Theor Chem Acc (2016) 135:18
DOI 10.1007/s00214-015-1784-6

REGULAR ARTICLE

Novel approach for predicting partition coefficients of linear perfluorinated compounds

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Received: 22 October 2015 / Accepted: 1 December 2015
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Abstract A new approach for predicting octanol–water partition coefficients (Log P) of linear perfluorinated compounds is described, making use of the limited experimental data available, previous observations and the consistent similarities observed between the experimental and calculated (with electronic structure methods and using EPI Suite) slopes of the linear plots of Log P values with the number of carbon atoms ($N = 2$–11). Eight families of linear organic compounds were investigated: carboxylic acids, perfluorinated carboxylic acids, sulfonic acids and perfluorinated sulfonic acids, together with their corresponding conjugate bases.

Keywords Octanol–water partition coefficients · Log P · K_{ow} · Linear perfluorinated compounds · Carboxylic acids · Perfluorinated carboxylic acids · Sulfonic acids · Perfluorinated sulfonic acids · Conjugate bases

1 Introduction

Long-chain linear perfluorinated acids (PFAs), such as perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), and their conjugate bases, perfluorocarboxylates (PFC) and perfluorosulfonates (PFS), have received significant attention in the past few years. Substitution of hydrogen by fluorine confers new physicochemical and biological properties to these molecules [1, 2]. They show resistance to both chemical and biological degradation, which allows those with more than seven carbon atoms in their structure to bioaccumulate in living organisms, increasing the potential risk associated with their concentrated action [3, 4]. Measurable quantities of branched perfluorinated acids have been found in mixtures analyzed by several groups [5–7]. However, the linear isomers predominate. These compounds have even been found in the arctic and the troposphere [8, 9]. Furthermore, they have been detected in animals and in human blood [10–12], which raises awareness about the need for a deeper understanding of their possible degradation pathways and routes of environmental distribution [13].

PFAs have been postulated to exist almost completely dissociated; hence, some papers ignore the non-dissociated species in calculations of the environmental fate of these compounds [14, 15]. However, several studies have tried to demonstrate the potential mistake of this approach by showing the need for taking both species into account [16–18]. The importance of considering both species arises when studying the chemical exchange between different environments (e.g., aqueous or non-polar solutions) involved in the global fate of these compounds. Much remains to be done to better understand how PFAs bioaccumulate and how they get to reach waters, soil, air and humans. To that end, the determination of physicochemical properties such as acid dissociation constants (K_a, $pK_a = -\log K_a$) and partition (or distribution) coefficients is a key factor to understand how these molecules behave in the environment or interact with the biota.

Electronic supplementary material The online version of this article (doi:10.1007/s00214-015-1784-6) contains supplementary material, which is available to authorized users.

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Published online: 31 December 2015

The experimental determination of octanol–water partition coefficient (Log *P* or Log *D*) values of PFCAs and PFSAs is a challenging task [19]. Hence, most values have not been determined, and estimated data are mainly used [17, 18, 20–23]. Zhao and Abraham [24] studied a large group of linear ionic organic salts and found a strong linear correlation between their Log P values and the number of carbon atoms in these species. They also found that the slopes of the graphs for the neutral and the charged species were different and that the difference between the Log *P* of cations and their neutral counterparts becomes less as the length of the linear carbon chain increases. Jing et al. [25] recently reported octanol–water partition coefficients for a homologous series of carboxylates and perfluorocarboxylates and for one sulfonate and perfluorosulfonate, determined by a voltammetry method. They observed that the lipophilicity of perfluorinated anionic compounds was two orders higher than that of their non-fluorinated counterparts. Furthermore, applying a fragment method, they demonstrated that perfluoroalkyl and alkyl chains of the same length have similar contributions to molecular lipophilicity. This result led them to hypothesize that the lipophilicity difference is determined by the charged head group ($-CO_2^-$ or $-SO_3^-$) and the electron-withdrawing effect upon it by the fluorine substitution on the alkyl chain. Like Zhao and Abraham [24], they found a strong linear correlation between the number of carbons in the linear chain and Log *P* of the ionic species analyzed.

Using isocratic reversed-phase high-performance liquid chromatography–mass spectrometry experiments, de Voogt et al. [26] found that the hydrophobicity of some PFAs, which they expressed as their capacity factors, is linearly related to the number of fluorinated carbon atoms in these molecules. Rayne and Forest [27] analyzed the apparently constant CF_2 fragment contribution to a set of K_{oc} (soil organic carbon–water partition coefficient) values reported by Higgins and Luthy [28] for linear PFCAs. After plotting the same experimental data of Log K_{ow} values with the length of the perfluoroalkyl chain differently, Rayne and Forest suggested that the previously observed linear CF_2 contribution is debatable, as they observed an apparent change of CF_2 contribution with the increase in chain length. When discussing the results obtained by Jing et al., Rayne and Forest claimed that lack of consideration of the chemical interface could be a factor for the constant slope observed with the increase in the number of CF_2 group. Another study [29] used a water-saturated sediment column to calculate sediment-dissolved partition coefficients. The values they obtained were almost half a unit different from those reported by Luthy and Higgings [28]. The observed differences were attributed to variations in sediment texture and water chemistry. A more recent study [30] confirmed the linear relationship between the experimental Log *P* values reported by Jing et al. [25] for the linear PFCs with the number of fluorine atoms.

