Role of Chain Length and Electrolyte on the Micellization of Anionic Fluorinated Surfactants in Water

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ABSTRACT

The micellization of ionic surfactants in aqueous media reflects a balance between the hydrophobic attraction of surfactant tails and the electrostatic repulsion of surfactant headgroups. We investigate here the effect on surfactant micellization of the hydrophobic chain length and electrolyte composition, by focusing on the fluorinated surfactants sodium perfluorohexanoate (NaPFHx) and sodium perfluorooctanoate (NaPFO) in aqueous solution without/with NaCl, and analyzing experimental data from surface tension, pyrene fluorescence, small-angle neutron scattering (SANS), and viscosity techniques. The CMC of NaPFHx in water was 200 mM, much higher than that of NaPFO, 30 mM, due to the additional two -CF_2- groups of the latter. Upon addition of 0.25 M NaCl to the aqueous solution, the CMC of NaPFHx and NaPFO decreased by about 50% and 80%, respectively. The NaPFHx and NaPFO micelles are both ellipsoid in shape. NaPFHx forms smaller micelles compared to NaPFO: the association number for NaPFHx in D_2O was 15 compared to 25 for NaPFO. Upon NaCl addition, the micelle shape became more elongated. This is the first report on the NaPFHx micelle structure. The information presented here supports the re-formulation and replacement of long-chain fluorinated surfactants with relatively safer long-chain surfactants.

KEYWORDS: PFAS, perfluoroalkyl carboxylates, small-angle scattering, self-assembly, formulations

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INTRODUCTION

The self-assembly of surfactants in aqueous media results from a balance between the hydrophobic "attraction" of tails and the repulsion of headgroups which, in the case of ionic surfactants, is due to electrostatic interactions. The presence of other ions (counterions or additional salt) in the aqueous media reduces the electrostatic repulsion between the headgroups of ionic surfactants, and thus favors the formation of micelles.[1] The critical micelle concentration (CMC) of ionic surfactants decreases by a factor of four when the valency of inorganic counterions increases from one to two, whereas organic counterions (such as tetramethylammonium, TMA^+)[2] decrease the CMC compared to inorganic counterions.[1, 3, 4] Furthermore, adding one -CH_2- group to the surfactant alkyl chain decreases the CMC by a factor of about two in the case of ionic surfactants in water with no added salt.[1, 5, 6]

In fluorinated surfactants, fluorine atoms replace hydrogen atoms in the alkyl chain. The fluoroalkyl chains are bulkier than hydrogenated ones due to the significantly larger size of the fluorine atom compared to the hydrogen atom.[7, 8] The more electronegative fluorine atom makes fluorinated surfactants repel hydrocarbons, in addition to repelling water.[9] Due to the low polarizability of fluorine, van der Waals interactions between fluorinated chains are weak, resulting in their very low surface tensions, high fluidities, low dielectric constants, high vapor pressures, high compressibilities, and high gas solubilities.[7, 10, 11] Perfluorination of the surfactant alkyl chain leads to a drastic decrease of the CMC by about one or two orders of magnitude.[1] Cylindrical and discoid micelles with smaller association number and higher degree of dissociation have been reported for fluorinated surfactants of six to eight carbon atoms.[12, 13]

On the basis of their unique physicochemical properties, fluorinated surfactants are useful for several applications including polymer manufacturing, textiles, paper packaging, leveling agents for paints, mist suppression, lubricants, firefighting foams, and biomedical imaging.[4, 14, 15] At the same time, fluorinated compounds can be deleterious to health, leading to, e.g., weight loss, liver enlargement, disturbance of lipid metabolism, as well as cancer in organs such as liver, pancreas, and testis.[16] Moreover, fluorinated surfactants are extremely resistant to degradation, bioaccumulate in food chains, and have long half-lives in humans.[16-21] More than 3000 per- and polyfluoroalkyl substances (PFAS) have been identified on the global market, many of which are fluorinated surfactants that have been recently introduced to replace legacy fluorosurfactants that had been banned.[19] Due to inadequate knowledge of the physicochemical properties of PFAS surfactants present in new and old formulations, the removal of these compounds from the environment is challenging.[17]

PFAS surfactants having C_8-C_{14} chains and their sodium and ammonium salts are listed as regulatory substances in the European Union due to their persistent and bioaccumulative nature. In response, manufacturers have introduced short-chain and ultra-short-chain PFAS as safer alternatives to long-chain substances.[20] Data submitted to regulatory authorities and from published studies show that short-chain PFAS are eliminated more rapidly from the body and are less toxic than long-chain PFAS.[22-24] Some studies[25] have shown that the general human population exposures to short-chain PFAS such as perflurohexanoic acid (PFHxA) are low and the margin of safety for PFHxA is high. In terms of relative potency, PFHxA is approximately four orders of magnitude less toxic than perfluorooctanoic acid (PFOA).[25] However, short-chain PFAS surfactants can have lower performance than long-chain surfactants.[20] To protect the environment from the detrimental effects of non-biodegradable long-chain (>C_6) fluorosurfacants, safer alternatives must be designed. The self-assembly properties of fluorinated surfactants could be modulated through changing the fluorocarbon chain chemistry and length.[26] Further research is needed to understand the PFAS surfactant sorption, transport, and bioaccumulation behavior as affected by the hydrophobic chain length and the presence of salt in water.[19] The study of perfluorinated surfactant self-assembly will provide information on properties (including CMC, surface tension, adsorption, etc.) in different solution conditions, which could lead to the replacement of long-chain fluorosurfactants with relatively safer and still effective short-chain molecules.

In this work, we address the effects of the fluorocarbon chain length on fluorinated surfactant micellization in water, and also effects of added salt on the micelle formation and structure for fluorinated surfactants with varied chain lengths. Specifically, we investigate sodium perfluorohexanoate (NaPFHx) and sodium perfluorooctanoate (NaPFO) in aqueous solutions without and with added NaCl. Surface tension, small angle neutron scattering (SANS), pyrene fluorescence spectroscopy, and viscosity measurements have been utilized to probe the micelle formation and structure. Surface tension data were used to estimate the CMC, maximum surface excess concentration, $\Gamma_{\max}$, minimum area occupied by a surfactant molecule (A_{min}) at the air/liquid interface, as well as surfactant critical packing parameter (CPP). Pyrene fluorescence data were used to obtain the CMC and the free energy of micellization (ΔG_{mic}) in aqueous solution without or with salt. Analysis of SANS data provided the association number, shape and size of NaPFHx and NaPFO micelles. The shape, size, volume fraction and hydration of micelles were obtained from the analysis of relative viscosity (η_r) data.

This is the first report on the NaPFHx micelle structure. The micellization of NaPFO was previously studied by conductivity, surface tension, fluorescence, and viscosity.[27] Alkyl chain length effects on heat capacities, surface tension and viscosities have been discussed for sodium perfluoroalkyl carboxylates including NaPFO but not NaPFHx.[11] Limited literature is available on the effect of salts on the self-assembly of fluorinated surfactants in water.[3, 8, 12, 28, 29] No literature is available on the effect of salts on the self-assembly of NaPFHx in water. The effect of added salt on the NaPFO micelle structure has not been previously reported.

MATERIALS AND METHODS

Materials

Sodium perfluorohexanoate (NaPFHx) ($C_5F_{11}COONa$, CAS number: 2923-26-4, MW=336.04 g/mol), also known as sodium undecafluorohexanoate or undecafluorohexanoic acid sodium salt, was obtained from SynQuest Laboratories (98% purity). Sodium perfluorooctanoate (NaPFO), ($C_7F_{15}COONa$, CAS number: 335-95-5, MW=436.05 g/mol), also known as sodium pentadecafluorooctanoate or pentadeca-perfluorooctanoic acid, sodium salt, or sodium perfluoro-n-octanoate, was obtained from SynQuest Laboratories (97% purity). Sodium chloride (NaCl), ≥ 99% pure, was obtained from EMD Chemicals Inc. Deuterium oxide (D, 99.9%), (D_2O, MW = 20.03 g/mol) was obtained from Cambridge Isotope Laboratories, Inc. (99.5% purity). All samples, except those for SANS, were prepared using milli-Q water. Samples for SANS were prepared using deuterated water. Sufficient equilibration time was allowed following mixing.

NaPFHx and NaPFO that comprise fluorocarbon chains with 5 and 7 carbon atoms, respectively, and NaCl, the most abundant salt on earth, are used here to study chain-length and salt effects. To decide on the salt concentration used in this study, we tested the miscibility of NaPFHx and NaPFO in aqueous solutions at 20 °C in the presence of NaCl, by dilution from higher salt concentration to lower, until the surfactant became completely miscible. Both NaPFHx and NaPFO are soluble at 0.25 M NaCl, but the solubility of NaPFO in aqueous 0.25 M NaCl solution was limited to 30 mM surfactant (Figure S1 in Supplementary Information).

