Hydrophobic Sorption Properties of an Extended Series of Anionic Per- and Polyfluoroalkyl Substances Characterized by C18 Chromatographic Retention Measurement

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Partitioning from water to nonaqueous phases is an important process that controls the behavior of contaminants in the environment and biota. However, for ionic chemicals including many per- and polyfluoroalkyl substances (PFAS), environmentally relevant partition coefficients cannot be predicted using the octanol/water partition coefficient, which is commonly used as a hydrophobicity indicator for neutral compounds. As an alternative, this study measured C18 liquid chromatography retention times of 39 anionic PFAS and 20 nonfluorinated surfactants using isocratic methanol/water eluent systems. By measuring a series of PFAS with different perfluoroalkyl chain lengths, retention factors at 100% water (k0) were successfully extrapolated even for long-chain PFAS. Molecular size was the most important factor determining the k0 of PFAS and non-PFAS, suggesting that the cavity formation process is the key driver for retention. The log k0 showed a high correlation with the log of partition coefficients from water to phospholipid membrane, air/water interface, and soil organic carbon. The results indicate the potential of C18 retention factors as a predictive descriptor for anionic PFAS partition coefficients and the possibility of developing a more comprehensive multiparameter model for partitioning of anionic substances in general.

Keywords
PFAS, LFER, liquid chromatography, adsorption, retention time, anionic surfactant

Introduction
The concept of solute hydrophobicity has been of extensive use in environmental chemistry to estimate the extent of sorption or partitioning of organic contaminants from water to nonaqueous phases such as natural organic matter, carbon surfaces, and biological lipids. For neutral organic compounds, the octanol/water partition coefficient (Kow) has been considered as a scale of solute hydrophobicity because Kow correlates well with various relevant partition coefficients, including soil/sediment organic carbon/water (Kow) and biological phospholipid membrane/water (Ksw) partition coefficients on the log-log scale, particularly when only a specific set of compounds with similar interaction properties (e.g., nonpolar aromatic compounds) are considered.1-4 For this reason, Kow is accepted or being introduced as chemical assessment criterion to account for the environmental mobility and bioaccumulation potential of chemicals in regulations such as the EU CLP and REACH regulations and the Stockholm Convention.5,6 However, for ionic compounds, i.e., compounds carrying one or more charges, the equilibrium concentration ratio between octanol and water highly depends on the coexisting electrolyte concentrations, and thus the Kow of ionic compounds cannot be defined in isolation from the experimental conditions.5,10 Moreover, even if Kow at a specific condition is chosen as a reference, the bulk partition of ionic compounds between octanol and water may not represent their actual environmental and biological partition mechanisms and thus such Kow does not serve as a useful metric.11,12

Per- and polyfluoroalkyl substances (PFAS) have been of high environmental concern due to their recalcitrance to degradation. PFAS are a diverse group of chemicals with perfluorocarbon atoms13 and include a number of ionic compounds. For example, PFAS of highest concern to date, such as perfluorooctane sulfonate (PFOS) and carboxylate (PFOA) and many of their industrial substitutes, are anionic. Capturing sorption and partition properties for legacy, emerging, and premarket anionic PFAS is a prerequisite for their environmental fate assessment14 but is not possible by using Kow for the reasons stated above.

Recently, de Voogt et al.15,16 proposed isocratic reversed-phase liquid chromatography (LC) retention (or capacity) factors (k) measured with an octadecyl group bonded silica (C18) column as a hydrophobicity indicator for fluorinated and nonfluorinated anionic surfactants. They measured k at varying volume fractions of methanol (φMeOH) in the aqueous eluent and extrapolated k at 100% water (k0) for each surfactant. Since k0 reflects the actual sorption behavior from water to an organic solid phase (i.e., C18 phase), it can serve as a useful hydrophobicity indicator. While there have been decades of research employing LC retention measurements to characterize hydrophobic partition properties,17 most studies have been aimed at estimating Kow values for LC retention. The use of an LC approach is particularly sensible for anionic compounds because an alternative to Kow is required for this group of compounds. While de Voogt et al.15,16 used perfluoroalkyl carboxylates (PFCAs) and sulfonates (PFSAs) with different alkyl chain lengths, the PFAS of current concern are more diverse and thus an extension of the data set may be warranted. In addition, they performed the LC retention measurement at relatively high MeOH concentrations, primarily at φMeOH ≥ 0.5, and extrapolated k0 over a long range, which could introduce substantial uncertainty in the derived k0 values.

