What Is So Special about the Sorption Behavior of Highly Fluorinated Compounds?

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Highly fluorinated organic compounds are often said to exhibit unique sorption and partition properties. Terms such as “fluorophilicity” have been used to describe these properties, and fudge factors depending on the degree of fluorination have been used in predictive partition models to make them work for fluorinated solutes. Here we demonstrate that highly fluorinated compounds differ from other molecules only in that they exhibit van der Waals interactions much smaller than those of other molecules of same size. A simple cavity model for partitioning is shown to give good results for fluorinated compounds if the nonspecific interactions are correctly parametrized.

Introduction

There are numerous experimental data that show a partition and adsorption behavior of highly fluorinated compounds that differs clearly from other compounds. It has therefore been suggested that a special fluorination factor has to be introduced into models so that the partitioning of highly fluorinated compounds can be predicted.[1] Similarly, partitioning into highly fluorinated solvents also appears to be special.[2] Obviously, it is unsatisfying if purely empirical fudge factors are needed to make the partition behavior of highly fluorinated compounds predictable. Here we show that an ordinary cavity model can explain the partitioning of highly fluorinated compounds if adequate parameters are used.

The following data illustrate the peculiar partition behavior of highly fluorinated compounds. Figure 1 shows a plot of logarithmic hexadecane/air partition coefficients versus molar volume for 695 organic compounds covering a large number of compound classes: aliphatic and aromatic compounds, halogenated compounds, alkanes, alkenes, ketones, esters, ethers, aldehydes, alcohols, thiols, carboxy acids, nitriles, and others (data from refs 3−5). There is a reasonable correlation between log $K_{\mathrm{hexadecane/air}}$ and the molecular volume of these compounds, and although there is some scatter, one can identify a distinct window in which all data lie. Only the highly fluorinated compounds (with a F/C ratio of >1.5) appear as substantial outliers in this plot. A similar picture can be seen in Figure 2 where the saturated liquid vapor pressure is plotted versus molar volume for a large number of compounds that do not form H-bonds with themselves (aliphatic and aromatic compounds, halogenated compounds, alkanes, alkenes, ketones, esters, ethers, aldehydes, thiols, and tertiary alkylamines). (See the Appendix for the calculation of the molar volumes that are used throughout this paper.)

Theory

The transfer of molecule *i* from one phase to another requires that interactions between molecules are given up while new interactions become possible. The logarithm of the partition constant is proportional to the change in the free energy of intermolecular interactions of the solute in the two phases. The air/condensed phase partitioning of a solute *i* depends only on the interactions in the condensed phase because interactions in the air are negligible. Interactions in the condensed phase involve two steps, the first being (a) creation of a cavity in the condensed phase for molecule *i*. For this step, free energy is required to separate the phase molecules from each other so that a cavity of the size of *i* can be formed. The free energy required for this cavity formation depends on the interaction free energy between the like molecules of the condensed phase, i.e., the cohesive free energy in this phase, and on the size of the required cavity, i.e., the volume of molecule *i*. In the second step (b), after creation of a cavity molecule *i* can interact with its new neighbors. These interactions always comprise nonspecific van der Waals interactions and, in addition, specific interactions such as H-bond interactions provided that solute *i* and the phase molecules have the required complementary properties (e.g., H-bond donor and H-bond acceptor). Applying this mechanistic model to the partitioning between air and any bulk phase x (such as hexadecane) that does not undergo specific interactions with

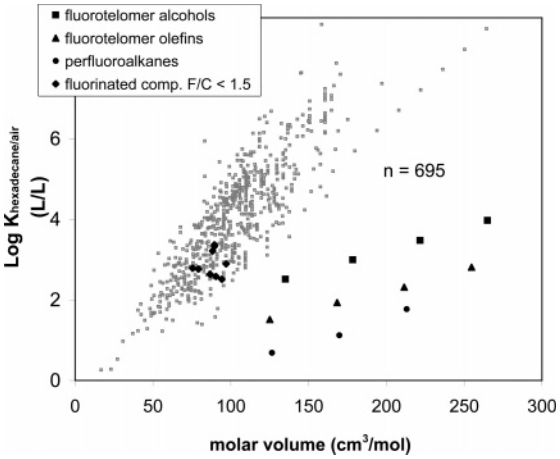

Figure 1. Logarithmic hexadecane/air partition coefficients plotted vs molar volume. The fluorotelomer alcohols have the general form F_3C-$(CF_2)_n$-CH_2-CH_2-OH, and the fluorotelomer olefins have the general form F_3C-$(CF_2)_n$-CH=CH_2. Data taken from refs 3−5.

