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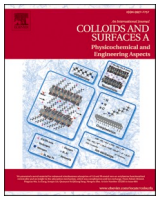

# Counterion influence on perfluorooctanoate micelle characteristics: Shape, size, and interactions

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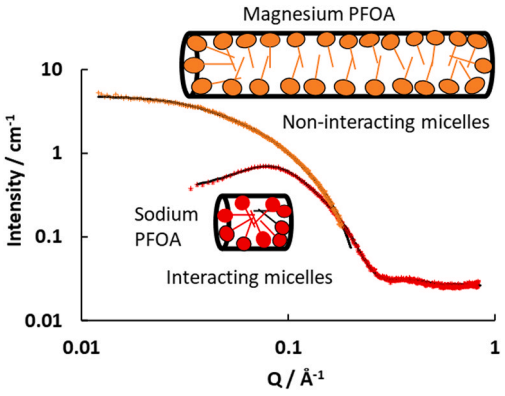
## HIGHLIGHTS

- Micelles of perfluorooctanoate salts are anisotropic influencing transport.
- Magnesium perfluorooctanoate micelles are longer than those of monovalent salts.
- Low temperatures and higher concentrations increase anisotropy.
- Sodium perfluorooctanoate exhibits distinctive phase behaviour even at low concentrations.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

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## ABSTRACT

Counter-ions have large effects on the self-assembly and dispersion of per- and polyfluoroalkyl substances (PFAS) in aqueous solution. PFAS have been recognized as emerging contaminants of concern due to their ubiquitous distribution in the environment and persistent and potential toxic characteristics. The aim of this study was to investigate how different counter-ions affect perfluorooctanoate micelle assembly and interactions. Small-angle X-ray scattering was used to determine the influence of ions ($Li^+$, $Na^+$, $NH_4^+$, $Mg^{2+}$) on the micelles and their interactions. The micelles formed by perfluorooctanoate in the presence of monovalent counter-ions ($Li^+$, $Na^+$, $NH_4^+$) were characterized as highly charged cylinders that became more elongated as the surfactant concentration increased. In the presence of added sodium chloride, the sodium perfluorooctanoate micelles were more elongated and, with 0.2 M NaCl, electrostatic interactions were screened almost completely. The micelles formed by perfluorooctanoate in the presence of the divalent magnesium ions were cylinders and the length increased markedly at higher concentrations and at lower temperatures. The interactions were screened by the divalent ions without further added electrolyte. As the formation of micelles influences the transport and dispersion of PFAS in the environment, the results will be valuable in understanding processes related to pollution and improving remediation methods.

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## 1. Introduction

Fluorocarbon amphiphiles known as per- and polyfluoroalkyl substances (PFAS) are recognized as widespread pollutants due to their persistent and potential toxic nature [1]. Perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are the most common classes of PFAS detected in the environment. This class of PFAS are amphiphiles due to their hydrophobic tail and hydrophilic head group. Due to their unique properties [1], they are used in a variety of consumer and industrial applications such as aqueous firefighting foam, and as water and oil repellents [2]. However, PFAS are extremely persistent and detected ubiquitously in the environment and biota [3]. Once in the environment surfactants are transported from contamination sites into surrounding ecosystems such as surface water bodies, ground water systems and soil [4,5]. Previous studies have observed that perfluorooctanesulphonic acid (PFOS) binds to soils with higher organic carbon content due to their hydrophobic interactions [6]. In surface water bodies, perfluorooctanoic acid (PFOA) and PFOS were transported downstream in rivers from contamination sources [5]. The aggregation to form micelles that occurs at elevated concentrations can influence the distribution by increasing molecular transport [7] and change the free energy of the molecules causing differences in chemical potential that drive, for example, adsorption to be significantly modified [8–10]. The transport of surfactants in aqueous environments is influenced by the aggregates that are formed because of the increased solubility, and particularly as the rate of diffusion varies with their size and shape. Micelles will typically move more slowly than individual surfactant molecules but as they transfer more molecules, they provide more efficient transport [7]. The effect is most important for shapes when the aggregation number increases with concentration significantly faster than the hydrodynamic radius.

