Partitioning behavior of fluorinated telomer alcohols and olefins

Kai-uwe Goss, Hans Peter Arp[1], Guido Bronner[1], Christian Niederer, Torsten Schmidt[2], Monika Hertel[2]

[1]ETHZ
[2]University of Tübingen

Introduction

The transport and accumulation of organic chemicals in the environment is governed by their physico-chemical properties, i.e. their equilibrium partitioning between various media such as water, air, soil, plants, etc. Recently a number of physico-chemical data (vapor pressures, Henry's Law constants and octanol-air partitioning) have been published for the Fluorinated Telomer Alcohols (FTOHs) [1,2]. Based on some of these data it has been postulated that the H-bond properties of the OH-group in the fluorinated alcohols is suppressed [1]. This would have consequences for all kinds of environmental partitioning of this compound class. However, data from others contradict these findings [3]. Besides this uncertainty, we have concluded before that vapor pressures or octanol-air partition constants are no suitable predictors for the environmental partitioning of organic compounds [4,5].

Here, we present a different approach, i.e. polyparameter-LFERs, in order to achieve a good understanding of the partition behavior of fluorinated telomer alcohols and olefins.

These pp-LFERs contain separate descriptors to characterize the various types of interactions that a compound can undergo. In the past we have successfully applied this concept to a diverse set of organic compounds and various sorbates [5,6]. In the work presented here we set out to determine the interaction descriptors (also called LSER descriptors) of the fluorinated telomer alcohols and olefins and validate them by a comparison with measured environmental partitioning data for air/water, air /quartz surface and air/humid acid partitioning.

Methods

In order to derive the LSER descriptors of a compound one needs to acquire a set of partition constants that differ in their sensitivity to van der Waals and H-bond-donor/acceptor interactions. We chose to rely mainly on chromatographic partitioning systems for this purpose because these experiments were easy to perform and gave reliable and consistent data. Some of the data are shown in Fig. 1 and 2 plotted versus their carbon number in comparison with some standard compounds. This type of comparison allows for a number of important consistency checks on the experimental data. a) Compounds from different, homologue compound classes must have identical slopes when their logarithmic partition constants are plotted versus the number of carbon atoms (unless the repeating unit has an electron-withdrawing property and is added in close vicinity to a functional group); b) if the slope for the fluorinated compounds is shallower than the slope of the respective hydrogenated compounds then the absolute partition constants also must be smaller. In fact, in most cases one can expect that an extrapolation of the experimental partition data of the fluorinated telomers down to two carbon atoms should yield values close to those measured for ethanol and ethane, respectively.

Results

Fig. 1 and 2 show some of our measured data and how these pass our consistency tests.

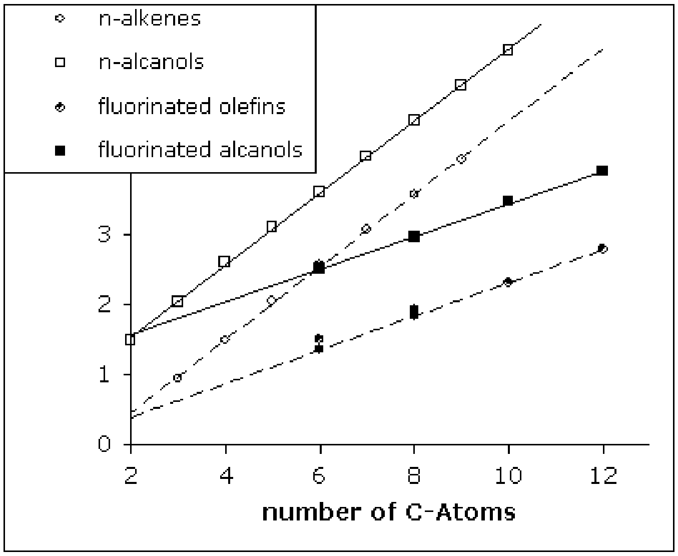

Fig. 1: Experimental values of L_{i16} of the fluorinated telomer alcohols and olefins at 25°C in comparison with data for the analogous hydrogenated compounds taken from [7].