Log *P* values used in the vast majority of publications dealing with global fate predictions and partitioning behavior of PFAs have been obtained using available software packages (e.g., EPI Suite, CLog *P* and SPARC [20]) which provide very fast results and have demonstrated their applicability for predicting other properties. Even though no software package is able to accurately predict Log *P* values for all PFAs [22], they continue to be used [17, 18, 20–23].

Wang et al. [31] used the quantum chemistry-based model COSMOtherm [32, 33] to estimate the octanol–water partition coefficients of several perfluorocompounds, including some PFCAs and PFSAs. Their estimations were limited to the neutral species, but they proposed a method to estimate distribution coefficients (Log *D* values, accounting for both neutral and anionic species) using pK_a values. However, they noted that the calculated pK_a values significantly depend on the conformation chosen for both species and the software used was unable to obtain a set of reliable conformers of the anions.

This work deals with the calculation of octanol–water partition coefficients for the linear PFAs with 2 to 11 carbon atoms (PFCAs and PFSAs, as well as their conjugate bases). The non-fluorinated analogues of these compounds are also studied. A new approach which makes use of electronic structure calculations, empirical observations and the limited experimental data available to predict the octanol–water partition coefficients of PFAs is described. This study considers all the molecules studied as monomers, ignoring the effect of the formation of molecular aggregates.

2 Methodology

2.1 Calculation of partition coefficients

A solute S partitions between *n*-octanol and water according to Eq. 1. The octanol–water partition equilibrium constant or coefficient, *P*, describes this process according to Eq. 2 which uses activities.

$$S_{\text{water}} \rightleftarrows S_{n\text{-octanol}} \tag{1}$$

$$P = a(S_{n\text{-octanol}})/a(S_{\text{water}}) \tag{2}$$

The standard Gibbs free energy change of this equilibrium, $\Delta G^{\circ}_{\text{ow}}$, can be determined from the difference between the calculated standard Gibbs free energies of formation ($\Delta_f G^{\circ}$) of the solute in the two partitioning media as shown in Eq. 3. Log *P* values can then be determined using Eq. 4, where *R* is the ideal gas constant and *T* is the temperature in Kelvin.

$$\Delta G^{\circ}_{\text{ow}} = \Delta_f G^{\circ}_{\text{o}}(S) - \Delta_f G^{\circ}_{\text{w}}(S) \tag{3}$$

$$\text{Log}\,P = -\Delta G^{\circ}_{\text{ow}}/(RT\ln 10) \quad (4)$$

Two approaches were followed to calculate the $\Delta_f G^{\circ}$ values in octanol and water, $\Delta_f G^{\circ}_{o}$ and $\Delta_f G^{\circ}_{w}$, respectively. The simplest approach, which led to the best results reported in this paper, involved the application of solvent effects through a single-point energy calculation using gas-phase optimized geometry and frequency corrections. The $\Delta_f G^{\circ}$ values in either octanol or water were obtained by combining the uncorrected energy in solution, E_o or E_w (for octanol and water, respectively), with the gas-phase thermal correction to the Gibbs free energy, TCG_{gas}; Eq. 4 then becomes Eq. 5.

$$\text{Log}\,P = (E_w - E_o)\big/(RT\ln 10) \quad (5)$$

Another approach considers solvent effects in both geometry optimizations and frequency calculations. The $\Delta_f G^{\circ}$ values in solution are calculated by combining the energy in solution with the corresponding TCG value. Since experimental data have been obtained between 295.15 and 298.15 K, this second approach was applied to verify that using a temperature of 298.15 K in our calculations had no significant effect on the calculated Log *P* values. Convergence problems during the optimization of the carboxylic acids and carboxylates prevented us from using this procedure; however, the overall results for the neutral acids were not better than when using solvent effects only on the energies.

Log *P* (also represented as Log K_{ow}) is the value most frequently reported when referring to neutral solutes. The partitioning behavior of ionizable molecules is usually described through the distribution coefficient, Log D, which depicts how the dissociated/undissociated pair distributes between these two phases (water and octanol). At high enough pH values, PFAs can be assumed to be completely dissociated, since the reported pK_a values are close to zero (a range of values from −0.5 to 3.8 has been reported, and debate is still ongoing) [34–37]. Thus, the Log D values of the anionic species can be considered equal to Log *P* under these conditions. This approach was used by Jing et al. [25] for reporting the first experimental Log *P* values for PFCs and perfluorooctane sulfonate (the PFS with $N = 8$). In this paper, the octanol–water partition coefficient of anions will also be denoted Log *P*.

2.2 Computational details

The bulk of the Log *P* calculations reported in this paper are based on electronic structure calculations performed with the Gaussian 09 software package [38]. The B3LYP functional [39, 40] was applied with the 6-31++G(*d*,*p*) basis set. Solvent effects were accounted for by means of the SMD method [41]. A previous study by our group [42] on the thermodynamic stability of the perfluorooctanesulfonic acid isomers led to B3LYP/6-311++G(*d*,*p*) results in close agreement with previous B3LYP/6-31++(*d*,*p*) calculations for the mono-methylated isomers [43]. Based on this, the smaller basis set was chosen for the current study. Stationary points were verified as legitimate minima by a harmonic frequency calculation at the same level of theory. Since there is experimental evidence (confirmed by computations) of the helical conformation of perfluorinated compounds [46–50], to avoid optimizing other conformers of higher energy, the geometries of the species studied were built starting from the helical optimized structure of the acid with eight carbon atoms, as done in our previous studies [42, 44, 45]. Calculations were also performed using the M06-2X functional [51, 52], and the results obtained were not significantly different from the B3LYP results discussed in the following sections.