Perfluorooctanoate salts self-assemble in aqueous solutions forming micelles and, at higher concentrations, various ordered phases [11,12]. The significant differences in phase behaviour with temperature described in those studies are naturally of interest given the variations relevant to environmental conditions. The micellar size and shape are determined to a significant extent by the packing of the individual surfactant molecules, which is influenced by the head group area and charge, and the length and volume of the perfluorocarbon hydrophobic tail [13]. The increased stiffness of the perfluorocarbon chain [14,15] causes them to be slightly longer than the corresponding hydrocarbon molecules. The interfacial area per molecule in an assembly is also affected by the hydration and ionic association of the polar head group [13]. The shape of the molecules determines how the surfactant molecules fit within micelles and other ordered phases found at higher concentrations, and is described by a packing parameter [13]. The counter-ions influence the self-assembly and dispersion of the perfluorooctanoate in aqueous media. For example, sodium and ammonium perfluorooctanoate form elongated micelles [14,16], while caesium perfluorooctanoate is reported as packing as flat assemblies forming oblate micelles [15]. Previous scattering studies [14–19] focused on the salts of perfluorooctanoate with monovalent counter-ions such as $Na^+$, $NH_4^+$ and $Cs^+$ and have described the micelles as either elongated cylinders or ellipsoids (Table S1 in the Supplementary Information). Information about micellar assembly is therefore important in understanding accumulation and remediation processes.

The present study investigates systematically how counter-ions affect perfluorooctanoate micelles using small-angle X-ray scattering. Specifically, we i) investigate effects of perfluorooctanoate concentration, ii) assess the impact of temperature, and iii) evaluate the influence of counter-ions ($Li^+$, $Na^+$, $NH_4^+$, $Mg^{2+}$) on the micelle shape, size, and interactions. Complementary information about the mobility is obtained from measurements of conductance of solutions. Apart from the straightforward identification of the critical micelle concentration when a change in gradient occurs, estimates of the aggregation number and the degree of ionic dissociation of micelles can be made. [20,21]

## 2. Materials and methods

### 2.1. Chemicals

Perfluorooctanoic acid ($C_7F_{15}COOH$, purity: 95 %) was purchased from Sigma Aldrich. Sodium hydroxide (NaOH, 98 % pellets), ammonium hydroxide solution ($NH_4(OH)$, 28–30 % $NH_4OH$), and lithium hydroxide (LiOH, 98 %, powder) were purchased from Sigma-Aldrich and magnesium hydroxide ($Mg(OH)_2$, 95–100 %) was purchased from Fluka. The solutions were prepared using deionized water with a resistivity of 18.2 MΩ cm. Details of the sample preparation are provided in the Supplementary Information (Section 2).

### 2.2. Conductivity

The electrical conductivity of aqueous solutions were measured at 23 ± 1 °C using a Hanna HI 8733 conductivity meter calibrated to 12.8 mS $cm^{-1}$ using a total dissolved solids (TDS) calibration solution at 25 °C. The gradient of the conductivity vs surfactant concentration graph, and specifically, the point at which the gradient changes, is used to determine the critical micelle concentration of the solutions.