Here, we report C18-LC retention factors measured for a vastly extended set of anionic PFAS including alternatives to PFOA or PFOS. Nonfluorinated compounds from three groups of alkyl surfactants (i.e., carboxylates, sulfonates, sulfates) are also tested for comparison. The use of a shorter C18 column than in past studies15,16 allows measurement at φMeOH < 0.5. Mathematical models are fitted to the k data to extrapolate or interpolate k values at φMeOH of 0 (k0), 0.25 (k25), and 0.5 (k50). k25 and k50 are also included because they can be interpolated more frequently and determined more accurately than k0. For all k values, 95% confidence intervals (CIs) are provided to account for uncertainty. These k values are compared to environmentally relevant partition coefficients available in the literature to evaluate their potential as hydrophobic sorption indicators.
Materials and Methods
Reagents
MeOH and ultrapure water for LC/MS were purchased from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan). Solutions of 1 M ammonium acetate (Fujifilm Wako Pure Chemical Corporation) and 25% ammonia (Merck, Darmstadt, Germany) were used to prepare the LC eluent as described below.

The 43 anionic PFAS, including PFCAs, PFASs, fluorotelomer carboxylic acids (FTCAs) and sulfonic acids (FTSs), and perfluoroalkyl ether carboxylic acids (PFECA) and sulfonic acids (PFSAs), and 21 nonfluorinated anionic surfactants were subjected to LC analysis. All these compounds are listed in Table S1 with the abbreviations used in this article. Reagents were purchased from Tokyo Chemical Industry (Tokyo, Japan), Fujifilm Wako Pure Chemical Corporation (Osaka, Japan), Matrix Scientific (Columbia, USA), SynQuest (Alachua, USA), Sigma Aldrich Japan (Tokyo, Japan), and Toronto Research Chemicals (Columbia, USA), SynQuest (Alachua, USA), Sigma Aldrich Japan (Tokyo, Japan), and Toronto Research Chemicals (Toronto, Canada), as detailed in Table S1. For 19 PFAS, reagents were purchased in the form of acid, K salt, or NH₄ salt. These acids and salts were dissolved in MeOH at a concentration of 5 mg/L. In addition, seven commercially available mixtures of PFAS were purchased from Wellington Laboratories (Guelph, Canada) with the product names PFAC-MXG, PFAC-MXA, FTC-MIX-B, FTS-3 MIX, PAP-5MIX, New PFC-4MIX, and PFC-PFS MIX (see Table S1 for the components of the mixtures). The concentrations of individual PFASs in the mixtures ranged from 0.2 to 5 mg/L. Carboxylic acids were obtained as pure acids, while alkyl sulfonates and sulfates were sodium salts. These nonfluorinated surfactants were also dissolved in MeOH to obtain a concentration of 5 mg/L.

LC/MS retention time measurement
The retention time (t_r) of each PFAS was measured using an LC system (1260 Infinity II) equipped with a single quadrupole mass selective detector (MSD) from Agilent Technologies (Santa Clara, USA). Nitrogen gas generated by an AT-10NP-CS nitrogen generator (Airtech Corporation, Yokohama, Japan) was used to spray the sample solution into the ionization chamber. The fragmentor voltage was 25 V, which was relatively low to minimize fragmentation of unstable PFAS. A mass chromatogram was obtained by using the negative selected ion monitoring (SIM) mode. The monitored ions are shown in Table S2. Most compounds were measured with an m/z value that corresponds to the deprotonated form of the acids ([M − H]⁻). Fragment ions were monitored for C₇-C₁₄ PFCA, NDFHA, and HFPO-DA.

