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Predicting the Partitioning Behavior of Various Highly Fluorinated Compounds[†]

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Due to their high degree of fluorination, highly fluorinated compounds (HFCs) have unique substance properties that differ from many other organic contaminants. To predict the environmental behavior of HFCs, models that predict both absorptive and adsorptive partitioning are needed; however, the accuracy of existing models has not heretofore been thoroughly investigated for these compounds. This report has two parts: first we show that a well-established polyparameter linear free energy relationship used to predict experimental adsorption constants underestimates values for HFCs by several orders of magnitude. We found a mechanistic explanation for the model's inaccuracy and adjusted it accordingly. In the second part of this report, we evaluate various models that predict saturated subcooled liquid vapor pressure (p_L*), air−water partition constant (K_{aw}), and the octanol−water partition constant (K_{ow}) based on molecular structure. These parameters are typically required for general environmental fate and transport models. Here, we found that SPARC and COSMOtherm make predictions usually within 1 order of magnitude of the experimental value, while the commonly used EPI SUITE and ClogP perform more inaccurately. The least accurate predictions occurred with ClogP for the fluorotelomer alcohols, where the estimated values were off by 2 to almost 5 orders of magnitude.

Introduction

Various types of highly fluorinated compounds (HFCs) have been reported as being capable of both long-range transport and environmental persistence (*1*). HFCs of concern include perfluoroalkylsulfonamides, fluorotelomer alcohols (FTOHs), fluorotelomer olefins (FTolefins), and perfluorinated carboxylic and sulfonic acids (*2*, *3*), which are appearing more frequently in environmental samples (*1*, *4*), wildlife samples (e.g. dolphins (*5*)), and human samples (*6*).

Partitioning coefficients commonly required for environmental models are the saturated subcooled liquid vapor pressure (p_L*), air−water partition constant (K_{aw}), and the octanol−water partition constant (K_{ow}). However, for many emerging chemicals like the HFCs these data are missing, and one has to revert to estimated data. To this end, there are a variety of models that one can choose from (*7*). However, HFCs were not likely incorporated into the training or validation sets of these models, and thus the capability and robustness of models to handle HFCs is currently uncertain. Misleading interpretations, false risk assessments, wasted resources, and misguided policies are just some of the potential side effects that can result from inaccurately estimated (or determined) partitioning coefficients (for an example, see ref *8*). In this study, we compare a number of experimental partition coefficients that have been carefully checked for consistency and reliability with values predicted from four types of software packages: EPI Suite, ClogP, SPARC, and COSMOtherm.

During earlier experiments with the HFCs we recognized that these compounds exhibit a relatively high tendency to *ad*sorb from air to surfaces, such as laboratory glassware (*9*). This may indicate that these compounds also adsorb intensively to environmental surfaces (water droplets, minerals, etc). Here, in the first part of this study, we therefore also present measured *ad*sorption constants, $K_{i\ \mathrm{surf/air}}$, of FTOHs and FTolefins to three surfaces: quartz, α-Al_2O_3, and $CaCO_3$. These adsorption constants are then used to validate a polyparameter linear free energy relationship (pp-LFER) that has been shown before to successfully estimate the $K_{i\ \mathrm{surf/air}}$ values for a large variety of organic chemicals to natural surfaces such as minerals (*10*), salts (*11*), soot (*12*), water droplets (*13*), and snow (*14*).

Experimental Section

Chemicals. The FTOHs and FTolefins have the general structure $F_3C\text{-}(CF_2)_x\text{-}CH_2\text{-}CH_2\text{-}OH$ and $F_3C\text{-}(CF_2)_x\text{-}CH{=}CH_2$, where *x* is an odd number. They are listed here using the shorthand *Y*-2, where "*Y*" refers to the number of carbons on the fluorinated section. The CAS numbers and sources for the chemicals used are 4-2 FTOH (2043-47-2; Aldrich, Buchs, Switzerland), 6-2 FTOH (647-42-7; Clariant, Sulzbach, Germany), 8-2 FTOH (678-39-7; Clariant), 10-2 FTOH (865-86-1; Fluorochem, Derbyshire, U.K.), 4-2 FTolefin (19430-93-4, Aldrich), 6-2 FTolefin (25291-17-2, Clariant), 8-2 FTolefin (21652-58-4, Clariant), 10-2 FTolefin (30389-25-4, Fluorochem), and 12-2 FTolefin (67103-05-3, Clariant). All other chemicals were ordered from Fluka (Buchs, Switzerland).

Solid-Phase Materials. Quartz (mean diameter 120 μm, Merck, Dietlikon, Switzerland), α-Al_2O_3 (mean diameter 6 μm, Alcan Chemicals), and $CaCO_3$ (precipitated, mean diameter 1 μm, Fluka) were the same as used in previous work (*10*, *15*).

Gas-Chromatographic Analysis. $K_{i\ \mathrm{surf/air}}$, the equilibrium ratio of the number of molecules of compound *i* on a surface (in mol/m^2) to the number of molecules in the air phase (mol/m^3), was quantified using inverse-gas chromatography (IGC). A detailed description of the method can be found in ref *15*. Quartz was measured at a relative humidity (RH) of 90% and at 15, 25, 35, 45, and 55 °C, and the enthalpy of adsorption, $\Delta_{ads}H_i$, was determined using the van't Hoff equation (see the Supporting Information (SI)); α-Al_2O_3 and $CaCO_3$ were measured at a RH of 70% and 15 °C.