Surface tension

The surface tension was measured by the Wilhelmy plate method using a Kruss model K100 tensiometer with an accuracy of ≤ 0.5%. Following the addition of surfactant molecules to an aqueous solution, the surface tension (γ) decreases and reaches an almost constant value above the CMC.[30, 31] For monovalent surfactant ion and counterion in aqueous solution in the presence of the electrolytes, the maximum surface excess concentration $\Gamma_{\max}$, the minimum area occupied by a surfactant molecule (A_{min}) at the air/liquid interface, and the critical packing parameter (CPP) are given by:[30, 32-34]

$$\Gamma_{max} = -\frac{1}{2.303RT}\left(\frac{1}{1+(c_0/(c_0+c_e))}\right)\left(\frac{d\gamma}{dlogC}\right)_{T,P} \tag{1}$$

$$A_{min} = \frac{1}{N\Gamma_{max}} \tag{2}$$

$$CPP = \frac{V_0}{A_{min}l_c} \tag{3}$$

where c_0 CMC in the presence of electrolyte (mM), c_e electrolyte concentration (mM), R universal gas constant (8.314 J mol^{-1} K^{-1}), T absolute temperature, N Avogadro number, V_0 volume and l_c extended length of the surfactant hydrophobic chain (refer to SI for details).[1, 34, 35] Our system meets all the conditions under which equation (1) has been derived: both surfactant and salt are strong electrolytes and have the same counterion, and the solutions are dilute. Perfluoroalkane carboxylic acids are considered as strong acids since equivalent conductance and potentiometric titration experiments have shown that they are completely dissociated in water.[36, 37] The dissociation constants of perfluoroalkanoic acids (from perfluoropropanoic to perfluorododecanoic acid) reported in the literature ranged from pK_a = 0.32 to 3.13.[36, 38]

Micropolarity

The micropolarity of aqueous surfactant solutions is probed using pyrene fluorescence spectroscopy. Pyrene fluorescence emission spectra were recorded using a Hitachi model F-2500 fluorescence spectrophotometer in the wavelength range of 340–460 nm and excitation wavelength of λ=335 nm. The intensity ratios of the first and the third vibronic peaks (I1/I3) of the pyrene emission spectrum depend strongly on the polarity experienced by pyrene.[30, 31, 39-41] The CMC values are obtained from the change in I1/I3 ratios with surfactant concentration (refer to SI for details).[30, 31, 39]

Small-angle neutron scattering (SANS)

Aqueous surfactant solutions can be characterized using SANS to determine the surfactant micelle structure.[31, 42-47] For this study, SANS measurements of aqueous surfactant solutions were performed on the NG-7 and NG-B 30 m SANS instrument at the Center for Neutron Research (NCNR), National Institute of Standards and Technology (NIST), Gaithersburg, MD (refer to SI for information on SANS data collection and reduction).

SANS data from NaPFHx and NaPFO micelles in D_2O have been fitted with the core-shell ellipsoid form factor and the Hayter–Penfold structure factor with rescaled mean spherical approximation (RMSA),[45] considering the micelle core to comprise of only fluorocarbon chains (dry core), and the micelle shell to include carboxylate headgroups, counterions, and associated water molecules.[46] The expressions describing the form factor and structure factor models, and the micelle structure/composition are presented in detail in SI.

The micelle core volume V_{core} (in Å^3) is calculated from the surfactant association number N_{agg} and the volume of the perfluroalkyl carboxylate fluorocarbon chain ($V_{t,NaPFHx}$ = 250.4 Å^3 and $V_{t,NaPFO}$ = 333.6 Å^3), using $V_{core} = \frac{4}{3}\pi ab^2 = N_{agg}V_t$, where a is the major and b is the minor radius of the ellipsoid micelle core. The micelle shell volume V_{shell} (in Å^3) is calculated from the volume contributions of the surfactant hydrophilic headgroups, counterions, and associated water molecules, using $V_{shell} = N_{agg}\left(V_{COO^-} + (1-\alpha)V_{Na^+} + N_H V_{D_2O}\right)$, where V_{COO^-} is the volume of the carboxylate headgroup, V_{Na^+} volume of the Na^+ counterion, α = Z/N_{agg} is the fractional charge on a micelle, V_{D_2O} volume of a D_2O molecule, and N_H is the hydration number of a surfactant molecule. Scattering length densities of the micelle core ρ_{core} or the micelle shell ρ_{shell} are calculated from the scattering length contributions of the groups/atoms present in the micelle core or shell, and the volumes of the micelle core V_{core} or the shell V_{shell}, respectively. The scattering length density of the solvent $\rho_{solvent}$ was calculated using the scattering lengths and concentrations of deuterated water, surfactant and any salt present.

The key assumptions in analyzing the SANS data are that the micelle core minor radius (b) is equal to the extended length of the surfactant fluorocarbon chain, the ratio of shell thickness at pole to that at the equator ϵ = 1 (uniform shell thickness), and the number of water molecules hydrating (N_H) NaPFO = 14 and for NaPFHx = 10. The main parameters resulting from the fit to the SANS data are the micelle association number (N_{agg}), charge on a micelle (Z), and micelle volume fraction (φ). Please refer to SI for details.

Viscosity

A Cannon-Fenske capillary viscometer (size 50) was used to measure the viscosity of aqueous surfactant solutions. The relative viscosity ($\eta_r = \eta/\eta_o$) of the solution is obtained from the ratio of the kinematic viscosity of the solution (η) (calculated by multiplying the efflux time with the viscometer calibration constant provided by the manufacturer, Cannon Instrument Co, State College, PA) and the kinematic viscosity of the pure solvent (η_o). The relative viscosity (η_r) of a micellar solution is related to the micelle size, shape volume fraction (φ) and hydration,[27, 48] and can be expressed as:[30, 49, 50]

$$\eta_r = 1 + \nu\phi + k_1(\nu\phi)^2 + O(\phi)^3 \tag{4}$$

where ν is a shape factor representing the micelle shape and $\phi = V_s^{hyd}(c_s - c_1)$, is the volume fraction of micelles including the water of hydration, where V_s^{hyd} is the hydrated volume of a surfactant molecule, c_s, c_1 are the total surfactant concentration and unassociated surfactant concentration (CMC), respectively (refer to SI for further information).[50]

RESULTS AND DISCUSSION

Aqueous solution properties of the surfactants sodium perfluorohexanoate (NaPFHx) and sodium perfluorooctanoate (NaPFO) have been studied in the absence or presence of NaCl using surface tension, pyrene fluorescence spectroscopy, small-angle neutron scattering, and viscosity measurements. The adsorption and micellization behavior NaPFHx and NaPFO have been assessed by surface tension, and the polarity of the micellar microenvironment by pyrene fluorescence. The micelle size, shape, and hydration were determined by SANS and viscosity.

Interfacial Properties and Micelle Formation

Surface tension data of NaPFHx or NaPFO in aqueous solution in the absence and in the presence of 0.25 M NaCl are plotted in Figure 1 as a function of surfactant concentration. Various properties obtained from analysis of surface tension data are reported in Table 1. The temperature dependence of the CMC for the surfactants of interest to this study is rather weak. For example, for a 5 °C change in temperature, the CMC of NaPFO changed by only 1 mM.[51]

Table 1. *Solution and surface properties of NaPFHx and NaPFO: CMC, maximum surface excess concentration (Γ_{max}), minimum area occupied by a surfactant molecule (A_{min}) at the air/liquid interface, critical packing parameter (CPP), and surface tension (ST) at the CMC.*

Surfactant	NaCl (M)	Temperature (°C)	CMC (mM)	$\Gamma_{\max}$ x 10^{26} (mol/Å^2)	A_{min} (Å^2)	CPP	ST at CMC (mN/m)
NaPFHx	0	21	200 (±2)	2.62 (±0.1)	63.4 (±2.6)	0.46 (±0.02)	28.9 (±0.08)
NaPFHx	0.25	25	100 (±3)	2.89 (±0.2)	57.3 (±3.4)	0.51 (±0.03)	25.7 (±0.08)
NaPFO	0	20	30	2.80 (±0.1)	59.4 (±1.8)	0.50 (±0.02)	25.5
NaPFO	0.25	25	5 (±0.2)	3.36 (±0.2)	49.5 (±3.0)	0.60 (±0.03)	19.1 (±0.09)