A Kinetex EVO C18 column (5 mm particle size, 2.1 mm i.d. × 30 mm) connected to a guard column of the same i.d. was used. This column is said to be stable with 100% water and in a pH range of 1 to 12, suitable for this work. A short column with relatively large particles was opted so that retention times of long-chain compounds could also be measured. Mixtures of MeOH/water containing 10 mM ammonium acetate and 0.2 mM ammonia were used as the eluent. The small amount of ammonia kept the pH of the eluent around 8 so that -COOH was fully deprotonated. These MeOH/water mixtures were prepared in a bottle by mixing predetermined volumes of MeOH, pure water, 1 M ammonium acetate and 0.2 M aqueous ammonia solution. The mixer equipped with the LC pump was not used to mix the eluent components because preliminary experiments that used the LC mixer showed substantial difference in t_r values from those determined with premixed eluent.

Retention time measurements were performed using isocratic elution with φ_MeOH starting at 0.8 and decreasing to 0 by a decrement of 0.1. Samples (1.0 μL) were injected into the column using an autosampler. The flow rate and column oven temperature were set at 0.4 mL/min and 40 °C, respectively. The measurement ran was terminated after 2–3 h even if no peak appeared. All peaks were symmetrical and the peak top time was recorded to obtain t_r.

Data analysis
The value of k was calculated from t_r and the column dead time (t₀) using the following equation:

$$k = \frac{t_r - t_0}{t_0} \quad (1)$$

To determine t₀, three candidate tracers were measured at each φ_MeOH: uracil, DL-glyceric acid (GA), and D(-)-quinic acid (QA). The previous studies 15,16 determined t₀ using uracil, which is mostly neutral (pK_a, 9.4). The measured retention time of uracil at low φ_MeOH was slightly longer than that of GA and QA (Figure S1), suggesting the possibility of weak retention for uracil. In addition, anionic compounds may undergo an anion exclusion effect with silica-based stationary phases,18 which are negatively charged near neutral pH, and thus the use of an anionic tracer may be more appropriate.19 Since GA showed a slightly shorter retention time than QA, we decided to use t₀ of GA for t₀.

Results and Discussion
Retention time at varying ammonium acetate concentrations
In preliminary experiments, the dependence of t_r for anionic PFAS on the concentration of ammonium acetate ([NH₄CH₃COO]) was examined. For each compound, the value of t_r increased slightly with increasing [NH₄CH₃COO] from 1 to 50 mM (Figure S2). Similar results were reported by Hammer et al. 16 Retention was substantially weaker when no electrolyte was added to the eluent, suggesting that control of ionic strength is important to obtain stable results. Based on these results, we chose [NH₄CH₃COO] of 10 mM for further measurements. Although the exact retention mechanism is unknown, we surmise that anionic surfactants sorb primarily to the interface between the C₈ phase and the mobile phase, with the anionic head group oriented toward the mobile phase and the hydrophobic tail in the C₈ phase. Higher ionic strength in water reduces the repulsive interactions between the negative charges of the silica particles and the anionic analytes. Ion-pair formation is unlikely to be the main retention mechanism because of the relatively small influence of [NH₄CH₃COO] on t_r.

k at varying volume fractions of MeOH
All retention times measured with 10 mM NH₄CH₃COO and 0.2 mM NH₃ for PFAS and non-PFAS are tabulated in Table S3. For each compound, k values were obtained at 2–7 concentrations of MeOH in the eluent. No significant retention was obtained for butyric acid (BA), the smallest test compound, even at φ_MeOH of 0. Conversely, no peak appeared for long-chain compounds within the run time (2–3 h) at low φ_MeOH. Identification of FTCAs was unclear, possibly due to the use of a single quadr uplet MS in this work and peak overlap with FTCAs. No peak was obtained for 11Cl-PF3ODs due to inadequate m/z setting for this chemical, which became apparent after all measurements. In the end, we obtained k data for 39 PFAS and 20 nonfluorinated surfactants at least for two values of φ_MeOH.