### 2.3. Small-angle X-ray scattering (SAXS)

Small-angle X-ray scattering (SAXS) measurements of aqueous perfluorooctanoate solutions were performed with a Xeuss 2.0 Q-Xoom (Xenocs, Grenoble, France) SAXS/WAXS instrument with a Pilatus 300 R detector and a Peltier temperature stage at the Biomedical Centre (BMC), Uppsala University. The samples in the concentration range of 100–300 mmol $dm^{-3}$ for aqueous solutions of sodium perfluorooctanoate (NaPFO), ammonium perfluorooctanoate ($NH_4$PFO), lithium perfluorooctanoate (LiPFO) and 50–150 mmol $dm^{-3}$ for magnesium perfluorooctanoate ($Mg(PFO)_2$) were sealed into 1.0 mm diameter borosilicate glass capillaries supplied by Hilgenberg. The data are presented as plots of intensity of scattered radiation vs the scattering vector $Q = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength and θ is the scattering angle. In scattering experiments, the vector Q represents the momentum transfer between the incoming wave and the scattered wave. The Q range for this experiment was $0.01 < Q < 1$ $Å^{-1}$. The samples were measured at temperatures in the range of 10–50 °C using a Peltier controlled stage and held in vacuum during measurements. Further details about the data reduction are provided in the Supplementary Information (Section 3). The samples were measured at various concentrations above the respective critical micelle concentrations which were determined from the conductivity measurements or taken from the literature values listed in Table S2.

### 2.4. Zeta potential

Complementary data about the hydrodynamic interaction potential for the micelles were obtained using a Malvern Zetasizer Pro (Malvern Panalytical, Malvern, UK) to measure the zeta potential of the micellar solutions at concentrations of 100 mmol $dm^{-3}$ at 25 °C. Results were calculated assuming the Smoluchowski approximation for high ionic strength solutions [22] and with assumed refractive indices of 1.30 for the fluorocarbon surfactants and 1.33 for water.

## 3. Results and discussion

### 3.1. Critical micelle concentration

Conductivity measurements were made on magnesium perfluorooctanoate to determine the critical micelle concentration at different temperatures. The results shown in Fig. S1 (Supplementary Information) compare the conductivity of magnesium perfluorooctanoate with that of lithium, sodium, and ammonium

perfluorooctanoate. The critical micelle concentration of magnesium perfluorooctanoate was 7.8 ± 0.5 mmol dm$^{-3}$ at 23 °C, which is three times lower than that of the monovalent salts. As the temperature increased from 10 °C to 55 °C, the critical micelle concentration only decreased slightly as shown in Fig. S2. In previous studies, sodium perfluorooctanoate and lithium perfluorooctanoate showed a similar initial decrease, with a small increase observed at higher temperatures [23,24]. The previous and present data on critical micelle concentration of various perfluorooctanoate salts have been summarised in Table S2. Previous studies [25] on the conductivity showed that similar conductivity was observed for sodium perfluorooctanoate in the same concentration range.

### 3.2. Micelle shape, size, and interactions

Small angle X-ray scattering data for lithium, sodium, ammonium, and magnesium perfluorooctanoate at 25 °C are shown for a concentration of 100 mmol dm$^{-3}$ together with the corresponding model fits in Fig. 1. There is a clear difference with the divalent counter-ion. For $Mg^{2+}$, the pronounced peak associated with micellar interactions is not apparent, due to the large screening effect of the magnesium counter-ions. The presence of the divalent magnesium reduces the Debye-screening length due to the increased ionic strength, therefore reducing the inter-micellar interactions [26]. In contrast, for the monovalent ions ($Li^+$, $Na^+$, $NH_4^+$), the peaks arising from the interaction between micelles were pronounced and the fitted structure factor was determined by the volume fraction of micelles as well as their charge. The data for the samples with monovalent counter-ions were fitted with the Hayter-Penfold rescaled mean spherical approximation as a structure factor that accounts for the screened electrostatic interactions between the micelles. The parameters for the models are shown in Table S3 in the supplementary material. The total charge on a micelle is the product of the aggregation number and the fractional charge per molecule that is the degree of ionic dissociation of the molecules. For lithium perfluorooctanoate the fractional charge increased from 0.4 to 0.8 in the concentration range 100–300 mM. However, for sodium and ammonium perfluorooctanoate, the fractional charge of the micelles remained approximately constant (Table S3). In this range there are only small changes in the aggregation number.