For both surfactants, the surface tension value attained at the CMC (Table 1) is lower in the presence of NaCl, suggesting a greater adsorption of the ionic surfactant at the air/water interface. The maximum surface excess concentration $\Gamma_{\max}$ increased and the minimum area occupied by a surfactant molecule A_{min} decreased with the addition of salt for both surfactant systems. For NaPFHx in water, addition of 0.25 M NaCl increased $\Gamma_{\max}$ by 10% and decreased A_{min} by 10%, while for NaPFO, addition of NaCl increased $\Gamma_{\max}$ by 20% and decreased A_{min} by 17%. In agreement with these results, a neutron reflection study on ammonium PFO found that addition of 0.20 M NH_4Cl increased $\Gamma_{\max}$ by 30% and decreased A_{min} by 23%.[29]

The critical packing parameter (CPP) of both NaPFHx and NaPFO increased upon salt addition, suggesting more elongated micelles in the presence of salt compared to plain water. In general, the shape of surfactant micelles changes from sphere to elongated and, further on, to lamellar with the addition of salt.[1] For example, a sphere-to-rod transition occurs at 25 °C for sodium dodecyl sulfate (SDS) micelles in aqueous solution when the concentration of NaCl reaches 0.45 M,[32, 52] allowing SDS micelles to grow with an increased association number.[53-55] The addition of salt in aqueous surfactant solution decreases the difference between interfacial and bulk ion concentrations and, consequently, decreases the entropy loss from counterion binding, favoring micelle formation and lowering the CMC.[1] Further, this allows closer packing of the surfactant headgroups in the micelle shell, resulting in lower effective area per surfactant headgroup.[1] Hence, A_{min} decreases and CPP increases upon salt addition.

Pyrene fluorescence intensity I_1/I_3 ratio values for NaPFHx or NaPFO aqueous solutions in the absence and in the presence of 0.25 M NaCl are plotted as a function of surfactant concentration in Figure 2. The I_1/I_3 ratios at surfactant concentrations above the CMC of both NaPFHx and NaPFO in aqueous 0.25 M NaCl solution are lower compared to the I_1/I_3 ratios of NaPFHx and NaPFO in plain water. At a certain surfactant concentration, the micelles in the presence of 0.25 M NaCl have smaller surface area per headgroup and greater CPP compared to the case with plain water, suggesting greater association number and, therefore, surfactant molecules are closely packed in micelles in the presence of salt, affording a more hydrophobic environment for pyrene. This could be the reason for lower I_1/I_3 values in presence of salt. The CMC values of NaPFHx or NaPFO obtained from pyrene I1/I3 data in water in the absence and in the presence of 0.25 M NaCl are consistent with those obtained from surface tension. Above the CMC, fluorinated surfactants generally exhibit higher pyrene I_1/I_3 ratio than their hydrocarbon analogues.[56, 57] The value of I_1/I_3 is related to the density of packing, degree of water penetration and the location of solubilized pyrene in the micelles. The bulkiness and rigidity of fluorocarbon chains induce smaller association numbers and allow relatively more water to come in contact with the micelle interior, consistent with higher pyrene I_1/I_3 ratio.[30, 57] Higher I_1/I_3 ratios in fluorinated surfactants were also ascribed to the lower solubility of pyrene in fluorinated surfactant micelles due to the lipophobic nature of the fluorocarbon chains.[58] Pyrene had a higher binding coefficient K and K/N_{agg} ratio in perfluorinated surfactants than hydrocarbon surfactants, due to the stronger hydrophobicity of the perfluorinated tail.[6]

Figure 3 shows the relative viscosity of aqueous solutions of NaPFHx or NaPFO in the absence and in the presence of 0.25 M NaCl, plotted as a function of the total surfactant concentration in the solution. The concentrations where the viscosity slope changes (indicated by the intersection of straight lines fitted to data below and above the concentration where the slope changes) are in good agreement with the CMC values obtained from surface tension. The relative viscosity of NaPFO solutions in the presence of salt is greater compared to that of plain water at a given surfactant concentration (Figure 3b), whereas for NaPFHx solutions there is no big difference in the relative viscosities in the absence and in the presence of salt (Figure 3a). Below the CMC, the relative viscosity η_r of NaPFHx and NaPFO in plain water can decrease due to the effect of the unmicellized monomer disrupting the structure of water.[27]

The CMC values of NaPFHx (200 mM) or NaPFO (30 mM) in aqueous solution in the absence of salt are in agreement with CMC values reported in the literature.[5] The tendency of NaPFO toward micellization is higher than NaPFHx because NaPFO has a longer fluorocarbon chain. The CMC of NaPFHx and NaPFO decreased by 50% and 80%, respectively, in the presence of 0.25 M NaCl. The addition of salt facilitated the micellization of fluorinated surfactants due to the screening of electrostatic repulsion of the surfactant headgroups. The decrease in the CMC due to 0.25 M NaCl is greater in NaPFO (80% decrease) compared to NaPFHx (50% decrease). The decrease in A_{min} and the increase in $\Gamma_{\max}$ upon 0.25 M NaCl addition were also greater in NaPFO (17%, 20%) than NaPFHx (10%, 10%). The stronger salt effect observed in NaPFO compared to NaPFHx is discussed in the section "Micellization Thermodynamics" on the basis of the various contributions to the free energy of micellization.

Rather limited literature is available on the effect of salts on the micellization of fluorinated surfactants in water.[3, 8, 12, 28, 29] The CMC values of ammonium PFO (APFO), NaPFO, lithium perfluorooctanoate (LiPFO) trimethylammonium perfluorooctanoate (TMHPFO) and triethylammonium perfluorooctanoate (TEHPFO) in aqueous solutions with different concentrations of added NaCl are summarized in Table 2.[8, 12, 28, 29] The CMC of NaPFO decreased by 47% with the addition of 0.1 M NaCl, and the CMC of LiPFO decreased by 92% with the addition of 1 M LiCl.[3] The CMC of APFO decreased by 48%, 75%, and 76 % with the addition of 0.1, 0.3, and 0.5 M NaCl, and by 44%, 61%, and 75 % with the addition of 0.05, 0.1, and 0.2 M NH_4Cl, respectively. For the same salt molar concentrations, the decrease in the CMC of APFO is higher in the case of NH_4Cl (same counterion) compared to NaCl. For TMHPFO and TEHPFO, the CMC decreased to a small extent (16%, 7%) when the concentration of NaCl was low (0.1 M) but, when the NaCl concentration was larger (0.3 M, 0.5 M), the CMC increased, which the authors attributed to ion exchange between Na^+ and $N(CH_3)_3^+$ or $N(CH_2CH_3)_3^+$.[28] The CMC of the hydrocarbon surfactant SDS decreased by 90% and A_{min} decreased by 27% upon addition of 0.25 M NaCl.[32] The relative decrease in the CMC or A_{min} of SDS with salt addition is slightly higher than that of NaPFO, but much higher than that of NaPFHx. This could be ascribed to the longer hydrocarbon chain of SDS.

***Table 2**. CMC values (in mM) of fluorinated surfactants and of SDS in aqueous solutions in the presence of added NaCl at various concentrations at 25 °C.[8, 28, 29, 53]*

NaCl	APFO	NaPFO	TMHPFO	TEHPFO	SDS
0 M	27.3, 26	31.2	7.3	7.2	8.1
0.05 M	20.4	-	-	-	2.3
0.1 M	14.3, 16.0	16.6	6.1	6.7	1.49
0.2 M	10.7	-	-	-	0.94
0.3 M	6.9	-	8.0	9.4	0.83
0.5 M	6.5	-	11.1	5.2	0.52

Micellization Thermodynamics

In this section, we determine the free-energy contributions that give rise to the chain length and salt effects reported in the previous section, on the basis of an analysis of the various free-energy contributions associated with micelle formation by NaPFHx and NaPFO. Our study also reports on the effect of chain length on the micellization of perfluoroalkyl carboxylates in the presence of salts, which had not previously reported. Further, the calculation and analysis of the various contributions to the free energy of micellization had not been previously reported for aqueous salt solutions of perfluoroalkyl carboxylates. The Gibbs free energy of micellization (ΔG_{mic}) is the net free-energy gain for transferring a free surfactant molecule and its counterion from the bulk aqueous solution to a micelle. For ionic surfactants, ΔG_{mic} is related to the CMC by the following equation (5)[51]

$$\Delta G_{mic} = (2-\alpha)RTlnX_{CMC} \quad (5)$$

where X_{CMC} is the surfactant mole fraction at the CMC, and α the degree of counterion dissociation. α values for NaPFHx (α = 0.68) and NaPFO (α = 0.54) aqueous micellar solutions in the absence of NaCl are taken from reference.[5] α values for NaPFHx and NaPFO aqueous micellar solutions in the presence of NaCl are calculated using the Corrin–Harkins equation:[32]

$$lnX_{CMC} = A - \beta lnX_C \quad (6)$$

where X_C is the total concentration of free counterion in the solution at the CMC in mole fraction units, and β = (1-α) is the degree of counterion binding. In the absence of NaCl, X_{CMC} equals X_C and A = (1+β)lnX_{CMC} = $\Delta G_{mic}/RT$. Since we know the ΔG_{mic} values in the absence of NaCl, the constant A can be calculated from the previous equation, and then used in calculating β=(1-α) values for NaPFHx and NaPFO aqueous solutions in the presence of 0.25 M NaCl. α values obtained from this calculation are reported in Table 3 together with the corresponding ΔG_{mic} values. For both NaPFHx and NaPFO, ΔG_{mic} becomes more negative with salt addition.

