

# EVALUATION OF A PREDICTIVE MODEL FOR AIR/SURFACE ADSORPTION EQUILIBRIUM CONSTANTS AND ENTHALPIES

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**Abstract**—A model used to predict equilibrium adsorption to surfaces using a poly-parameter linear free-energy relationship as well as an empirical model used to predict enthalpies of adsorption of volatile compounds were evaluated with new experimental data to cover semivolatile compounds and a larger variability of compound classes. Equilibrium adsorption constants on a quartz surface ranging over seven orders of magnitude were measured for 142 compounds, and enthalpies of adsorption on a quartz surface from -33.7 to -99.8 kJ/mol were measured for 76 compounds. Agreement between experimental and predicted data was within a factor of two (82.1%) or three (100.0%) for the equilibrium adsorption constants and within 20% for the enthalpy of adsorption values. Thus, the scatter in the validation data sets reported here were practically the same as that for the calibration data sets used to derive the models. The few outliers that we identified in the prediction of equilibrium adsorption constants likely are caused by either shortcomings of the reported sorbate parameters or the occurrence of chemical speciation in the water layer on the surface of the quartz.

Keywords—Adsorption Enthalpy Semivolatile Organic compounds Partitioning

# INTRODUCTION

Adsorption, which is the partitioning between the air and the surface of condensed phases, such as mineral particles, dry soil, aerosols, water droplets, and snow, plays a significant role in the environmental fate of volatile and semivolatile organic substances, both in terms of transport and in terms of transformation. Thus, much work has been done recently to better understand adsorptive partitioning to environmental phases under ambient conditions (for a critical review, see Goss [1]). The adsorptive partitioning constant for a given substance, *i*, to a given surface,  $K_{i surfair}$ , is defined in Equation 1:

$$K_{i\,\text{surf/air}} = \frac{mol_{i\,\text{surf}}/SA_{\text{surf}}}{mol_{i\,\text{air}}/V_{\text{air}}} \tag{1}$$

where  $mol_{i \text{ surf}}$  and  $mol_{i \text{ air}}$  are the number of molecules of *i* on the surface and in the air at equilibrium,  $SA_{\text{surf}}$  is the surface area of the condensed phase, and  $V_{\text{air}}$  is the volume of air. The units of  $K_{i \text{ surf/air}}$  are explicitly given as mole m<sup>3</sup>/mole m<sup>2</sup>, but for the sake of simplicity, they will be given as m throughout the present work. In earlier works, we have shown that a vast number of adsorption constants  $K_{i \text{ surf/air}}$  for a diverse set of volatile organics to various surfaces can be described with the poly-parameter linear free-energy relationship (LFER) [1] shown in Equation 2:

$$\log K_{i \text{ surf/air}}(15^{\circ}\text{C}) = 0.136 \cdot L \cdot \sqrt{\gamma_{\text{surf}}^{vdW}} + 5.13 \cdot B \cdot EA_{\text{surf}} + 3.67 \cdot A \cdot ED_{\text{surf}} - 8.47 \qquad (2)$$

where *L*, *B*, and *A* are the sorbate's hexadecane/air partitioning constant (describing the van der Waals [vdW] interaction capability), the effective hydrogen bond basicity (describing the electron-donating [ED] capability), and the effective hydrogen

bond acidity (describing the electron-accepting [EA] capability), respectively. In previous publications, we used the terms  $K_{i\,\text{hexadecane/air}}$ ,  $\Sigma\beta_{12}^{H}$ , and  $\Sigma\alpha_{12}^{H}$  for the sorbate descriptors. In the present work, however, we use *L*, *B* and *A*, respectively, because they have become more common in the literature. Corresponding to the sorbate descriptors are the analogous surface descriptors,  $\sqrt{\gamma_{\text{surf}}^{vdW}}$ ,  $EA_{\text{surf}}$ , and  $ED_{\text{surf}}$ , which are the square root of the van der Waals component of the surface free energy, the electron-accepting activity of the surface, and the electrondonating activity of the surface, respectively. The surface descriptors are dependent on surface type and on ambient humidity if the surface is hydrophilic. The values of such descriptors are scattered throughout the literature. A rather large list of sorbate descriptors can be found [2–4], and a list of surface descriptors has been compiled by Goss [1].