An interesting comparison of the micellar interactions can be made with the measured zeta potentials for the micelles that were found to be −55 ± 10, −59 ± 10, −66 ± 10, and −18 ± 3 mV for $Li^+$, $Na^+$, $NH_4^+$, and $Mg^{2+}$ respectively. This potential is likely to be correlated with that controlling the micellar interactions and thus provides further corroboration for the lack of observed inter-micellar correlations seen with the micelles of the $Mg^{2+}$ salt. The positions of the peaks in the scattering data are inversely related to the mean separation distance between the micelles. The widths of the peaks provide directly information about the interactions and are inversely correlated with the potentials.

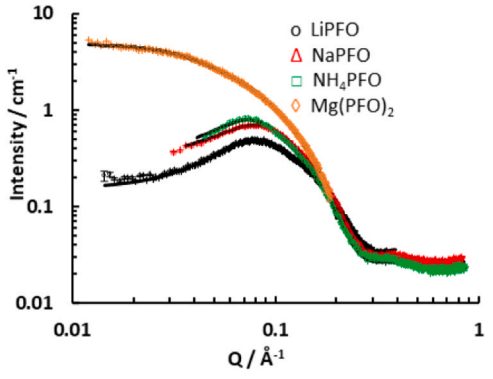


**Fig. 1.** Intensity of small angle X-ray scattering for 100 mmol dm$^{-3}$ lithium perfluorooctanoate, sodium perfluorooctanoate, ammonium perfluorooctanoate and magnesium perfluorooctanoate measured at 25 °C. The continuous lines are the fits of models for cylinders (lithium, sodium and ammonium perfluorooctanoate) with the Hayter-Penfold structure factor and non-interacting cylinders (magnesium perfluorooctanoate) with the parameters listed in Table S3.

The micelles of lithium, sodium, ammonium and magnesium perfluorooctanoate were all modelled as monodisperse cylinders, although adequate fits as prolate ellipsoids were also possible. Adding some polydispersity did not change the fitting parameters significantly and the effects of resolution were also negligible. Models for both cylinders and ellipsoids showed fits that were essentially indistinguishable, with parameters such as volume and aggregation number varying by only 5–10 %, that are within the uncertainties of the measurements (see Fig. S3). The fits on magnesium perfluorooctanoate solutions showed that they formed cylindrical micelles with a radius of 14.3 Å. This radius was slightly longer than the perfluorooctanoate molecular length (13 Å) that has been suggested previously [15]. However, this extended radius accounts for the headgroup as well as the perfluorocarbon chain length. These micelles were longer than those with monovalent cations ($Li^+$, $Na^+$, $NH_4^+$) and they became more elongated as the surfactant concentration increased (see Table S3).

The changes with surfactant concentration were investigated over a range of 100–300 mmol dm$^{-3}$ for the monovalent salts and 50–150 mmol dm$^{-3}$ for magnesium perfluorooctanoate (Figs. S4-S6). For the monovalent salts, only small changes in the parameters describing the micelles were observed but the effects of micellar concentration are clearly apparent from the changes observed in the peak position and intensity. The parameters for the fitted models are shown in Table S3. In contrast, for the magnesium perfluorooctanoate, increasing the concentration caused an increase in length from 65 to 101 Å with a radius of 14.3 Å. In comparison, the length of the sodium perfluorooctanoate micelles length increased only from 30 to 34 Å with a radius of 13 Å.

While the other perfluorooctanoate salts ($Li^+$ and $NH_4^+$) showed small changes with increasing concentration, sodium perfluorooctanoate exhibited a distinctive phase behaviour. Up to concentrations of 200 mmol dm$^{-3}$ at 25 °C, a homogenous dispersion of micelles was formed (Fig. S5). However, at 300 mmol dm$^{-3}$ it formed an ordered structure that separated into a concentrated phase. The scattering data at this concentration are shown in Fig. S5 and an extra peak at 0.045 Å$^{-1}$ is seen in addition to that from the nearest neighbour micelle correlation. This single extra peak did not provide sufficient insight to determine full details of the structure for this phase. It is interesting to note that this ordered phase is temperature-sensitive and exhibits supercooling and superheating behaviour. At lower temperatures, this phase became more pronounced as seen by the increasing intensity of the peak at lower Q (Fig. S7).

