

Octanol/water distribution coefficients of the C₁ through C₇ perfluoro-n-alkyl sulfonates: Comparison of the IEFPCM-UFF, CPCM, and SMD solvation models

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The octanol/water distribution coefficients ($\log D_{ow}$) of the C₁ through C₇ perfluoro-n-alkyl sulfonates (PFSA) were calculated using the M062X/6-311++G(d,p) and MP2/6-311++G(d,p)//M062X/6-311++G(d,p) levels of theory and the IEFPCM-UFF, CPCM, and SMD solvation models. At both levels of theory with all solvation models, absolute $\log D_{ow}$ calculated for the straight chain C₁ through C₇ PFSA display a substantial negative bias against available experimental data and expected trends by several log units. However, the SMD solvation model achieves accurate relative $\log D_{ow}$ accuracy, yielding fragmental contributions of a -CF₂- group towards the $\log D_{ow}$ of 0.51 ± 0.02 to 0.54 ± 0.01 units (-3.0 ± 0.1 to -3.1 ± 0.1 kJ mol⁻¹), in good agreement with the experimental value of 0.61 units (-3.4 ± 0.1 kJ mol⁻¹). In contrast, the IEFPCM-UFF and CPCM solvation models exhibit either invariant $\log D_{ow}$ with increasing perfluoro-n-alkyl chain length (CPCM) or a modestly decreasing trend (IEFPCM-UFF).

Perfluoroalkyl sulfonic acids (PFSA; Figure 1) are widely used industrial materials that have also become an important class of environmental contaminants [1]. With pK_a values $\ll 0$, these compounds are effectively entirely dissociated in aqueous solution [2] [3]. Consequently, when assessing the partitioning behavior of PFSA, the anionic form is relevant, warranting use of equilibrium constants such as the octanol/water distribution coefficient ($\log D_{ow}$) [4] [5] [6].

Few experimental studies have been conducted on the partitioning of PFSA (and other perfluoroalkyl

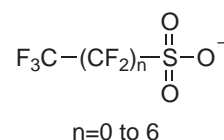


Figure 1: General structure of the C₁ to C₇ perfluoro-n-alkyl sulfonates.

compounds) between pure gas, liquid, solution, and solid phases. Previous work has provided experimental fragmental contributions of a -CF₂- group ($f(\text{CF}_2)$) towards the $\log D_{ow}$ for perfluoro-n-alkyl oxyacids (PFSA and perfluoro-n-alkyl carboxylic acids [PFCAs]) at 0.61 $\log D_{ow}$ units, or -3.4 ± 0.1 kJ mol⁻¹ [7]. In the current study, solution phase standard state (298.15 K, 1 mol L⁻¹) density functional theory calculations in n-octanol and water model solvents were conducted using the M062X/6-311++G(d,p) [8] [9] [10] method in Gaussian 09 [11] on the C₁ (trifluoromethyl sulfonate) through C₇ (perfluoro-n-heptane sulfonate) straight chain PFSA anions with the IEFPCM-UFF [12], CPCM [13] [14], and SMD [15] solvation models. Computationally derived $\log D_{ow}$ at these levels of theory were obtained from the respective Gibbs free energies with thermal and zero-point corrections for comparison with the experimental data. Single point calculations were also performed at the SMD-MP2/6-311++G(d,p)//M062X/6-311++G(d,p) level of theory, yielding theoretical $\log D_{ow}$ estimates based on the corresponding single point energies.

At both levels of theory with all solvation models, absolute $\log D_{ow}$ calculated for the straight chain C₁ through C₇ PFSA display a substantial negative bias by several log units. For example, the MP2/6-311++G(d,p)//M062X/6-311++G(d,p) calculated $\log D_{ow}$ for n-perfluorooctane sulfonate (n-PFOS; straight chain C₈ PFSA) is -1.8, compared to the experimental value of +2.4 [7]. Based on the ex-

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perimental $\log D_{ow}$ for n-PFOS and the corresponding n-perfluoroalkyl $f(\text{CF}_2)$ of 0.61 $\log D_{ow}$ units for octanol/water partitioning, linearly distributed $\log D_{ow}$ values ranging from -1.8 (C_1 PFSA) to +1.8 (C_7 PFSA) are expected for the compounds under consideration. By comparison, calculated values at the M062X/6-311++G(d,p) and MP2/6-311++G(d,p)//M062X/6-311++G(d,p) levels range from about -6 (C_1 PFSA) to -2 (C_7 PFSA; Figure 2) depending on the theoretical method and solvation model employed.

