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Perfluorinated Pollutants in Water: Diffusion Coefficient of Perfluorosulfonic Acids by Molecular Dynamics Simulations

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Abstract

Intra-diffusion coefficients of five perfluorinated surfactants (PFAS) (perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorodecanesulfonic acid (PFDS), perfluorododecanesulfonic acid (PFDodS) and the perfluorooctanesulfonate anion (PFOS⁻)) in water were determined by molecular dynamics simulation at infinite dilution, as a function of temperature. The results show an excellent agreement with the scarce amount of experimental data available in the literature, lending confidence to the values obtained for PFDS and PFDodS, for which no experimental results could be found. Arrhenius-like equations were adjusted to the temperature dependence of the diffusion coefficients, correlating the diffusion coefficients within the estimated uncertainties. Together with previous studies for perfluorinated alcohols, the data reported is essential for the development of dispersion models of perfluorinated pollutants in water and remediation strategies.

Keywords

Diffusion coefficient in water

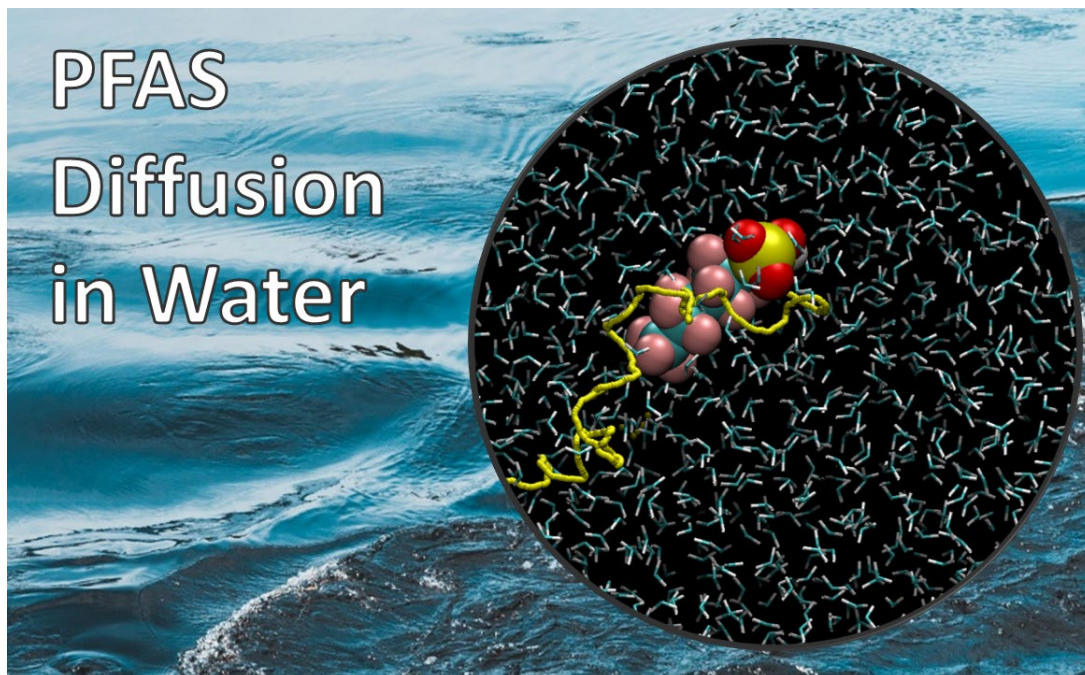
Per- and polyfluoroalkyl substances (PFAS)

Molecular dynamics simulations

Perfluorosulfonic acids

Temperature effect

Graphical Abstract



1. Introduction

Per- and polyfluoroalkyl substances (PFAS, defined by OECD as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom) are synthetic compounds that combine several exceptional properties such as chemical inertness, simultaneous hydrophobic and lipophobic character, low surface tensions, high density, low dielectric constants and high ability to dissolve gases, which make them very attractive for countless practical applications. Highly fluorinated surfactants, in particular, have increasingly found over the 20th century a truly ubiquitous use. For example, PFAS surfactants are used as both emulsifiers and emulsion breakers, from the oil industry to cosmetics, in both water- and oil-repellent surface coatings and as wetting agents in inks or pesticides, in fire-fighting foams and powders.¹ This widespread use, allied to the extreme chemical inertness has led to the accumulation of these compounds in the environment and PFAS earning the epithet of “Forever Chemicals.” Although PFAS were initially considered inert and biocompatible, several studies have demonstrated their bio accumulative potential² and established probable links between the presence of PFAS in blood serum and severe health issues including cancer.³

