determined by van der Waals interactions only (e.g., alkanes, PCBs), this question may be answered by combining the information provided by the slope m and the absolute sorption constants K. If, in these cases, *ad*sorption governs gas/particle partitioning, the slope m equals $-0.133(\gamma^{\mathrm{vdW}})^{1/2}$ (case a see above) and eq 10 can be rewritten as

$$\ln K_i^{\mathrm{ads}}\ (\mathrm{m}^3/\mathrm{m}^2) = m\ (\ln p^\circ_{i\mathrm{L}} - 15.7) - 19.5 \qquad (12)$$

This equation allows the calculation of the adsorption constant K^{ads} of compounds such as alkanes or PCBs with a given vapor pressure (in Pa) on the considered surface. Such calculated adsorption constants can be compared to the experimental sorption constants after conversion to same units. Using Sheffield and Pankow's (*24*) estimate of the specific surface area of urban particulate matter of about 2.1 m^2/g and switching from ln to log, eq 12 becomes

$$\log K_i^{\mathrm{ads}}\ (\mathrm{m}^3/\mu\mathrm{g}) = m \log p^\circ_{i\mathrm{L}} - 6.83\ m - 14.6 \qquad (13)$$

It should be noted that eq 13 has been derived for 20 °C. However, when assuming that the heats of sorption and the heats of condensation are similar—an assumption that is supported by many experimental data—eq 13 can also be used as a first approximation to estimate K^{ads} values at other temperatures. Table 4 shows the difference between experimental and calculated (eq 13) K values for alkanes and PCBs for field data sets from Table 3. For the calculations, the experimentally determined m values were used (Table 3). As is evident, in most of the cases, the experimental K values are one to several orders of magnitude higher than

TABLE 4. Comparison of Experimental Sorption Constants[a] and Estimated Adsorption Constants Estimated for Surfaces That Exhibit the Same Slope as the Experimental Data (Assuming a Specific Surface Area of 2.1 m^2/g for the Aerosols)

compd class	exptl slope	$\log K_{exp} - \log K_{est}$[b]	temp. (°C)	ref
alkanes	−1.03	0.64	37	*25*
alkanes	−0.86	2.83	5	*6*
PCBs	−0.95	1.91	5	*6*
PCBs	−0.97	0.57	25	*7*
PCBs	−0.86	1.78	25	*7*
PCBs	−0.90	2.48	3.1	*15*
PCBs	−0.76	3.88	1.8	*15*
PCBs	−0.61	5.29	−0.2	*15*
PCBs	−0.59	5.72	3.7	*15*
PCBs	−0.83	2.35	2.3	*15*
PCBs	−0.82	2.85	0.9	*15*
PCBs	−0.59	5.48	2.4	*15*

[a] Data from Table 3. [b] Eq 13.

predicted from eq 13. These findings suggest that sorption from the gas phase to urban particles is governed primarily by *ab*sorption and not *ad*sorption, a conclusion that has recently also been drawn by Liang et al. (*25*) based on a different reasoning.

A strict interpretation of slopes *m*, as discussed in this paper, also sheds some new light on the interpretation of published data from laboratory experiments on gas/particle sorption. Goss and Eisenreich (*26*) published data on the adsorption of volatile organic compounds on soot. From a reasonable agreement between the measured absolute adsorption coefficients *K* on soot and some field data on gas/particle partitioning, they concluded that adsorption to soot might be similar to the gas/particle partitioning occurring in the atmosphere. However, this interpretation failed to consider that the slopes in the ln *K* vs ln p_L° plots happened to be significantly different. While the slopes obtained for the adsorption on soot were between −1.06 and −1.10 depending on RH (see Table 2), the slopes for the field data were significantly shallower (−0.84 and −0.74 for alkanes). This clearly indicates that adsorption to soot as measured by Goss and Eisenreich must have been different from the dominating sorption process in the referenced field data on gas/particle partitioning.