The value of k decreased with increasing φ_MeOH (Figure 1; all data are shown in Figure S3). For each compound, the linear equation (eq 2) approximated a relationship between log k and φ_MeOH:

$$\log k = \alpha \phi_{MeOH} + \beta \quad (2)$$

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$\alpha$ and $\beta$ are compound-specific fitting parameters. However, weakly sorbing compounds (e.g., PFBA) showed slightly concave downward curves, and strongly sorbing compounds (e.g., PFDA) showed slightly concave upward curves. For such compounds, the quadratic equation (eq 3) fit the data better than eq 2.

\[
\log k = a \phi_{\text{MeOH}}^2 + b \phi_{\text{MeOH}} + c \tag{3}
\]

where $a$, $b$, and $c$ are fitting parameters. All fitting parameters for eqs 2 and 3 as well as the standard deviations of the residuals are listed in Table S4.

### Extrapolation/Interpolation of $k_0$, $k_{25}$, and $k_{50}$

The linear (eq 2) or quadratic equation (eq 3) could be used for extrapolation and interpolation of $k_0$, $k_{25}$, and $k_{50}$. However, for long-chain compounds, the uncertainty in the extrapolated $k_0$ value is high no matter if eq 2 or 3 is used because there are no measured $k$ data in the low $\phi_{\text{MeOH}}$ range. The reliability of the extrapolation may be improved by using the strong linear relationship between log $k$ and the number of CF$_2$ or CH$_2$ for a given class of compounds (Figure S4).

\[
\log k = z n_{\text{CF2}} + \text{const.} \tag{4}
\]

where $n_{\text{CF2}}$ is the number of CF$_2$ of the PFAS and $z$ is the slope of log $k$ against $n_{\text{CF2}}$. For alkyl substances, $n_{\text{CF2}}$ should be replaced by $n_{\text{CH2}}$, the number of CH$_2$.

If all compounds within a given class (e.g., PFCAs) satisfy both eqs 3 and 4, all log $k$ data for that class must follow eq 5.

\[
\log k = n_{\text{CF2}}(a_1 \phi_{\text{MeOH}}^2 + b_1 \phi_{\text{MeOH}} + c_1) + a_2 \phi_{\text{MeOH}}^2 + b_2 \phi_{\text{MeOH}} + c_2 \tag{5}
\]

Transforming eq 5, we obtain,

\[
\log k = (a_1 n_{\text{CF2}} + a_2) \phi_{\text{MeOH}}^2 + (b_1 n_{\text{CF2}} + b_2) \phi_{\text{MeOH}} + (c_1 n_{\text{CF2}} + c_2) \tag{6}
\]

The six fitting parameters ($a_1$, $a_2$, $b_1$, $b_2$, $c_1$, $c_2$) were obtained by nonlinear least-squares fitting using the nls() function of the statistical software R. Using eq 6, $k_0$ for a given compound can be extrapolated as a cross section of the two conditions represented by eqs 3 and 4, based on all data available for the

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**Figure 1.** Examples of measured log $k$ vs volume fraction of MeOH in the eluent (10 mM NH$_4$CH$_3$COO, 0.2 mM NH$_3$, 0.4 mL/min flow rate). Black and blue lines indicate the linear (eq 2) and quadratic (eq 3) fits, respectively. The bands show the 95% CIs. Data for all other compounds are shown in Figure S3.