The temperature effect on the size of magnesium perfluorooctanoate micelles is shown in Fig. 2 with a decrease in intensity as the temperature increased from 10 to 50 °C. For 100 mmol dm$^{-3}$ magnesium perfluorooctanoate this corresponded to a decrease in the aggregation number from 223 to 58 (Table S4). The trend (Fig. 3) was consistent across a range of concentrations from 50 to 150 mmol dm$^{-3}$, showing that lower temperatures and higher concentrations both resulted in longer micelles. This effect was also observed with the monovalent perfluorooctanoate salts ($Li^+$, $Na^+$, $NH_4^+$) (Figs. S8 and S9, Table S5) although the changes were small and only significant for the ammonium salt .

A comparison of the anisotropy of magnesium perfluorooctanoate, sodium perfluorooctanoate, and ammonium perfluorooctanoate revealed variations with concentration and temperature (Fig. S10). As the concentration of magnesium perfluorooctanoate increased from 50 to 150 mmol dm$^{-3}$ , anisotropy exhibited a linear increase at lower temperatures. In contrast, for the monovalent surfactants, sodium, and ammonium perfluorooctanoate, anisotropy also increased with

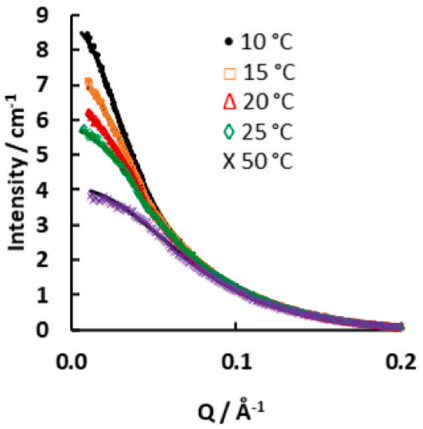


**Fig. 2.** Small-angle X-ray scattering data for magnesium perfluorooctanoate at 100 mmol dm$^{-3}$ showing the effect of changing temperature in the range 10–50 °C. The continuous lines are model fits for cylinders with the parameters listed in Table S4.

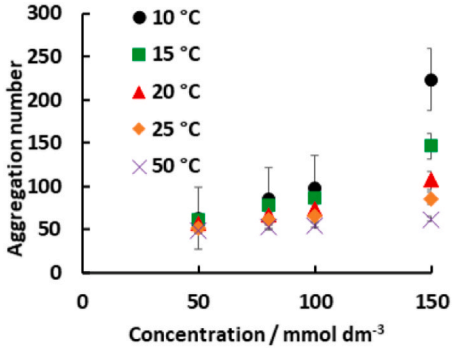


**Fig. 3.** Micelle aggregation number as a function of concentration for magnesium perfluorooctanoate at temperatures from 10 to 50 °C. As the temperature increased, the size of the micelles decreased.

concentration (100–300 mmol dm$^{-3}$) but was lower than that of the magnesium perfluorooctanoate micelles (Fig. S10). This suggests that at lower temperatures the micelles are longer for the divalent salt as compared to the monovalent salts.