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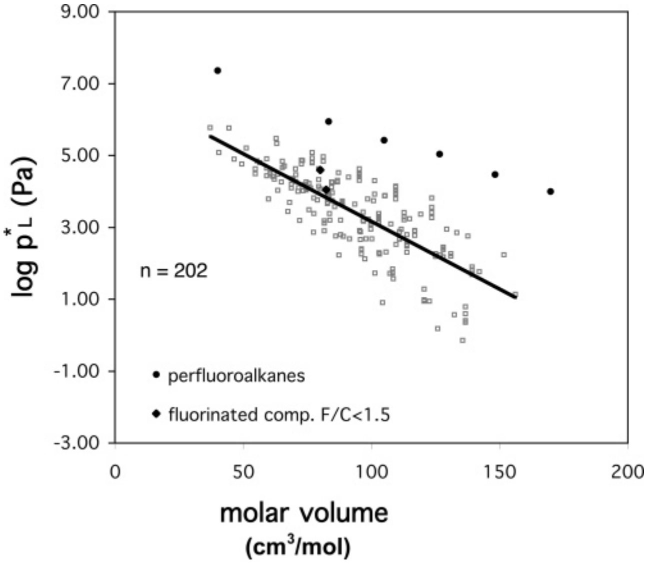

Figure 2. Saturated liquid vapor pressures at 25 °C of 200 organic compounds and six perfluorinated alkanes plotted vs their molar volume. Data from refs 15−17.

any solute suggests that the log $K_{ix/\mathrm{air}}$ values of different organic compounds should simply be proportional to their free energy of cavity formation ($\Delta G_{ix}^{\mathrm{cavity}}$) and their van der Waals interaction free energy ($\Delta G_{ix}^{\mathrm{vdW}}$) in that phase.

$$\log K_{ix/\mathrm{air}} \propto \Delta G_{ix}^{\mathrm{cavity}} + \Delta G_{ix}^{\mathrm{vdW}} \qquad (1)$$

$\Delta G_{ix}^{\mathrm{cavity}}$ must be proportional to the cohesive energy in x, $E_{\mathrm{x}}^{\mathrm{cohesion}}$, and the molar volume of solute i, V_i. The van der Waals interactions ($\Delta G_{ix}^{\mathrm{vdW}}$) between solute i and condensed phase x are dominated by London dispersive interactions[6] and are roughly proportional to[7]

$$\Delta G_{ix}^{\mathrm{vdW}} \propto \frac{n_{\mathrm{x}}^{2} - 1}{n_{\mathrm{x}}^{2} + 2} V_i \frac{n_i^{2} - 1}{n_i^{2} + 2} \qquad (2)$$

where V_i is the molar volume of i and n_i and n_{x} are the refractive indices of compound i and phase x, respectively, at the Na line. It follows that a general model for the partitioning of solutes i between bulk phase x and air should assume the following form (if no specific interactions occur between the solute and solvent):

$$\log K_{ix/\mathrm{air}} \propto -E_{\mathrm{x}}^{\mathrm{cohesion}} V_i + \frac{n_{\mathrm{x}}^{2} - 1}{n_{\mathrm{x}}^{2} + 2} \mathrm{mr}_i \qquad (3)$$

with the molar refraction of i, mr_i, defined as

$$\mathrm{mr}_i \equiv V_i (n_i^{2} - 1)/(n_i^{2} + 2) \qquad (4)$$

For describing the variability of hexadecane/air partition coefficients of different organic molecules, this reduces to

$$\log K_{i\mathrm{hexadecane/air}} = aV_i + b\mathrm{mr}_i \qquad (5)$$

where a is a scaling coefficient that contains the cohesive energy of hexadecane and b is a scaling coefficient that contains the refractive index term of hexadecane. Figure 3 shows that this type of model does indeed give satisfactory results for all compounds from Figure 1.