The knowledge of the thermodynamic and thermophysical properties of PFAS, and particularly of their diffusion behaviour in water, is crucial for modelling their environmental dispersion and transport in natural waters and soils,^{4,5,6,7,8} and even for the development of specific chemical sensors.⁹ On the other hand, it can also be important for the design and optimization of remediation technologies, which typically require the removal of the perfluorinated pollutants from the contaminated matrix and their subsequent concentration and destruction by other methods.^{10,11} The more usual separation processes include adsorption methods,¹² either in activated carbon or anionic exchange resins;¹³ membrane processes,¹⁴ either through nanofiltration or reverse osmosis; or flocculation, using specific proprietary chemical additives. Very recently, foam fractionation has emerged as a novel remediation method that separates PFAS by adsorption to the interface of rising air bubbles in a column of water, with the consequent increase of concentration on the layer of foam that is formed at the top of the column and extracted.^{15,16,17}

Even though all these modelling and technological applications would greatly benefit from a detailed knowledge of the dependence of the diffusion coefficients on temperature and on the molecular structure of the solutes, very limited data has been published on this subject. A few experimental studies can be found in the literature that report diffusion coefficients of perfluorinated carboxylic or sulfonic acids in water, albeit always at a single temperature (either 293 K or room temperature). Nordstierna *et al.* studied the aggregation behaviour of sodium perfluorooctanoate in water by nuclear magnetic resonance techniques, having determined the diffusion coefficient of the perfluorooctanoate (PFOA⁻) monomer.¹⁸ The diffusion coefficient of the perfluorobutanesulfonate anion (PFBS⁻) was reported based on the modelling of cyclic voltammetry curves,¹⁹ and Schaefer *et al.*²⁰ determined in a single experiment the diffusion coefficient of a series of PFAS in synthetic groundwater at room temperature, using the capillary method. Very recently, Islam and Arrigan²¹ proposed values for the diffusion coefficients of the anionic forms of PFBS, PFHxS, PFOS and PFOA, also from the modelling of ion-transfer voltammetry experiments.

In previous work by our group, the diffusion behaviour of a related class of PFAS, linear fluorotelomer alcohols $F(CF_2)_nCH_2OH$ with $n=1-4$, was studied. Their intra-diffusion coefficients in dilute aqueous solutions were experimentally determined as a function of temperature using pulsed field gradient NMR and also calculated from molecular dynamics (MD) simulations. It was

found that the intra-diffusion coefficients of these simple surfactants show a regular trend with chain length and molecular weight, like the linear hydrogenated alcohols, but also that fluorinated alcohols diffuse faster in water than their hydrogenated counterparts with the same molecular weight. This is likely due to the enhanced hydrophobicity of the perfluoroalkyl chain.^{22,23} The agreement between simulated and experimental results lent confidence to the MD predictions of the diffusion coefficients of perfluorosurfactants PFOA and PFOS at infinite dilution. To the best of our knowledge, these were the first reported studies of the diffusion behaviour of these regulated pollutants in water as a function of temperature.

In this work, intra-diffusion coefficients in water at infinite dilution are determined by MD for the series of the linear perfluorosulfonic acids ($C_4 - C_{12}$) comprising the range of chain lengths of the most important and regulated PFAS pollutants.²⁴ The results obtained are compared with the available experimental data from the literature. MD simulations are performed at temperatures between 283 K and 313 K, allowing the assessment of the effect of temperature on the mobility of these pollutants in water. This temperature range covers a significant part of the environmental and remediation process temperatures. The effect of the equilibrium between the neutral (protonated) and anionic forms of the studied compounds on the diffusion coefficient is also discussed and quantified.