The effects of addition of sodium chloride to 200 mmol dm$^{-3}$ sodium perfluorooctanoate were also investigated as shown in Fig. 4. As the concentration of the added sodium chloride increased, the shape of the pronounced peak broadened until it was not observed with

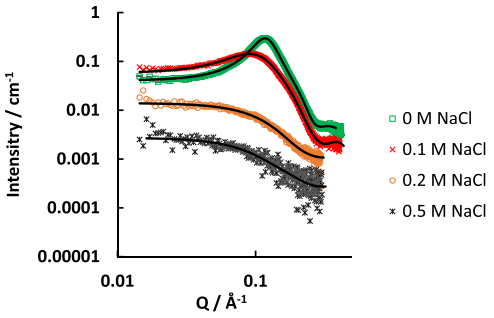


**Fig. 4.** Small-angle X-ray scattering data for sodium perfluorooctanoate (200 mmol dm$^{-3}$) at 25 °C with different concentrations of added NaCl. The continuous lines show the fits for a model of cylindrical micelles with the Hayter-Penfold structure factor. The micelles become elongated and less strongly interacting as the salt concentration increases. The parameters of the fitted models are listed in Table S6.

0.2 mol dm$^{-3}$ NaCl as is expected by the screening effect of the salt ions [27]. The data for these micelles were also fitted as cylinders and the parameters are listed in Table S6. For sodium chloride concentrations of 0.2 M and 0.5 M, the micelles could be adequately fitted with no electrostatic interactions. The micelles increased in length from 38 Å to 54 Å with a 14 Å radius with an increase in salt concentration.

It is interesting to discuss the consequences of the presented results. The present study has identified the micelles formed by lithium, sodium and ammonium perfluorooctanoate as elongated. This contrasts with a study of sodium perfluorooctanoate micelles [17] using small-angle neutron scattering describing the micelles as spheres with a 15 Å radius. However, the fit parameters were not plausible for short amphiphiles that are unlikely to extend to 15 Å. Burkitt *et al.* [14] described the ammonium perfluorooctanoate micelles in $NH_4Cl$:$NH_4OH$ buffer solutions as rod-like with a 10 Å radius and 48 Å length but also commented that they could be modelled as ellipsoids. These parameters correspond well with our data for solutions without any added buffer salts (see Table S3).

Iijima et al. [15] described caesium perfluorooctanoate micelles as oblate rather than prolate ellipsoids although the scattering data and fitted parameters for both models were indistinguishable. However, they determined that the molecules were unlikely to extend to 15.5 Å, instead suggesting a more physically realistic extended chain length of approximately 13 Å. This length was longer than the 10.4 Å described by Tanford [28] for the corresponding hydrocarbon chain. This difference allows for the rigidity and conformation of the perfluorocarbon chains and the carboxyl head group. Kancharla *et al.* [16,19] described sodium and ammonium perfluorooctanoate micelles as core-shell ellipsoids. However, their reported fit parameters suggest that the sodium and ammonium perfluorooctanoate micelles were smaller than observed in the present study. Unfortunately, the parameters of their fits were not clearly presented, making direct comparisons difficult.

In contrast to micelles formed with monovalent cations, magnesium perfluorooctanoate micelles were considerably elongated at 25 °C. This elongation was influenced by both concentration and temperature, with the effect being particularly pronounced for magnesium perfluorooctanoate at lower temperatures and higher concentrations. The molecular packing parameter, $p$, describing the approximate shape of a surfactant molecule plays a crucial role in determining micelle shape and arrangement [13]. It is defined as $p = V / (a\,l)$ where $V$ is the volume of the molecule, $a$ is the headgroup cross-sectional area and $l$ the length of the molecule [13].

A large headgroup area would favour assembly with high curvature such as spherical micelles as it represents a conical shape while molecules that resemble more closely cylinders tend to favour less curved interfaces and thus larger objects or flatter micelles [13]. In general, it is suggested that spherical micelles form when the packing parameter, $p < 1/3$, while ellipsoidal and cylindrical occur when $1/3 < p < 1/2$. In this study magnesium perfluorooctanoate molecules with their rigid fluorocarbon tails tend to pack more densely than those of sodium and ammonium perfluorooctanoate. The headgroups influence the micellar shape also through their interactions with the ions in solution. At lower temperatures, the molecular packing became more ordered and denser.