**Figure 2.** Log $k$ vs volume fraction of MeOH for PFCA (C$_4$ to C$_{14}$ from bottom to top). The same experimental data are shown in both panels, and the data are fitted with (A) eq 3 and (B) eq 6. The lines indicate the results of the model fitting, and the colored bands indicate the 95% CIs.
respective class of compounds and is thus expected to be more accurate than \( k_0 \) determined on an individual compound basis using eq 3. As an example, the two panels of Figure 2 show the same experimental data but with different fitted models (eq 3 and eq 6). Fitting eq 3 to individual compounds resulted in broad 95% CI bands for long-chain compounds in the low \( \varphi_{\text{H/OH}} \) range, demonstrating the problem of extrapolation. In contrast, the CI bands were much narrower when eq 6 was used, due to the additional model constraint represented by eq 4 as well as the large amount of the data. Note that perfluoroalkyl ethers (PFECAs and PFESAs) are not a group of compounds with just different perfluoroalkyl chain lengths, but with more variation in terms of, e.g., the number of ether oxygens and the presence of a partially fluorinated carbon atom. For these compounds, eq 6 cannot be used, and thus \( k_0 \) had to be estimated compound by compound using eq 3. The values of \( k_{25} \) and \( k_{50} \) were also obtained from eq 6 or eq 3. Apparently, there must be at least 3 data points for eq 3 to fit. We were not able to obtain \( k_0, k_{25}, \) and \( k_{50} \) values for any of diPAPs because only a few data at high \( \varphi_{\text{H/OH}} \) were available for these strongly sorbing PFAS.

The values obtained for log \( k_0, \log k_{25}, \) and log \( k_{50} \) ranged from -0.03 to 10.12, -0.59 to 6.81, and -1.10 to 3.93, respectively (Table 1, Figure S5). Apparently, \( k_0 \) has the broadest range of these three \( k \)'s and is the most sensitive to the structural variation of the compounds. However, the CIs of \( k_0 \) were broader than those of \( \log k_{25} \) and \( \log k_{50}, \) reflecting the fact that the determination of \( k_{25} \) and \( k_{50} \) values was often an interpolation rather than an extrapolation. In particular, the 95% CIs of \( k_0 \) for long-chain compounds determined via eq 3 (e.g., 9CI-PF3ONS) range over 1 log unit or more, which may raise concerns about their practical use as a property descriptor. For such chemicals, \( k_{25} \) or \( k_{50} \) may serve as an alternative descriptor.

**Influence of PFAS molecular structure on \( k_0 \)**

The values of \( k_0 \) are linearly related to the number of CF2 (\( n_{\text{C2}} \)) for PFAS and CH2 (\( n_{\text{CH2}} \)) for non-PFAS (Figure 3A). The slope of \( \log k_0 \) against \( n_{\text{C2}} \) was 0.94 (mean of PFECAs and PFESAs) and that for \( n_{\text{CH2}} \) was 0.66 (mean of SOs, SAs, and CAs). A higher slope for PFAS than non-PFAS indicates a stronger hydrophobic effect on CF2 than CH2. These results agree qualitatively with those of Hammer et al.,\(^{16} \) who reported incremental values of 0.56/CF2 and 0.47/CH2 for log \( k_0 \) on C8. The difference from the result of the present study may be due to the different experimental setups or, in part, to the long-range linear extrapolations from high methanol concentrations made by Hammer et al. In the literature, the log of the hexadecane/water partition coefficient has been reported to increase by 0.74/CF2 and 0.64/CH2 for neutral compounds.\(^{20} \) Similarly, log \( K_{\text{H/O}} \) increases by ~0.6/CF2,\(^{21,22} \) and 0.54/CH2,\(^{23} \) for neutral compounds. The log \( k_0 \) derived in the current study appears to be relatively sensitive to the number of perfluorocarbon atoms, which may indicate that the cavity formation energy required for a perfluoroalkyl compound to partition into the C18 phase is low compared to the other phases mentioned above.

The types of nonfluorinated structure also have a significant influence on the values of \( k_0 \). The log \( k_0 \) values are in the order X:2 FTS > X:3 FTCA > X:2 FTCa > PFSA > PFCA when compounds with the same \( n_{\text{C2}} \) are compared. Specifically, log \( k_0 \) of X:2 FTS is 1.29±0.23 greater, X:3 FTCA is 0.91±0.02 greater, X:2 FTCa is 0.56±0.34 greater, and PFSA is 0.45±0.01 greater than that of PFCA at the same \( n_{\text{C2}} \). The fluorotelomer substances have nonfluorinated carbon atoms, which make log \( k_0 \) greater than perfluoroalkyl compounds with the same \( n_{\text{C2}} \). Sulfonates appear to be more retained by the C18 column than carboxylates with the same number of (perfluoro)carbon atoms. Log \( k_0 \) values of perfluoroalkyl ether acids are also greater than those of PFCA with the same \( n_{\text{C2}} \) but the difference varies widely (by 0.75±0.45 for PFECAs, 1.36±0.76 for PFESAs), reflecting the variable structure of ether-containing PFAS.