Models. *Adsorption Model.* The adsorption model tested was recently validated for a large variety of compound classes consisting of 143 compounds (*15*) and is given in eq 1

$$\log K_{i\ \mathrm{surf/air}}(m{,}15\ °\mathrm{C}) = 0.135(\pm 0.003) \cdot L_i \cdot \sqrt{\gamma_{\mathrm{surf}}^{\mathrm{vdW}}} + 5.11(\pm 0.15) \cdot B_i \cdot \mathrm{EA}_{\mathrm{surf}} + 3.60(\pm 0.28) \cdot A_i \cdot \mathrm{ED}_{\mathrm{surf}} - 8.47 \quad (r^2 = 0.996,\ rmse = 0.253) \quad (1)$$

where L_i, B_i, and A_i are sorbate descriptors used to describe the van der Waals (vdW) interaction capability, the electron donor capability, and the electron acceptor capability,

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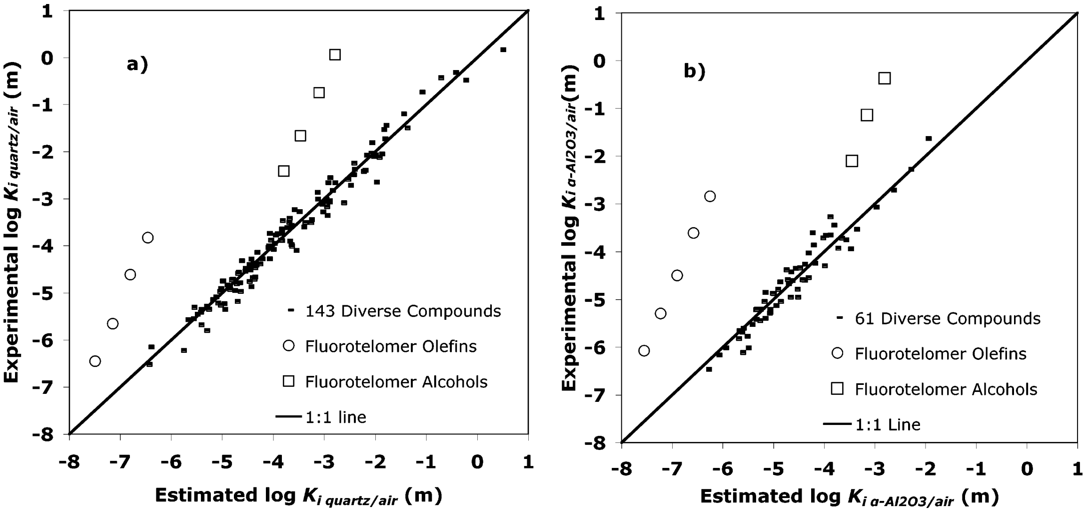


FIGURE 1. Comparison of experimental and estimated log $K_{i\ \mathrm{surf/air}}$ values for the (a) quartz surface (15 °C, 90% RH) and the (b) α-Al_2O_3 surface (15 °C, 70% RH). Estimations are from eq 1, which uses L_i as the vdW descriptor and leads to severe underpredictions for the fluorotelomers. Data are reported in Table S2 in the SI.

respectively. For the FTOHs and FTolefins these descriptors have been determined in an earlier work (*9*) and are reported in Table S1 of the SI together with the descriptors of other compounds used here. Corresponding to the sorbate descriptors are the analogous surface descriptors $\sqrt{\gamma_{\mathrm{surf}}^{\mathrm{vdW}}}$, EA_{surf}, and ED_{surf}, which are the square root of the vdW component of the surface free energy, the electron acceptor capability, and the electron donor capability of the surface, respectively. The surface descriptors for the surfaces at the tested RH come from ref *10*.

General Partitioning Models based on Molecular Structure. The U.S. EPA's EPI Suite (Estimations Programs Interface) is one of the most frequently used models for environmental purposes. It uses a variety of quantitative structure−activity relationships (QSARs) (*16*, *17*). Recent reviews suggest that EPI Suite is among the best performing software packages for the prediction of K_{ow} and K_{aw} values available (*18*−*21*). It requires simply the input of a SMILES string to predict a partitioning constant, and it is publicly accessible online (http://www.epa.gov/opptintr/exposure/docs/episuite.htm).

ClogP is commonly used to calculate the K_{ow} value, and it is available for free use online and requires only the input of a SMILES string (http://www.daylight.com/daycgi/clogp). It is considered widely to be the most accurate QSAR available (*19*) and is quoted (along with EPI Suite) as being able to ascertain K_{ow} values within experimental uncertainty (*7*).

SPARC explicitly calculates various solute−solvent interactions by using various molecular descriptors that are determined by the their molecular structure (*22*, *23*). SPARC also requires only the input of a SMILES string to predict a parameter, and it is publicly accessible on the Internet (http://ibmlc2.chem.uga.edu/sparc/). During the work on this publication a revised version of SPARC was published. While the Web site does not give any information as to the kind of revisions that were made, we noticed that the estimated partition coefficients for the HFCs differed considerably between those that were first retrieved in spring 2005 and those retrieved in February 2006. These two data sets are here referred to as "Old SPARC" and "New SPARC", respectively.