For volatile compounds, Equation 2 is applicable to all surfaces and at all humidities studied so far (including mineral surfaces [5,6], salt surfaces [5], organic liquid surfaces [7], the water's surface [8], snow [9], Teflon<sup>®</sup> [7], graphite [10], and so on) and for a large variety of compound classes. Furthermore, Equation 2 gives much better predictions than previously used single-parameter LFERs, such as those that relate  $K_{i \text{ surf/air}}$  to the subcooled liquid vapor pressure of the pure com pound,  $p_i^*$ , or to the partitioning constant between octanol and air,  $K_{i \text{ oa}}$ . The reasons for this have been discussed previously [1,11].

The calibration of Equation 2, however, was limited to rather volatile compounds, although many compounds of environmental interest can be expected to exhibit significantly larger  $K_{i \text{ surf/air}}$  values to natural surfaces. This is particularly true for larger molecules, including pesticides, hormones, and pharmaceuticals, which, as is inherent by their size, have a greater tendency to adsorb intensively because of their larger van der Waals forces and the possible H-bonding from multiple functional groups. Furthermore, the larger the molecule, the less favorable *ab*sorption would be into bulk water, such as into a

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water droplet, because of the increased cost of the cavity energy, which would favor adsorption on the droplet's surface. The performance of Equation 2 at predicting  $K_{i \text{ surf/air}}$  values for such semivolatile compounds has not been checked before. Furthermore, it also remains to be tested if Equation 2 is applicable to compound classes other than those used for the calibration, such as compounds with untested moieties or combinations of moieties.

For this purpose, the adsorption on the quartz surface was measured for a much larger chemical data set than that used previously, which included new compound classes as well as several substances exhibiting quartz/air equilibrium partitioning constants,  $K_{i \text{ quartz/air}}$ , that were three orders of magnitude higher than those measured previously. Quartz was chosen as a model surface for these verification experiments, because quartz exhibits strong  $EA_{\text{surf}}$  and  $ED_{\text{surf}}$  interactions and, therefore, displays all the types of relevant interactions an adsorbent can have with an adsorbate.

When  $K_{i \text{ surf/air}}$  values at temperatures other than 15°C are desired, instead of using different equations of the type given in Equation 2, it is more practical to use a prediction for the enthalpy of adsorption,  $\Delta_{ads}H_i$  (kJ/mol), such as the empirical relationship shown in Equation 3 (from Goss and Schwarzenbach [12]):

$$\Delta_{\rm ads} H_i = -9.83 \log K_{i \, \rm surf/air}(15^{\circ} \rm C) - 90.5$$
(3)

and then use the van't Hoff Equation (Eqn. 4):

$$\log K_{i \text{ surf/air}} = -\frac{\Delta_{\text{ads}}H_i + RT_a}{2.303R}\frac{1}{T} + constant$$
(4)

where *R* is the ideal gas constant and  $T_a$  is the average temperature of the temperature range considered. As with Equation 2, however, the applicability of Equation 3 to substances exhibiting  $\Delta_{ads}H_i$  values more negative than -50.2 kJ/mol, which was the most negative value for those substances measured previously, had not been checked. For mineral surfaces, we now have extended the data set to substances exhibiting values from -31.7 to -99.8 kJ/mol.

### MATERIALS AND METHODS

The quartz sand was obtained from Merck (Dietlikon, Switzerland) and washed under mild heating (at 60°C) for 3 d in a solution of 10% H<sub>2</sub>O<sub>2</sub> in water. The specific surface area was determined by the Brunauer-Emmett-Teller nitrogen adsorption method for both dry quartz and quartz equilibrated at 50% relative humidity (RH). In both cases, the surface area was 0.26 m<sup>2</sup>/g. The size distribution of the quartz sand was as follows: 0.3% < 63  $\mu$ m, 32.5% < 177  $\mu$ m, 89.1% < 355  $\mu$ m, 99.0% < 710  $\mu$ m, and 100% < 1 mm. All chemicals were ordered from Fluka (Buchs, Switzerland).