The log \( k_0 \) values were plotted against indicators of molecular size. The Goss-modified McGowan molar volume (\( V_{\text{Goss}} \))\(^{24} \) showed an excellent linear relationship with log \( k_0 \) for both PFAS and non-PFAS combined (Figure 3B). \( V_{\text{Goss}} \) has been successfully used as a descriptor of the polyparameter linear free energy relationship model for neutral compounds.\(^{22,24-26} \) The linear relationship with \( V_{\text{Goss}} \) suggests that the difference in cavity formation energy between the C18 phase and water is the main driver of PFAS partitioning and that \( V_{\text{Goss}} \) may also be useful in describing partition coefficients of anionic substances, irrespective of the degree of fluorination. The data for 6:2 and 8:2 monoPAPs deviate somewhat from the trend, likely because these compounds are the only divalent anions in the data set. The original McGowan molar volume, which uses a slightly different atomic incremental volume for F,\(^{27} \) also showed a high correlation with log \( k_0 \) for PFAS, but the non-PFAS compounds are slightly off the regression line for PFAS (Figure S6). Molecular weight also exhibited a linear relationship with log \( k_0 \) for PFAS, although non-PFAS are far from the PFAS regression line.

![Figure 3](https://example.com/figure3.png)

Figure 3. (A) Log \( k_0 \) vs the number of CF2 (\( n_{\text{C2}} \)) for PFAS and CH2 (\( n_{\text{CH2}} \)) for non-PFAS. \( n_{\text{C2}} \) and \( n_{\text{CH2}} \) include the number of CF2 and CH2, respectively. (B) Log \( k_0 \) vs Goss-modified McGowan molar volume (\( V_{\text{Goss}} \)). Error bars indicate the 95% CIs of log \( k_0 \). Arrows indicate 6:2 and 8:2 monoPAPs. 9CI-PF3ONS was excluded from the plot due to the high CI.
Table 1. Interpolated/extrapolated log k<sub>0</sub>, log k<sub>25</sub>, and log k<sub>50</sub> values using eq 3 or 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>log k&lt;sub&gt;0&lt;/sub&gt; value</th>
<th>95% CI</th>
<th>log k&lt;sub&gt;25&lt;/sub&gt; value</th>
<th>95% CI</th>
<th>log k&lt;sub&gt;50&lt;/sub&gt; value</th>
<th>95% CI</th>
<th>fitted eq</th>
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<td>EDA</td>
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<td>[2.83,2.97]</td>
<td>2.17</td>
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<td>[3.75,3.95]</td>
<td>2.28</td>
<td>[2.25,2.30]</td>
<td>0.73</td>
<td>[0.71,0.75]</td>
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<td>[4.65,4.94]</td>
<td>2.88</td>
<td>[2.84,2.92]</td>
<td>1.01</td>
<td>[1.08,1.11]</td>
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<tr>
<td>PFHpS</td>
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<td>[5.55,5.94]</td>
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<td>[1.44,1.48]</td>
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<td>[7.04,7.38]</td>
<td>5.30</td>
<td>[5.25,5.35]</td>
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<td>[2.49,2.53]</td>
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<td>[6.50,6.90]</td>
<td>5.10</td>
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<td>[0.82,0.86]</td>
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<td>3.23</td>
<td>[3.19,3.26]</td>
<td>1.49</td>
<td>[1.46,1.52]</td>
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<td>[-0.38,-0.29]</td>
<td>-0.91</td>
<td>[-0.96,-0.85]</td>
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<td>0.60</td>
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<td>[-0.33,-0.24]</td>
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<td>2.88</td>
<td>[2.82,2.93]</td>
<td>1.54</td>
<td>[1.52,1.56]</td>
<td>0.34</td>
<td>[0.31,0.37]</td>
<td>eq 6</td>
</tr>
<tr>
<td>DA</td>
<td>4.18</td>
<td>[4.09,4.27]</td>
<td>2.48</td>
<td>[2.45,2.51]</td>
<td>0.96</td>
<td>[0.94,0.98]</td>
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<td>HxA</td>
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<td>0.04</td>
<td>[0.01,0.07]</td>
<td>-0.48</td>
<td>[-0.51,-0.45]</td>
<td>eq 6</td>
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<tr>
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<td>[1.18,1.38]</td>
<td>1.01</td>
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<td>0.15</td>
<td>[0.12,0.17]</td>
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<tr>
<td>DA</td>
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<td>[3.20,3.33]</td>
<td>1.98</td>
<td>[1.95,2.02]</td>
<td>0.78</td>
<td>[0.76,0.79]</td>
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<tr>
<td>TeDA</td>
<td>6.01</td>
<td>[5.87,6.15]</td>
<td>3.91</td>
<td>[3.86,3.96]</td>
<td>2.04</td>
<td>[2.02,2.06]</td>
<td>eq 6</td>
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<tr>
<td>HxDA</td>
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<td>[7.20,7.56]</td>
<td>4.87</td>
<td>[4.81,4.94]</td>
<td>2.67</td>
<td>[2.64,2.70]</td>
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Comparison of \( k_0 \), \( k_{25} \), and \( k_{20} \) to relevant partition coefficients

