Environmental fate predication via atom-based computer simulations

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Project Introduction

The purpose of this project was to develop a new perfluorocarboxylic acid model by optimizing dihedrals of perfluorobutanoic acid in order to calculate different physical properties of those compounds.

State of Knowledge

Perfluorocarboxylic acids are man-made surfactants that are used in many household objects such as cleaning products, fire-fighting foam, and packaging [1]. Because of the strong carbon-fluorine bonds, these compounds do not biodegrade on their own, have very long half-lives, and can bioaccumulate in nature. This bioaccumulation has led to liver and kidney problems in animals [2]. Unfortunately, little work has been done in developing solid model parameters to use during computer simulations for perfluorocarboxylic acids. Computer simulations can be useful to calculate different properties that can identify how harmful these compounds are to the environment and aid in synthesizing new replacement materials that have similar properties but are not harmful to the environment.

$$E = \sum_{\text{bonds}} K_b(b - b_0)^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 + \sum_{\text{dihedrals}} K_\phi(1 + \cos(n\phi - \delta)) + \sum_{\text{improper}} K_\varphi(\varphi - \varphi_0)^2 + \sum_{\text{Urey-Bradley}} K_u(u - u_0)^2 + \sum_{i<j} 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_{i<j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

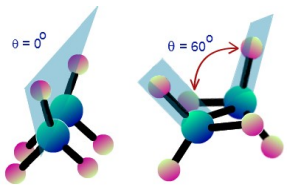

Figure 1
Equation behind model development (left) and example of rotation of dihedrals, which was optimized using Gaussian (right).

Approach

Molecular dynamics programs NAMD and VMD were used to validate a previous model [3] and eventually create a new one. Density and free energy of hydration (ΔG) were calculated using the old model to highlight its instability. In the new model, dihedrals were optimized using OPLS-AA force field and Gaussian.

Results

The newly developed model shows less error as seen in Table 1. Figure 1 shows the theory behind the new aspect of the model. The dihedrals were optimized fairly well as seen by the overlapping of scans in Figure 2. Figure 3 shows bulk solutions of butanoic acid and perfluorobutanoic acid, respectively, with highlighted dimers, trimers, and quadrimers showing interactions between molecules. The radial distribution between the hydroxyl hydrogen and carbonyl oxygen for butanoic acid and perfluorobutanoic acid is shown in Figure 4.

	ΔG (kcal/mol)	Error	Density (g/cm^3)	Error
Perfluoroethane	2.815	6.67%	1.674	5.28%
Perfluoropropane	2.564	9.18%	1.861	16.30%
Perfluoropentane	3.262	11.36%	1.824	14.03%
Perfluorohexane	3.689	12.86%	1.901	13.46%
Perfluoroheptane	3.788	12.50%	1.939	n/a
Perfluorooctane	3.089	13.43%	2.190	25.08%
Perfluorobutanoic Acid	n/a	n/a	1.708	3.50%

Table 1
Shown above are free energies of hydration (ΔG) and densities of perfluoroalkanes, as well as perfluorobutanoic acid, with associated percent errors. High errors in perfluoroalkanes led to new model development.

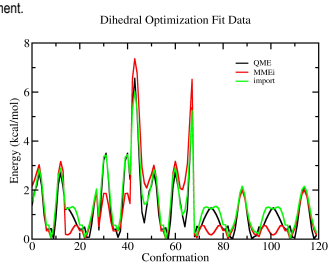

Figure 2
Dihedral scans based on Newman conformations from perfluorobutanoic acid model development shown above. The red line represents the initial scan, while green and black represent the optimized scan.

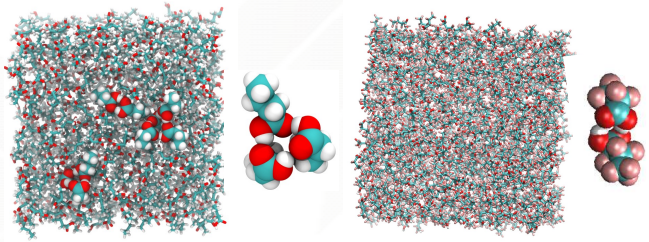

Figure 3
A bulk solution of butanoic acid with a highlighted dimer, trimer, and quadrimer is shown at left. The trimer has been enlarged for detail, showing interactions between the hydroxyl hydrogen and carbonyl oxygen. A bulk solution of perfluorobutanoic acid is shown at right, with an enlarged dimer from the bulk solution.

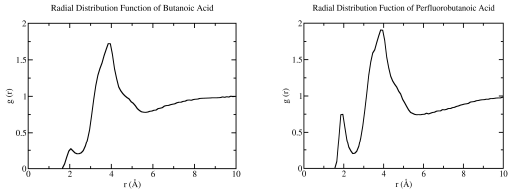

Figure 4
Shown above are the radial distribution function graphs between the hydroxyl hydrogen and carbonyl oxygen of butanoic acid (left) and perfluorobutanoic acid (right). These graphs show the similarities in properties between the two compounds.

Conclusions

Based on the percent error and the minor differences in the dihedral scan, the model developed could be optimized even more, which would lead to even better results. Butanoic acid and perfluorobutanoic acid have some similar properties as evidenced by the appearance of dimers in both bulk solutions. Future work will include testing this model more thoroughly and calculating free energy of longer-chain PFCAs.

Relation Sustainable Mg.

Longer-chain perfluorinated carboxylic acids are used during the manufacturing of semiconductors and household objects. This research will assist in the process of learning more about these compounds and finding sustainable replacements in the future to help the environment.

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About Me

Jessica Maass is entering her third year studying chemical engineering at Missouri University of Science and Technology. This is her first research experience.

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