It is important to note that the described work is part of a much wider project aiming at characterizing the thermodynamic behaviour of perfluorinated substances either pure, in aqueous solution or mixed with hydrogenated species. This study has included the study of bulk, interfacial and transport properties. For example, vapour pressures, liquid densities, and surface tensions of pure perfluorinated alcohols^{25,26,27} have been recently reported. Mixtures of fluorinated and hydrogenated alcohols have also been recently studied, both in the liquid^{28,29,30,31,32} and the gaseous phases.³³ All this information is essential to develop efficient dispersion models and remediation processes. The simultaneous presence of perfluorinated and hydrogenated amphiphiles is particularly relevant as it is well known that perfluorinated and hydrogenated chains are mutually phobic, displaying liquid-liquid immiscibility and large volumetric,³⁴ dynamic,³⁵ conformational³⁶ and interfacial^{37,38} anomalies. Ultimately, this mutual phobicity leads to the formation of nano-domains^{39,40} and different types of supramolecular organization.^{41,42,43,44}

2. Simulation Details

The fluorinated surfactants studied (perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorodecanesulfonic acid (PFDS), perfluorododecanesulfonic acid (PFDodS) and the perfluorooctanesulfonate anion (PFOS-)) were modelled using the optimized potentials for liquid simulations (OPLS-AA) atomistic force field.⁴⁵ Chemical structures of these compounds are shown as Figure S1 of the Supporting Information. The parameters for the perfluoroalkyl moieties were taken from the work of Watkins and Jorgensen.⁴⁶ The neutral form of the sulfonic acid group was modelled with the parameterization of Sunda and Venkatnathan,⁴⁷ using the point charges determined from quantum mechanical calculations in a previous work,²² and its anionic form (sodium salt) was modelled with the sulfonate group parameters⁴⁸ of the Canongia Lopes & Pádua force field (CL&P) and with the sodium ion parameters by Aqvist.⁴⁹ The TIP4P/2005 model for water by Abascal and Vega⁵⁰ was used as it provides an accurate nonpolarizable forcefield in very good

agreement with experimental data for a wide range of water properties, including the self-diffusion coefficient.⁵¹ The dispersive interactions between different types of atoms were calculated using geometric mean rules for both the size and energy Lennard-Jones parameters, following the OPLS force field parameterization.

Molecular dynamics simulations were performed and analysed using the Gromacs 5.0.7 open-source package,⁵² for systems consisting of one molecule of perfluorinated surfactant and 999 molecules of water in cubic boxes with periodic boundary conditions. Since a single solute molecule is present, the simulated systems correspond to a condition of infinite dilution, even if the nominal concentration exceeds the experimental solubility values. For each studied system, an initial low-density random molecular configuration was generated and subjected to an energy minimization using the steepest descent method to relax unphysical high-energy contacts. A random velocity distribution was assigned to the atoms, according to the Maxwell distribution at the desired temperature, and a 2 ns NpT pre-equilibration run was performed at 100 bar to achieve a dense liquid configuration. The equilibrium volume of each box was then obtained from an 11 ns NpT simulation at 1 bar, of which the first ns was discarded from the analysis. The final configuration from this run was then resized to the average NpT volume and used in a NVT simulation for a further 11 ns, of which the last 10 ns were used to compute the diffusion coefficient. The equilibrated simulation box sizes were always slightly larger than $3.1 \times 3.1 \times 3.1 \text{ nm}^3$.

The equations of motion were integrated in 1 fs timesteps, using the leapfrog algorithm, with all bonds involving hydrogen atoms constrained to their equilibrium distance by the LINCS algorithm. A 1.2 nm cutoff (1.1 nm for the pre-equilibration) was used for both dispersive and electrostatic interactions, applying standard analytic tail corrections for energy and pressure to the dispersion terms and treating the long-range coulombic interactions using the particle-mesh Ewald method. The Verlet cutoff scheme was used to update the neighbour lists, with a minimum frequency of 10. The Berendsen thermostat and barostat, with coupling constants of 0.3 and 4 ps, respectively, were used during the pre-equilibration stage, whereas the Nosé-Hoover thermostat and the Parrinello-Rahman barostat were applied in the production stage runs with coupling constants of 0.2 and 1.0 ps. Gromacs input files with the full set of forcefield and simulation parameters are given as Supplementary Information.

The intra-diffusion coefficients of the different solutes in water (D) were calculated from the linear part of the mean square displacement (MSD) of the centre of mass of the solute molecule according to the Einstein equation,

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \quad (1)$$

where $\mathbf{r}_i(t)$ is the vector position of the centre of mass of each molecule i at time t , and the $\langle \rangle$ brackets indicate the time average. The diffusion coefficient reported for each state point is the average of 20 independent simulations, obtained from generating different random velocity distributions at the pre-equilibration stage. An example set of MSD curves, for the 20 trajectories of the PFOS- anion at 298.15 K, is shown as Figure S2 of the Supplementary Information. The reported uncertainties u were calculated according to

$$u = \frac{\sqrt{\frac{\sum(D-\bar{D})^2}{n-1}}}{\sqrt{n}} \times t(0.05; n - 1) \quad (2)$$

where n is the number of samples (i.e., 20), D the diffusion coefficient calculated for each simulation, \bar{D} the average diffusion coefficient for the state point and $t(0.05; n - 1)$ the t -distribution critical value for $n-1$ degrees of freedom and a confidence level of 95%.