The  $K_{i \text{ quartz/air}}$  constants were determined by inverse gas chromatography (IGC), which uses dynamic adsorption experiments where the adsorbent serves as the stationary phase in a gas chromatograph (GC) system. When substance *i* is injected onto the column under isothermal conditions, the retention observed is a measure of its adsorption intensity. The  $K_{i \text{ surf/air}}$  can be derived from Equation 5 (from Conder and Young [13]):

$$K_{i \, \text{surf/air}} = \frac{(V_i - V_{\text{tracer}})}{SA_{\text{surf}}}$$
(5)

where  $V_i$  is the retention volume of *i* and  $V_{\text{tracer}}$  is the elution volume of a nonretained tracer. The volumes  $V_i$  and  $V_{\text{tracer}}$  are

determined from the retention time of the respective peaks marked by the peak center and the volumetric flow rate of the carrier gas corrected for the pressure drop in the IGC system [13]. Equation 5 requires that the organic compounds are present at low concentrations (i.e., in the linear range of the adsorption isotherm) and that the adsorption kinetics are fast enough to guarantee equilibrium conditions during the chromatographic process. A sample chromatogram along with a description of its interpretation is given in the *Supporting Information* (SETAC Supplemental Data Archive, Item ETC-25-01-01; http://etc.allenpress.com).

The IGC used was a Carlo Erba MFC500 (Carlo Erba, Milan, Italy) equipped with a flame-ionization detector. The quartz sand was packed into stainless-steel, high-pressure liquid chromatograph columns ( $1.0 \times 0.3$  or  $3.5 \times 0.6$  cm). No frits were used, because the sand grains were sufficiently large to remain in the column. The GC capillaries used were made of stainless steel and had an internal diameter of 0.5 mm. For measurements at 15 and 25°C, a water bath was used to ensure temperature equilibrium. For measurements at 35, 45, and 55°C, the oven on the GC unit was used to heat the column, and the injector temperature was set to 100°. No temperature gradient was used. To obtain the desired RH of 90%, the carrier gas (nitrogen) was passed through a water saturator in a water bath before it entered the GC. The temperature of the water saturator was selected according to the column temperature and the pressure drop between the water saturator and column [14]. To ensure that no condensation occurred in the capillaries joining the water saturator and injector, a heating cable (Polytetrafluoroethene 2.2 mm KteS; Wisag, Zurich, Switzerland) ran parallel to either side of the capillaries and was secured and insolated by completely wrapping the heating cable and capillaries first with Teflon tape and then with aluminum foil. The quartz was equilibrated with the carrier gas for at least 15 h after initial installation of the column. Gas flow rates between 5 and 80 ml/min were controlled by a needle valve and measured with a mass flowmeter (F-111C-HAD-11-V; Bronkhorst, Reinach, Switzerland). The pressure drop in different parts of the system from the water saturator to the column was measured with a pressure transducer (26PCCFB6G; Honeywell, Seelze, Germany). This information was used to adjust the temperature of the water saturator and to correct the pressure of the measured volumetric gas flow rate. When adjusting to different temperatures, the carrier gas flow was stopped, the temperature of the column and water saturator adjusted appropriately, and the gas flow restored when the desired temperatures were reached.