Storey et al. (*27*) found a consistency of their own experimental adsorption constants on quartz fiber filters and data by others for a pure silica surface. However, the slopes *m* for the alkanes were between −1.01 and −1.11 (depending on RH) in their work and between −0.68 and −0.82 in the referenced work (*28*). Thus, the two surfaces must have had different properties.

Additional Possibilities for Characterizing Sorbents by Gas-Phase Sorption of Probe Molecules. The attempt to gain information about unknown sorbents from the parameter *m* as discussed above suffers from a serious shortcoming: it requires a linear relationship between ln *K* and ln p_L°. Since this linearity is most likely obtained only if the differences between the studied compounds are due to differences in their van der Waals interactions, the information contained in *m* is principally limited because it is based on only this type of interaction. As a consequence, for example, the *ab*sorbents heptane and diethyl ether (Table 1) or the *ad*sorbents polyethylene and α-Fe_2O_3 (50% RH) (Table 2) cannot be distinguished based on *m* values derived from experiments with alkanes. Obviously the distinction of different sorbents could be more selective if it was also based on the more specific Lewis acid−base interactions. However, in many cases (PAHs are an exemption), this would not yield linear relationships between ln *K* and ln p_L° anymore.

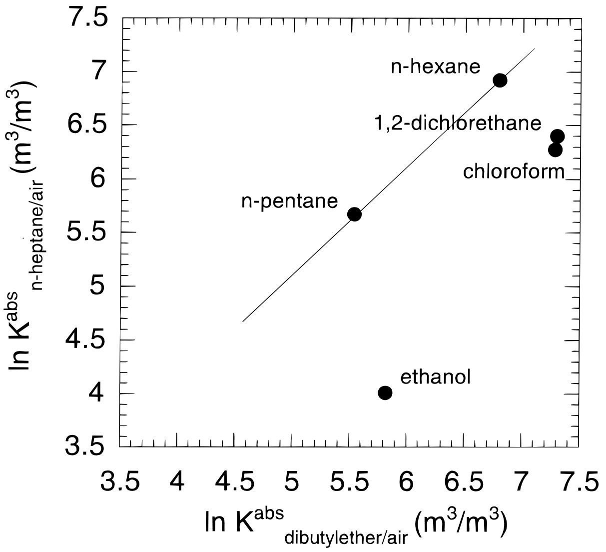

FIGURE 4. Absorption constants of various compounds from air into dibutyl ether plotted against those from air into *n*-heptane. Data from ref *32*.

This problem can be overcome in those cases where a direct comparison of two different sorbents is desired. In this case, the sorption coefficients of compounds *i* for both sorbents, ln K_{i1} and ln K_{i2}, should not be plotted against ln p_{iL}° but against each other. If the sorbents are the same, then K_{i1} and K_{i2} must be identical or, if they have different or not appropriate dimensions (see above discussion), they differ only by a constant factor independent of the studied compounds. In any case, a plot of ln K_{i1} vs ln K_{i2} must give a straight line with a slope of 1.0 for *all* compounds if sorbent 1 and 2 were the same. Such a plot does not necessitate the use of compounds of one compound class. In fact, it is even most informative if the compounds differ as much as possible in their interactions with the sorbents. If there is only a single compound that deviates significantly from the regression line or if the slope deviates significantly from unity, the two sorbents must have been different.

A slope of 1.0 in a plot of ln K_{i1} vs ln K_{i2} provides, of course, no final evidence for the identity of two sorbents, but it is at least indicative for a high chemical similarity of both sorbents if very different sorbates have been included in the comparison. Figures 4 and 5 serve as an illustration. The two absorbents *n*-heptane and dibutyl ether cannot be distinguished by the relative absorption behavior of *n*-alkanes. The slopes in the ln K_i vs ln p_{iL}° plots are identical (see Table 1), and in a plot of ln $K_{i\ \mathrm{heptane/air}}$ vs ln $K_{i\ \mathrm{ether/air}}$, the alkanes lie on a line with a unity slope (Figure 4). However, if other, hydrogen-bonding compounds such as ethanol are included in the comparison, it can be clearly seen that both sorbents behave quite differently and the data points cannot be fitted by a straight line (Figure 4). In contrast, all compounds including those that are capable of forming H-bonds lie on a straight line with a unity slope ($m = 1.04 \pm 0.05$, $r^2 = 0.99$) if *n*-heptane and *n*-octane, two similar absorbents, are compared (Figure 5).

