Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2021

Supplementary Information for:

Controlling the Self-Assembly of Perfluorinated Surfactants in Aqueous Environments

Dengpan Dong, ¶† Samhitha Kancharla, ¶‡ Justin Hooper, † Marina Tsianou, ‡

Dmitry Bedrov, †* Paschalis Alexandridis, ‡*

† Department of Materials Science and Engineering, University of Utah, 122 South Central Campus Drive, Room 304, Salt Lake City, UT 84112

‡ Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York (SUNY), Buffalo, NY 14260-4200

¶: Joint first authors

Corresponding Authors

- * Paschalis Alexandridis: palexand@buffalo.edu
- * Dmitry Bedrov: d.bedrov@utah.edu

1. EXPERIMENTS: DETAILED ANALYSIS AND ADDITIONAL RESULTS

Micropolarity

The analysis of pyrene I1/I3 data to obtain CMC can vary depending on the authors and the system under investigation. ^{1,2,3,4,5}, For the PFOA solutions, the concentration value obtained from the intersection of straight lines fitted to the first plateau region of the I1/I3 vs surfactant concentration curve and the linear part of I1/I3 decrease region (near the inflection point) gives a CMC value that is consistent with the CMC obtained here from conductivity.⁶ To follow changes in the micropolarity of surfactant micelles upon ethanol addition, we observed the pyrene fluorescence intensity I1/I3 ratio of PFOA in ethanol-water mixtures as a function of ethanol concentration (Figure S1). The I1/I3 ratio at 20 mM PFOA decreased by 8% or 14%, and at 100 mM decreased by 4% or 6% with the addition of 10% or 20% ethanol, respectively. In aqueous PFOA solutions (no ethanol present), pyrene molecules are expected to locate in the palisade layer of PFOA micelles.⁸ Previous work has shown that pyrene prefers to locate inside hydrocarbon micelles over fluorinated micelles, and in some fluorinated surfactants such as tetraalkylammonium perfluorooctanoates, pyrene locates in the counterion layer instead of the fluorinated micelle core due to the presence of alkyl chains in the counterions.¹ Considering this, we speculate that, in the case of PFOA in ethanol + water mixtures, ethanol may solubilize in PFOA micelles and create its own environment into which pyrene prefers to locate instead of the fluorocarbon domains. As a result, the I1/I3 ratio of aqueous PFOA solutions would decrease with ethanol addition. Figure S1, shows that the micropolarity sensed by pyrene decreased with ethanol concentration. Figure S1 also shows the decrease in I1/I3 ratio of aqueous solution (no surfactant present) with the addition of ethanol, which indicates an increase in the aqueous

solution hydrophobicity upon ethanol addition. For pyrene and conductivity (discussed in the main manuscript) data the error-bars are smaller than the symbols in the plots.



Figure S1. Variation with ethanol concentration of pyrene fluorescence intensity I1/I3 ratio of PFOA in aqueous solutions. The PFOA concentrations are shown inside the graph.

Surface tension

The surface tension decrement of PFOA in 10% ethanol-water mixture when plotted in logarithmic scale is very gradual, and the surface tension when plotted in a linear scale is too steep, hence, the CMC value cannot easily be extracted from the surface tension data. Above the CMC, the surface tension of PFOA in aqueous solution reached a constant value of ~18 mN/m in the absence of ethanol and ~22.5 mN/m in the presence of 10% ethanol. The greater surface tension of PFOA in 10% ethanol aqueous solutions system when compared to PFOA in pure water system above the CMC may be due to the adsorption of some ethanol molecules along with PFOA molecules at the air/liquid interface in the 10% ethanol /water system. For PFOA in

aqueous solution at 24 °C, the slope $(d\gamma/dlogC)$ determined at CMC is -29.6 mN/m, Γ_{max} calculated from the slope $(d\gamma/dlogC)$ is 2.6 x 10⁻¹⁰ mol cm⁻² and the A_{min} is 64 ± 2 Å², while for PFOA in 10% ethanol – water mixture $d\gamma/dlogC = -9.45$ mN/m, $\Gamma_{max} = 8.3$ x 10⁻¹¹ mol cm⁻²,

 V_0

and $A_{min} = 200 \pm 4$ Å². The critical packing parameter (CPP = $\overline{A_{min}l_c}$) of amphiphiles can be estimated from the A_{min} , the volume of a surfactant alkyl chain (tail volume) in the surfactant assembly V₀, the extended length of the surfactant alkyl chain (tail length) l_c.⁷ The volume (V₀) and extended length of the PFOA fluorocarbon chain (l_c) are 333.6 Å³ and 11.16 Å, respectively.⁶ The CPP of PFOA in aqueous solution in the absence and in the presence of 10% ethanol are 0.47 and 0.15, respectively. For spherical micelles, CPP \leq 0.33 and for cylindrical micelles, 0.33 < CPP < 0.5.⁸ The CPP of PFOA in aqueous solution decreased by ~70% with the addition of 10% ethanol, suggesting that PFOA micelles in 10% ethanol-water should be spherical.