Most of the software packages frequently used for Log *P* determinations [20] base their calculations on molecular structure and atomic or fragment contributions. The Log *P* values obtained for PFAs using several versions of these software packages have been compared with some limited experimental results, and the inaccuracies found are in the order of one unit or more, which shows the need for more research in this field [20, 22]. The analysis of recent improvements in the predictions of some of these packages suggests that better parameterizations have been performed. However, doubts still remain as to whether these new results are a product of a specific parametrization to fit some particular groups of perfluorinated compounds or whether there have been major changes to the software that could improve the calculation of Log *P* values for any group of molecules [22]. Table S1, of the electronic supplementary material (ESM) section, shows some of the previously calculated/reported values for PFCAs, which are also displayed in Figure S1.

The estimation of Log *P* in this work was also performed using EPI Suite [53, 54], one of the most widely used tools for predicting physicochemical properties of molecules, especially for environmental purposes. This freeware software bases its calculations on quantitative structure–activity relationships [55, 56]. It requires a SMILES (Simplified Molecular Input Line Entry System) string as the input structure; examples for neutral and anionic species are shown in Section S1 of the ESM. EPI Suite calculates Log *P* values of neutral and ionic species making use of the KOWWIN module. Anionic species are calculated as sodium, potassium or lithium salts, and the SMILES string used should indicate the cation chosen, even though it does not affect the Log *P* calculation. In this work, anions are calculated as sodium salts when using EPI Suite.

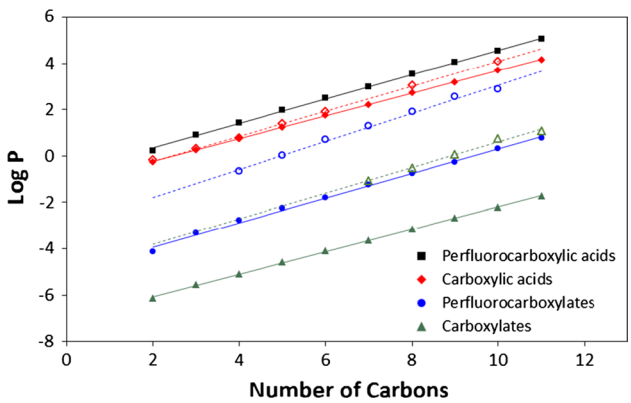

Fig. 1 Plot of the experimental (*broken lines* and *unfilled markers*) and calculated (using Eq. 5, *solid lines* and *filled markers*) Log *P* values (reported in Table 1) with the number of carbon atoms for carboxylic acids, perfluorocarboxylic acids and their conjugate bases

3 Results and discussion

3.1 Ab initio calculation of Log *P* values of carboxylic acids, perfluorocarboxylic acids and their conjugate bases

Figure 1 shows the linear correlation between experimental and calculated (using Eq. 5) Log *P* values with the number of carbon atoms (*N*) for the two families of carboxylic acids and their conjugate bases studied. Figure S2 of the ESM section contains the independent graphs for the experimental and calculated data. Remarkably high linear correlations ($R^2 > 0.997$) are obtained for the four curves shown. Similar R^2 values are obtained when correlating the experimental and calculated sets of data with each other. Table 1 displays the experimental [25, 57–62] and calculated Log *P* values for the four groups of species. Experimental values

Table 1 Experimental (or predicted) and calculated (using EPI Suite and from electronic structure calculations) Log *P* values of carboxylic acids, perfluorocarboxylic acids (PFCAs) and their conjugate bases

N[a]	Carboxylic acids $CH_3(CH_2)_{N-2}COOH$			Carboxylates $CH_3(CH_2)_{N-2}COO^-$			PFCAs $CF_3(CF_2)_{N-2}COOH$			PFCs $CF_3(CF_2)_{N-2}COO^-$		
	Exp[b]	EPI Suite	Calc	Exp[c]	EPI Suite	Calc	Exp[f]	EPI Suite	Calc	Exp[c]	EPI Suite	Calc
2	−0.17	0.09	−0.26	[−3.87]	−3.72	−6.15	−2.1[d]; [−0.2][e]	0.50	0.24	[−1.78]	−3.31	−4.12
3	0.33	0.58	0.25	[−3.31]	−3.23	−5.57	[0.41]	1.47	0.91	[−1.17]	−2.34	−3.32
4	0.79	1.07	0.78	[−2.75]	−2.74	−5.10	[1.01]	2.14	1.43	−0.66	−1.67	−2.78
5	1.39	1.56	1.24	[−2.19]	−2.25	−4.59	[1.62]	2.81	1.98	0.03	−1.00	−2.25
6	1.92	2.05	1.74	[−1.63]	−1.76	−4.11	[2.22]	3.48	2.49	0.7	−0.34	−1.78
7	[2.48]	2.54	2.22	−1.1	−1.27	−3.63	[2.83]	4.15	3.00	1.30	0.33	−1.23
8	3.05	3.03	2.72	−0.51	−0.78	−3.15	[3.44]	4.81	3.53	1.9	1.00	−0.76
9	[3.56]	3.52	3.19	0.07	−0.29	−2.67	[4.04]	5.48	4.06	2.57	1.67	−0.25
10	4.09	4.02	3.69	0.74	0.20	−2.20	[4.65]	6.15	4.55	2.9	2.34	0.31
11	[4.63]	4.51	4.17	1.08	0.70	−1.71	[5.25]	6.82	5.08	[3.68]	3.01	0.79
Slope[g]	0.539	0.491	0.490	0.561	0.491	0.488	[0.606]	0.685	0.529	0.606	0.685	0.529
Intercept[g]	−1.295	−0.895	−1.214	−4.993	−4.703	−7.059	[−1.412]	−0.671	−0.714	−2.991	−4.483	−4.977