In a recent publication by Finizio et al. (*16*), correlations between octanol/air partitioning constants (K_{oa}) and particle/air partitioning (K_p) have been reported with a slope of 0.79 ($n = 10$, $r^2 = 0.97$) for PAHs and a slope of 0.55 ($n = 22$, $r^2 = 0.79$) for PCBs and pesticides. These slopes are considerably smaller than unity and suggest that the sorbing properties of octanol are quite dissimilar from those of the sampled particles. At the same time, the absolute sorption constants K_{oa} and K_p for PCBs and PAHs were found to be rather similar, which seems to suggest similarities between both sorbents.

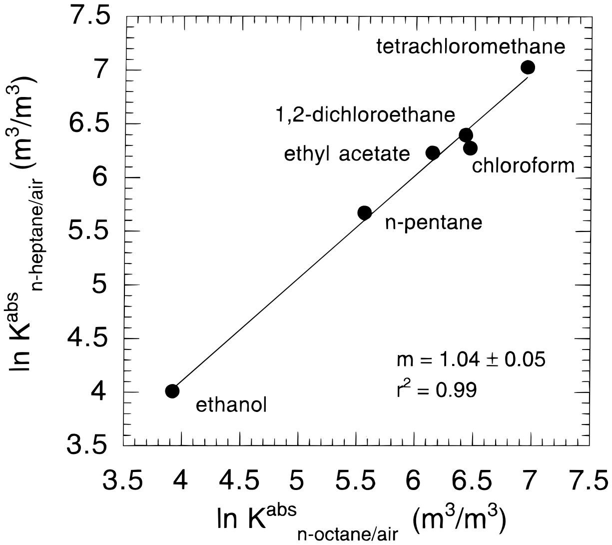

FIGURE 5. Absorption constants of various compounds from air into *n*-octane plotted against those from air into *n*-heptane. Data from ref *32*.

This again is a manifestation of the problem discussed above that a comparison of absolute K values does not allow unambiguous conclusions if the sorption constants are not normalized to the correct sorbent property. Especially for heterogeneous sorbents this is an almost impossible task. In contrast, the conclusion drawn from the slopes, i.e., that the octanol phase and the particle phase must have been considerably different, is compelling.

Finally it is interesting to look at the plant/air partitioning of organic compounds. For PCBs this partitioning has been investigated for five different plant species (ryegrass, clover, plantain, hawk's beard, yarrow) by Kömp and McLachlan (*29*). Plots of log K_{plant} vs log K_{oa} yielded linear regression lines ($r^2 = 0.86-0.98$) with slopes that ranged from 0.57 to 1.15. The authors concluded that this points to a high chemical variety of the sorbing tissues of the plant species, a conclusion that is in agreement with the discussions outlined here. Deviations from a unity slope further indicate that many plant tissues have sorbing properties different from that of octanol (*29*). Despite these differences, log K_{oa} works as a useful predictor for a given class of compounds (e.g., PCBs) as is demonstrated by the good linearity of the regression lines. However, the larger the chemical difference between octanol and the sorbing phase, the more likely it is that a single regression line will not hold for compounds of different compound classes. Only if there is a high chemical similarity between octanol and the sorbing phase will organic compounds from different compound classes fall on the same regression line log $K_{\text{plant/air}}$ vs log K_{oa}, which will then exhibit a unity slope.

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