Table 3. *Free energy of micellization (ΔG_{mic}) and contributions to ΔG_{mic} [transfer free energy (ΔG_{tr}), interfacial free energy (ΔG_{int}), packing free energy (ΔG_{pack}), steric free energy (ΔG_{st}), electrostatic free energy ($\Delta G_{elec} = \Delta G_{dis} + W_{elec}$), and entropic free energy (ΔG_{ent})] for NaPFHx and NaPFO in water and in 0.25 M NaCl aqueous solution.*

	NaCl (M)	CMC (mM)	α	ΔG_{mic}	ΔG_{tr}	ΔG_{int}	ΔG_{pack}
NaPFHx	0	200	0.68[5]	-17.9	-34.4	9.6	7.3
NaPFHx	0.25	100	0.79	-18.9	-34.9	7.8	7.4
NaPFO	0	30	0.54[5]	-26.8	-45.4	8.4	5.8
NaPFO	0.25	5	0.68	-30.3	-46.2	5.6	5.9
	NaCl (M)	ΔG_{st}	ΔG_{dis}	W_{elec}	ΔG_{elec}	ΔG_{ent}	$-\beta kTln(X_ce)$
NaPFHx	0	2.0	-3.1	-2.3	-5.4	1.8	3.5
NaPFHx	0.25	2.0	-2.6	0.3	-2.3	1.4	2.1
NaPFO	0	2.7	-4.3	-1.2	-5.5	2.2	7.4
NaPFO	0.25	3.0	-3.0	1.6	-1.4	1.8	3.4

All ΔG values are reported in kJ/mol units; α: degree of counterion dissociation; β = (1- α): degree of counterion binding; X_c: mole fraction of counterions in the bulk aqueous solution; e: exponential constant 2.718

In order to decouple the hydrophobic and electrostatic/headgroup contributions to ΔG_{mic}, we considered the molecular thermodynamic framework developed by Blankschtein and co-workers.[13] ΔG_{mic} includes contributions of both the micelle core containing the surfactant tails, and the micelle shell containing headgroups and the bound counterions. ΔG_{mic} is given by:

$$\Delta G_{mic} = \Delta G_{tr} + \Delta G_{int} + \Delta G_{pack} + \Delta G_{st} + \Delta G_{elec} + \Delta G_{ent} - \beta kTln(X_c e) - kT \quad (7)$$

where k is the Boltzmann constant. The contributions to the overall free energy from the transfer free energy (ΔG_{tr}), interfacial free energy (ΔG_{int}), and packing free energy (ΔG_{pack}) are associated with the formation of the micelle hydrophobic core. The steric free energy (ΔG_{st}), electrostatic free energy (ΔG_{elec}), and entropic free energy (ΔG_{ent}) represent free energy contributions related to the formation of the micelle hydrated shell.[13] The term $-\beta kT\ln(X_c e)$ reflects the translational entropy lost by the counterions upon binding onto the micelle charged surface.[13]

The transfer free energy, ΔG_{tr}, is given by:[13]

$$\Delta G_{tr} = [-2.30(n_c - 1) - 2.55]kT \tag{8}$$

where (n_c-1) is the number of carbon atoms in the fluorocarbon tail of the surfactant. ΔG_{tr} is more negative for NaPFO compared to NaPFHx due to greater chain length, and ΔG_{tr} does not change in the presence of salt (Table 3). The CMC values of both fluorinated and hydrogenated surfactants decrease as the carbon number of the surfactant tail increases. Figure 4 shows that lnCMC varies linearly with n_c for two surfactant series (sodium perfluoroalkyl carboxylates, $C_nF_{2n-1}COONa$ and sodium alkyl sulfates, $C_nH_{2n+1}OSO_3Na$). This linearity of lnCMC vs. n_c arises primarily from the transfer free energy ΔG_{tr} contribution.

The interfacial free energy, ΔG_{int}, is determined by the following equation:[13]

$$\Delta G_{int} = \sigma_s \left(a - a_{o,s}\right) \tag{9}$$

where σ_s is the micelle core-water interfacial tension, a interfacial area per surfactant molecule, and $a_{o,s}$ interfacial area per surfactant molecule screened from contact with the aqueous solvent due to the physical connection of the surfactant tail to the surfactant head. a depends on the micelle geometry and is determined by:[13]

$$a = \frac{SV_t}{l_c} \tag{10}$$

where S is a shape factor (3 for spheres, 2 for infinite sized cylinders, and 1 for infinite-sized disks or bilayers), V_t surfactant tail molecular volume, and l_c micelle core minor radius. ΔG_{int} values (Table 3) for NaPFHx and NaPFO are estimated from the σ_s and $a_{o,s}$ values given in reference.[13] For the ΔG_{int} calculation, we considered the interfacial area per surfactant molecule a values to be equal to the A_{min} values obtained from surface tension. ΔG_{int} for NaPFHx is slightly higher than ΔG_{int} for NaPFO. In the presence of salt, ΔG_{int} decreases for both NaPFHx and NaPFO.

The packing free energy (ΔG_{pack}) is the free energy change per surfactant molecule related to the constrained arrangement of the surfactant tails inside the micelle core. For spherical micelles, the chain is in a less confined state as l_c increases, and ΔG_{pack} decreases.[13] The ΔG_{pack} values for NaPFHx and NaPFO were taken from Figure 3 of reference[13] for spherical micelles. ΔG_{pack} is higher for NaPFHx compared to NaPFO due to the shorter fluorocarbon chain length in the micelle core. The penalty involved in the confinement of the chain within the micelle core for spherical micelles is higher for shorter fluorocarbon chains.[13]

The steric free energy, ΔG_{st}, associated with steric repulsions between the surfactant headgroups and the counterions bound at the micelle surface of charge is determined by:[13]

$$\Delta G_{st} = -kT(1+\beta)\ln\left(1 - \frac{a_{h,s} + \beta a_{h,c}}{a}\right) \tag{11}$$

where $a_{h,s}$ and $a_{h,c}$ are the effective cross-sectional areas of the surfactant headgroup and of the counterion, respectively. The $a_{h,s}$ and $a_{h,c}$ values are estimated from the hydrated radii of surfactant headgroup and counterion.[13]

The entropic free energy (ΔG_{ent}) originates from mixing the surfactant headgroups and the counterions bound at the micelle surface of charge, and is given by:[13]

$$\Delta G_{ent} = -kT\, ln\left(\frac{1}{1+\beta}\right) - \beta kT\, ln\left(\frac{\beta}{1+\beta}\right) \tag{12}$$

For both NaPFHx and NaPFO, counterion binding decreases in the presence of salt. As a result, the ΔG_{ent} contributions to ΔG_{mic} decrease for both surfactants (Table 3).

The electrostatic free energy, ΔG_{elec}, related to the electrostatic repulsions between the surfactant ionic headgroups at the micelle surface, is determined by:[13]

$$\Delta G_{elec} = \Delta G_{dis} + \int_0^{qf} \varphi_0(q)\, dq \tag{13}$$

where ΔG_{dis} is the electrostatic self-atmosphere energy[13] released by the surfactants and the counterions when they are discharged in the bulk aqueous solution and assembled to form an initially neutral micelle surface. $\Delta G_{dis} = \Delta G_{dis,s} + \beta\Delta G_{dis,c}$, where $\Delta G_{dis,i}$ represents the electrostatic self-energy released by species i (i = surfactant, s, and i = counterion, c).[7] $\Delta G_{dis,i}$ is given by:[7]

$$\Delta G_{dis,i} = -\frac{z_i^2 e_0^2}{2\epsilon_b r_{h,i}(1+\kappa r_{h,i})} \tag{14}$$

where e_0 is the electronic charge, z_i valence, $\epsilon_b = 4\pi\epsilon_r\epsilon_0$ (ϵ_0 dielectric permittivity of vacuum, ϵ_r dielectric constant of water), and $r_{h,i}$ the hydrated radius of ionic species i in the bulk aqueous solvent. $\kappa = (8\pi e_0^2 I/\epsilon_b kT)^{1/2}$ is the inverse of the Debye screening length of this ionic aqueous solution, where I denotes the solution ionic strength.[7] κ values calculated for NaPFO + water, NaPFO + 0.25 M NaCl, NaPFHx + water, NaPFHx + 0.25 M NaCl are 0.057 Å^{-1}, 0.164 Å^{-1}, 0.146 Å^{-1}, and 0.192 Å^{-1}, respectively. ΔG_{dis} values for NaPFHx and NaPFO increased by 17% and 30%, respectively, in 0.25 M NaCl compared to the case of plain water.