COSMOtherm C2.1 (*24*−*27*) is a commercial software that performs density functional quantum chemical continuum-solvation calculations with statistical thermodynamics. Input files for COSMOtherm are generated with other software packages like Turbomole or Gaussian.

It should be noted here that when using partitioning models that are based on training sets, such as EPI Suite and ClogP, one should first establish whether or not the given molecule belongs to the model's chemical applicability domain. Applicability domains are, however, difficult to determine even if the training data set of the respective model is accessible, such as in the case of the Help Menu Files of EPI Suite. The Web sites on which these models are made available do not currently provide users with a readily available way to ascertain whether a given molecular structure belongs to the model's applicability domain or not. However, one study actually indicates that perfluorocompounds do belong to EPI Suite's applicability domain for the determination of K_{ow} values (*28*). COSMOtherm, on the other hand, uses very little empirical calibration due to its fundamental nature and is thus expected to be very robust when it comes to new or more complex structures; thus, there is no need for the user to establish the applicability domain.

Results and Discussion

Adsorption Model Predictions. Experimental $K_{i\ \mathrm{surf/air}}$ values for the fluorotelomer compounds were found to be several orders of magnitude higher than those estimated with eq 1 for all surfaces tested. Figure 1 shows this for the quartz and α-Al_2O_3 surfaces. In the SI a similar plot for $CaCO_3$ can be found (Figure S2) along with all $K_{i\ \mathrm{surf/air}}$ values (Table S2).

The reason for the innaccuracy of this predictive model lies in the use of the L_i parameter (i.e. log hexadecane/air partition coefficient) as a descriptor for the vdW interactions of the sorbate molecule. L_i depends not only on vdW interactions but also on the cavity energy in hexadecane. For almost all compounds both vdW interactions and the cavity energy in hexadecane exhibit a similar proportionality to the molecular volume; however, this is not the case for HFCs, and thus L_i is inappropriate as vdW descriptor for these molecules. This is discussed in more detail in ref *29*. As a consequence, an adsorption model that covers HFCs along with other compounds must use a more universal vdW descriptor. To this end the best descriptor that we could find is the molar refraction of a compound defined as

$$\mathrm{mr}_i = V_i\,(n_{Di}^{\ 2} - 1)/(n_{Di}^{\ 2} + 2) \qquad (2)$$

where V_i is the molar volume here calculated as the McGowan volume in units of (100 cm^3/mol) (*30*), and n_{Di} is the refractive index of molecule *i*. The molar refraction of *i* is directly related

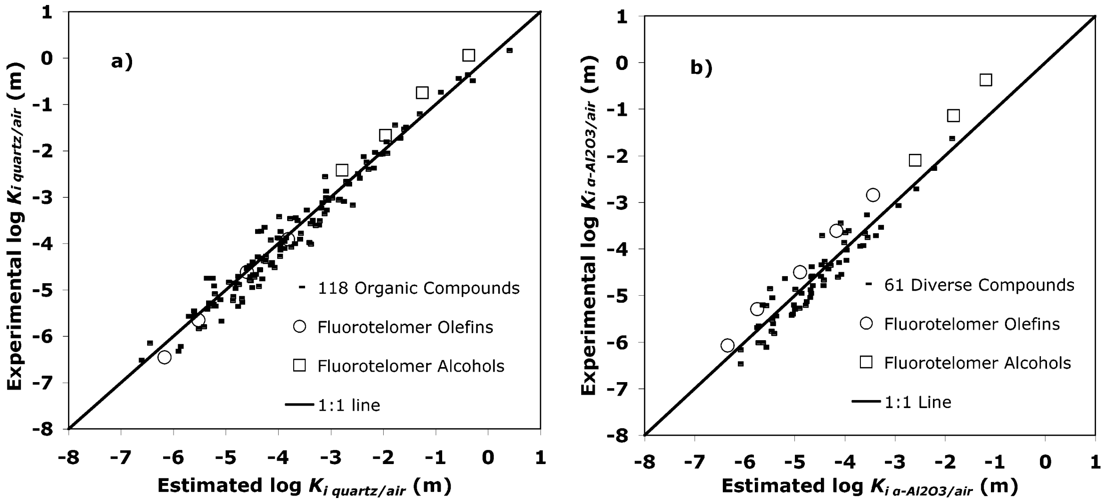


FIGURE 2. Comparison of experimental and estimated log $K_{i\ \mathrm{surf/air}}$ values for the (a) quartz surface (15 °C, 90% RH) and the (b) α-Al_2O_3 surface (15 °C, 70% RH). Estimations are from eq 4, which uses mr$_i$ as the vdW descriptor. The r^2 and *rmse* for the training sets (which do not include the HFCs) are 0.997 and 0.28 (m, log units) for quartz and 0.993 and 0.31 (m, log units) for α-Al_2O_3. Data are reported in Table S2 in the Supporting Information.