SANS analysis

Scenario 1: The micelle core consists of PFOA fluorocarbon chains and the CD_3CD_2 parts of the d-ethanol molecules that are solubilized in PFOA micelles, while the micelle shell consists of PFOA carboxylate head groups, counterions, -OD groups of the d-ethanol molecules solubilized in PFOA micelles, and associated water molecules.

The major fitting parameters to describe the scattering from PFOA micelles in D₂O and in D₂O + 10% or 20% d-ethanol are the surfactant association number η , micelle volume fraction φ , charge on a micelle Z, and number of ethanol molecules per micelle η_E . The micelle core minor radius (b) was taken to be the extended length of a fluorocarbon chain $l_{f,c} = 11.14$ Å. The micelle core volume V_{core} (in Å³) was calculated given the surfactant association number, η , and the number of ethanol molecules per micelle η_e using:

$$V_{core} = \eta V_{t,APFO} + \eta_E V_{t,ethanol} \tag{1}$$

where $V_{t,PFOA} = 333.6 \text{ Å}^3$ is the volume of a PFOA fluorocarbon chain, and $V_{t,ethanol}$ is the volume of the ethanol hydrocarbon chain.⁶ The volume of the ethanol hydrocarbon chain $V_{t,ethanol}$ was obtained from Tanford's formula:

$$V_{t,alcohol} = 27.4 + 26.9N_c \tag{2}$$

where N_c is the number of carbon atoms in the hydrocarbon chain of the alcohol molecule (N_c is 2 for ethanol and V_{t,ethanol} = 81.2 Å³). The molecular volume of ethanol calculated from the partial molar volume (58.6 cm³/mol) reported in the literature is 97.29 Å³. This value matches well with the ethanol volume (CD₃CD₂ volume (81.2 Å³) + polar –OD group volume (15.80 Å³)) that we considered in this study.

Considering the volume contributions from surfactant head-groups, counterions, polar – OD groups of alcohol, and associated water molecules, the micelle shell volume can be written as:

$$V_{shell} = \eta \left(V_{COO^{-}} + (1 - \alpha) V_{NH_{4}^{+}} + N_{H} V_{D_{2}O} \right) + \eta_{E} (V_{OD} + N_{HE} V_{D_{2}O})$$
(3)

where ${}^{V}_{COO^{-}}$ is the volume of the PFOA head-group, ${}^{V}_{NH}{}^{+}_{4}$ the volume of the counterion ${}^{NH}{}^{+}_{4}$, ${}^{V}_{D_{2}O}$ the volume of a D₂O molecule, and N_H and N_{HE} are the hydration numbers, i.e., the number of water molecules associated per surfactant molecule and alcohol molecule, respectively. $\alpha =$

 Z/η is the fractional charge on a micelle. We fixed N_{HE} = 2.⁹ An 'ab initio' quantum computational study of PFOA/H₂O system reported that, in average, 8 water molecules can be accommodated in the polar head group of the PFO⁻ ion.¹⁰ The reported hydration numbers for NH₄⁺ ion vary from 4 to 11.^{11,12} On the basis of the reported hydration numbers for NH₄⁺ ion and PFO⁻ ion, we fixed N_H = 12.

The scattering length density of the micelle core is calculated by equation (4)

$$\rho_{core} = \frac{\eta b_{CF_3(CF_2)_6} + \eta_E b_{CD_2CD_3}}{V_{core}}$$
(4)

where b_i is the coherent scattering length of molecule i. b_i values reported are shown in Table S1.

Table S1. Scattering lengths and parameters, and hydration numbers of ions reported in the literature used for fitting SANS data of PFOA aqueous solutions. Σb_i is the scattering length of species *i* (the sum of the scattering lengths of atoms present in the group), v_i is the molecular volume of species *i*, ρ_i is the scattering length density of species *i*, and MW_i is the molecular weight of species *i*.