[a] Number of carbon atoms

[b] From Ref. [57] [values in square brackets have been predicted using the experimental slope and intercept]

[c] From Ref. [25] (see Section S2) [values in square brackets have been predicted using the experimental slope and intercept]

[d] From Refs. [58–60]

[e] From Refs. [60–62]

[f] Values in square brackets have been predicted using one value reported in the literature (−0.2, $N = 2$) and the experimental slope of PFCs (0.606)

[g] From a linear regression analysis: Log P = slope × N + intercept (excluding predicted values, unless the slope and intercept are shown in square brackets)

for the PFCs were determined using the data provided by Jing et al. [25], as described in the ESM (see Section S2 and Table SS2). The calculated (uncorrected) energies in solution, E_w and E_o, for the four families of linear compounds are reported in Tables S2a and S2b of the ESM section.

The calculated Log *P* values are slightly underestimated for the carboxylic acids with an average error of −0.18 units, which is an excellent result. Larger underestimated values are obtained for the anions, with average errors of −2.74 for the carboxylates and −2.50 for the PFCs. The calculated error tends to increase with the size of the species considered. Calculations predict these compounds, especially the anions, to be less lipophilic than they have been found to be experimentally. However, the general trends are well reproduced. Calculated and experimental values correlate linearly with *N*. Log *P* values for PFCs determined by Jing et al. [25] are almost two orders of magnitude higher than the values of the carboxylates with the same number of carbon atoms; our results also reproduce this. Furthermore, the calculated lipophilic order (carboxylates < PFC < carboxylic acids) corresponds with the experiment [25, 61].

Our calculations indicate that, as expected [25], the perfluorinated species have greater Log *P* values than the non-fluorinated ones. The increase in Log *P* is much greater for the anions than for the neutral acids, which is to be expected based on polarity arguments and the charge of these species. The electron-withdrawing effect of the fluorine atoms in the alkyl chain reduces the negative charge of the head group, making the anions more thermodynamically stable and increasing the acidity of the corresponding PFCAs. Calculated Mulliken atomic charges (see Table S3a) clearly indicate this effect which increases when going from the gas phase to octanol and water. Larger negative charges on the oxygen atoms bonded to the acidic hydrogen atom also explain the higher acidity of the PFCAs relative to their non-fluorinated analogues (the same situation applies to PFSAs and PFSs, see Table S3b).

Table 1 also displays the slopes and intercepts of the linear correlations between the experimental and calculated Log *P* values with *N* for the four groups of species. A very interesting observation is the fact that the curves for the carboxylic acids and the carboxylates, using both experimental and calculated data, are almost parallel, with slopes of 0.538–0.561 (experimental) and 0.491 (calculated). The same situation arises between the calculated curves for the PFCAs and the PFCs with slopes of 0.529 (calculated), which are just slightly greater (by 0.04 units) than the calculated slopes of the non-fluorinated species. From this it is not difficult to imagine that the corresponding slope for the linear correlation using the experimental Log *P* values of the PFCAs may be very close to 0.606, the value obtained for the slope using the experimental Log *P* values of the PFCs. The calculated slopes for the carboxylic acids, the carboxylates and the PFCs are only 0.05–0.08 units smaller than the corresponding experimental curves.

Log *P* values were also obtained from calculations including solvent effects by means of the IEF-PCM solvation method [63–65] using both the UFF and UAHF radii to define the solvent cavities. Even though the Log *P* versus *N* curves obtained showed strong linear correlations, the slopes were negative in contradiction to the experimental data. Previous computational studies have also indicated that SMD is the continuum solvation method used to predict an increase in lipophilicity with an increase in chain length for acids with more than two carbon atoms [36].

To the best of our knowledge, there are no experimental Log *P* values reported for PFCAs with more than two carbon atoms in their structure. The calculation for trifluoroacetic acid ($N = 2$) seems to be overestimated (by 0.44 or 2.34 units; see follow-up discussion in Sect. 3.2.1), and at this point, not much more can be said about the calculated Log *P* values of other PFCAs. The parallel relationships previously identified between experimental and calculated (based on electronic structure calculations) Log *P* values for the two groups of acids with their corresponding conjugate bases, are investigated in the following section using online calculators based on molecular structure.