It is known that diffusion coefficients computed from molecular dynamics simulations display a significant dependence on the size of the simulated system. This effect, which arises from self-interactions in periodic systems, was first studied by Dünweg and Kremer⁵³ and later revisited by Yeh and Hummer.⁵⁴ According to these studies, the diffusion coefficient computed directly from an MD simulation with periodic boundary conditions D^{PBC} is linearly dependent on the inverse of the lateral size L of the simulation box according to

$$D^\infty = D^{PBC} + \frac{k_B T \xi}{6\pi\eta L} \quad (3)$$

where D^∞ is the diffusion coefficient in the thermodynamic limit (infinite system size), k_B is Boltzmann's constant, T is the absolute temperature, ξ is a dimensionless constant equal to 2.837298 for periodic cubic systems and η is the shear viscosity. This equation is commonly known as the Yeh-Hummer correction, and its validity has been demonstrated for a very wide range of systems.^{55,56,57} The diffusion coefficients reported in this work were thus corrected with equation 3. Since the simulated systems correspond to infinite dilution conditions, we have assumed their shear viscosities to be equal to those of pure TIP4P/2005 water, and obtained the values at the studied temperatures by interpolating the results of González and Abascal.⁵⁸ As the box size L was also essentially the same for all the simulations performed, the applied Yeh-Hummer corrections were constant and equal to $0.15 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ at 283.15 K, $0.23 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ at 298.15 K and $0.33 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ at 313.15 K.

3. Results and discussion

Intra-diffusion coefficients at infinite dilution in water, at three temperatures (283.15 K, 298.15 K and 313.15 K), have been obtained by MD simulation for perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorodecanesulfonic acid (PFDS), perfluorododecanesulfonic acid (PFDodS) and for sodium perfluorooctanesulfonate (NaPFOS), the anionic form of perfluorooctanesulfonic acid. The obtained values are reported in Table 1 and represented in Figure 1. As can be seen, the intra-diffusion coefficients increase with temperature and decrease gradually along the chemical family, in parallel with the experimental results previously obtained^{22,23} for the shorter chained fluorinated alcohols. Since all of the solutes share the same polar group, the gradual decrease of the diffusion coefficient with the length (and mass) of the apolar fluorinated tail corresponds to the expected behaviour. Moreover, the values predicted in this work for the perfluorinated sulfonic acids are lower than those displayed by the perfluorinated alcohols of equivalent chain length. This could be expected not only due to the higher mass and molecular volume of the sulfonic group, but also to an expectable higher tendency to coordinate water molecules.

Table 1. Intra-diffusion coefficients at infinite dilution in water of the studied PFAS, obtained by MD simulation.

	$D / 10^{-9} \text{ m}^2 \text{ s}^{-1}$		
	283.15 K	298.15 K	313.15 K
PFBS	0.56 ± 0.03	0.80 ± 0.06	1.20 ± 0.09
PFHxS	0.48 ± 0.04	0.74 ± 0.05	1.09 ± 0.07
PFOS [22]	0.47 ± 0.02	0.70 ± 0.03	0.98 ± 0.04
PFOS ⁻	0.42 ± 0.02	0.62 ± 0.03	0.88 ± 0.07
PFDS	0.40 ± 0.03	0.61 ± 0.04	0.91 ± 0.08
PFDodS	0.36 ± 0.02	0.55 ± 0.03	0.78 ± 0.04