Interestingly, one usually finds a close linear correlation between V_i and mr_i for organic molecules (see Figure 4) because n_i varies only little (typically between 1.35 and 1.6). This explains why we also see a reasonable correlation between log $K_{i\mathrm{hexadecane/air}}$ and the molar volume in Figure 1. However, Figure 4 also reveals that the highly fluorinated compounds have a substantially smaller van der Waals interaction energy than all other organic compounds of similar size and must therefore occur as outliers in a plot such as Figure 1. For the saturated liquid vapor pressure in Figure 2, the situation is analogous. The vapor pressure of compounds that do not form H-bonds with themselves depends only on van der Waals interactions and cavity formation and is therefore correlated with the molecular volume of the compounds. The fluorinated compounds exhibit vapor pressures that are orders of magnitude higher than one would expect from their molecular volume because of their much weaker van der Waals interaction energy. Linear relationships such as those in Figure 1 or 2 present a truncated cavity model in that they implicitly assume a correlation between the molar volume of the solute and both the cavity energy and the van der Waals interaction energy between the solute and the phase. Where this assumption does not hold, as in the case of highly fluorinated compounds, the cavity model in its full form (eq 5) has to be used. However, even if a partition model uses two separate descriptors for cavity energy and van der Waals interactions, it might not give good predictions for the highly fluorinated compounds if the calibration data do not contain any highly fluorinated compounds

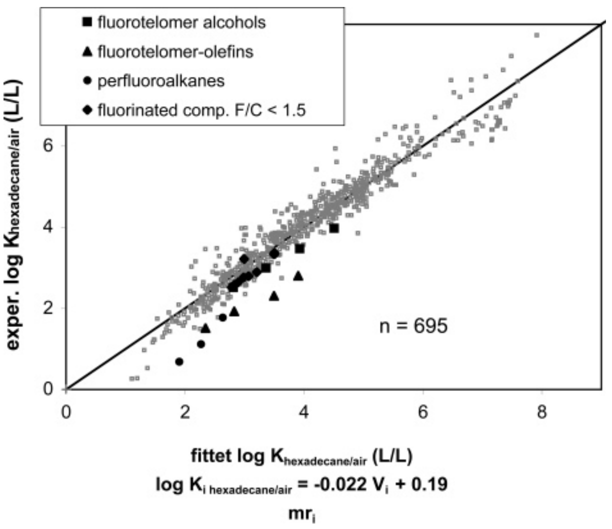

Figure 3. Experimental log $K_{\mathrm{hexadecane/air}}$ partition coefficients vs values fitted with eq 5.

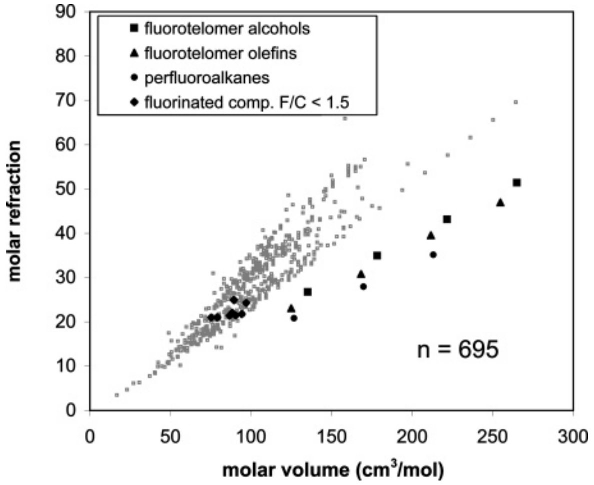

Figure 4. Molar volume plotted against molar refraction.

TABLE 1: Partition Coefficients (in units of liters per liter) of a Highly Fluorinated Solute and a Nonfluorinated Solute of Similar Size between PFMCH and Toluene, Toluene and Air, and PFMCH and Air

solute	V (cm^3/mol)	log $K_{\text{PFMCH/toluene}}$[a]	log $K_{\text{toluene/air}}$[b]	log $K_{\text{PFMCH/air}}$[c]
tetradecane	208	−1.71	6.01	4.30
$CF_3-(CF_2)-CH_2{=}CH_2$	212	1.16	2.89	4.05

[a] From ref 1. [b] Calculated with a LSER equation from ref 13 with LSER descriptors from refs 3 and 5. [c] Calculated from the other data using the thermodynamic cycle.

because of the high intercorrelation that occurs between V_i and mr$_i$ for all other compounds.

