

The effect of fluorination on the physical properties and the free energies of hydration of 1-alcohols

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ABSTRACT

Because of the widespread use of fluorinated compounds and their subsequent release into the environment, these chemicals have been subjected to a great deal of scrutiny in the past years to determine the extent of their toxicity. In order to better understand the interactions of perfluorinated alcohols and fluorotelomer alcohols in aqueous environments, molecular dynamics simulations are utilized to determine environmental predictors, such as the free energy of hydration. In this work, the predictions of two different force fields, the united-atom Transferable Potentials for Phase Equilibria (TraPPE) and the all-atom Optimized Potentials for Liquid Simulations (OPLS) are compared against available experimental data. Both force fields yield reliable predictions for liquid densities, heats of vaporization and hydration free energies. Investigation of the local solvation environment around the hydroxyl group reveals that fluorination of carbons closest to the hydroxyl group has the greatest effect on the overall hydration free energy.

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1. Introduction

Fluorotelomer-based compounds are used in a widespread array of consumer products, including coatings for cookware and stain resistant coatings for fabrics. Concurrent with their widespread use in consumer products, these materials are now widely distributed in the ecosystem, with significant levels being found in the blood of wildlife and humans [1]. Studies have shown that various fluorotelomer-based compounds, including alcohols, olefins, iodines and acrylates can be oxidized in the environment to form perfluorocarboxylic acids $[\text{CF}_3(\text{CF}_2)_x\text{COO}^-]$ (PFCA) [2–7] of which perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are the most common. PFCAs are persistent in the environment, and have been shown to induce liver tumors and developmental defects in rodents [1,8,9]. Studies of workers at facilities that produce PFOA have shown long term exposure may lead to increased risk of developing prostate cancer [10]. Concerns over PFOA and PFOS bioaccumulation eventually lead to a reformulation of Scotchguard fabric treatment in 2000 after 34 years on the market [11].

In recent years, there has been widespread interest in understanding the partitioning, transport and degradation of fluorinated surfactants in the environment. Properties such as

octanol–water ($\log K_{ow}$) and water–air partition coefficients ($\log K_{aw}$) are of particular interest because these are required inputs for environmental fate models, such as the BETR Global Model [12]. In the case of fluorinated surfactants, carboxylic acids [13] and alcohols [14,15], experimental data are limited, and in some cases conflicting [16]. Therefore, many key parameters for the prediction of environmental fate have been estimated using Quantitative Structure Property Relationships (QSPR) [17–23]. The use of QSPR on perfluorocarboxylic acids and perfluoroalcohols is problematic, since typical QSPR programs such as Sparc, EPI Suite and COSMOtherm yield inconsistent results for typical environmental predictors, such as $\log K_{ow}$ and $\log K_{aw}$ [14,24,25].

Atom-based computer simulations provide another route to the prediction of physical properties and free energies of transfer that are required for prediction of environmental fate. Methods such as thermodynamic integration, free energy perturbation and adaptive biasing force have been used to determine free energies of hydration of alkanes [26,27], energetic materials [28], amino acid side chains [29,30], ionic liquids [31], and a variety of other small organic solutes [32–34]. While extensive simulations have been performed on 2,2,2-trifluoroethanol [35–37], other fluoroalcohols and fluorotelomers have yet to be studied by computer simulation.

In this work, molecular dynamics simulations are used to predict the physical properties and hydration free energies of perfluorinated alcohols and fluorotelomer alcohols. Calculations are performed with two force fields, the Optimized Potentials for Liquid Simulations All-Atom (OPLS-AA) and the Transferable

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Potentials for Phase Equilibria United-Atom (TraPPE-UA). In addition, the effect of water model on the predicted hydration free energies is assessed. The predictions of simulation are compared to available experimental data, and used to predict free energies of hydration for compounds where no experimental data are known to exist. The effect of fluorination on the hydration behavior of alcohols is identified, and explained from changes observed in the local microstructure of water around the solute.

2. Force field

Calculations are performed using the Optimized Potentials for Liquid Simulations (OPLS), and the Transferable Potentials for Phase Equilibria (TraPPE) force fields. These force fields were selected because each provides the most accurate representation of perfluoroalkane condensed phase physical properties in their class (all-atom or united-atom). Simulations performed on these two force fields provide insight on the effect of the united-atom approximation on the prediction of free energies of hydration for perfluoroalcohols. In both force fields, interactions between atoms are described by pairwise-additive 12-6 Lennard-Jones potentials combined with partial charges to represent Coulombic interactions

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}} \quad (1)$$

where r_{ij} , ϵ_{ij} , σ_{ij} , q_i , and q_j are the separation, LJ well depth, pseudo-atom diameter and partial charges, respectively, for the pair of interaction sites i and j and ϵ_0 is the permittivity of vacuum. For OPLS, an all-atom representation is used, with non-bonded parameters taken from Watkins and Jorgensen for fluorine and associated carbon atoms [38], and Jorgensen et al. for the hydroxyl and alkyl groups [39]. In TraPPE, a united-atom representation is used for all CF_x and CH_x groups; *i.e.*, hydrogen or fluorine atoms bonded to carbon atoms are not represented explicitly and are instead combined with carbon atoms to form a single interaction site or “pseudo-atom.” Lennard-Jones parameters and partial charges were taken from the original publications for CF_3 and CF_2 [40], CH_3 and CH_2 [41], and OH [42] and used without modification. Parameters for unlike interactions were determined using the standard Lorentz–Bethelot combining rules [43,44] for calculations using TraPPE, while for OPLS a geometric combining rule $\sigma_{ij} = \sigma_i \sigma_j^{1/2}$, $\epsilon_{ij} = \epsilon_i \epsilon_j^{1/2}$ was used for both σ_{ij} and ϵ_{ij} [39]. Non-bonded parameters for both force fields are listed in Table 1.