The second term in eq 13 represents the work (W_{elec}) done in recharging the discharged ions (surfactant headgroups and bound counterions) on the micelle surface of charge, which leads to the formation of a charged micelle surface and the accompanying formation of the diffuse counterion cloud which balances the charge of the bare micelle.[13] The calculation of W_{elec} requires solution of the Poisson-Boltzmann equation which is beyond the scope of this work, hence we obtained W_{elec} values by subtracting all the known terms in eq 7 from ΔG_{mic}.

Comparing the free energy contributions associated with the formation of the micelle hydrophobic core between the two surfactants considered here, NaPFHx and NaPFO, in plain water, the ΔG_{tr}, ΔG_{int}, and ΔG_{pack} terms decreased by 32%, 12%, and 20%, respectively, with the increase in 2 -CF_2- groups in the hydrophobic part of the surfactant. Whereas, the free energy contributions associated with the formation of the micelle hydrated interfacial shell, ΔG_{st}, and ΔG_{ent} increased by 35% and 22%, respectively, while ΔG_{elec} did not change much. The ΔG_{st} and ΔG_{ent} contributions to ΔG_{mic} are much lower compared to the ΔG_{tr}, ΔG_{int}, and ΔG_{pack} contributions. The ΔG values presented in Table 3 clearly show that the chain length effects are mainly due to the free energy contributions associated with the formation of the micelle core, primarily ΔG_{tr}. ΔG_{tr} is more negative for fluorocarbon tails than for hydrocarbon tails with the same number of carbon atoms (ΔG_{tr} = -23.3 kJ/mol for n_c = 6 and ΔG_{tr} = -30.5 kJ/mol for n_c = 8).[13] This greater hydrophobicity of the fluorocarbon tails is the reason for the lower CMC of a fluorocarbon surfactant having the same carbon chain length, polar headgroup and counterion as a hydrocarbon surfactant.

Addition of salt did not change ΔG_{tr}, however ΔG_{int} and ΔG_{ent} decreased by 19% and 22% for NaPFHx, and by 33% and 18% for NaPFO, respectively. ΔG_{st} increased by 11% for NaPFO with the addition of salt, while it remained the same for NaPFHx. ΔG_{elec} increased by 57% and 75% for NaPFHx and NaPFO, respectively, with salt addition, while the entropy lost by the counterions upon binding onto the charged micelle surface ($-\beta kT\ln(X_c e)$) decreased by 40% and 54%, respectively. On the basis of these ΔG values, we can conclude that the ΔG_{elec} contribution and the entropy lost by counterions are the main reasons for the salt effects.

The change in the ΔG_{elec} term of NaPFO with salt addition is greater (75%) compared to that of NaPFHx (57%). The decrease in the entropy loss with the addition of salt is also greater for NaPFO (54%) compared to NaPFHx (40%). The ΔG_{elec} contribution and the entropy lost by the counterions upon binding to the micelle surface are the reasons for the stronger salt effect observed in NaPFO compared to NaPFHx.

Micelle Structure

The chain length effect is discussed in this section in the context of the micelle size and shape of fluorinated surfactants in aqueous solution. Previously published papers[5, 59] have reported the alkyl chain length dependence on the CMC and the free energy of micellization of perfluoroalkyl carboxylates, however, the effect of chain length on the micelle structure of perfluoroalkyl carboxylates has not been previously reported. The SANS absolute intensity profiles of NaPFHx and NaPFO in D_2O are shown in Figure 5. The correlation peak reflects repulsive interactions between charged micelles. At 110 mM NaPFHx (which is below its CMC), the scattering is almost flat, suggesting no micelles present in the solution. The intermicelle distance d can be estimated from the q value at the peak maximum: $d = 2\pi/q_{max}$. SANS data for

NaPFHx and NaPFO micelles in D_2O were analyzed using the form and structure factors described in the Materials and Methods section to obtain the association number, micelle shape and size (results summarized in Table 4). Structural information on NaPFHx micelles was not previously available in the literature.

Table 4. *Parameters obtained by fitting SANS data of NaPFHx and NaPFO in D_2O, corrected for D_2O scattering, using the core-shell ellipsoid form factor and the Hayter rescaled MSA structure factor considering dry (water-free) core. C_{Tot} is the total surfactant concentration in the aqueous solution, N_{agg} micelle association number (number of surfactant molecules per micelle), α fractional charge or charge per surfactant molecule in a micelle, φ volume fraction of the micelles, b micelle core minor radius, ε ratio of micelle core major to minor axis, δ shell thickness, V_m micelle volume including bound counterions and associated water molecules, R_{eq} equivalent spherical radius of micelle, d inter-micelle distance, and I_{peak} intensity at the correlation peak maximum. χ_R^2 is a statistical parameter that quantifies the differences between the calculated and experimental SANS intensities. The uncertainties in the major parameters (shown in parenthesis) are calculated by applying propagation of errors using statistical uncertainties of the fitting parameters.*

C_{Tot} (mM)	N_{agg}	α	φ x 10^3	b (Å)	ε	δ (Å)	V_m (Å^3)	R_{eq} (Å)	d (Å)	I_{peak}	χ_R^2
110 NaPFO	24.5 (±0.3)	0.28 (±0.01)	34.9 (±0.9)	11.14	1.41 (±0.02)	4.42	20425 (±206)	16.96 (±0.06)	74.8	0.078	2.54
555 NaPFHx	14.7 (±0.2)	0.27 (±0.01)	161.1 (±2.1)	8.54	1.41 (±0.02)	3.40	9220 (±85)	13.00 (±0.04)	38.1	0.080	5.48
1106 NaPFHx	17.2 (±0.1)	0.56 (±0.01)	296.8 (±1.2)	8.54	1.65 (±0.01)	3.46	10620 (±42)	13.63 (±0.02)	30.6	0.230	3.65
608 NaPFHx + 0.25 M NaCl	17.4 (±0.2)	0.41 (±0.01)	159.3 (±2.2)	8.54	1.67 (±0.02)	3.52	10840 (±110)	13.73 (±0.05)	39.3	0.095	1.23

NaPFHx forms smaller micelles when compared to NaPFO. The association numbers of NaPFHx micelles in D_2O are 14.7 and 17.2 at 555 mM and 1106 mM, respectively. The association number of NaPFO micelles in D_2O is 24.5 at 110 mM. In the presence of 0.25 M NaCl, NaPFHx forms micelles with association number 17.4 at 608 mM. The micelle association number and micelle size (volume) of NaPFHx micelles at 608 mM in the presence of 0.25 M NaCl are very close to the micelle association number and micelle size (volume) of NaPFHx micelles at 1106 mM in the absence of NaCl. This indicates that micelles grow in size upon addition of salt. The association number of NaPFO obtained from our SANS analysis matches well with the literature values.[42] We considered here the fluorinated surfactant micelle core to comprise of only fluorocarbon chains. Such water-free core was previously used in SANS analysis for NaPFO, APFO, and cesium perfluorooctanoate (CsPFO).[42-44, 60] Following the consideration of possible water present in the fluorocarbon region of the micelle, a previous SANS study[42] on NaPFO concluded that dry micelle core gave the best fit to their SANS data.

In order to compare the chain length effects on micelle structure between fluorocarbon and hydrocarbon surfactants, the micelle structure dependence on hydrocarbon chain length is discussed below for the hydrocarbon surfactants sodium octanoate ($CH_3(CH_2)_6COONa$) (CMC = 360 mM)[61], and sodium dodecanoate ($CH_3(CH_2)_{10}COONa$) (CMC = 27 mM).[60] Sodium octanoate (NaO) micelles in the 600 – 1200 mM surfactant concentration range at 28 °C have been studied by SANS using the core-shell sphere form factor and Hayter-Penfold structure factor.[61] The association number and radius of NaO micelles increased from 15 and 11.7 Å at 600 mM, to 23 and 13.5 Å at 1200 mM. Sodium dodecanoate (NaDoD) micelles have been studied by SANS in the 160 – 530 mM surfactant concentration range at 25 °C using the core-shell prolate ellipsoid form factor and screened Coulombic potential plus hard sphere repulsion structure factor with RMSA.[60] The association number and equivalent spherical radius of NaDoD micelles increased from 57 and 23.0 Å at 160 mM to 70 and 24.7 Å at 530 mM.