We generally conclude that highly fluorinated compounds will show a much weaker tendency to partition from the gas phase into any kind of condensed phase, be it aqueous or organic, than other organic molecules of similar size and similar specific interactions because the fluorinated compounds exhibit much smaller van der Waals interactions (while the cavity energy is the same due to the same molecular size). Figure 4 suggests that this peculiar behavior of fluorinated compounds increases with an increase in relative fluorine content. A significant effect becomes observable for compounds whose F/C ratio is ≥1.5. This is supported by the data in Figure 1.

To predict the partition behavior of highly fluorinated compounds between two condensed phases, x and y, we must consider the cavity energies and interaction energies between the solute and the bulk phase molecules for both phases with opposite sign (for reasons of simplicity, we, again, restrict this discussion to cases in which no specific interactions between the solutes and the bulk phases occur). In analogy to eq 3 we then obtain

$$\log K_{i\text{xy}} \propto -[V_i(E_{\text{x}}^{\text{cohesion}} - E_{\text{y}}^{\text{cohesion}})] + \text{mr}_i\left(\left[\frac{n_{\text{x}}^{2}-1}{n_{\text{x}}^{2}+2} - \frac{n_{\text{y}}^{2}-1}{n_{\text{y}}^{2}+2}\right]\right) \qquad (6)$$

TABLE 2: Free Energies of Absorption and Adsorption for a CH$_2$ Fragment As Compared to a CF$_2$ Fragment

	ΔG_{CH_2} (kJ/mol)[a]	ΔG_{CF_2} (kJ/mol)[a]
absorption from air		
water/air at 25 °C[b]	0.68	5.36
polyurethane/air at 60 °C[c,e]	−2.30	−0.96
poly(ethylene glycol)/air at 100 °C[c,e]	−1.72	−0.68
pentadecylphenol/air at 70 °C[d]	−2.26	−0.90
hexadecane/air at 25 °C[c]	−2.85	−1.26
trifluoropropylmethylpolysiloxane/air at 70 °C [c,e]	−1.97	−1.44
adsorption from air		
quartz/air at 15 °C and 90% relative humidity[f]	−2.43	−2.32
α-Al_2O_3/air at 15 °C and 70% relative humidity[f]	−2.32	−2.32
$CaCO_3$/air at 15 °C and 70% relative humidity[f]	−2.51	−2.31

[a] Calculated from the difference in the sorption constants of consecutive members of a homologue, hydrogenated compound class according to the relation $\Delta G_{CH_2} = -RT(\ln K_{C_{n+1}} - \ln K_{C_n})$ and from a homologue, fluorinated compound class according to the relation $\Delta G_{CF_2} = -RT(\ln K_{C_{n+1}} - \ln K_{C_n})$ (see also ref 14). [b] From ref 3. [c] From ref 5. [d] From ref 9. [e] Polymer phase. [f] Unpublished results.

If we compare molecules on the basis of the same molar volume, it is obvious that the difference in their partitioning can come from only the van der Waals interaction term. This van der Waals interaction term will be considerably smaller for highly fluorinated solutes than for other solutes of the same size due to the smaller mr$_i$ of the highly fluorinated solutes. Hence, the highly fluorinated compounds will exhibit a smaller preference than other organic molecules for the solvent with the higher refractive index (i.e., stronger van der Waals interactions). This effect should become most distinct in the partitioning between a highly fluorinated solvent and a nonfluorinated solvent because the former has a refractive index much smaller than the latter. Indeed, it is widely known that fluorinated solutes have a strong tendency to partition from a nonfluorinated solvent like toluene into a highly fluorinated solvent like PFMCH [perfluoro-(methylcyclohexane), $CF_3C_6F_{11}$)], while other solutes prefer the nonfluorinated solvent.[1,2,8] Highly fluorinated compounds have therefore often been described as fluorophilic,[1,2,8] which, from a mechanistic point of view, is misleading. This becomes clear if, for example, we compare the two solutes tetradecane and $CF_3(CF_2)CH_2{=}CH_2$. They are similar in size and exhibit only nonspecific interactions (cavity energy and van der Waals interactions), but they differ by 3 orders of magnitude in their PFMCH/toluene partitioning (Table 1). However, the preference of $CF_3(CF_2)CH_2{=}CH_2$ for PFMCH as compared to tetradecane's preference for toluene is not due to a preference of highly fluorinated solutes for highly fluorinated solvents but due to the weak interactions of highly fluorinated solutes in nonfluorinated solvents such as toluene. This becomes obvious if we look at the PCMCH/air and toluene/air partition coefficients. The $K_{\text{PFMCH/air}}$ values in Table 1 show that tetradecane actually has a stronger preference for PFMCH than $CF_3(CF_2)CH_2{=}CH_2$ (due to its stronger van der Waals interactions) and might therefore be regarded as more "fluorophilic". But the preference of tetradecane for the toluene phase is even more distinct compared to that of $CF_3(CF_2)CH_2{=}CH_2$. This indicates that highly fluorinated compounds are by no means fluorophilic in a strict sense; i.e., they do not like fluorous solvents more than other solutes do. But they lack the same preference for nonfluorinated solvents that other organic solutes have. This critique of the term fluorophilic is also supported by the observation that highly fluorinated compounds have exceptionally high saturated vapor pressures (i.e., a strong tendency to escape from their own liquid phase into air; see Figure 2).