Methane was used as the nonsorbing tracer. Depending on the amount of chemical needed to give a noticeable peak, 0.5 to 10,000 µl of the vapor of the sorbates were injected. If peaks were deemed to be too large or too small, injections were redone with a more appropriate injection volume. For some substances exhibiting particularly low vapor pressures and low detectabilities, solid-phase microextraction (SPME) needles (7-µm polydimethylsiloxane needle; Supelco, Bellefonte, PA, USA) were used to collect the sample and to inject it into the system. The SPME sampling was done by placing the headspace vials on a mildly heated hot plate, inserting the SPME needle through the septum, and waiting for 30 s to 5 min for the sample to partition into the fiber. The SPME injections were 5 s in length. The SPME needles were then cleaned by purging at 100°C and letting an 80 ml/min stream of helium strip off the chemical for at least 20 min. The back-

Table 1. Comparison of chemical data sets used in the present and a previous study for the determination of the quartz/air partitioning constant  $K_{i \text{ quartz/air}}$  values

Parameter/descriptor <sup>a</sup>	Previous study <sup>b</sup>	Present study	
Maximum L	5.79	7.63	
	l-Methyl naphthalene	Phenanthrene	
Maximum A	0.57	0.74	
	2,2,2-Trifluoroethanol	3,4-Dichlorophenol	
Maximum B	0.56	0.88	
	2-Propanol	Dimethyl phthalate	
Smallest $K_{i \text{ quartz/air}}$	4.34E-07	3.16E-07	
(m)	Trichloroethene	Dichloromethane	
Largest $K_{i \text{ quartz/air}}$ (m)	4.02E-04	1.54	
• rquuusuu	2-Nitrotoluene	Diethyl phthalate	
Least negative $\Delta_{ads}H_i$	-31.7	-33.7	
(kJ/mol) <sup>c</sup>	Chlorobenzene	Toluene	
Most negative	-50.2	-99.8	
$\Delta_{ m ads} H_i (kJ/mol)^c$	Ethyl acetate	Decanol	

<sup>a</sup> *L*, *A*, and *B* are the sorbate's hexadecane/air partitioning constant, the effective hydrogen bond acidity, and the effective hydrogen bond basicity, respectively.

<sup>b</sup> From Goss and Schwarzenbach [6] unless otherwise indicated.

<sup>c</sup> Enthalpies of adsorption ( $\Delta_{ads}H_i$ ) from Goss [15].

ground  $V_i$  was obtained by measuring the  $V_i$  in the IGC system with an empty column attached (with all other conditions identical) and was subtracted from the  $V_i$  obtained with the column filled with quartz sand. The background  $V_i$  usually was less than 15% of the total  $V_i$  with the small quartz column except for large apolar molecules (e.g., dodecane) when performing headspace injections and for most molecules when performing SPME injections.

Not every chemical was measured at every experimental temperature because of various experimental and practical reasons. The  $\Delta_{ads}H_i$  values were determined using Equation 4 only when data at three or more temperatures (from the present study and from Goss and Schwarzenbach [6]) were measured. For chemicals where  $K_{i \text{ quartz/air}}$  at 15°C was not measured, the values were extrapolated using the experimentally determined  $\Delta_{ads}H_i$  values via Equation 4, and when that was not available, the estimated  $\Delta_{ads}H_i$  from Equation 3 and the  $K_{i \text{ quartz/air}}$  measured at the lowest temperature were used.

### RESULTS

The  $K_{i \text{ quartz/air}}$  for a total of 143 compounds were measured, 130 of which had solute descriptors available, 45 of which were repeats of the 55 compounds for which  $K_{i \text{ quartz/air}}$  was previously reported in literature [6] and that had been used to calibrate the surface descriptors of the quartz surface at 15°C and 90% RH. Seventy-six compounds were measured at three temperatures or more, allowing for the  $\Delta_{ads}H_i$  to be determined via Equation 4. Table 1 summarizes how the data set *L*, *B*, and *A* of the chemicals measured here compares to the previously used chemical data set for  $K_{i \text{ quartz/air}}$  determinations [6]. Also in this table is a comparison of the range of  $K_{i \text{ quartz/air}}$  and  $\Delta_{ads}H_i$  values both reported here and reported previously [6,12,15].