For magnesium perfluorooctanoate, the packing parameter calculated from the fitted parameters of micelle volume, surface area and radius, was 0.41 at 25 °C (Table S7). As the temperature decreased to 10 °C and the concentration increased, the packing parameter increased to 0.46 indicating slightly denser molecular packing and less curvature of the micelle surface. In comparison, at 100 mmol dm$^{-3}$, sodium perfluorooctanoate had a packing parameter of 0.36, while ammonium perfluorooctanoate had a packing parameter of 0.37 based on the dimensions obtained from the present SAXS data (Table S7). Comparing these values with those calculated with molecular parameters from the literature for sodium perfluorooctanoate and ammonium perfluorooctanoate, the packing parameters were calculated as 0.74 and 0.66 respectively. These used the molecular length from Iijima *et al.* [15]

of 13 Å, the 381 Å$^3$ volume derived from density measurements from fluoroalkane liquids with a carboxyl headgroup [29] and the area of the molecule for sodium and ammonium perfluorooctanoate as 41 Å$^2$ and 45.9 Å$^2$ calculated by Downes *et al.* [30] from interfacial tension measurements. The smaller area of the molecule reported by Downes *et al.* [30] probably arises from the different packing at planar solution/vapour interfaces. In contrast, the present study found the area per perfluorooctanoate molecule to be about 1.7 times larger for micelles where the interface was significantly curved (Table S3).

As reported in Section 3.2 of the results, the micelles have been modelled as cylinders but could also be represented as ellipsoids. A comparison of the scattering data for cylindrical and ellipsoidal micelles showed that both models fitted and their geometries were indistinguishable (Fig. S10). For example, at 100 mmol dm$^{-3}$ magnesium perfluorooctanoate could be fitted as a prolate ellipsoid with 14.5 Å equatorial radius and a cylinder of 14.3 Å radius (Table S4). The corresponding surface areas were 8140 Å$^2$ and 8600 Å$^2$, and the volumes 49,000 Å$^3$ and 52,000 Å$^3$, respectively. The differences were minimal, confirming that both models provided a good description of the micelles. The similarity of these shapes and the molecular assembly is illustrated schematically in Table S4.

This study has shown that increasing concentration and decreasing temperature had analogous effects. For concentrations much higher than the critical micelle concentration, e.g., 150 mmol dm$^{-3}$, and at low temperatures, the length of magnesium perfluorooctanoate micelles increased from 101 to 211 Å (Table S4) on cooling from 25 °C to 10 °C. At 10 °C and 100 mmol dm$^{-3}$, the aggregation number was 110, whereas, at the same concentration at 25 °C the aggregation number was 67 (Table S4). In other studies, for ammonium perfluorononanoate and tetramethylammonium perfluorononanoate at concentrations greater than 10 % by weight, micelles were found to become more elongated leading to the formation of a nematic phase [31]. This phase was characterised by the orientation of micelles as they pack. However, caesium perfluorooctanoate micelles form disc-like micelles as the concentration increased [11]. This change in shape was due to the transition from the nematic phase to a stable lamellar phase driven by interactions between the micelles [11]. In contrast, the fluorinated sulphonic acids (PFSAs) form two distinct phases, a micellar phase that transforms to a lamellar phase as the concentration by weight increases [32]. In the present study, an ordered phase was observed for sodium perfluorooctanoate at 300 mmol dm$^{-3}$ at even though this concentration was below the suggested 10 % by weight (Fig. S5). The packing of the various surfactants to form different aggregates may be related to the density of ionised groups. In this context, it is interesting to observe that the zeta potential for micelles with the $Mg^{2+}$ salt is lower than that for the various monovalent salts and the micellar packing shows less curvature. As seen in Table S4 the area per fluoroalkyl chain is smaller than for the monovalent counter ions. This suggests that further systematic studies of ionisation and hydration of polar groups would be interesting.