Above, we were able to explain qualitatively the preference of fluorinated solutes for fluorinated solvents relative to nonfluorous solvents from eq 6. If our analysis is correct, then we should also expect the cavity model to quantitatively fit the PFMCH/toluene partition constants while a correlation with molar volume alone should fail. Panels A and B of Figure 5 show that this is indeed the case. The fitting equation for the experimental data in Figure 5B is

$$\log K_{i\text{PFMCH/toluene}} = 0.0335V_i - 0.141\text{mr}_i \qquad (7)$$

The signs of the fitted coefficients are consistent with our expectations from eq 6. A larger molar volume shifts partitioning to the less cohesive PFMCH phase, while a larger molar refraction shifts the partitioning to the toluene phase because there the gain in van der Waals interaction energy is larger than in PFMCH.

We can also extend our conclusions to adsorption from air to surfaces: this process does not require the formation of a cavity and therefore depends on only the direct interactions between the surface and the sorbing compound. Again, the molar volume or a related term serves as a good descriptor for the

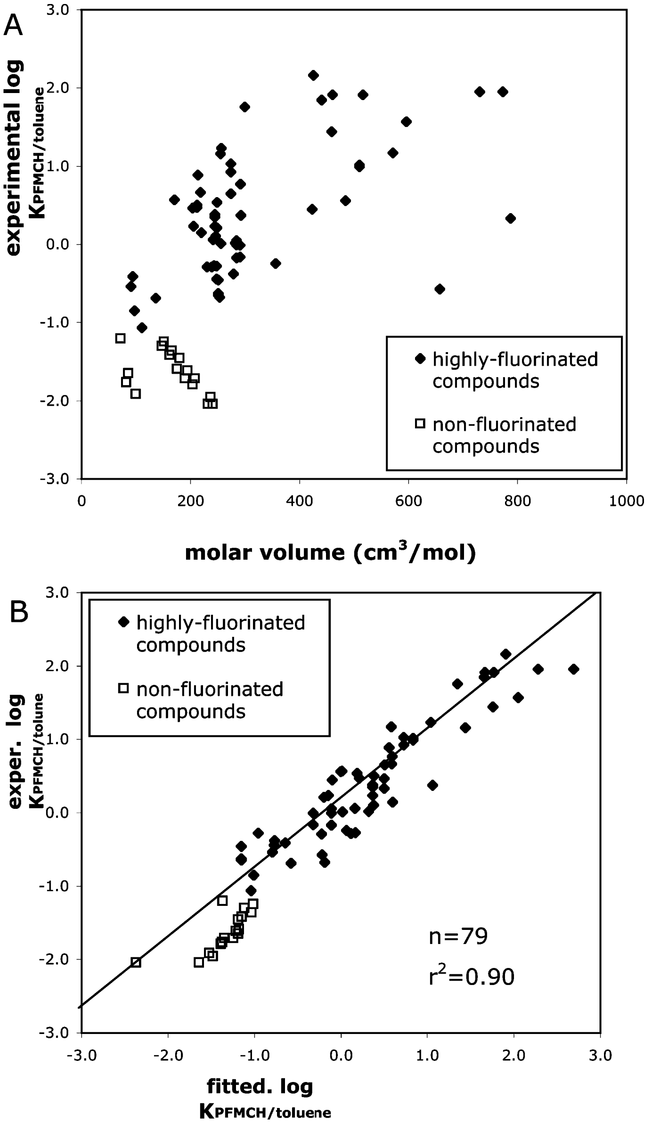

Figure 5. Experimental PFMCH/toluene partition coefficients plotted vs molar volume (A) and vs values fitted with eq 7 (B). Experimental data were taken from the collection in ref 1. The refractive indices were calculated with the on-line version of SPARC (http://ibmlc2.chem.uga.edu/sparc). The following compounds from the collection of ref 1 were not used in the fit: (a) five compounds for which SPARC did not calculate any n_i, (b) 12 compounds that have a strong H-bond donor property because their specific interactions with toluene as an H-bond acceptor would have to be ascribed to an additional interaction term, and (c) two aromatic esters that appear to be experimental outliers.

involved van der Waals interactions as long as no highly fluorinated compounds are involved. However, such a model fails to predict the adsorption constants of highly fluorinated compounds by several orders of magnitude.[9] This discrepancy can be reconciled if molar refraction is used as a descriptor of the van der Waals interactions.[9]