Phospholipid membranes are among the most important phases for the bioaccumulation of anionic chemicals including PFAS.\textsuperscript{28} The log phospholipid membrane/water partition coefficients \( (K_{\text{mem/w}}) \) from Droge et al.,\textsuperscript{29} consisting of 10 PFAS and 9 nonfluorinated anionic surfactants, correlate well with the \( k_0 \) obtained in this study \( (R^2, 0.92; \text{Figure 4A}) \). It is encouraging that both per- and nonfluorinated surfactants fall into a single correlation. The log \( K_{\text{mem/w}} \) data set for 12 PFAS from Ebert et al.,\textsuperscript{30} includes ether-containing PFAS and also correlates well with log \( k_0 \) \( (R^2, 0.84; \text{Figure 4B}) \). This \( R^2 \) value is higher than would be obtained by correlating log \( K_{\text{mem/w}} \) with \( n_{C22} \) \( (R^2, 0.62) \), because \( n_{C22} \) cannot account for the influences of ether oxygen atoms of PFCAs and PFESAs, \(-\text{CHF}-\text{of ADONA, or -CCIF; of 9CI-PF3ONS on log} \ K_{\text{mem/w}}\).

Adsorption at the air/water interface is a relevant process for surfactants. Increased retention during transport in unsaturated porous media\textsuperscript{31} and significant transport from seawater to the atmosphere via sea spray\textsuperscript{32,33} have been reported for PFAS, and these interesting phenomena occur due to the strong interfacial adsorption properties of PFAS relative to bulk partitioning. The log of air/water interfacial adsorption coefficients at infinite dilution \( (K_{\text{IW}}) \) cm; i.e., the partition coefficient between the air/water interface and bulk water) collected by Le et al.\textsuperscript{34} is linearly related to \( k_0 \) (Figure 4C). This data set includes both anionic perfluoroalkyl and nonfluoroalkyl substances. Note that only \( K_{\text{IW}} \) data for Na- or K-salt are considered here, as the \( K_{\text{IW}} \) data for acids show considerable differences from the corresponding salts, as reported in the original article\textsuperscript{34}.