species	$\Sigma_i b_i (\text{\AA})$	ν_i (Å ³)	$\rho_i (\text{\AA}^{-2})$	MW _i	Hydration number
NH4 ⁺	-5.596 x 10 ⁻⁵	20.2	-2.77x 10 ⁻⁶	18	$4 - 11$, ¹³ 8, ¹⁴ $4 - 13^{15}$
COO-	1.825 x 10 ⁻⁴	47.4	3.85 x 10 ⁻⁶	44	4, ¹⁶ 11 ^{17,18}
CF ₃	2.361 x 10 ⁻⁴	84.0	2.81 x 10 ⁻⁶	69	-
CF ₂	1.795 x 10 ⁻⁴	41.6	4.315 x 10 ⁻⁶	50	-
D ₂ O	19.145 x 10 ⁻⁵	30.19	6.341 x 10 ⁻⁶	20	-
H ₂ O	-1.675 x 10 ⁻⁵	29.9	-0.56 x 10 ⁻⁶	18	-
$CF_3(CF_2)_6$	1.313 x 10 ⁻³	333.6	3.936 x 10 ⁻⁶	369	-
CF ₃ (CF ₂) ₆ COO ⁻	1.496 x 10 ⁻³	381	3.926 x 10 ⁻⁶	413.1	819
OD	1.247 x 10 ⁻⁴	15.80	7.892 x 10 ⁻⁶	18	220
CD ₃	2.67 x 10 ⁻⁴	54.30	4.917 x 10 ⁻⁶	18	-
CD ₂	2.0 x 10 ⁻⁴	26.90	7.435 x 10 ⁻⁶	16	-
CD ₃ CD ₂	4.67 x 10 ⁻⁴	81.2	5.745 x 10 ⁻⁶	34	-
CD ₃ CD ₂ OD	5.917 x 10 ⁻⁴	97.0	6.1 x 10 ⁻⁶	52	213

 b_i of the molecules are calculated using scattering lengths of individual atoms as suggested by Kline et al. using the NIST online calculator.²¹

The scattering length density of the micelle shell is calculated using equation (5), which includes the individual contributions to the scattering from surfactant hydrophilic headgroups, counterions, polar –OD groups of alcohol and associated water molecules.

$$\rho_{shell} = \frac{\eta \left[b_{coo^{-}} + (1 - \alpha) b_{NH\frac{+}{4}} + N_{H} b_{D_{2}0} \right] + \eta_{E} \left[b_{OD} + N_{HE} b_{D_{2}0} \right]}{V_{shell}}$$
(5)

The scattering length density of the solvent $\rho_{solvent}$ was calculated using the scattering lengths and concentrations of alcohol, surfactant, and heavy water. The concentration of PFOA present in the bulk solution was considered as its CMC. The dielectric constant values used for different water–alcohol mixtures were obtained from the literature.²² A dielectric constant value of 78.25 was used for plain water, 73.88 for 10% ethanol-water and 67.98 for 20% ethanol-water.

SANS intensity data from PFOA + D₂O corrected for solvent (D₂O) scattering have been fitted by considering the ratio of micelle core major to minor axis (ε), shell thickness (δ), volume fraction of the micelles (φ), and total charge on a micelle (Z) as free parameters. We fixed the core minor radius (b) to be equal to the extended PFOA fluorocarbon chain length, and the ratio of the micelle shell thickness at pole to equator equal to 1 (uniform shell thickness). The scattering length density of the solvent ($\rho_{solvent}$) and the core (ρ_{core}) have been fixed. We varied the shell thickness (δ) from 3 Å to 5 Å, and calculated the volume of the micelle core (V_{core}) and the shell (V_{shell}). From V_{core} and V_{shell}, using equations 1 and 3 ($\eta_E = 0$), we calculated the surfactant association number (η). During the fit, we adjusted the shell thickness ($\delta = 4.1$ Å) such that the association number (η) calculated from V_{core} (equation 1) equals the η value calculated from V_{shell} (equation 3). From the η , α , and V_{shell} values thus obtained, we calculated the scattering length density of the shell (ρ_{shell}).

SANS intensity data from PFOA + 10% d-ethanol D₂O, corrected for solvent (10% dethanol in D₂O) scattering, have been fitted by considering as free parameters the ratio of micelle core major to minor axis (ϵ), volume fraction of micelles (ϕ), and total charge on a micelle (Z). We fixed the core minor radius (b) equal to the extended PFOA fluorocarbon chain length, and the ratio of micelle shell thickness at pole to equator equal to 1 (uniform shell thickness). The scattering length density of the solvent $\rho_{solvent}$ has been fixed. We varied the shell thickness from 3 Å to 4 Å, and calculated the fitting parameters (η , η_E , α). If the thickness was low (≤ 3.3 Å), the fractional charge or the charge per surfactant molecule in a micelle $\alpha > 1$ (unrealistic). If the thickness was high (\geq 3.6 Å), the number of ethanol molecules per micelle η_E was negative (unrealistic). The calculated fitting parameters η , η_E , α are realistic for shell thickness in the range 3.4 Å - 3.5 Å. The two other fitting parameters, scattering length density of the core (ρ_{core}) and the shell (ρ_{shell}), depend on η , η_E , α , V_{shell} , V_{core} (i.e., on b, ε , δ). We fixed the shell thickness at 3.4 Å or 3.5 Å, and performed iterations until the ρ_{core} and ρ_{shell} given by the fitting software match with the ρ_{core} and ρ_{shell} values calculated from equations 4 and 5. Shell thickness = 3.4 Å gave unrealistic fitting parameters ($\alpha > 1$) after 2 iterations, while the shell thickness 3.5 Å gave all realistic fitting parameters.