Figure 6 shows select SANS structural parameters plotted for sodium perfluoroalkyl carboxylates (our results and data from the literature[42]) and sodium alkyl carboxylates (literature[60, 61]). The association number of NaPFHx is close to the association number of 8-carbon hydrogenated surfactant NaO at almost equal total surfactant concentrations. At a total surfactant concentration of about 3 times its CMC value, the association number of the fluorinated surfactant NaPFO is 24.5, for NaPFHx is 14.7, and the association number of the hydrogenated surfactant NaO is 23 and NaDoD is 55 (extrapolated from Figure 6). For sodium perfluoroalkyl carboxylates, upon an increase in the hydrophobic tail of the surfactant by 2 –CF_2– groups, the micelle association number increases by 70% and the size increases by 30%. For sodium alkyl carboxylates, upon increase in 2 –CH_2– groups in the hydrophobic part of surfactant, the association number increases by 75% and the micelle size increases by 35%. Fluorinated carboxylate surfactants have lower CMC and larger association number compared to their hydrocarbon analogues of equal carbon chain length. This is due to the greater alkyl chain hydrophobicity and the smaller effective charge of the fluorinated surfactant headgroups.[42] Due to the differences in electronegativities (EN) between fluorine (EN = 4.0) and hydrogen (EN = 2.1), fluorine tends to withdraw electron charge from the carboxyl headgroup: fluorinated carboxylates carry less charge, and the headgroups can pack closer to one another, allowing for a lower CMC and larger association number.[42]

Micelle Hydration

The effects of chain length and salt are also manifested in the viscosity of the fluorinated surfactant solutions. Figure 7 shows the relative viscosity of aqueous solutions of NaPFHx or NaPFO in the absence and in the presence of 0.25 M NaCl, plotted as a function of micellized surfactant concentration (C - CMC) which accounts for the contribution of only the micelles. A second-degree polynomial equation (Equation (4), neglecting the $O(\phi)^3$ term) was fitted to the viscosity data sets in Figure 7 and, from the x-coefficient value obtained, the hydrated volume of a surfactant molecule V_s^{hyd} is calculated. The shape factor ν was calculated using equations 7-9 in reference.[30] The axial ratio of a cylindrical micelle (L/d), where L the length of a cylindrical micelle, including contribution from the two hemispherical ends, and d the micelle diameter required in the shape factor ν calculations are obtained from the SANS results presented above.

For NaPFHx aqueous solutions in the absence of salt, the shape factor ν obtained from our SANS analysis at 555 mM NaPFHx is 2.54 and the hydrated volume of a NaPFHx molecule

V_s^{hyd} is 670.1 Å^3. After subtracting from this number the "dry" molecular volume of NaPFHx (337.3 Å^3), the volume of water hydrating a NaPFHx molecule is estimated 332.9 Å^3 which corresponds to ~11 water molecules. The shape factor v is also calculated at 1106 mM NaPFHx concentration. For a doubling of the NaPFHx concentration, from 555 mM to 1106 mM, the micelle length increased by 14%, while the micelle diameter remained almost the same; the shape factor v increased by 1.7% and the corresponding number of water molecules hydrating a NaPFHx molecule decreased by 0.4. The change in the v or hydration number is very small and hence the micelle size/shape changes do not affect the viscosity analysis. For NaPFHx aqueous solutions in the presence of salt, the shape factor ν estimated from our SANS analysis is 2.59. The V_s^{hyd} of a NaPFHx molecule in the presence of salt is 596.1 Å^3 and the volume of hydration water 258.8 Å^3 (~9 water molecules). The hydration of a NaPFHx molecule changed to some extent (~23%) due to salt. For NaPFO aqueous solutions in the absence of salt, the shape factor ν estimated from our SANS results is 2.54, the hydrated volume of a NaPFO molecule V_s^{hyd} is 862.9 Å^3, the dry molecular volume of NaPFO is 420.5 Å^3, and the volume of hydration water is 442.4 Å^3 (~15 water molecules). For NaPFO aqueous solutions in the presence of salt, for which case SANS results were not available, we assumed the hydrated volume of a NaPFO molecule V_s^{hyd} to be the same as in NaPFO in the absence of salt with about 23% uncertainty, and then estimated the shape factor. The ν obtained is 6.01 ± 1.79 and the corresponding axial ratio of the cylindrical micelle (L/d) value is 6.17 ± 1.61, which is much higher than the axial ratio of NaPFO micelle in the absence of salt (L/d = 1.29).

SANS results for APFO in 0.5 M NH_4Cl aqueous solution have shown rod-like micelles with radius 16 Å and length 300 Å (L/d = 9.37).[62] The shape factor ν for APFO micelles in 0.5 M NH_4Cl aqueous solution is 9.82 while for APFO micelles in plain water is 2.61[31]. The shape factor ν for APFO micelles in 0.25 M NH_4Cl aqueous solution obtained from the interpolation of ν values at 0 M and 0.5 M NH_4Cl is 6.21, which is almost equal to the ν value estimated above for NaPFO micelles in 0.25 M NaCl aqueous solution. This suggests that NaPFO forms rod-like micelles in 0.25 M NaCl solution. Assuming the diameter of NaPFO micelles in 0.25 M NaCl solution to be the same as in NaPFO in the absence of salt (d = 31.12 Å), the length of NaPFO micelles in 0.25 M NaCl solution could be 192 ± 50 Å.

The viscosity results support further the greater effect of salt on NaPFO micelles compared to NaPFHx micelles. Unlike NaPFHx, the relative viscosity of NaPFO increased sharply for NaPFO with the addition of salt, suggesting rod-like micelles for NaPFO in 0.25 M NaCl solution. This agrees well with the greater decrease in A_{min} and the greater increase in CPP with the addition of salt for NaPFO compared to NaPFHx.

CONCLUSIONS

This work explores effects of chain length and electrolyte on the self-assembly of anionic perfluorinated surfactants, with an ultimate goal to facilitate the replacement of environmentally toxic, long chain fluorosurfactants with relatively safer surfactants that have shorter carbon chain length. To this end, we investigate here the micellization of sodium perfluorohexanoate (NaPFHx) and sodium perfluorooctanoate (NaPFO) in aqueous media without or with added NaCl, following analysis of surface tension, pyrene fluorescence, SANS, and viscosity data.

The CMC of NaPFHx and NaPFO in water is 200 mM and 30 mM, respectively. The greater propensity to form micelles (lower CMC and more negative micellization free energy, ΔG_{mic}) by NaPFO compared to NaPFHx is due to the longer fluorocarbon chain (additional two -CF_2- segments) of NaPFO, which results in a more negative transfer free energy ΔG_{tr} (by 32%) and lower interfacial free energy ΔG_{int} (by 12%) and packing free energy ΔG_{pack} (by 20%), compared to the corresponding ΔG_{tr}, ΔG_{int}, and ΔG_{pack} contributions to the ΔG_{mic} for NaPFHx. The micelles are ellipsoid in shape for both surfactants. NaPFHx formed smaller micelles with association number of 14.7 (at 555 mM in D_2O) compared to NaPFO with association number of 24.5 (at 110 mM in D_2O) due to shorter chain length. For the sodium perfluoroalkyl carboxylates considered here, this 70% increase in the association number and 30% increase in the micelle size upon increase in 2 –CF_2– groups in the hydrophobic part of surfactant match well with findings for sodium alkyl carboxylate surfactants, where the association number increased by 75% and micelle size increased by 35% upon 2 –CH_2– increase. Fluorinated carboxylate surfactants have lower CMC and larger association number compared to their hydrocarbon analogues of equal carbon chain length due to the fluorinated surfactants' greater alkyl chain hydrophobicity and smaller headgroup charge.[42] In the case of hydrocarbon surfactants, the ΔG_{mic} decreased by 38% with increase in 2 –CH_2– groups for sodium alkyl carboxylates (ΔG_{mic} = -24.0 kJ/mol for NaD and ΔG_{mic} = -33.1 kJ/mol for NaDoD).[63] The ΔG_{mic} decreased to a great extent, by 50%, with increase in 2 –CH_2– groups for sodium perfluoroalkyl carboxylates (ΔG_{mic} = -17.9 kJ/mol for NaPFHx and ΔG_{mic} = -26.8 kJ/mol for NaPFO).