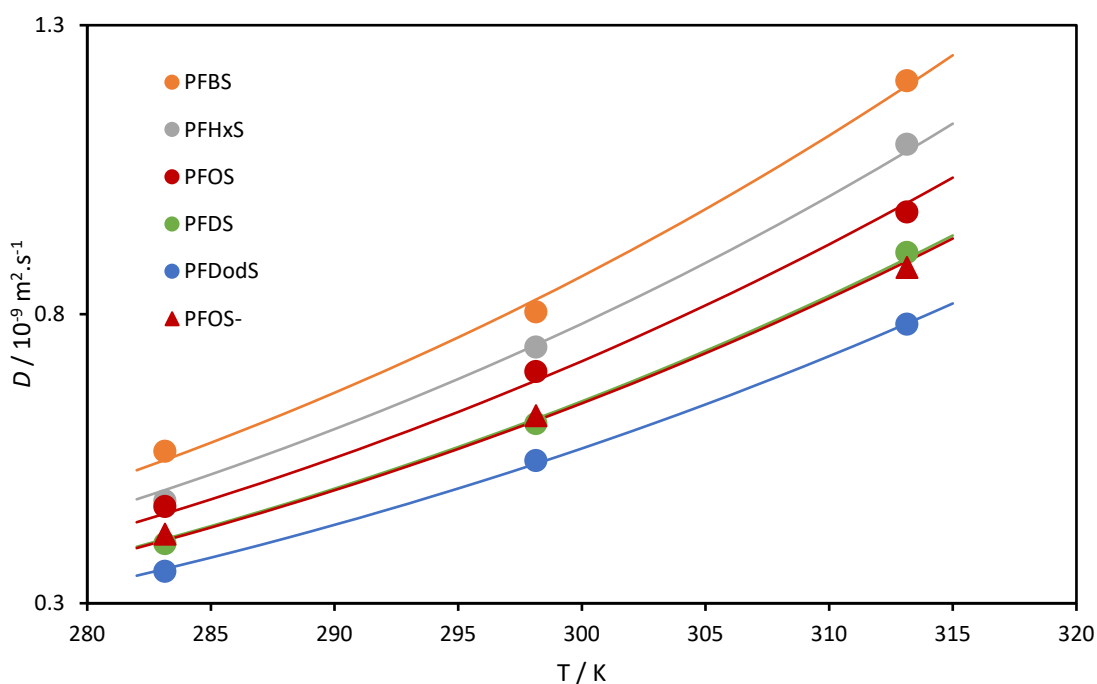


Figure 1. Intra-diffusion coefficients at infinite dilution in water of the PFASs studied, as a function of temperature, obtained by MD simulation. Symbols represent simulation data and lines the Arrhenius correlations (Model II). Error bars have been omitted for clarity.

The MD results at 298.15 K, including the data by Pereira *et al.*²² for PFOS and PFOA, are compared with the available literature values in Figure 2. Experimental and molecular simulation data for the previously studied fluorotelomer alcohols have been included for comparison.^{22,23}

The diffusion coefficients obtained in our previous work have also been corrected for finite-size effects according to Eq. 3.

As can be seen, the available experimental data for both the sulfonic and carboxylic compounds display a large scatter, with values by different authors differing by up to 100%, and with the data by Schaefer *et al.*²⁰, in particular, showing irregular behaviour with increasing molecular size for both families. The MD results presented decrease regularly with chain length and fall well within the dispersion of the experimental data. After the correction for finite-size effects, our previous MD results for the three longer fluorotelomer alcohols agree quantitatively with the experimental results, obtained by pulsed field gradient NMR. This imparts a very good degree of confidence to the new simulation data, which was obtained with the same simulation procedure and similar molecular force-fields.