The new substances and substance classes that were measured in the present study include cycloalcohols, carboxylic acids, phenols (cresols and chlorophenols), chloroaniline, phthalates, thiophenol, dibenzofuran, biphenyl, three-ring polyaromatic hydrocarbons, tetrachlorobenzenes, pentachlorobenzene, hexachlorobenzene, methyl benzoate, acetophenone, benzyl acetates, benzyl alcohol, benzonitrile, dimethyl car-



Fig. 1. Quartz/air partitioning constant values  $(K_{i quartz/air})$  values at 15°C and 90% relative humidity (RH) determined by direct measurement or extrapolations from higher temperatures compared to estimated  $K_{i quartz/air}$  value for 15°C and 90% RH from Equation 2. + = previous measurements;  $\bigcirc$  = measurements at 15°C;  $\blacktriangle$  = measurements extrapolated using Equation 4;  $\blacklozenge$  = measurements extrapolated using Equation 3; - = 1:1 line.

bonate, naphthol, azobenzene, 4-nitroanisole, and lindane. A complete list of all chemicals, sorbate descriptors,  $K_{i \text{ quartz/air}}$  measurements, and experimental  $\Delta_{ads}H_i$  values can be found in *Supporting Information*.

In Figure 1, the newly and previously measured values are compared with the predicted values using Equation 2. For this prediction, the surface descriptors for quartz sand equilibriated at 90% are those previously reported [6]; that is,  $\sqrt{\gamma_{surf}^{vdW}}$ , *EA*<sub>surf</sub>, and *ED*<sub>surf</sub> are 5.31, 0.88, and 0.85, respectively.

The 76 measured  $\Delta_{ads}H_i$  values are compared with the estimated values (following Eqn. 3) in Figure 2.

#### DISCUSSION

### K<sub>i quartz/air</sub> values

A comparison of the calibration data set [6] used to derive Equation 2 and the evaluation data set, after removing the outliers discussed below, can be found in Table 2. From Table 2 and Figure 1, it is evident that the scatter for our newly measured data set is almost the same as for the calibration data set. This is a very good result, considering that the diversity of the data set has been expanded considerably. Many of the compounds that differed by a factor of three or more belonged to similar compound classes, such as the polychlorobenzenes and carboxylic acids. These outliers are depicted graphically in Figure 3.

Such deviations as those depicted in Figure 3 can result from various causes, such as inaccurately reported solute descriptors, chemical transformation (e.g., speciation) at the moist quartz surface, an inherent flaw in the model for a certain compound class, and bad experimental data. For the compounds used here, inaccurately reported solute parameters and chemical transformation are the most relevant. This will now be discussed for the individual compounds and compound classes.



Fig. 2. Comparison of experimentally determined enthalpy of adsorption  $(\Delta_{ads}H_i)$  values from measured quartz/air partitioning constant  $(K_{i,quartz/air})$  values at three or more temperatures with the  $\Delta_{ads}H_i$  predicted from Equation 3.

Polychlorobenzenes. With the tri-, tetra-, and pentachlorobenzenes, the measured values are substantially higher than the predicted values. In the literature, the A and B values are reported as being 0.00 [2,4,16]. In a recent paper [17], polychlorobiphenyls, which are structurally quite similar, are stated to exhibit a noticeable B value. In a paper by Slasinski et al. [18], hydrogen-bond formation between polychlorobenzenes and hexamethylphosphoramide was observed when cyclohexane, but not carbon tetrachloride, is used as a solvent. Thus, we consider the possibility of the polychlorobenzenes exhibiting weak hydrogen bond as still an open issue and worthy of further investigation.

*4-Nitroanisole.* The experimental  $K_{i \text{quartz/air}}$  is higher than the predicted value by a factor of four. This is considered to be caused by an underestimation of both the obtained *A* (0.00) and *B* (0.40) descriptors [19]. A prediction of these compound descriptors with the program COSMOtherm (Conductorlike Screening Model) [20], according to the method described by Zissimos et al. [21], gave the following numbers: A = 0.09,



Fig. 3. Major outliers between the comparison of the experimental and estimated quartz/air partitioning constant ( $K_{i \text{quartz/air}}$ ) values following Equation 2. × = lindane;  $\bigcirc$  = 4-nitroanisole; + = pyridine;  $\triangle$  = diethyl amine;  $\bigcirc$  = tri-, tetra-, and pentachlorobenzenes;  $\square$  = carboxylic acids; - = 1:1 line.

and B = 0.46. Using these numbers in Equation 2 yields a very good agreement between the predictive (1.13E-02 m) and experimental (1.39E-02 m)  $K_{i \text{ quartz/air}}$  values. This seems to indicate that the literature descriptor values for 4-nitroanisole are not correct. However, the overall precision of sorbate parameters calculated with COSMOtherm is not good enough to be used as a reliable source of missing sorbate parameters [21].