3.1.1 Calculation of Log P values using EPI Suite

EPI Suite is the online calculator used in this work because, since its creation, PFAs have been included in its training set for the calculation of octanol–water partition coefficients. The values obtained for the carboxylic and perfluorocarboxylic acids and their conjugate bases are displayed in Table 1 (and plotted in Figure S3). Once again, the calculated Log *P* values linearly correlate with *N* for each of the four groups of compounds. Interesting similarities between the slopes of these graphs when using both EPI Suite Log *P* values and those derived from electronic structure calculations can be observed. The EPI Suite slopes for the carboxylic acids and the carboxylates are identical to each other (parallel graphs with 0.491 slope) and to the slopes of the graphs that use the calculated Log *P* values previously presented. These slopes are only 0.05–0.06 units smaller than the slopes of the quasi-parallel experimental graphs. Parallel lines (with slopes of 0.685) are also obtained for the PFCAs and PFCs; the slopes of the previously calculated graphs of these compounds were 0.529. In addition, the experimental lipophilic order (carboxylates < PFCs < carboxylic acids) and the slightly greater slope obtained for the PFCs relative to the non-fluorinated compounds using experimental data are well matched by the Log *P* predictions made with EPI Suite.

Values calculated with this software depend on the version used (see Table S1 in the ESM section). When EPI Suite 2009 is used, the slope of the Log *P* versus *N* graph for PFCAs (0.966) is much larger than when using the 2012 version (0.685) or when using the experimental Log *P* values of PFCs (0.606). The 2009 EPI Suite values from Rayne and Forest [22] seem to be identical to a set of values reported in 2006 [20]. Both EPI Suite versions (2006 and 2009) made use of the KOWWIN module v1.67; however, the results reported in this paper use the latest version, v1.68. The differences between these two versions of the KOWWIN module are due to the inclusion of a correction factor for the chain length of the internal CF_2 core (−0.3 log units per CF_2) [54].

3.2 Predicting Log *P* values for perfluorinated acids

3.2.1 Assessing the available Log P values for trifluoroacetic acid

To the best of our knowledge, the only PFCA for which Log *P* values have been reported is trifluoroacetic acid (TFAA, $N = 2$; see Table 1): −2.1 [58–60] and −0.2 [60–62]. The reported value of −2.1 is much smaller than the −1.78 value derived by Jing et al. [25] for trifluoroacetate (TFA, $N = 2$) by extrapolation from the Log *P* versus *N* curve using their experimental values for PFCs. As can be seen from our previous discussion using the data reported in Table 1, the Log *P* values of the acids are always larger than those of their corresponding conjugate bases. Hence, the −2.1 value might need to be revised.

Using a fragment method, Jing et al. [25] demonstrated that a perfluoroalkyl chain is as lipophilic as a non-fluorinated alkyl chain with the same number of carbons (i.e., CH_2 and CF_2 groups contribute similarly to the lipophilicity of these compounds). In addition, they explained the differences between the Log *P* values of the anions (PFC vs. carboxylates) due to the strong electron-withdrawing effect of the fluorine atoms that quenches the negative charge of the head group of PFCs. According to this explanation, the affinity of PFCs for water is less than that of carboxylates and the overall effect is that PFCs have greater P (and Log *P*) values than their analogue carboxylates. If these ideas are applied to neutral compounds (the PFCAs and the carboxylic acids with similar carbon chain lengths), then given that the head group is not charged, much smaller differences between their Log *P* values would be expected (as can be seen from the calculated curves displayed in Fig. 1). Their lipophilicity would be very similar, and the absence of a charged head group would also make their interaction with water similar between fluorinated and non-fluorinated carboxylic acids.[1]

[1] Ideas shared with Dr. Shigeru Amemiya, corresponding author of Ref. [25], through a personal communication.

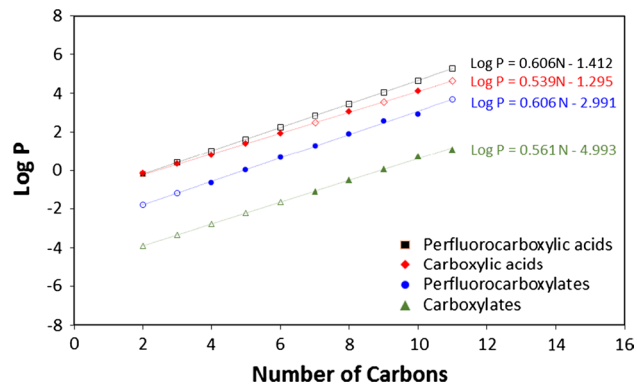

Fig. 2 Plot of the experimental (*filled colored marker*) and predicted (*unfilled marker*) Log *P* values (reported in Table 1) with the number of carbon atoms for carboxylic and perfluorocarboxylic acids and their conjugate bases

The −0.2 value [60–62], which follows the expected trend for this compound given the estimated value for its conjugate base −1.78), was obtained by the Rekker's fragment additivity scheme [66]. Furthermore, this value is not too different from the −0.17 Log *P* value reported for acetic acid ($N = 2$), in agreement with the ideas previously shared. Hence, we have taken this Log *P* value as the most probable one for TFAA.