Molecules were modeled as fully flexible, with bond stretching and bending governed by a harmonic potential

$$U_{b-a} = k(x - x_0)^2 \quad (2)$$

where U_{b-a} corresponds to the bond stretching or angle bending energy; x and x_0 are the instantaneous (bond length or angle) and equilibrium (bond length or angle), respectively. Traditionally, the TraPPE force field uses fixed bond lengths; however, in this work flexible bonds were used to simplify the implementation of the force field in molecular dynamics simulations [45]. Bond stretching and bending constants were taken from the OPLS force field [38,39] and are listed in the Supplementary material.

Rotations around dihedral angles were described with a cosine series

$$U_{\text{torsion}} = \sum_{i=1}^m k_i (1 + \cos(n_i \phi - \delta)) \quad (3)$$

where k_i are force constants, n is the periodicity or multiplicity, ϕ is the dihedral angle and δ the phase shift. Existing torsional potentials for the C–C–C–C backbone for n -alkanes and perfluoroalkanes in the OPLS and TraPPE force fields were refit

Table 1

Non-bonded parameters for alcohols, fluoroalcohols and fluorotelomer alcohols.

Group	ϵ/k_B (K)	σ (Å)	q_i
OPLS-AA			
FC (fluorine)	26.7	2.95	−0.12
CF (carbon in CF_3)	33.2	3.50	0.36
CF (carbon in CF_2)	33.2	3.50	0.24
CH (carbon in CH_3)	33.2	3.50	−0.18
CH (carbon in CH_2)	33.2	3.50	−0.12
CH (alpha carbon)	33.2	3.50	0.145
HC (alkane hydrogen)	15.1	2.5	0.06
OH (alcohol oxygen)	85.5	3.12	0.418
HO (alcohol hydrogen)	0.0	0.0	−0.683
TraPPE-UA			
CH_3	98.0	3.75	0.0/0.265 ^b
CH_2	46.0	3.95	0.0/0.265 ^b
CF_3	87.0	4.36	0.0/0.265 ^b
CF_2	27.5	4.73	0.0/0.265 ^b
O (alcohol)	93.0	3.02	−0.70
H (alcohol)	0.0	0.0	0.435
TIP3P			
O	3.15	76.544	−0.834
H	0.0 ^a /0.4	0.0 ^a /23.15	0.417
SPC			
O	3.167	78.21	0.820
H	0.0	0.0	0.410

^a Simulations with the TraPPE force field use the original TIP3P force field.

^b Partial charges for the alpha carbon bonded to oxygen.

to use the form of Eq. (3). Constants for all dihedral potentials are listed in the Supplementary material.

Additional required Fourier coefficients for perfluoroalcohols and telomers were optimized to reproduce rotational barriers determined from MP2/6–31+g(d,p) *ab initio* calculations. These calculations were performed in Gaussian 09 [46]. Gas phase energy minimizations were performed in CHARMM v36b2 with Fourier constants set to zero to determine the contribution of Lennard-Jones and Coulombic interactions to the rotational barrier. Fourier coefficients were then fit to reproduce the difference between the rotational barrier and the predictions of *ab initio* calculations. For the OPLS force field, 1–4 Lennard Jones and Coulombic interactions were scaled by 0.5. For consistency with prior TraPPE parameterizations [47], all 1–4 interactions were set to zero, and therefore

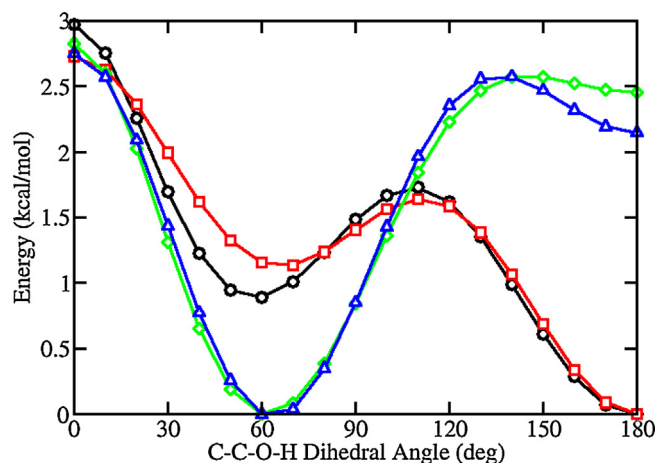


Fig. 1. Rotational barrier for C–C–O–H dihedral for fluoroalcohols. MP2/6–31+g(d,p) *ab initio* calculations (black circles) and optimized OPLS parameterization (red squares) for perfluoroethanol. MP2/6–31+g(d,p) *ab initio* calculations (green diamonds) and OPLS-AA parameterization (blue triangles) for 2,2,2-trifluoroethanol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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