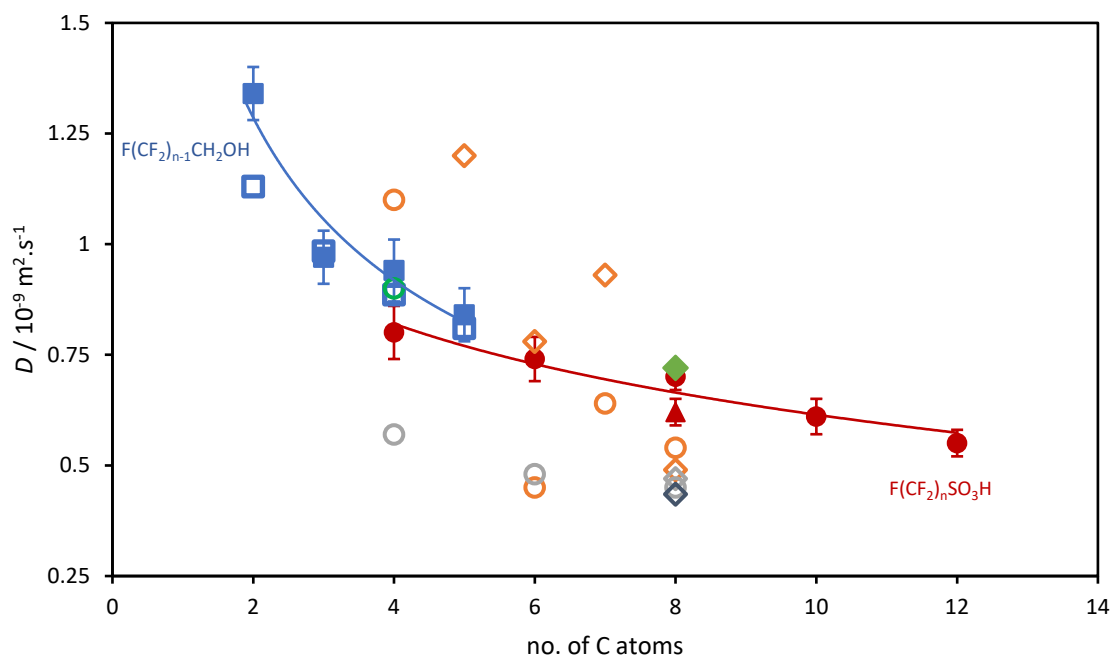


Figure 2. Comparison between the MD results and experimental results from the literature, at 298.15 K or room temperature, as a function of the carbon chain length. Full symbols represent simulation data (lines are guides to the eye) and empty symbols experimental data. $F(CF_2)_nSO_3H$, this work - ●; $F(CF_2)_8SOO^-$, this work - ▲; $F(CF_2)_{n-1}CH_2OH$ - □^{22,23}; $F(CF_2)_{n-1}CH_2OH$ - ■^{22,23}; $F(CF_2)_7COOH$ - ◆²²; Perfluoro sulfonic acids - ◆²⁰, ◆²¹, ◆¹⁹; Perfluoro carboxylic acids - ◆²⁰, ◆²¹, ◆¹⁸.

It is important to note that the studied compounds are acids. Therefore in aqueous solution neutral PFAS molecules co-exist in equilibrium with the deprotonated anions. Thus, data of PFAS in aqueous solution can often be regarded as an average value of the properties of the neutral and the ionic forms at the equilibrium concentration. In the literature, the reported acidity constants for perfluorinated carboxylic acids vary by several orders of magnitude.⁵⁹ However, it is generally accepted that they have pK_a values lower than 4, being thus stronger acids than their

hydrogenated counterparts. For perfluorinated sulfonic acids, a similar survey points to pK_a values lower than 1,^{60,61} indicating that these compounds behave as quite strong acids. At relevant environmental conditions the exact degree of dissociation will obviously depend on the solute concentration, on the composition of the aqueous matrix and particularly on pH. In terms of diffusion coefficient, it is reasonable to assume that the neutral forms should diffuse faster than their charged counterparts, due to the latter's increased effective mass and volume originated by a larger number of coordinated water molecules. This stronger coordination can be confirmed in Figure S3 of the Supporting Information, where it is seen that the first peak of the radial distribution function between the oxygen atoms of the sulfonate group and those of the water molecules is much higher for the anionic form than for the protonated form of PFOS. The diffusion coefficients of the neutral and anionic forms can be thus envisaged as upper and lower bounds to the effective mobility of the PFAS in aqueous solution. To evaluate and quantify this effect, the diffusion coefficient at infinite dilution of the PFOS⁻ anion was also obtained by MD and found to be about 10% lower at all the studied temperatures. This difference likely decreases with the size of the diffusing molecule, as the number of coordinated water molecules should depend essentially on the nature of the polar group and be independent of the chain length. For longer solutes, the interaction with water (and hence its mobility) is increasingly governed by the fluorinated chain length in comparison with the role played by the polar group.

The predicted intra-diffusion coefficients for the perfluorinated sulfonic acids (PFSA) are also represented in Figure 3 as a function of the carbon chain length. As can be seen, at constant temperature the coefficients decrease linearly with chain length. These linear fits reproduce the data within the estimated uncertainties and can thus be used to interpolate the diffusion coefficients for the odd members of the series. Other empirical methods,⁶² such as the Wilke-Chang equation, were tested to correlate the diffusion coefficients with the chemical structure of the solutes, but the results were significantly worse than the linear relations now obtained. For chains lengths considerably longer than those now reported, it is likely that the linear dependence should gradually change to an asymptotic limiting behaviour. However, within the range of temperatures and chain lengths studied, which span most of the environmentally relevant conditions and compounds, the linear correlations provide a quantitative description of the present results.