Lindane. Lindane was measured to be a factor of eight lower than what is predicted by Equation 2. For lindane and other hexachlorohexanes, some scatter is reported in the literature in regards to their various partition coefficients on which the solute parameters are based, which has led to discrepancies between LFER-based predictions of phase-partitioning properties and measured values [22]. Another explanation for the discrepancy in this case is considered to be based on the equa-

Table 2. Comparison of the statistical parameters from the calibration and evaluation data sets for poly-parameter linear free-energy relationship models used to determine logarithmic quartz/air partitioning constant (log  $K_{i \text{ quartz/air}}$ ) values at 90% relative humidity

	Equation 2 <sup>a</sup>		Poole [27] <sup>b</sup>	
	Calibration	Evaluation	Calibration	Evaluation
n	51	118	51ª	95°
Average error <sup>d</sup>	0.01	-0.04	0.00	0.14
Absolute average	0.19	0.19	0.12	0.26
Error				
$r^2$	0.91	0.97	0.96	0.94
Standard deviation	0.23	0.22	0.15	0.31

<sup>a</sup> The calibration data set is from Goss and Schwarzenbach [6], and the evaluation data set is from the present study.

<sup>b</sup> Poole used only 41 data points from the 51 referenced in Goss and Schwarzenbach [6]. Which 41, however, are unknown to us; thus, the resulting statistics reported in Poole [27] are different than the statistics reported here.

<sup>c</sup> The compounds and data used are the 95 compounds with both dipolarity/polarizability (*S*) and excess molar refraction (*E*) parameters available, as listed in the *Supporting Information* (SETAC Supplemental Data Archive, Item ETC-25-01-01; http://etc.allenpress.com).

<sup>d</sup> Error is defined as (estimated value – experimental value).

torial/axial conformation of lindane, which would make it impossible for all the chloro-substituents to be in contact with the flat surface; thus, the apparent *B* value for adsorption would be less than the reported *B* value (0.66 in Abraham et al. [23]).

Pyridine and diethyl amine. These peaks exhibited extreme asymmetries, making them unacceptable for evaluation (and, thus, not to be considered as one of the 143 chemicals where  $K_{i \text{ quartz/air}}$  values were obtained). This tailing, which also was observed for other amines, pyridines, and formamides (not shown), is hypothesized to be related to their ability to act as a strong Lewis base, where they pick up a proton in the outer water layer that causes them to have a charge and, thus, to adsorb much more strongly (or, potentially, to form covalent bonds) to the quartz surface and making Equation 2 no longer valid (Eqn. 2 does not apply to nonneutral species). The surface charge of quartz in water is negative above pH 2, which implies that the hydroxyl groups on the surface are acidic (see Fig. 3.1 of Stumm [24]); thus, the water layer adsorbed to the surface in the present study is expected to be acidic, thereby making it extremely likely that pyridine and diethyl amine are protonated in the water layer. Note that 2-chloroaniline, which is very weakly basic (having an acid dissociation constant  $[pK_{ia}]$  of 2.65 in the protonated form [25]), does not exhibit this asymmetry and is not an outlier in this adsorption model. It may be possible to estimate the pH of the hydrated quartz surface by using a set of basic compounds with an increasing set of  $pK_{ia}$  values and seeing at what  $pK_{ia}$  value the peaks become significantly asymmetric. One must be aware, however, that different quartz surfaces from different sources may have different amounts of hydroxyl groups; thus, the hydrated quartz surfaces can have different pHs.