3.2.2 Predicting Log P values for PFCAs and related compounds

From the observation of the various pairs of similar slopes (using experimental, EPI Suite or electronic structure calculation Log *P* values) for the Log *P* versus *N* graphs of carboxylic acids and carboxylates, and separately for PFCAs and PFCs (see Table 1), better predictions of Log *P* values for the PFCA group with three to eleven carbons in the linear chain can be attempted. Given that the slope of the experimental Log *P* values of PFCs is 0.606 [25], we could anticipate the same slope for the graph of the experimental Log *P* values of PFCAs. With the slope of the line that these points would form, and knowing one of these points (the Log *P* value for TFAA ($N = 2$) is −0.20), the Y-intercept can be calculated (−1.412). Equation 6 can then be used to calculate the desired Log *P* values for each value of *N*.

$$\text{Log}\,P = \text{Slope} \times N + \text{Intercept} = 0.606 \times N - 1.412 \quad (6)$$

The predicted Log *P* values for PFCAs are shown in square brackets in Table 1. As expected from our previous discussion, these values are very similar to the experimental Log *P* values of the carboxylic acid analogues [57]. Because the slope of the carboxylic acids is smaller (0.538) than the slope of the PFCAs (0.606), the Log *P* values of

Table 2 Predicted and calculated (using EPI Suite and from electronic structure calculations) Log P values of sulfonic and perfluorosulfonic (PFSAs) acids and their conjugate bases

N[a]	Sulfonic acids $CH_3(CH_2)_{N-1}SO_2OH$			Sulfonates $CH_3(CH_2)_{N-1}SO_2O^-$			PFSAs $CF_3(CF_2)_{N-1}SO_2OH$			PFSs $CF_3(CF_2)_{N-1}SO_2O^-$		
	Pred[b]	EPI Suite	Calc	Pred[c]	EPI Suite	Calc	Pred[d]	EPI Suite	Calc	Pred[e]	EPI Suite	Calc
2	0.41	−1.89	−1.71	−2.77	−4.04	−6.90	0.41	0.48	−0.60	−1.19	−1.67	−4.63
3	0.95	−1.40	−1.23	−2.21	−3.55	−6.38	1.01	1.15	−0.09	−0.58	−1.00	−4.12
4	1.49	−0.91	−0.72	−1.64	−3.06	−5.92	1.62	1.82	0.42	0.03	−0.33	−3.55
5	2.03	−0.42	−0.23	−1.08	−2.56	−5.41	2.22	2.49	0.99	0.63	0.34	−3.03
6	2.57	0.07	0.25	−0.52	−2.07	−4.95	2.83	3.16	1.49	1.24	1.01	−2.5
7	3.11	0.56	0.74	0.04	−1.58	−4.46	3.44	3.82	1.99	1.84	1.68	−2.03
8	3.64	1.06	1.22	0.6 [g]	−1.09	−3.98	4.04	4.49	2.51	2.45 [g]	2.35	−1.49
9	4.18	1.55	1.71	1.16	−0.60	−3.50	4.65	5.16	3.07	3.06	3.02	−0.98
10	4.72	2.04	2.20	1.72	−0.11	−3.01	5.25	5.83	3.55	3.66	3.68	−0.46
11	5.26	2.53	2.68	2.28	0.38	−2.52	5.86	6.50	4.08	4.27	4.35	0.03
Slope[f]	0.539	0.492	0.488	0.561	0.491	0.484	0.606	0.669	0.521	0.606	0.669	0.518
Intercept[f]	−0.668	−2.876	−2.681	−3.888	−5.021	−7.850	−0.804	−0.855	−1.643	−2.398	−3.006	−5.644

[a] Number of carbon atoms

[b] Predicted values using the experimental slope of the carboxylic acids (0.539, see Table 1) and the predicted value for $N = 2$ (Log $P = 0.41$, see Sect. 3.2.3)

[c] Predicted values using the experimental slope of the carboxylates (0.561, see Table 1) and one experimental value (Log $P = 0.6$, $N = 8$)

[d] Predicted values using the experimental slope of PFCAs (0.606, see Table 1) and the predicted value for $N = 2$ (Log $P = 0.41$, see Sect. 3.2.3) are the values of the PFCAs with the same perfluorinated chain length (i.e., $N + 1$)

[e] Predicted values using the experimental slope of the PFCs (0.606, see Table 1) and one experimental value (Log $P = 2.45$, $N = 8$)

[f] From a linear regression analysis: Log P = slope × N + intercept

[g] Experimental values from Ref. [25] (see Section S2)

the latter become slightly greater as the length of the linear carbon chain increases. The differences in Log P values between these two families go from −0.03 (for $N = 2$) to 0.62 (for $N = 11$). Using the slope and intercept of the curve that best fits the experimental points for the carboxylic acids, carboxylates and PFCs (see Table 1), the unavailable experimental data have been predicted and these values are shown in square brackets in Table 1. Experimental and predicted values for the four groups of compounds are displayed in Fig. 2.

3.2.3 *Predicting Log P values for sulfonic acids, sulfonates, PFSAs and PFSs*

Electronic structure calculations of Log P values for the linear sulfonic acids, PFSAs and their conjugate bases were also performed, together with EPI Suite calculations. The calculated (uncorrected) energies in solution, E_w and E_o, are reported in Tables S2c and S2d of the ESM section. The values obtained and details of the linear correlations (slopes and intercepts) of the different sets of Log P values with the number of carbon atoms in the linear chain (N) are reported in Table 2. Strong linear correlations were found in all cases (see Figs. 3 and S4).