to its ability to undergo van der Waals interactions as can be derived theoretically (*31*). Using mr$_i$ for the vdW descriptor the general adsorption model takes the following form

$$\log K_{i\ \mathrm{surf/air}} \cdot a \cdot \mathrm{mr}_i \cdot \sqrt{\gamma_{\mathrm{surf}}^{\mathrm{vdW}}} + b \cdot B \cdot \mathrm{EA}_{\mathrm{surf}} + c \cdot A \cdot \mathrm{ED}_{\mathrm{surf}} - 8.47 \quad (3)$$

where *a*, *b*, and *c* are linear regression coefficients, and the constant "−8.47" is derived from the standard state of adsorption by de Boer ((*32*) p 110, see also ref *13*). The values *a*, *b*, and *c* were determined as in ref *13*, i.e. by performing a multilinear regression with log $K_{i\ \mathrm{surf/air}}$ values for the bulk water surface as the dependent variable and setting $\sqrt{\gamma_{\mathrm{surf}}^{\mathrm{vdW}}}$, EA$_{\mathrm{surf}}$, and ED$_{\mathrm{surf}}$ to those of the bulk water surface, which are 4.69 (mJ/m^2), 1, and 1, respectively. This resulted in

$$\log K_{i\ \mathrm{surf/air}}(m^3/m^2, 15\ ^\circ\mathrm{C}) = 0.84(\pm 0.21) \cdot \mathrm{mr}_i \cdot \sqrt{\gamma_{\mathrm{surf}}^{\mathrm{vdW}}} + 5.22(\pm 0.19) \cdot B_i \cdot \mathrm{EA}_{\mathrm{surf}} + 3.55(\pm 0.35) \cdot A \cdot \mathrm{ED}_{\mathrm{surf}} - 8.47 \quad (r^2 = 0.993,\ rmse = 0.323) \quad (4)$$

Note that the coefficients for *b* and *c* in eq 4 are almost the same as the corresponding coefficients in eq 1, though *a* is quite different. This is due to *a* being based on a different vdW-energy descriptor scale, but *b* and *c* being based on the same descriptors as before. For mineral surfaces, the surface descriptors published before had been derived from experimental adsorption coefficients of various compounds using a multilinear regression based on eq 1. The surface parameters ED$_{\mathrm{surf}}$, EA$_{\mathrm{surf}}$, and $\sqrt{\gamma_{\mathrm{surf}}^{\mathrm{vdW}}}$ should theoretically be the same for a given surface whether they are calculated from multilinear regressions based on eqs 1 and 4; however, due to statistical uncertainties in both models, the resulting surface parameters may differ slightly. Thus, before seeing if eq 4 could predict $K_{i\ \mathrm{surf/air}}$ values for the HFCs, the surface parameters were recalculated following a multiple-linear regression based on eq 4 for a variety of surfaces; the values can be found in Table S3 of the SI.

This revised adsorption model predicted the majority of compounds in the training set within a factor of 2 (see Table S2 of the SI for experimental values and predictions). When placing the HFCs in the *validation set* of this revised model, the predictions were mostly within a factor of 3 and always well within an order of magnitude, as is shown for quartz and α-Al_2O_3 in Figure 2 and Table S2. A similar plot for $CaCO_3$ can be found in Figure S3 of the SI. This is much better than the predictions of eq 1, which were off by up to a factor of 2500. The success of the predictions for the three different surfaces tested indicates the robustness of the revised model and that it should work for other surfaces as well.

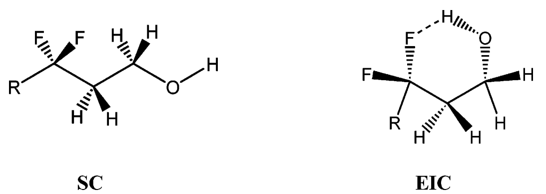
While the new model works well for HFCs and most other tested compounds, it systematically underpredicts polychlorinated aromatic compounds and compounds containing a nitro group (see Table S2) by a factor of 4−6. Though mr$_i$ is a more sound vdW descriptor than L_i, there are likely still some, although not severe, shortcomings which we currently do not understand.

Enthalpy of Adsorption Measurements and Model Predictions. $K_{i\ \mathrm{surf/air}}$ values were measured at various temperatures on quartz at 90% RH in order to derive adsorption enthalpies (see Table S4 for data). The determined $\Delta_{\mathrm{ads}}H$ are as follows: 6-2 FTolefin (−39.3kJ/mol), 8-2FTolefin (−46.3kJ/mol), 10-2 FTolefin (−69.6 kJ/mol), 4-2 FTOH (−70.8 kJ/mol), 6-2 FTOH (−79.1kJ/mol), 8-2 FTOH (−93.0 kJ/mol), and 10-2 FTOH (−105.8 kJ/mol). The enthalpy values fit well with the empirical relationship reported earlier (*15*), i.e.

$$\Delta_{\mathrm{ads}}H = -9.83 \log K_{i\ \mathrm{surf/air}}(15\ ^\circ\mathrm{C}) - 90.5 \quad (5)$$

A plot comparing experimental and predicted $\Delta_{\mathrm{ads}}H$ values from eq 5 is given in Figure S4 of the SI. Based on this linearity between $\Delta_{\mathrm{ads}}H$ and log $K_{i\mathrm{quartz/air}}$ (r^2 = 0.95), it appears that the HFCs do not show any special behavior with respect to their relationship between their free energies and enthalpies of adsorption.