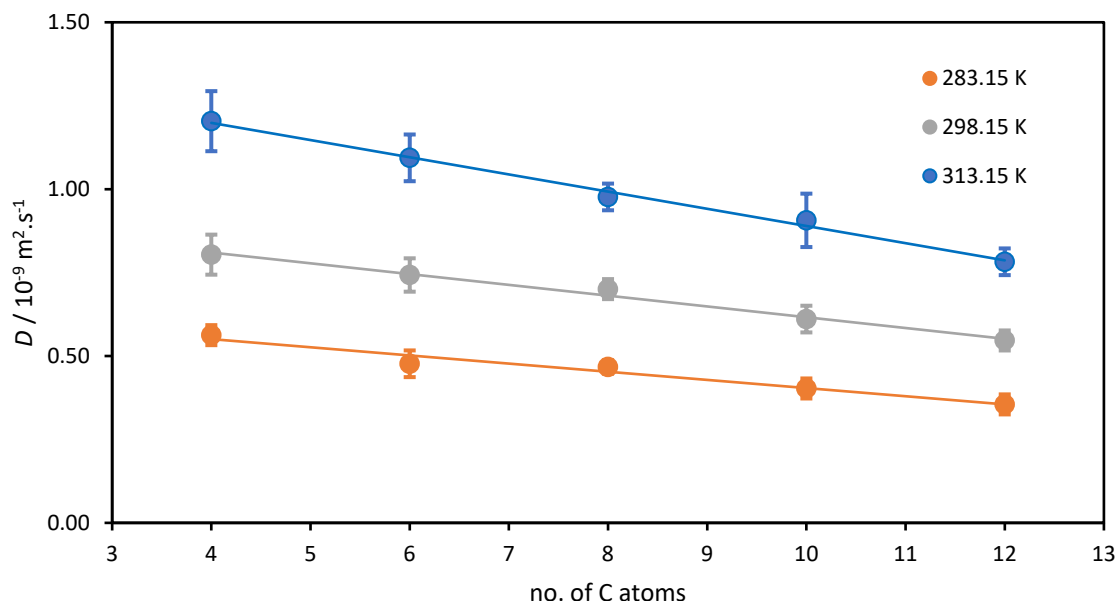


Figure 3. Intra-diffusion coefficients at infinite dilution in water of the studied PFAS, as a function of chain length, obtained by MD simulation.

The temperature dependence of the intra-diffusion coefficient of each solute in water was modelled by assuming that the diffusion process follows an Arrhenius-like behaviour:

$$D = A_D \exp\left(\frac{-E_D}{RT}\right) \quad (4)$$

where A_D is a pre-exponential factor and E_D the activation energy of diffusion. This latter parameter can be interpreted as the energy required for the diffusing molecule to break its solvation shell. Treating both parameters as constants, thus representing mean values within the studied temperature range, two models were tested. In Model I, equation 4 was fitted independently for all the studied PFSA, and the corresponding parameters are reported in Table 2. This model describes the simulated diffusion coefficients with a maximum deviation of 2.7% and an average deviation of 0.8%. As can be seen, neither the activation energies nor the pre-exponential factors of Model I present any trend within the chemical series and, moreover, the obtained E_D values are relatively similar for all the compounds.

As discussed previously,²² it is reasonable to consider that, at infinite dilution, the diffusion activation energy depends essentially on the solvent, as the solvation shell is exclusively formed by solvent molecules. A new fit of equation 4 was thus performed, assuming a common value of E_D for all the studied PFSA solutes. The new model parameters (Model II) are also presented in Table 2, and reproduce the simulated diffusion coefficients with maximum and average deviations of 4.0% and 1.7%, respectively. Despite being slightly larger than those of Model I, these deviations are well within the uncertainty of the determined diffusion coefficients. As can be seen in Figure 4, the pre-exponential factors of Model II now present a very regular linear trend, decreasing with the chain length of the solute. This model thus provides a very convenient

way to interpolate the diffusion coefficients at any temperature between 283.15 K and 313.15 K, for all the linear perfluorinated sulfonic acids.