Soil organic carbon/water partition coefficients \( (K_{oc}) \) also correlate well with \( k_0 \), as shown in Figure 4D. The log \( K_{oc} \) data considered were derived from data for the most organic-rich soil reported by Nguyen et al.\textsuperscript{35} to minimize the influence of other soil components on sorption. Nevertheless, short-chain PFAS (i.e., PFBA, PFPeA, PFBS) show similar log \( K_{oc} \) values independent of log \( k_0 \), likely because nonhydrophobic factors control their sorption, as suggested by the authors.\textsuperscript{35}

The slopes of the regression lines in the four panels of Figure 4 are all less than 1, again indicating that the \( C_{18} \) retention time is more sensitive to \( n_{C22} \) and \( n_{C18} \) than any of the partition phases considered here.

Log \( k_{25} \) and log \( k_{20} \) show similarly high correlations with log \( K_{\text{mem/w}} \), log \( K_{\text{IW}} \), and log \( K_{oc} \), albeit with different slopes and intercepts (Figures S7, S8). For long-chain compounds with uncertain \( k_0 \), these regressions may be a useful alternative to obtain estimates of the respective partition coefficients.

As expected from the high correlation between log \( k_0 \) and \( V_{\text{Goos}} \) (Figure 3B), the literature partition data shown in Figure 4 also correlate with \( V_{\text{Goos}} \). Thus, the partitioning of anionic compounds in all systems considered appears to be primarily controlled by the size of the molecules. \( V_{\text{Goos}} \) can equally well describe anion hydrophobicity, at least within the types of anionic PFAS and non-PFAS considered in this study. Since \( V_{\text{Goos}} \) can be calculated from the molecular structure, it appears to be a more convenient descriptor than log \( k_0 \). It is currently unknown to what extent \( V_{\text{Goos}} \) might correlate with different partition coefficients if a wider range of compounds were considered. As an experimentally derived value, log \( k_0 \) may have the advantage that it can at least reflect all relevant intermolecular interactions in the water phase, in contrast to \( V_{\text{Goos}} \), which only describes the difference in cavity formation. Data for more diverse structures, e.g., with branching, partial fluorination, and functional groups, are needed to evaluate the difference between \( k_0 \) and \( V_{\text{Goos}} \).

This study provided a large set of \( C_{18} \) retention factors as an empirical hydrophobicity index for anionic PFAS. The \( k_0 \) value, which is proportional to the \( C_{18} \)-bonded silica/water partition coefficient, shows a correlation with other partition coefficients, demonstrating its potential as a predictive descriptor for anionic

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**Figure 4.** Literature partition data vs log \( k_0 \). Literature data are from Droge et al.,\textsuperscript{29} Ebert et al.,\textsuperscript{30} Le et al. (Na and K-salt)\textsuperscript{34} and Nguyen et al. (Soil S6, pH 7.2).\textsuperscript{35}
PFAS partitioning. It is of interest whether the correlations shown in Figure 4 hold when more diverse anionic compounds are included. The actual intermolecular interactions that occur between PFAS and the phospholipid membrane, air/water interface, or soil organic matter should be different from those between PFAS and the C<sub>8</sub>-bonded silica. The simple correlations presented can be considered a first step in model development toward a more comprehensive multiparameter model for partitioning of anionic substances in general.

**Associated Content**

**Supporting Information**
Additional tables for the list of chemicals, monitored ions for LC/MS analyses, retention time data, and regression statistics; additional figures for tracer retention times, dependence of k on [NH4CH3COO], measured log k vs φ<sub>MW</sub>, dependence of log k on n<sub>C2</sub> and n<sub>C8</sub>, log k<sub>0</sub>, log k<sub>50</sub>, and log k<sub>50</sub> values, log k<sub>0</sub> vs V<sub>Migawa</sub> and molecular weight, and literature partition data vs k<sub>50</sub> and k<sub>SP</sub>.

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**Notes**
The authors declare no competing financial interest.

**Author Contributions**
Study design: SE. Experiment: SM. Data evaluation: SE, SM. Drafting of manuscript: SE. Revising of manuscript: SE, SM.

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**References**
20. Endo, S.; Hammer, J.; Matsuzawa, S. Experimental