Predictions of Other Partition Data. COSMOtherm. Before we compare the predictions of p_L*, K_{aw}, K_{ow}, and other partition constants from the various models it is necessary to discuss the results from COSMOtherm separately. The strength of COSMOtherm is the ability to consider different 3D conformations of a compound. Conformers with strong intramolecular interactions are especially important because they strongly influence the intermolecular interactions of a compound and therefore its partitioning behavior. In COSMOtherm calculations for single conformers can be performed along with calculations based on weighted contributions from all possible conformers. In the following we give a short overview on the relationship between conformer type and the partitioning behavior of some HFCs as calculated by COSMOtherm.



SC **EIC**

FIGURE 3. Stretched conformation (SC) and the intramolecular electrostatically interacting conformation (EIC) of the fluorinated telomer alcohols (FTOHs).

TABLE 1. Comparison of Predicted and Experimental Saturated Liquid Vapor Pressures, log p_L^* (Pa) at 25 °C for HFCs[f]

		deviation			
compound	exptl value[a]	COSMO-therm	new Sparc[c]	old Sparc[d]	EPI Suite[c]
4-2FTOH	2.33	−0.02	−0.26	−0.24	−0.79
6-2FTOH	1.26	−0.30	−0.75	−0.35	−0.85
8-2FTOH	0.6	0.07	−0.96	−0.14	−0.51
10-2FTOH	−0.69	−0.49	−1.86	−0.62	−0.84
MeFOSE	−2.70[b]	−0.04	−1.81	nd[e]	−1.38
EtFOSE	−2.07[b]	0.34	−1.07	nd[e]	−0.34
MeFOSEA	−2.68[b]	1.05	−0.87	nd[e]	−1.96
perfluorooctanoic acid	0.62	−0.50	−1.52	nd[e]	−0.98
perfluorononanoic acid	0.10	−0.59	−1.78	nd[e]	−1.10
perfluorodecanoic acid	−0.64	−0.84	−2.28	nd[e]	−1.45
perfluoroundecanoic acid	−0.98	−0.81	−2.40	nd[e]	−1.40

[a] From refs *4*, *33*, and *35*. [b] Measured at 23 °C. [c] Accessed February 2006. [d] Accessed April 2005. [e] nd = no data. [f] The standard deviations of the experimental values are estimated to be 0.2 log units. Model deviations are given as "experimental value − predicted value".

FTOHs. For the FTOHs the stretched conformation (SC) of the molecule as well as a conformer with a strong intramolecular electrostatic interaction (EIC) between the hydroxylic proton and the two fluorine atoms attached to the C-3 carbon (−O−H···F−, see Figure 3) were considered. Table S5 summarizes the partition coefficients calculated by COSMOtherm for the single conformers as well as the overall values based on the weighted coefficients of all conformers (weighting is done with the Boltzmann statistic, see ref *27*). The p_L^* data give a good basis for a discussion of the results, because the good agreement between experimental data and COSMOtherm predictions indicates that the calculations correctly account for this partition process (see Table 1). As expected, for all FTOHs the EIC-conformer has a considerably higher saturated p_L^* (almost 1 order of magnitude) than conformer SC, because part of the external H-bonding capacity of the EIC is used up by internal electrostatic interactions. The p_L^* weighted overall conformers lie closer to the EIC than to the SC. However, the calculated p_L^* of the EIC conformers are still 2 orders of magnitude lower than the p_L^* of the corresponding FTolefins, which completely lack any H-bond potential. This strongly indicates that even the EIC conformers with an intramolecular electrostatic interaction still form substantial H-bonds with their nearest neighbors. These findings are discussed in more detail in the SI. Hence, our results appear to disprove both the assumption of Krusic et al. (*33*), who postulated that this intramolecular interaction does not affect the p_L^*, and of Stock et al. (*34*), who concluded that this intramolecular interaction completely inhibits external H-bonding. Of course, the discussed conformer effects are also observable in air/water and octanol/air partitioning, where H-bonding to the surrounding phase also matters.

Perfluorinated Acids. In contrast to the FTOHs, the perfluorinated acids are completely fluorinated. For these compounds a strong intramolecular electrostatic interaction between the carboxylic proton and the fluorine atoms attached to the α-carbon is apparently not favorable due to steric reasons. An intramolecular interaction between the carboxylic proton and the fluorine atoms at the β-carbon is sterically possible, but the COSMOtherm calculations show that this conformer does not contribute to the weighted partition coefficients (see Table S5), probably because the energy expense of twisting the carboxy group to the ideal position for the intramolecular interaction is too high.

Perfluorooctane Sulfonamidoethanols. Unexpectedly, the experimental data show that the p_L^* of the larger *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) is higher than the p_L^* of the smaller *N*-methyl perfluorooctane sulfonamidoethanol (MeFOSE) (see Table 1). SPARC and EPI Suite do not show this counterintuitive behavior; however, the COSMOtherm calculations do so (see Tables 1 and S5) and may therefore provide an explanation. For both sulfonamidoethanols three different conformers were found and used in the calculations: (1) the stretched form (SC), (2) a conformer exhibiting an intramolecular H-bond between the hydroxy proton and the oxygens of the sulfonic acid (OxyEIC), and (3) a conformer with a strong intramolecular electrostatic interaction between the hydroxy proton and the fluorine atoms of the carbon directly linked to the sulfonamide group (EIC, see the SI for an illustration). The COSMOtherm calculations show that all conformers contribute significantly to all partition coefficients. The stretched conformers of both compounds exhibit the lowest p_L^* because the H-donor/acceptor properties of the hydroxyl group are fully available, and as expected the stretched MeFOSE has a higher p_L^* than the stretched conformer of EtFOSE. However, the p_L^* of the EIC of MeFOSE is lower compared to the corresponding conformer of EtFOSE. This effect appears to dominate the overall behavior of the compounds and explains their unexpected behavior.