Table 2. Diffusion activation energies and pre-exponential factors (eq. 2) for the studied PFSA molecules at infinite dilution in water. In Model I, E_D is fitted independently for each compound and in Model 2 a single E_D is used for all substances.

	Model I		Model II	
	$E_D / \text{kJ.mol}^{-1}$	$A_D / 10^{12} \text{ m}^2.\text{s}^{-1}$	$E_D / \text{kJ.mol}^{-1}$	$A_D / 10^{12} \text{ m}^2.\text{s}^{-1}$
PFBS	19.20	1.91	19.16	1.88
PFHxS	20.29	2.66		1.70
PFOS	17.91	0.95		1.56
PFDS	20.06	2.01		1.41
PFDodS	19.21	1.25		1.23
PFOS⁻	18.13	0.93		1.40

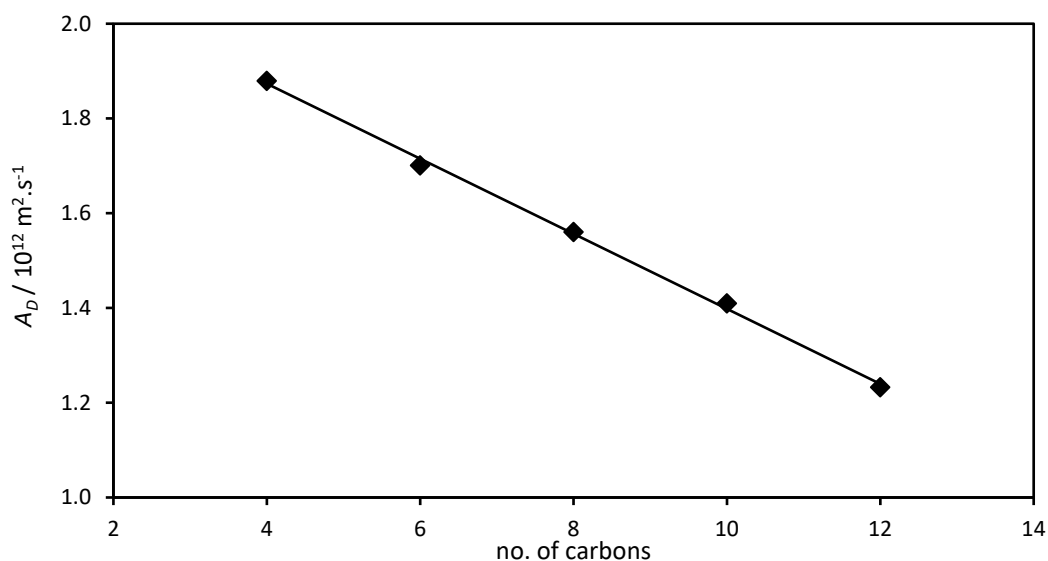


Figure 4. Pre-exponential factor A_D (Eq. 2) for the studied PFSA (Model II), as a function of the carbon chain length. The expression for the linear correlation is $A_D / (10^{12} \text{ m}^2.\text{s}^{-1}) = 2.1903 - 0.079221 \times (\text{no. of carbons})$.

4. Conclusions

Intra-diffusion coefficients at infinite dilution in water of several PFAS surfactants were obtained by molecular dynamics simulations, at three temperatures between 283 K and 313 K. The results obtained show an excellent agreement with the published experimental data, granting a high level of confidence to the MD predictions in the cases where no experimental results are

available for comparison. To the best of our knowledge, these are the first reported diffusion coefficients for the perfluorodecanesulfonic and perfluorododecanesulfonic acids in water, and for all other studied substances at temperatures different from room temperature. The diffusion coefficients of the studied perfluorosulfonic acids in water decrease gradually with the chain length of the solutes. It was observed that the anionic forms of the perfluorosulfonic acids diffuse more slowly than their neutral counterparts, and that for PFOS this decrease in the diffusion coefficient is of around 10% at all studied temperatures.

The temperature dependence of the diffusion coefficients obtained presents an Arrhenius-like behaviour for all compounds, and the results are well correlated using a single common value for the diffusion activation energy. A linear correlation of the pre-exponential factor with the PFSA chain length is proposed, which allows the description of the diffusion coefficients of this family of compounds, within the estimated simulation uncertainty, for all the range of chain lengths and temperatures studied.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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