*Carboxylic acids.* For these compounds the measured  $K_{i \text{ quartz/air}}$  values are higher than the estimation by factors of 3.4 to 5.1. At the temperatures used (15–55°C), carboxylic acids are dimerized in the vapor phase, which would account for them being outliers. Furthermore, if the pH of the water on the quartz surface is in a range similar to the  $pK_{ia}$  value of carboxylic acids (~4.8 [25]), the dimerized carboxylic acids could dissociate, causing them to sorb even more intensively. Note that high asymmetries were not observed for these compounds.

Others. Of the remaining 117 measured  $K_{i \text{ quartz/air}}$  with solute descriptors available, only 21 differ from the predicted value by more than a factor of two, and none differs by more than a factor of three. This is in agreement with the stated accuracy of such a prediction—that is, that the prediction of 80% of compounds differs from experimental values by less than a factor of two [1]. The cycloalkanes belonged to this set of 21 minor outliers, and the reasons for this have been discussed previously [1]. In short, the *L* descriptor overestimates the van der Waals interaction capability for adsorption of these molecules, because some steric effect exists that prohibits the entire molecule from making close contact with the surface compared to the *n*-alkanes.

# $\Delta_{\textit{ads}} H_i \ \textit{values}$

Of the 76  $\Delta_{ads}H_i$  values obtained in this study, 26 were off by 10% or more from the Equation 3 estimation, and of these, none was off by more than 20%. The absolute error was 0.2 kJ/mol, the absolute average error 4.3 kJ/mol, the standard deviation 5.75, and  $r^2$  0.82. This, along with a visual appraisal of Figure 2, shows that the estimation given in Equation 3 is reasonable and that for extrapolating  $K_{i \text{ quartz/air}}$  values within



Fig. 4. Log–log plot of quartz/air partitioning constant ( $K_{i \text{ quartz/air}}$ ) values versus the subcooled vapor pressure  $p_i^*$  (from Daubert and Danner [26]).  $\blacktriangle$  = nonpolar compounds; + = monopolar compounds;  $\blacklozenge$  = bipolar compounds.

an ambient temperature range, this prediction of  $\Delta_{ads}H_i$  is adequate for most practical purposes. The compounds with an experimental value that differed from the estimated value by more than 15% were cyclohexanol, toluene, bromobenzene, acetophenone, 1-methyl naphthalene, anthracene, phenanthrene, lindane, and 3-nitroanisole. It should be noted that this model underpredicts the results in general; however, a recalibration of Equation 3 with the old and new data would be unlikely to give much of an improvement in its applicability. In terms of outliers belonging to certain compound classes, no clear trends or, at best, only minor trends, such as near- to underprediction of the  $\Delta_{ads}H_i$  for the polyaromatic hydrocarbons, can be seen. Thus, no mechanistic explanation of the deviations can be given explicitly, especially considering that many of the deviations are influenced by experimental errors. Extrapolations of  $\Delta_{ads}H_i$  were based on only a few data points, and some minor differences in the quartz surface likely occurred on column aging or column replacement. Several columns were used to measure this data set, and our experience has shown that the resulting  $r^2$  from plotting  $\ln \Delta_{ads} H_i$  versus 1/T (after Eqn. 4) is usually best when the same column is used for measurements at all temperatures.