For perfluorooctanesulfonic acid, *N*-ethyl perfluorooctane sulfonamide (EtFOSA), *N*-methyl perfluorooctane sulfonamidoethylacrylate (MeFOSEA), and perfluorooctanesulfonamide, only one relevant conformer could be identified for each.

p_L^* Model Predictions. Experimental p_L^* values for the FTOHs (*33*), perfluorinated acids (*35*), and perfluoralkyl sulfonamides (*4*) together with model results are listed in Table 1. Largely diverging experimental data have been published for FTOHs. The ones used here are the only ones that are consistent with independent experimental findings and thermodynamic considerations (*9*). The reliability of the experimental values for the acids can be ascertained by the same consistency checks.

A comparison of the data in Table 1 reveals that COSMOtherm predictions agree within an order of magnitude with experimental values. The performance of New SPARC and EPI Suite is considerably worse (disagreement of >1 log unit in many cases) and is beyond the standard deviations (SD) reported for these models (i.e. a SD of 0.15 log units from the validation set for SPARC (*36*) and a SD of 96 Pa for EPI Suite (*7*)).

K_{aw} Model Predictions. Table 2 compares predicted log K_{aw} values for the FTOHs with experimental values that passed several consistency checks (*9*). Note that the log K_{aw} value of the 10-2FTOH was extrapolated from the three other experimentally determined data points. Here, SPARC underestimates by about 1 order of magnitude, and EPI Suite methods overestimate by up to 4 orders of magnitude. Again, this discrepancy is outside the reported SD of the validation sets of 0.44 log units for EPI Suite (*7*) and 0.10 for SPARC (*36*). COSMOtherm predictions performed well for the 4-2 and 6-2 FTOHs; however, predictions for the 8-2 and 10-2 FTOHs are off by nearly 1 order of magnitude.

K_{ow} Model Predictions. No K_{ow} values have been measured explicitly; however, "dry" K_{ow} values could be calculated from experimental K_{aw} and K_{oa} data for the 4-2, 6-2, and 8-2 FTOHs

TABLE 2. Comparison of Predicted and Experimental log K_{aw} (L/L) Values at 25 °C for the FTOHs[e]

		deviation				
compound	exptl value[a]	COSMO-therm	new SPARC[c]	old SPARC[d]	EPI Suite bond method[c]	EPI Suite group method[c]
4-2FTOH	−1.52	−0.03	1.12	0.36	−0.87	−1.35
6-2FTOH	−0.56	0.16	1.36	0.91	−1.35	−2.39
8-2FTOH	0.58	0.85	1.39	1.41	−1.65	−3.25
10-2FTOH	1.60[b]	0.94	0.89	1.59	−2.07	−4.23

[a] Reference *9*. [b] Extrapolated from data series based on plotting log K_{aw} values vs the number of carbons. [c] Accessed February 2006. [d] Accessed April 2005. [e] The standard deviations of the experimental values are estimated to be 0.2 log units. Model deviations are given as "experimental value − predicted value".

TABLE 3. Comparison of Predicted and Experimental log K_{ow} (L/L) Values at 25 °C for the FTOHs[a]

		deviation				
compound	exptl value[a]	COSMO-therm	New SPARC[c]	Old SPARC[d]	EPI Suite[c]	ClogP[c]
4-2FTOH	3.28 ± 0.3	0.98	1.06	0.47	−0.38	1.93
6-2FTOH	4.70 ± 0.3	1.38	1.07	0.52	−0.90	2.88
8-2FTOH	6.14 ± 0.3	1.84	0.83	0.43	−1.39	3.85
10-2FTOH	7.57 ± 0.3[b]	2.18	0.28	0.24	−1.89	4.81

[a] Calculated by adding experimentally determined log K_{oa} and log K_{aw} values from ref *9*. The standard deviations of the experimental values are estimated to be 0.3 log units. Model deviations are given as "experimental value − predicted value". [b] Extrapolated from data series based on plotting log K_{oa} and log K_{aw} values vs the number of carbons. [c] Accessed February 2006. [d] Accessed April 2005.

TABLE 4. Comparison of Predicted and Experimental log $K_{i\text{hexadecane/air}}$ (L/L) Values at 25 °C for the Fluorotelomer Compounds[e]

		deviation		
compound	exptl value[a]	COSMO	New SPARC[b]	Old SPARC[c]
4-2FTOH	2.52 ± 0.1	0.14	−0.44	−0.11
6-2FTOH	2.96 ± 0.1	0.12	−0.63	−0.43
8-2FTOH	3.47 ± 0.1	0.10	−0.58	−0.55
10-2FTOH	3.90 ± 0.1	0.13	−0.50	−0.69
4-2FTolefin	1.35 ± 0.1	−0.08	−0.42	nd[d]
6-2FTolefin	1.83 ± 0.1	−0.10	−0.23	nd[d]
8-2FTolefin	2.31 ± 0.1	−0.11	0.22	nd[d]
10-2FTolefin	2.79 ± 0.1	−0.11	0.69	nd[d]

[a] Reference *9*. [b] Accessed February 2006. [c] Accessed April 2005. [d] nd = no data. [e] Deviations are given as "experimental value − predicted value".