Calcium perfluorooctanoate could not be investigated due to the low solubility limit in the present study. Solutions in the range of concentrations from 10 to 50 mmol dm$^{-3}$ could not prepared and heating the solutions from 22 °C up to 60 °C did not improve solubility, suggesting a high Krafft temperature.

Sodium perfluorooctanoate micelles in the presence of 0.5 M NaCl were best modelled as cylinders with a radius of 13 Å and length of 54 Å. This is a significant increase from a length of 34 Å with no added salt. A similar observation was reported in a study of ammonium perfluorooctanoate salt in the presence of 0.5 mol kg$^{-1}$ $NH_4Cl$ [18]. At higher added salt concentrations, the molecules form disc-like micelles indicating a tendency towards a transition from a nematic to a lamellar phase driven by micellar interactions that was also observed for caesium perfluorooctanoate micelles [11].

The shape and size of the micelles is important because the state of aggregation influences the diffusivity and other behaviour in aqueous solutions. Counter-ions also influence the packing of molecules (Fig. 5).

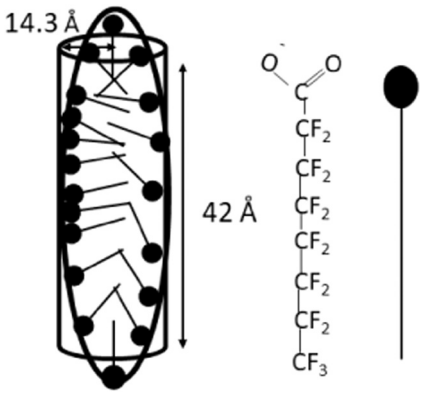


**Fig. 5.** Schematic illustration of the cylinder and prolate ellipsoid models for a micelle of a perfluorooctanoate surfactant.

For example, magnesium perfluorooctanoate has one cation associating with two perfluorooctanoate ions thus modifying the packing parameter causing molecules to pack more densely in less curved assemblies.

## 4. Conclusions

The present study demonstrates how micelle structure and shape in perfluorooctanoate surfactant systems are influenced by different counter-ions, added salt and temperature. The divalent salt ($Mg^{2+}$) had a lower critical micelle concentration than the monovalent salts. Increased concentration altered the micellar size with magnesium perfluorooctanoate micelles becoming more elongated while the micelles of monovalent counter-ions exhibited only a relatively small change of size with increased concentration from 50 to 150 mmol dm$^{-3}$. In contrast, at high concentrations, above 100 mmol dm$^{-3}$, sodium perfluorooctanoate formed an ordered structure that separated into a concentrated phase. This is particularly pronounced at low temperatures. The present study demonstrates that the divalent counter-ion, $Mg^{2+}$, provides more effective screening of electrostatic micellar interactions compared with the monovalent ions ($Li^+$, $Na^+$, $NH_4^+$). The addition of extra salt also decreased the interactions between the micelles by reducing the electrostatic screening length. Temperature further affected the magnesium perfluorooctanoate micelles; at lower temperatures they were twice as long.

PFAS have been detected in surface water at concentrations of 13 μg L$^{-1}$ [33]. Perfluorocarboxylates were the dominant PFAS in the surface water, reaching a concentration of approximately 0.019 μmol L$^{-1}$. Although these concentrations were lower than those in the present study, localized accumulation of these surfactants particularly near sites of active use can result in significantly elevated levels in the environment. In the environment, these surfactants typically interact with salts and minerals so they do not generally exist in the form of acids. The counterions can modify significantly the molecular packing and transport properties.

## CRediT authorship contribution statement

**Lutz Ahrens:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Formal analysis, Conceptualization. **Adrian R. Rennie:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Njelama Sanga:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

## 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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*Supplementary Information*

The supplementary information includes details of experimental procedures and plots of further data as mentioned in the text. Scattering data files are available on request.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2025.137912.

## Data availability

Data will be made available on request.

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