# Comparison of $K_{i \text{ quartz/air}}$ and $p_i^*$

Although the inadequacies of using  $p_i^*$  to estimate  $K_{i \text{ quartz/air}}$ have been established [1], this estimation method will be discussed further here because of its use in the literature. Figure 4 shows a log–log plot of experimentally determined  $K_{i \text{ quartz/air}}$ and  $p_i^*$  values (from Daubert and Danner [26]). Note that as log  $p_i^*$  is linearly related to  $\Delta_{\text{vap}}H_i$ , it does not matter if log  $p_i^*$  values at 25 or 15°C are used [12]. Looking at Figure 4, such an estimation clearly is inferior to that shown in Figure 1. Notice that for a variety of chemicals with a given  $p_i^*$ , their  $K_{i \text{ quartz/air}}$  value can vary by more than two orders of magnitude. Thus, the use of this correlation can certainly lead to very misleading interpretations. For individual compound classes, linear trends do appear. Nonpolar compounds (defined here as compounds having both *A* and *B* < 0.1) show a linear relationship when log  $p_i^*$  is plotted against log  $K_{i quartz/air}$ , as do the bipolar compounds (both *A* and *B* > 0.1). For a given  $p_i^*$ , however, the bipolar compounds adsorb much more strongly. For instance, undecane and phenol have roughly the same vapor pressure (45 and 55 Pa, respectively), but their  $K_{i quartz/air}$  values differ by more than a factor of 100 (2.85E-5 and 3.41E-3 m, respectively). With the monopolar compounds (one of either *A* and *B* > 0.1), however, some behave like the nonpolar compounds, some like the bipolar compounds, and some in between.

# Alternative sorbate descriptor model to predict equilibrium sorption constants

Recently, Poole [27] presented an alternative equation to Equation 2 to calculate the  $K_{i \text{ surf/air}}$  that contains six fitting parameters. Of course, such an extended equation (with three more fitting parameters than in our model) gives a better fit of the calibration data set. However, for the large validation data set presented here, the extended Poole equation performed considerably worse than the calibration data set and worse than our model that uses half the number of fitting parameters, as shown in Table 2. Hence, we conclude that our model is more robust and better suited for extrapolations than the Poole model. We also believe that our model is superior on mechanistic grounds. (A discussion on this will be published as a comment to Poole [27].)

# CONCLUSION

The data presented here demonstrate that using Equation 2 for the prediction of  $K_{i\,quartz/air}$  works, in general, for volatile and semivolatile compounds for a very diverse selection of compound classes. Furthermore, the estimation method for determining  $\Delta_{ads}H_i$  in Equation 3 gives adequate predictions for values ranging from -25 to -100 kJ/mol (and likely beyond). Both equations could be recalibrated with the new data, but it would not improve the estimations substantially. When using these estimations, one must be aware of the following limitations.

### Unknown or uncertain solute descriptors

Of course, poly-parameter LFERs like that in Equation 2 can be employed only if reliable compound descriptors are known. When these descriptors are unknown, several ways exist to estimate them. One way is to assume the data are similar to chemical homologues (e.g., all the *n*-alcohols having similar *A* and *B* values and a linear increase in log  $K_{i\,hexadecane/air}$  with the number of C atoms). For this, however, one must be very certain that the molecules are homologues. Certainly, the various dichlorophenols measured are not homologous in terms of their *A* and *B* values, nor are branched alcohols homologous with *n*-alcohols. There also are various computational ways that such descriptors could be estimated; however, we are unaware of any that are precise enough to be recommended for regulatory purposes.

# Untested compound classes

Even if the descriptors are known and have been found to work in poly-parameter LFERs to describe absorption, Equation 2 may still give a bad prediction for untested compounds classes for predicting adsorption. This is expected to be the case for multifunctional molecules in which all the functional groups (capable of H-bond formation) of the molecule are unable to have contact with a given flat surface at a given moment in time. Furthermore, we have found limitations in how well L can define van der Waals forces, as was the case with cycloalkanes and as will be shown in a forthcoming publication dealing with perfluorocompounds.

### Chemical transformation

One should always be aware of the possible speciation of the compound when considering partitioning onto surfaces that may contain water, because Equation 2 does not apply to ionic species. Furthermore, there also may be cases when the surface itself may react with solute, which would make the model invalid.

### Supporting information

All solute descriptor, measured  $K_{i \text{ quartz/air}}$ , and  $\Delta_{ads}H_i$  data are given (SETAC Supplemental Data Archive, Item ETC-25-01-01; http://etc.allenpress.com) and are compared to the predicted values. Furthermore, an explanation of how chromatograms are interpreted is provided along with a sample chromatogram.

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