Comparison of Fluorinated and Hydrogenated Analogues. Above we have compared highly fluorinated compounds with other organic compounds on the basis of their similar molar volumes. For the synthetic chemist, it often is of greater interest to know how the compound properties change if, for a given molecule, one or several hydrogens are replaced with fluorines. In this case, the molar volume of the compound increases considerably while its molar refraction and thus its dispersive van der Waals interactions stay almost the same. On the basis of the cavity model, one can thus predict the following effects on the partitioning of such a (partly or fully) fluorinated molecule compared to the hydrogenated analogue. (a) Partitioning between the gas phase and a condensed phase will shift to the gas phase for the fluorinated compound due to the larger volume that causes a larger energy expense for cavity formation. The extent of this effect will increase with the degree of fluorination (see Figure 6) and with the cohesive energy of the condensed phase; i.e., it will be largest for air/water partitioning. (b) The partitioning between two condensed phases will shift toward the phase with the lower cohesive energy again due to the increase in molar volume. For example, 1-dodecene has a log $K_{PFMCH/toluene}$ of −1.59 whereas $CF_3(CF_2)_9C{=}CH_2$ has a log $K_{PFMCH/toluene}$ of 1.16.[1] This effect will increase with the degree of fluorination and with the difference in the cohesive energy of the condensed phases; i.e., it will be largest for partitioning between water and a nonassociating, fluorinated organic liquid. (c) Adsorption on surfaces will remain unchanged because no cavity formation is required and the molar refraction (and thus the van der Waals interaction) stays unaltered (see Figure 7).

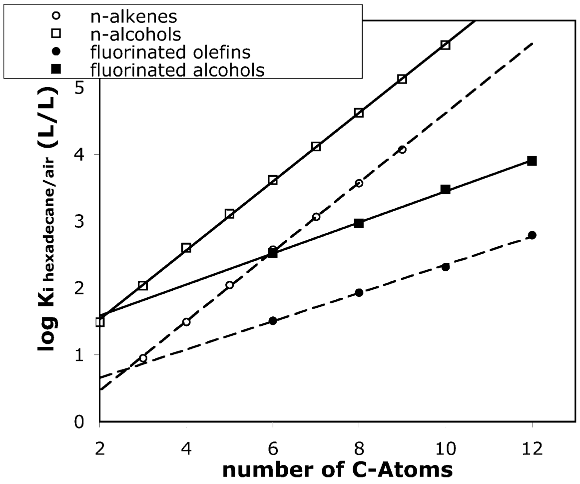

Figure 6. Hexadecane/air partition constants at 25 °C of fluorinated alcohols, $F_3C\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}OH$, and fluorinated olefins, $F_3C\text{-}(CF_2)_n\text{-}CH{=}CH_2$ (from ref 5), and their hydrogenated analogues (from ref 3).