(*9*) and are thus reported in Table 3. Note that the differences between dry K_{ow} values and "wet" values are usually off by less than a factor of 2−3 ((*37*) pp 186−187).

Interestingly, only the Old SPARC calculations gave reasonable results. The most extreme outliers came from the ClogP model, which was up to 5 orders of magnitude off the experimental value. The results for New SPARC (with the exception of 10-2FTOH) and EPI Suite (with the exception of 4-2FTOH) are outside the reported SD values of 0.18 (*36*) and 0.43 log units (*7*), respectively. COSMOtherm underpredicts values by 1−2 orders of magnitude.

Hexadecane/Air Model Predictions. Table 4 gives a comparison of the experimental log $K_{i\text{hexedecane/air}}$ constants (i.e. L_i) of FTOHs and FTolefins with those predicted with SPARC and COSMOtherm. Both predictive models give good predictions, though the predictions of COSMOtherm are noticeably better than with SPARC.

TABLE 5. Comparison of Predicted and Experimental log K_{oa} (L/L) Values at 25 °C[g]

		deviation			
compound	exptl data[a]	COSMO-therm	New SPARC[c]	Old SPARC[d]	EPI Suite[c,e]
C4-2 alcohol	4.80	0.95	0.13	0.30	0.49
C6-2 alcohol	5.26	1.14	−0.10	−0.22	0.45
C8-2 alcohol	5.56	0.89	−0.35	−0.80	0.26
C10-2 alcohol	5.97[b]	1.13	−0.40	−1.19	0.18
MeFOSE	7.45	−0.52	0.16	nd[f]	−1.59
EtFOSE	7.52	−0.12	0.25	nd[f]	−1.89
MeFOSEA	7.62	−0.81	0.31	nd[f]	−2.25

[a] References *4* and *9*. [b] Extrapolated from series. [c] Accessed April 2005. [d] Accessed April 2005. [e] EPI Suite obtained values from subtracting the log K_{aw} from the log K_{ow} giving a "wet" log K_{oa} value. [f] nd = no data. [g] The standard deviations of the experimental values are estimated to be 0.2 log units. Model deviations are given as "experimental value − predicted value".

K_{oa} Model Predictions. Table 5 gives a comparison of experimental and predicted octanol-air partition coefficients, K_{oa}. The experimental data for the perfluoroalkyl sulfonamides were measured with the identical procedure as the FTOHs. The predictions of SPARC and EPI Suite are both good, though for EPI Suite this is coincidental due to the overprediction of the K_{ow} value canceling out the underprediction of the K_{aw} value. COSMOtherm gives mostly underpredictions by 1 order of magnitude, except for MeFOSE, EtFOSE, and MeFOSEA.

Overall Performance of Predictive Models. There was no model that could predict all absorptive partitioning constants within an order of magnitude. COSMOtherm and SPARC, however, came closest to this goal. Table 6 shows that the predictions of partition constants where no experimental data exist also deviate over orders of magnitude between the various methods in some cases. Based on our previous validation we would expect COSMOtherm and SPARC again to give the best estimations. However, for a good understanding of the environmental behavior of these compounds reliable experimental data are necessary. To this end we actually recommend that the traditional octanol-based approaches are substituted by poly parameter LFERs because these do not only allow a more precise account of the partition behavior of polar organic compounds (*38*), but they also allow for a consistency check of experimental data. How important such consistency checks of experimental data are has been shown in various recent publications (*8*, *9*, *39*).

Based on the results of this study we believe EPI Suite and ClogP should not be used for HFCs. The largest deviation between experimental and predicted results occurred for the predictions of log K_{ow} by ClogP. According to the Stockholm Convention on Persistent Organic Pollutants (POPs) (*40*) one of the possible identifying characteristics of a POP is that it has a log K_{ow} greater than 5. Thus, according to experimental results, the C8-2 and C10-2 alcohols obey this criterion, having a log K_{ow} of 6.14 and 7.57, respectively. ClogP, however, assigns values of 2.29 and 2.76, respectively. EPI Suite, on the other hand, overpredicts the K_{ow} values by almost 2 orders of magnitude, which would at least allow C8-2 and C10-2 to qualify for this criterion as a POP, but at the same time it could lead to very inaccurate risk assessments and model predictions. EPI Suite's large discrepancy in determining K_{aw} values too brings the appropriateness of using EPI Suite for the screening of emerging chemicals also into question. One may argue that EPI Suite and ClogP have here been misused for the HFCs because they are not part of these models' applicability domains. However, we object to this argument because to our knowledge there is currently no available way for users to identify the model's applicability domain,