In aqueous 0.25 M NaCl, the CMC of NaPFHx and NaPFO decreased by 50% and 80%, respectively, compared to plain water. The surface area per headgroup A_{min} decreased by 10% for NaPFHx and by 17% for NaPFO with the addition of 0.25 M NaCl to aqueous surfactant solutions. The effect of NaCl was stronger on the micellization of NaPFO compared to that of NaPFHx. This is ascribed to the greater increase in ΔG_{elec} with the addition of salt for NaPFO (75%) compared to NaPFHx (57%), and to the greater decrease in the entropy lost by the counterions upon binding onto the charged micelle surface with the addition of salt for NaPFO (54%) compared to NaPFHx (40%). SANS results have shown that micelles grow in size upon addition of salt. Viscosity results suggest rod-like micelles for NaPFO in aqueous solution in the presence of 0.25 M NaCl. Upon addition of 0.25 M NaCl in aqueous solution, the CMC of the hydrocarbon surfactant SDS decreased by 90% and A_{min} decreased by 27%.[32]

Changes in the alkyl chain length and/or the presence of salt affect the self-assembly of ionic surfactants in water, modulate solution properties, and play a significant role in applications. The effect of added salt on the NaPFO micelle structure in aqueous solutions has not been previously reported in the literature. The chain length effect on fluorinated surfactant micellization in the presence of salts was not previously investigated. Stronger salt effect observed in NaPFO compared to NaPFHx. This is the first report on micelle formation and structure information of NaPFHx in the absence or in the presence of NaCl, which provides valuable information on the design of short chain fluorinated surfactants as potentially safer alternatives to long chain fluorinated surfactants. Further research on the physicochemical properties of fluorinated surfactants is needed to develop fundamental knowledge on various short chain fluorinated surfactants for their uses in different environmental conditions.

Acknowledgments

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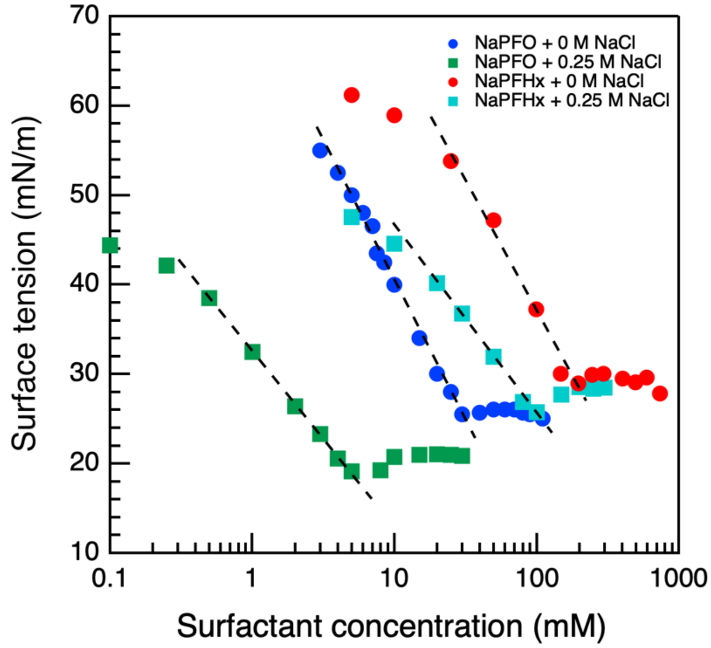


Figure 1. Surface tension of NaPFHx or NaPFO aqueous solutions in the absence (21 °C) and in the presence of 0.25 M NaCl (25 °C), plotted as a function of surfactant concentration. Linear fits have been applied to the data points where the surface tension decreases prior to reaching the CMC. The surface tension data of NaPFO in plain water are from reference.[27]

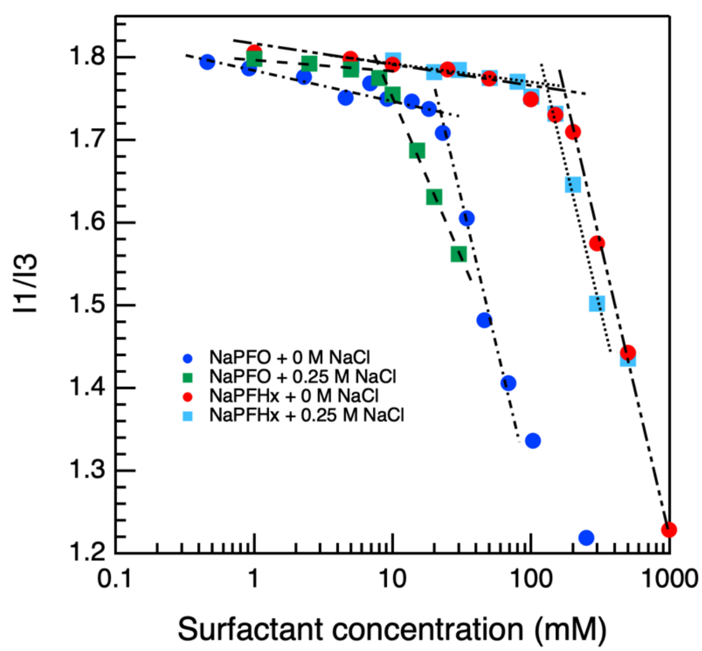
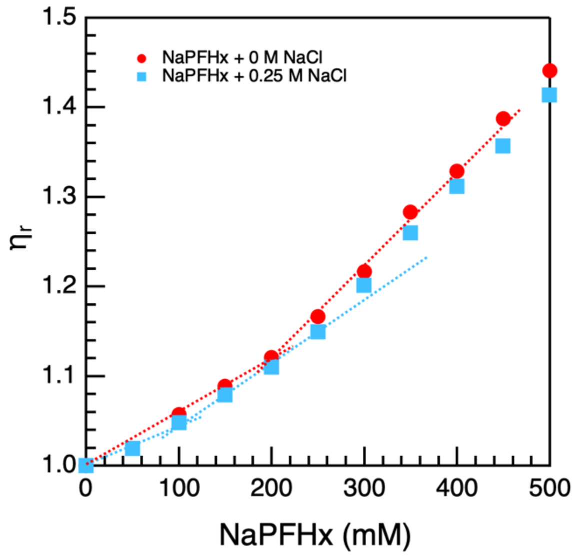
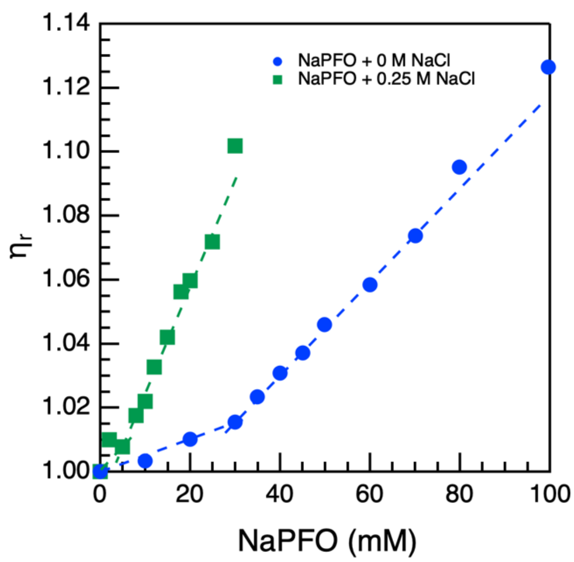


Figure 2. Pyrene fluorescence intensity I_1/I_3 ratio of NaPFHx or NaPFO aqueous solution in the absence or in the presence of 0.25 M NaCl, plotted as a function of surfactant concentration (22 °C).



(a)



(b)

Figure 3. Relative viscosity η_r, of (a) NaPFHx and (b) NaPFO aqueous solutions in the absence and in the presence of 0.25 M NaCl (21 °C), plotted as a function of total surfactant concentration.

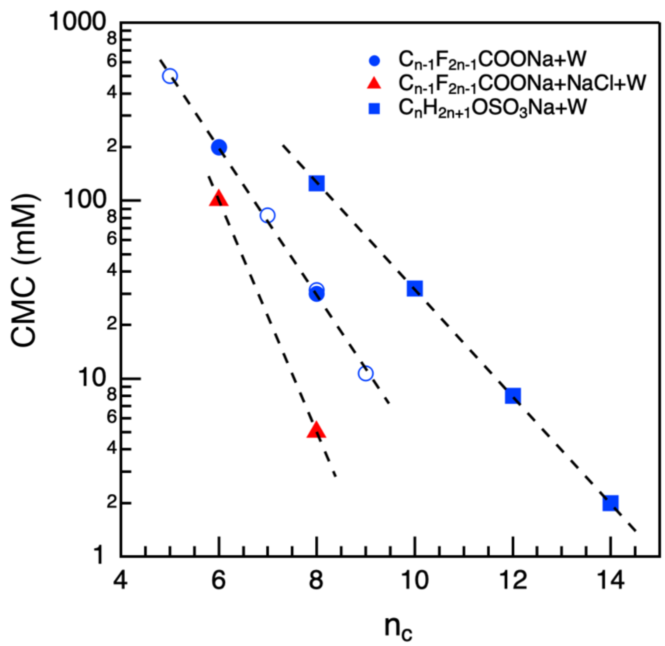


Figure 4. Dependence of CMC on the surfactant chain length (n_c) for the sodium perfluoroalkyl carboxylates, $C_{n-1}F_{2n-1}COONa$, studied here, without (filled circles) or with NaCl (0.25 M) (triangles) in water at 20 °C, from references[5, 64] at 25 °C (open circles) and for sodium alkyl sulfates, $C_nH_{2n+1}OSO_3Na$ (from reference[13]) at 30 °C.