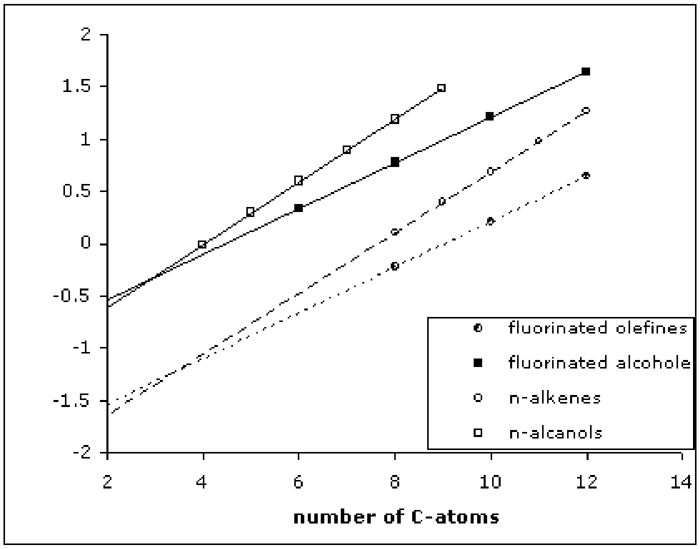

Fig. 2: Plot of retention volumes, Vnet, on a Rx-200 (crossbond trifluoropropylmethyl-polysiloxane) column at 70°C.

Derivation of LSER descriptors

Our experimental data could not be fitted satisfactorily with the traditional LSER parameters. We believe that this is due to the extreme R values of the fluorinated compounds that lie far outside the range of values that had been used in pp-LFERs before. However, this inconsistency can be reconciled with a slight change in the structure of the pp-LFER equations [8]. The LSER descriptors that can thus be determined are listed in Table 1. We are currently working on the determination of the missing B values.

Table 1: LSER descriptors of the fluorinated telomers based on a pp-LFER equation that uses a descriptor combination of log L_{i16} and V_i, S_i, A_i and B_i.

compound	S_i (former p_i)	A_i (former a_i)	Log L_{i16}
C4-2 alcohol	0.28 ±0.02	0.54 ±0.02	2.52
C6-2 alcohol	0.28 ±0.02	0.54 ±0.02	2.96
C8-2 alcohol	0.28 ±0.02	0.54 ±0.02	3.47
C10-2 alcohol	0.28 ±0.02	0.54 ±0.02	3.9
C4-2 olefin	-0.05 ±0.02	0	1.35
C6-2 olefin	-0.05 ±0.02	0	1.83
C8-2 olefin	-0.05 ±0.02	0	2.31
C10-2 olefin	-0.05 ±0.02	0	2.79

Environmental Partitioning

Our measurements for adsorption on a quartz surface (Fig. 3) nicely meet our consistency requirements and they give clear evidence that the H-bonding capability of the telomer alcohols must be similar to those of the hydrogenated analogues, i.e. no substantial suppression of the H-bonding capability.

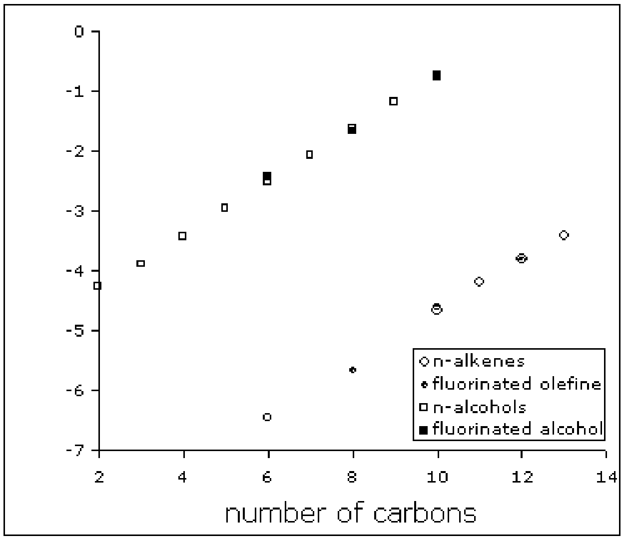

Fig. 9: Adsorption coefficients of various hydrogenated and fluorinated compounds measured on quartz sand at 15° C.

Measurements for air/water and air/humic acid partitioning were more difficult than expected. This work is ongoing.

References

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