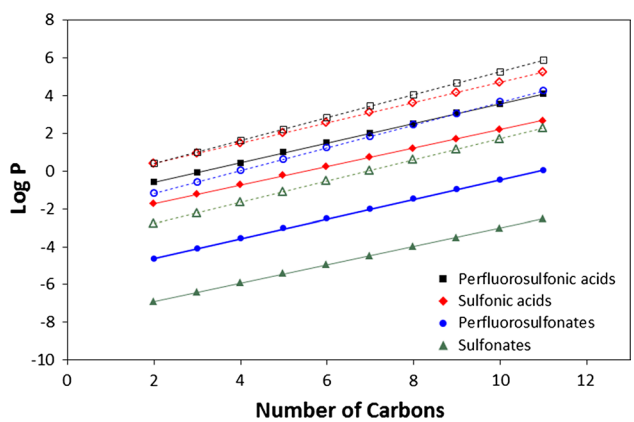

Fig. 3 Plot of the predicted (*unfilled marker*) and calculated (using Eq. 5, *color-filled marker*) Log P values (reported in Table 2) with the number of carbon atoms for sulfonic, perfluorosulfonic acids and their conjugate bases

Experimental Log P values have only been reported for octanesulfonate (0.6) and perfluorooctanesulfonate (2.45), $N = 8$ [25]. Using EPI Suite [using electronic structure calculations], the calculated values are −1.09 [−3.98] and 2.35 [−1.49] for octanesulfonate and perfluorooctanesulfonate,

respectively. Jing et al. [25] concluded that the 1.85 difference between the Log *P* values of these compounds (which is similar to the Log *P* difference of 2.16–2.50 units they obtained between PFCs and carboxylates) was due to the sulfonate group ($–SO_2O^–$), which is affected by the electron-withdrawing effect of the fluorine atoms that stabilizes the negative charge of the head group. The calculated Log *P* difference for these compounds is 3.44 (with EPI Suite) and 2.49 (with electronic structure calculations).

As previously observed for PFCAs/PFCs and carboxylic acids/carboxylates, the calculated curves of PFSAs and PFSs have greater slopes than those of their corresponding non-fluorinated analogues. A surprisingly interesting result is that the calculated slopes (using both EPI Suite and electronic structure calculations) for the carboxylic acids (0.491, 0.490), carboxylates (0.491, 0.488), PFCAs (0.685, 0.529) and PFCs (0.685, 0.529) are almost identical to the slopes of the corresponding sulfur compounds: sulfonic acids (0.492, 0.488), sulfonates (0.491, 0.484), PFSAs (0.669, 0.521) and PFSs (0.669, 0.518). Acids and their corresponding conjugate bases show the same Log *P* versus *N* slope in all cases as well. From these results, we could infer that the slopes of these curves are mainly determined by the presence of the alkyl or perfluoroalkyl chains in these compounds and not by the head group ($–COOH/–COO^–$ vs. $–SO_2OH/–SO_2O^–$). More importantly, this observation backs up the idea that the same equality in slopes would also be observed when comparing the slopes of experimental Log *P* values of these eight families of compounds. Given the almost complete absence of experimental data for the four families of sulfur-containing compounds under study, these ideas provide an interesting route for predicting their Log *P* values. That is, if the experimental slope for PFCAs and PFCs is 0.606, we should expect a similar slope when plotting the experimental Log *P* values of PFSAs and PFSs. Similarly, the experimental slopes of 0.539 and 0.561, for carboxylic acids and carboxylates, respectively, should also be the experimental slopes for sulfonic acids and sulfonates, respectively. Given that experimental values are only available for the sulfonate and PFS with $N = 8$, with a point and the slope, the intercept of what would be the experimental correlation line can be calculated and the remaining Log *P* values can be predicted. Predicted values for sulfonates and PFSs are given in Table 2. Figure 3 displays the combined plots of the predicted and calculated (using Eq. 5) Log *P* values; separate plots appear in Figure S4. Graphs that combine predicted and EPI Suite calculated Log *P* values are shown in Figure S3 of the ESM section. To undertake the prediction of Log *P* values for PFSAs and sulfonic acids, we make use of observations from previous studies.

Rayne and Forest [22] gave evidence of a strong relationship between linear PFSs and PFCs. They suggested, based on the results obtained by Jing et al. [25], Kelly et al. [21], and Higgins and Luthy [28, 67], that the Log D values obtained for the perfluorinated anions (sulfonic and carboxylic) should be the same as long as these molecules have the same perfluorinated chain length. The previous comparison could be made because the determinations upon which Rayne and Forest based their findings favoured the almost complete ionization of the corresponding acids that have pK_a values very close to zero. Apparently, as also observed from our calculations, the structural differences of the head group (sulfonate or carboxylate) do not produce Log *P* differences between PFSs and PFCs, as long as they have the same number of carbon atoms in the perfluorinated alkyl chain. That is, the Log *P* of the PFS with *N* carbon atoms should be very similar to the Log *P* value of the PFC with $N + 1$ carbon atoms. The experimental and predicted data we have gathered (see Tables 1, 2) fully support this idea. The average difference between the previously described pairs of Log *P* values for PFCs and PFSs is 0.01, and the mean absolute difference is 0.06.

The same correspondence between the Log *P* value of a PFSA (with *N* carbon atoms) and a PFCA with the same perfluorinated chain length (with $N + 1$ carbon atoms) should also be expected. Hence, we can assume that the Log *P* (0.41) for the PFSA of $N = 2$ is the predicted Log *P* value for the PFCA of $N = 3$. With this point and the predicted slope of 0.606, the remaining Log *P* values for PFSAs are predicted (see Table 2; Figs. 3 and S2).