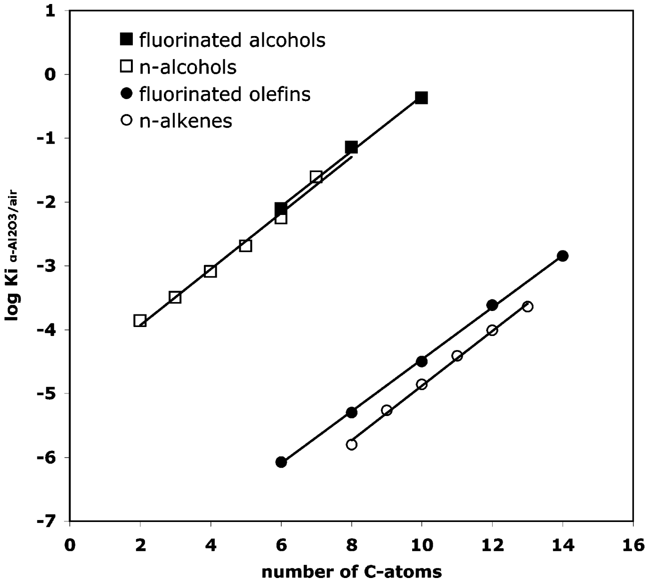

Figure 7. α-Al_2O_3/air adsorption constants at 15 °C and 70% relative humidity for fluorinated alcohols, $F_3C\text{-}(CF_2)_n\text{-}CH_2\text{-}CH_2\text{-}OH$, and fluorinated olefins, $F_3C\text{-}(CF_2)_n\text{-}CH{=}CH_2$ (from ref 9), and their hydrogenated analogues (from ref 9).

Adsorption and Absorption. The fact that highly fluorinated compounds and their hydrogenated analogues **adsorb** similarly to surfaces but **absorb** differently into bulk phases actually makes them suitable molecular probes for distinguishing both processes. In complex environmental media such as humic material or aerosols, a mixture of surfaces and bulk phases is available, and it is usually not possible to determine unambiguously which sorption process dominates for organic molecules. The use of highly fluorinated compounds in comparison to their hydrogenated analogues opens new possibilities here. Experimental data collected in Table 2 exemplify the similarity in the adsorption of analogue fluorinated and hydrogenated compounds and the differences in their absorption behavior. The free energy of absorption is always smaller for a CH_2 fragement than for a CF_2 fragment. The difference is largest for the most cohesive phase, water, and it is smallest for the least cohesive phase, trifluoropropylmethylpolysiloxane. This nicely corroborates conclusion (a) from the previous section. In contrast, the free energy of adsorption is the same for the CH_2 fragment and the CF_2 fragment, in agreement with conclusion (c) from the previous section. Hence, if, in a specific case, the relative sorption data of fluorinated and nonfluorinated compounds indicate that absorption is the dominating process for fluorinated compounds, then it must also be the dominating process for all other organic compounds because these have an even stronger preference for absorptive partitioning due to their higher van der Waals interaction-to-volume ratio.

Conclusion

Highly fluorinated compounds are special in that they have a much smaller van der Waals interaction energy per molecular contact area than nonfluorinated compounds.

This has consequences that appear to be counterintuitive. Fluorinated solutes, for example, have a stronger tendency to escape from any condensed phases into the gas phase than their hydrogenated analogues that are much smaller. Fluorinated solvents differ from other solvents in that their weaker van der Waals interactions lead to a much smaller cohesive energy, but more importantly, they also form weaker interactions with the solute. This lets especially nonfluorinated solutes prefer to partition in nonfluorinated solvents because of the greater gain in van der Waals interaction energy. The peculiar partition behavior of fluorinated solvents and solutes can be described by a simple cavity model if the cavity formation and the van der Waals interactions are parametrized correctly.

Appendix

There are various ways of calculating the molar volume of a compound. For the purpose of this paper, we needed a method that only gives reliable relative values for the molar volume. The simplest way to obtain such values is to add up tabulated volume increments for all molecular fragments of a molecule. The McGowan method[10,11] is such a method. Its results correlate 1:1 with values from a more complicated quantum chemical model such as COSMOtherm with one exception. For highly fluorinated compounds, the McGowan method predicts a smaller molar volume than COSMOtherm.[12] We believe that this is an error in the McGowan method caused by an insufficient calibration with fluorinated compounds due to the nonavailability of such data at that time. This is further supported by a comparison between the McGowan volume and the volume calculated from the density and the molar weight of the compounds.[5] For reasons of simplicity, we use the McGowan method here, however, with a corrected increment for the fluorine atom so that the calculated values are consistent with other methods.[5]

Note Added after ASAP Publication. This Article was published on Articles ASAP on July 13, 2006. In Table 1, the values in column 3 were interchanged. In the "Adsorption and Absorption" paragraph, Table 2 should have been referred to instead of Table 1. The corrected version was posted on July 14, 2006.

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