Despite the lack of absolute $\log D_{ow}$ predictive accuracy, the SMD solvation model achieves accurate relative $\log D_{ow}$ accuracy at both the M062X/6-311++G(d,p) and MP2/6-311++G(d,p)//M062X/6-311++G(d,p) levels of theory, giving the following $f(\text{CF}_2)$ values based on best fit linear regression of the predicted $\log D_{ow}$ values against the perfluoro-n-alkyl chain homolog number:

SMD-M062X/6-311++G(d,p):

$$r=0.999$$

$$p<10^{-7}$$

$$m[f(\text{CF}_2)]=0.54\pm 0.01 \text{ log units } (-3.1\pm 0.1 \text{ kJ mol}^{-1})$$

SMD-MP2/6-311++G(d,p)//M062X/6-311++G(d,p):

$$r=0.996$$

$$p<10^{-5}$$

$$m[f(\text{CF}_2)]=0.51\pm 0.02 \text{ log units } (-3.0\pm 0.1 \text{ kJ mol}^{-1})$$

In contrast, both the IEFPCM-UFF and CPCM solvation models exhibit either invariant $\log D_{ow}$ with increasing perfluoro-n-alkyl chain length (CPCM) or a modestly decreasing trend (IEFPCM-UFF):

IEFPCM-UFF-M062X/6-311++G(d,p):

$$r=-0.953$$

$$p=0.001$$

$$m[f(\text{CF}_2)]=-0.05\pm 0.01 \text{ log units } (0.2\pm 0.1 \text{ kJ mol}^{-1})$$

CPCM-M062X/6-311++G(d,p):

$$r=-0.289$$

$$p=0.53$$

$$m[f(\text{CF}_2)]=\text{not significant}$$

The results are consistent with our previous study at various levels of semiempirical, density functional, and composite method theory on the air to wa-

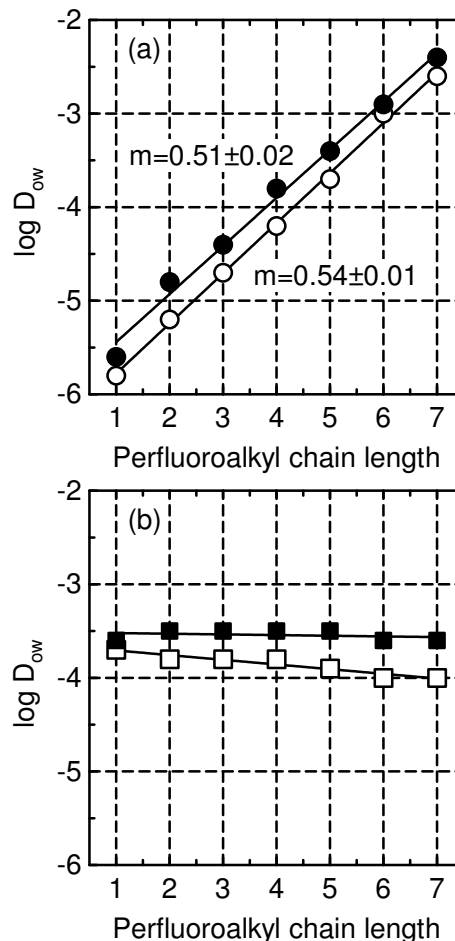


Figure 2: Computationally calculated $\log D_{ow}$ for the C_1 through C_7 perfluoro-n-alkyl sulfonates at the (a) SMD-M062X/6-311++G(d,p) (open circles) and SMD-MP2/6-311++G(d,p)//M062X/6-311++G(d,p) (filled circles) levels of theory and the (b) IEFPCM-UFF-M062X/6-311++G(d,p) (open squares) and CPCM-M062X/6-311++G(d,p) (filled squares) levels of theory.

ter solvation behavior of short-chain perfluoroalkanes, whereby only the SMD solvation model was observed to display the correct trend in solvation free energies with increasing perfluoro-n-alkyl chain length [16]. Despite not achieving absolute $\log D_{ow}$ accuracy, the SMD solvation model may have broad utility in developing relative quantitative structure-property relationships (QSPRs) for the solvation and partitioning behavior of perfluoroalkyl moieties (and related organic compounds) within and between various phases.

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