As previously discussed in Sect. 3.2.1, fluorinated and non-fluorinated carboxylic acids with the same carbon chain length should have similar Log *P* values, and this similarity is the greatest for the smallest family member ($N = 2$). Figure 2 shows this for the experimental and predicted Log *P* values of the PFCAs. If we extend this idea to the sulfonic acids and the PFSAs, we can estimate with some small error the Log *P* value of the sulfonic acid of $N = 2$ to be 0.41, and with the previously estimated slope of 0.539, the remaining Log *P* values can be estimated (see Table 2; Figs. 3, S2).

The predicted Log *P* values for the four sulfur-containing families of compounds are plotted in Figure S4. The strong similarities to the experimental plot of the fluorinated and non-fluorinated carboxylic acids (see Fig. 2) can be clearly appreciated. The perfluorinated anions (PFCs and PFSs) have greater Log *P* values than the non-fluorinated ones. The perfluorinated acids (PFCAs and PFSAs) have similar Log *P* values, just slightly higher as the length of the carbon chain increases, relative to the non-fluorinated acids. From a qualitative point of view, the relative order of the experimental or predicted curves is well reproduced by the calculated curves using Log *P* values derived from electronic structure calculations (see Figs. 1, 3). This consistency is not observed when comparing to the calculated

curves using EPI Suite, in particular when considering the sulfur-containing compounds (see Figure S3). In general, even though both electronic structure calculations and EPI Suite predictions of Log *P* values introduce consistent systematic errors when calculating Log *P* values that are different for fluorinated- and non-fluorinated compounds, the calculated curves of Log *P* values using electronic structure methods reproduce experiments better than the curves using EPI Suite predictions.

Given the lack of experimental Log *P* values to verify the predictions made, further investigation is needed. However, given that most environmental studies so far make use of Log *P* values which have been estimated by various softwares of similar nature to EPI Suite or using empirical results [17], the Log *P* values predicted in this study could provide a much better alternative for comparison when analyzing the environmental fate of these kinds of compounds.

3.3 Potential applicability of the Log *P* predictions made in this article

Because of their persistence and inertness to most degrading agents, concerns have been raised about the bioaccumulation of PFAs in the environment. It has been previously indicated that knowledge of their Log *P* values does not allow the correct prediction of their bioaccumulation because the potential association of PFAs with proteins instead of lipids changes their behavior relative to other bioaccumulative lipophilic compounds [4]. Nonetheless, estimated Log *P* values of PFAs are widely used in a variety of environmental studies, some of which have been compiled below.

Attempts have been made to relate Log *P* values to the trophic magnification factor at different trophic levels. Kelly et al. [21] took into account linear PFCAs ranging from seven to thirteen carbon atoms, as well as perfluorooctane sulfonic acid (PFSA with $N = 8$). These authors followed a methodology guided by empirical considerations as recommended by Dr. David Ellis, published 5 years later [9].

We found excellent agreement (with differences smaller than 0.5 units) between the Log *P* values they used and the ones predicted here for the PFSA with $N = 8$ (a value also in close agreement with our reported value for PFCA with $N = 9$) and the PFCAs with $N = 7, 8, 9$ (see Table S1 in the ESM section).

A long-term environmental fate simulation of PFCAs and PFCs with eight to thirteen carbon atoms was reported by Armitage et al. [18]. The Log *P* values used in their work were taken from the COSMOtherm and SPARC calculations published by Arp et al. [20], also shown in Table S1 and plotted in Figure S1. The COSMOtherm values are greater than the Log *P* values we predict in this work, but the differences become smaller and less significant as *N* increases. Similarly, the SPARC values are also greater than our predictions, but the differences increase as *N* increases. In our opinion, these simulations were performed using overestimated Log *P* values. In addition, Webster et al. [17] used a multispecies environmental fate model to predict the overall partitioning of the PFCA/PFC pair with $N = 8$ in different media. The Log *P* value predicted for the PFCA with $N = 8$, using previously published data by Higgins and Luthy [28], was 3.73, remarkably close to the 3.44 value predicted in this paper.

4 Conclusions

Partition coefficients (as well as acid dissociation constants) are key physicochemical properties when determining the environmental fate of chemical species. The lack of experimental determinations of Log *P* values, especially for fluorinated compounds, has led researchers to use limited predictive tools available when attempting to explain the observed environmental distribution and transport between different media of these compounds. However, the use of inaccurate values when performing environmental simulations could lead to incorrect long-term predictions, with important consequences.

Eight families of linear organic compounds were investigated: carboxylic acids, perfluorinated carboxylic acids (PFCAs), sulfonic acids and perfluorinated sulfonic acids (PFSAs), together with their corresponding conjugate bases. It has been shown that the consistent similarities observed between experimental and calculated (with electronic structure methods and using EPI Suite) slopes of the linear plots of Log *P* values with the number of carbon atoms ($N = 2$–11), together with the available experimental Log *P* data and previously published observations, provide a much better predictive alternative of Log *P* values to be used for comparison when modeling the environmental fate and transport of these compounds. The most relevant Log *P* predictions made in the present work refer to PFCAs, PFSAs and PFSs, but predictions were also made for the other families of linear organic compounds studied.

Acknowledgments The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support and would like to thank Information Technology Services at Thompson Rivers University.

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