TABLE 6. Predictions of Environmentally Relevant HFCs Where No Experimental Data Are Available

compound	COSMO-therm	New Sparc[a]	EPI Suite[a,b]	ClogP[a]
log p_L* (Pa)				
perfluorohexanoic acid	2.06	2.75	2.42	na[c]
perfluoroheptanoic acid	1.66	2.43	2.01	na[c]
EtFOSA	−1.04	1.01	1.77	na[c]
perfluorooctansulfonic acid	0.54	1.53	0.21	na[c]
perfluorooctane sulfonamide	−0.99	1.82	1.81	na[c]
log K_{aw} (L/L)				
MeFOSE	−3.08	−0.72	−1.75	na[c]
EtFOSE	−2.15	−0.47	−1.63	na[c]
MeFOSEA	−2.04	−0.73	−1.22	na[c]
perfluorohexanoic acid	−3.04	−2.48	−0.87	na[c]
perfluoroheptanoic acid	−2.66	−2.15	−0.15	na[c]
perfluorooctanoic acid	−2.37	−1.69	0.57	na[c]
perfluorononanoic acid	−2.03	−1.12	1.29	na[c]
perfluorodecanoic acid	−1.79	−0.45	2.01	na[c]
perfluoroundecanoic acid	−1.52	0.33	n.d.	na[c]
EtFOSA	−1.20	−1.27	2.34	na[c]
perfluorooctansulfonic acid	−2.40	−1.06	−0.35	na[c]
perfluorooctane sulfonamide	−3.92	1.71	1.88	na[c]
log K_{ow} (L/L)				
MeFOSE	4.80	6.90	7.29	3.34
EtFOSE	5.39	7.39	7.78	3.86
MeFOSEA	6.25	6.38	8.65	4.70
perfluorohexanoic acid	3.26	3.12	4.37	3.15
perfluoroheptanoic acid	3.82	3.82	5.33	3.39
perfluorooctanoic acid	4.30	4.59	6.30	3.62
perfluorononanoic acid	4.84	5.45	7.27	3.86
perfluorodecanoic acid	5.30	6.38	8.23	4.09
perfluoroundecanoic acid	5.76	7.40	9.20	4.33
EtFOSA	5.49	7.40	8.54	4.36
perfluorooctansulfonic acid	5.25	5.26	6.28	2.28
perfluorooctane sulfonamide	4.35	6.27	7.58	3.21
log K_i hexedecane/air (i.e., L_i) (L/L)				
MeFOSE	6.13	4.52	na[c]	na[c]
EtFOSE	6.54	4.81	na[c]	na[c]
MeFOSEA	7.92	4.95	na[c]	na[c]
perfluorohexanoic acid	2.28	2.40	na[c]	na[c]
perfluoroheptanoic acid	2.50	2.69	na[c]	na[c]
perfluorooctanoic acid	2.78	2.94	na[c]	na[c]
perfluorononanoic acid	2.99	3.16	na[c]	na[c]
perfluorodecanoic acid	3.26	3.35	na[c]	na[c]
perfluoroundecanoic acid	3.41	3.51	na[c]	na[c]
EtFOSA	5.19	3.85	na[c]	na[c]
perfluorooctansulfonic acid	3.44	3.14	na[c]	na[c]
perflourooctane sulfonamide	4.30	3.03	na[c]	na[c]
log K_{oa} (L/L)				
perfluorohexanoic acid	6.40	5.56	5.24	na[c]
perfluoroheptanoic acid	6.60	5.93	5.48	na[c]
perfluorooctanoic acid	6.80	6.25	5.73	na[c]
perfluorononanoic acid	7.01	6.55	5.98	na[c]
perfluorodecanoic acid	7.24	6.82	6.22	na[c]
perfluoroundecanoic acid	7.44	7.07	6.47	na[c]
EtFOSA	6.87	6.00	6.20	na[c]
perfluorooctansulfonic acid	7.80	6.17	6.63	na[c]
perfluorooctane sulfonamide	8.43	4.27	5.70	na[c]

[a] Accessed February 2006. [b] Log K_{aw} calculations done using the Bond Method approach. [c] na = not applicable.

excluding the one report that identifies some HFCs as actually belonging to EPI Suite's applicability domain for K_{ow} determinations (*28*). The one model that was able to predict K_{ow} for the telomer alcohols quite well, the old version of SPARC, is unfortunately no longer available online. This shows another problem with using software packages to predict partitioning parameters: changes are not always brought to user's notice and specific revisions over time are often not documented.

One can never be too confident about using models that predict partitioning parameters for untested compound classes, even if the models have been validated for thousands of compounds. Thus, upon the emergence of new compound classes, there should be a special bias to experimentally test the partitioning behavior of chemicals belonging to this class. Further, to improve the screening of chemicals, providers of partition models should put more effort into identifying the model's chemical applicability domain and to present this information to the users of the model.

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Supporting Information Available

Solute descriptors for compounds used in the adsorption study; measured $K_{i\ \mathrm{surf/air}}$ values and a comparisons to model predictions; recalibrated surface descriptors using eq 4; $\Delta_{\mathrm{ads}}H_i$ values for the fluorotelomers on quartz (90%RH); and illustrations and further discussions of the most stable conformers of various HFCs, as determined by COSMOtherm, along with predicted partitioning constants for the various conformers. This material is available free of charge via the Internet at http://pubs.acs.org.

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