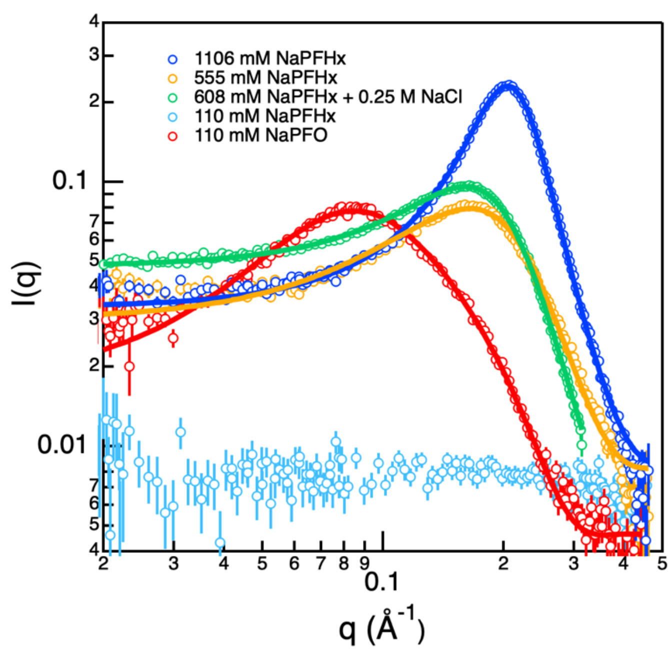
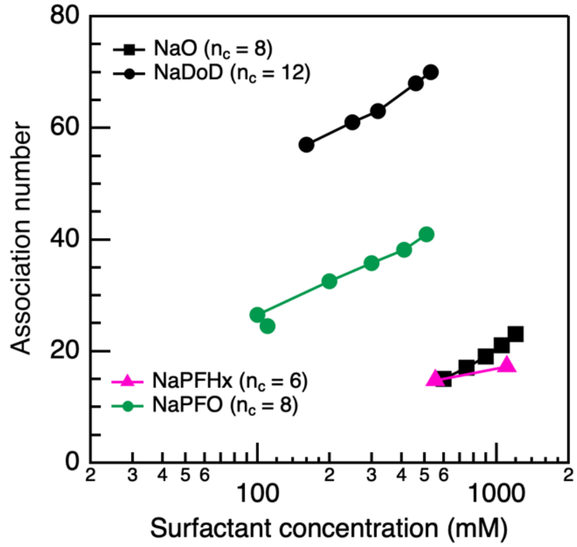
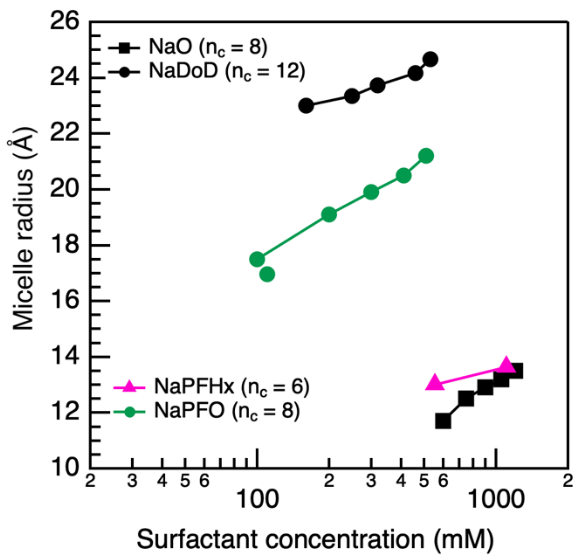


Figure 5. SANS absolute intensity profiles of 110 mM NaPFO in D_2O, 1106 mM, 555 mM, 110 mM NaPFHx in D_2O and 608 mM NaPFHx in 0.25 M NaCl + D_2O solutions at 22 °C (all corrected for solvent scattering). Markers represent experiment data and solid lines represent fits using the form factor and structure factor described in the text.

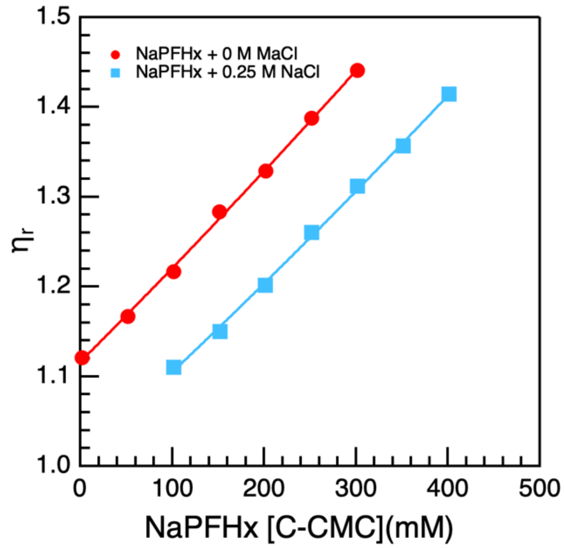


(a)

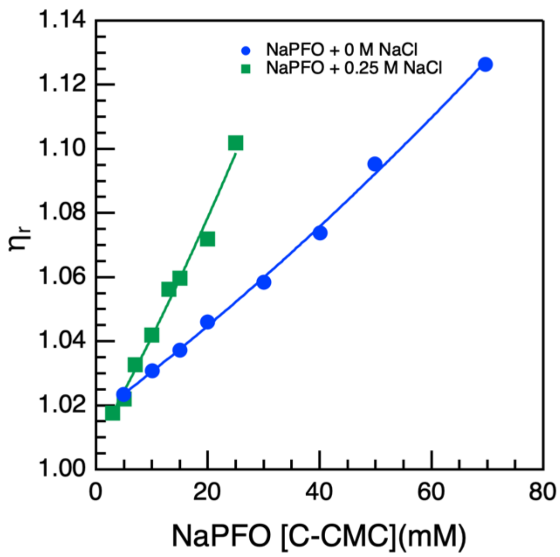


(b)

Figure 6. (a) Micelle association number (N_{agg}) and (b) micelle radius plotted as a function of surfactant concentration for the fluorinated surfactants NaPFHx and NaPFO (our results and results from ref[42]), and for the hydrocarbon surfactants sodium octanoate (NaO)[61], and sodium dodecanoate (NaDoD)[60].



(a)



(b)

Figure 7. Relative viscosity η_r, of (a) NaPFHx and (b) NaPFO aqueous solutions in the absence and in the presence of 0.25 M NaCl (21 °C), plotted as a function of micellized surfactant concentration. The lines through the viscosity data points are fits to equation (4).

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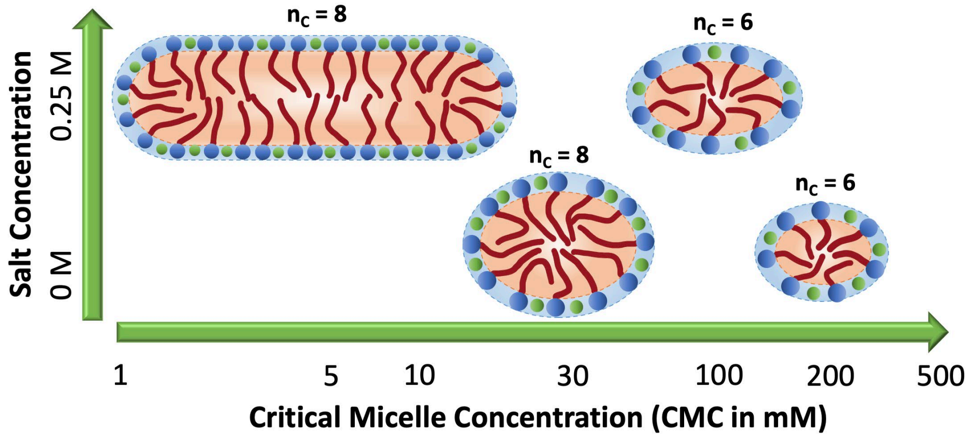

Changes in CMC and micelle size as a function of chain length (n_c) and added salt