# Octanol/water distribution coefficients of the $C_1$ through $C_7$ 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 $C_1$ through $C_7$ perfluoro-n-alkyl sulfonates (PFSAs) 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 $C_1$ through $C_7$ PFSAs 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 -$CF_2$- 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 (PFSAs; 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 PFSAs, 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 PFSAs (and other perfluoroalkyl compounds) between pure gas, liquid, solution, and solid phases. Previous work has provided experimental fragmental contributions of a -$CF_2$- group ($f(CF_2)$) towards the log $D_{ow}$ for perfluoro-n-alkyl oxyacids (PFSAs 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 $C_1$ (trifluoromethyl sulfonate) through $C_7$ (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.

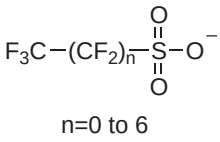


Figure 1: General structure of the $C_1$ to $C_7$ perfluoro-n-alkyl sulfonates.

At both levels of theory with all solvation models, absolute log $D_{ow}$ calculated for the straight chain $C_1$ through $C_7$ PFSAs 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 $C_8$ 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 $f(CF_2)$ 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 $f(CF_2)$ 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[$f(CF_2)$]=0.54±0.01 log units (-3.1±0.1 kJ $mol^{-1}$)

SMD-MP2/6-311++G(d,p)//M062X/6-311++G(d,p):
r=0.996
$p<10^{-5}$
m[$f(CF_2)$]=0.51±0.02 log units (-3.0±0.1 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[$f(CF_2)$]=-0.05±0.01 log units (0.2±0.1 kJ $mol^{-1}$)

CPCM-M062X/6-311++G(d,p):
r=-0.289
p=0.53
m[$f(CF_2)$]=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-

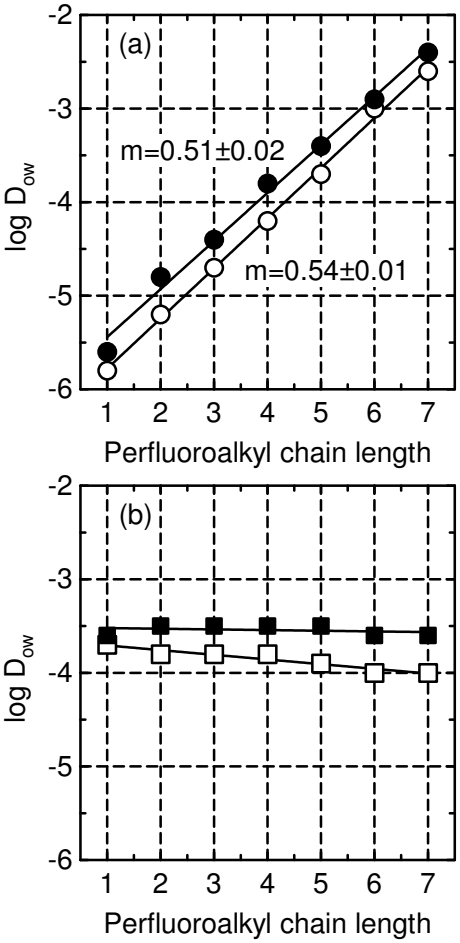


Figure 2: Computationally calculated log $D_{ow}$ for the $C_1$ through $C_7$ perfluoro-n-alkyl sulfonates at the (a) SMD-M062X/6-311++G(d,p) (open circles) and SMD-MP2/6-311++G(d,p)//M062X/6-311++G(d,p) (filled circles) levels of theory and the (b) IEFPCM-UFF-M062X/6-311++G(d,p) (open squares) and CPCM-M062X/6-311++G(d,p)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