Comment on "Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs)"

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In their article, Wang et al. [1] use the COSMOtherm software program in an attempt to shed some insights into the physicochemical properties of various poly- and perfluorinated compounds. The authors conduct COSMOtherm based pK_a calculations on the perfluoroalkyl carboxylic acids, and notably on n-perfluorooctanoic acid (PFOA), but appear to overlook relevant prior literature on the topic [2].

In their conformation dependent pK_a studies, the authors appear to make a critical error in their analyses that is evident in their statement that "the pK_a estimates are highly dependent on the chosen conformations of the neutral species and the anionic species." Dissociation of the acidic proton and any substantial conformational changes are not both included in calculations of the free energy of acid dissociation (from which the pK_a is calculated). The proton dissociation step is included in the energy calculation, but the perfluoroalkyl chain geometry of the dissociated anion must remain in a similar potential well orientation as that of the molecular acid form. Thus, during such calculations, the geometry of the acid form is optimized and the energy determined, and then the proton is removed and the corresponding anionic geometry is optimized and the energy determined, and the pK_a estimate obtained from the relative acid and anionic form energies.

What Wang et al. [1] appear to have allowed is a transition from an acid form geometry to a very different anionic form geometry, which is not a correct way of calculating free energy changes during acid dissociation. This error explains why the authors obtained widely ranging conformation dependent pK_a values for PFOA dissociation between 0.9 and 2.9. As has been previously shown [2], there are negligible conformation dependent effects on the pK_a value of PFOA.

References

[1] Z. Wang, M. MacLeod, I. Cousins, M. Scheringer, K. Hungerbuhler, Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs), Environmental Chemistry 8 (2011) 389–398.

[2] S. Rayne, K. Forest, Theoretical studies on the pKa values of perfluoroalkyl carboxylic acids, Journal of Molecular Structure THEOCHEM 949 (2010) 60–69.

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