The fitting procedure for SANS intensity data from PFOA + 20% d-ethanol D_2O corrected for solvent (20% d-ethanol in D_2O) scattering is the same as the procedure we followed for PFOA + 10% d-ethanol D_2O described above.

The uncertainties in the major parameters (shown in parenthesis) are calculated by applying Propagation of Errors (NIST/SEMATECH, 2013) using statistical uncertainties of the fitting parameters. The uncertainty for each calculated parameter can be expressed generally as:

$$\delta R = \sqrt{\left(\frac{\partial R}{\partial x_1}\delta x_1\right)^2 + \left(\frac{\partial R}{\partial x_2}\delta x_2\right)^2 + \dots + \left(\frac{\partial R}{\partial x_n}\delta x_n\right)^2}$$

where R is a function of measured variables $(x_1, x_2, ... x_n)$.²³ In our case, the measured variables are the ε , Z, φ , δ . We applied the above equation to expressions used to calculate η , η_E , α , v_{et} in order to estimate the uncertainty in each parameter. In the various tables presented below, uncertainties for each property represent $\pm \delta R$.

Table S2 summarizes the important parameters obtained by fitting PFOA SANS data considering scenario 1.

Table S2. Parameters obtained by fitting SANS data of 110 mM PFOA in D_2O + d-ethanol solutions corrected for solvent (D_2O + d-ethanol) scattering using core-shell ellipsoid form factor and Hayter rescaled MSA structure factor considering scenario 1.

C _{d-E} wt%	η	α	3	b (Å)	δ (Å)	χ^2_R
0	30.0 (±0.3)	0.31 (±0.01)	1.74 (±0.007)	11.14	4.1	1.32
10	16.8 (±0.2)	0.83 (±0.02)	1.19 (±0.014)	11.14	3.5	1.39
20	12.1 (±0.3)	0.86 (±0.03)	0.812 (±0.017)	11.14	3.1	0.82
C_{d-E} wt%	$\eta_{\rm E}$	V _{et}	φ x 10 ³	d (Å)	I _{peak}	
0	0	0	27.2 (±0.3)	82.67	0.095	
10	16.1 (±1.6)	10.3 (±1.05)	30.4 (±0.5)	67.56	0.080	
20	8.3 (±2.2)	7.8 (±2.1)	31.7 (±0.7)	59.27	0.055	

 C_{d-E} is d-ethanol concentration; η 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; η_E average number of ethanol molecules per micelle; v_{et} volume percent of ethanol in a micelle which comprises PFOA + hydration water + counterions + ethanol, b minor micelle core radius, ε ratio of major to minor micelle core axis; δ shell thickness; 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 data set.

The association number of PFOA micelles shown in Table S2 decreased by 44% and 60% with the addition of 10% and 20% ethanol, respectively. The fractional charge on a micelle α increased by 168% and 177%, and the micelle volume fraction φ increased by 12% and 16% with 10% and 20% ethanol addition, respectively. As shown in Table S2, the number of ethanol molecules solubilizing in a micelle at 10% ethanol is 16, and at 20% ethanol is 8. The number of ethanol molecules solubilized in PFOA micelles decreased when ethanol concentration increased from 10% to 20%, supporting a "cosurfactant" effect at 10% ethanol and a "cosolvent" effect at 20 % ethanol. The volume percent of ethanol in a micelle also decreased. The volume of a micelle (including bound counterions, hydration water, and ethanol) decreased by 34% and 55% with the addition of 10% and 20% ethanol, respectively.

Scenario 2: The micelle core consists of only PFAO fluorocarbon chains, and the shell consists of PFOA carboxylate head-groups, counterions, all the d-ethanol molecules associated with the micelles, and associated water molecules.

The major fitting parameters to describe the scattering from PFOA micelles in D₂O and in D₂O + 10% or 20% d-ethanol are the micelle association number η , micelle volume fraction φ , charge on a micelle Z, and number of ethanol molecules per micelle η_E .

The micelle core minor radius (b) was taken to be the extended length of a fluorocarbon chain $l_{f,c} = 11.14$ Å. The core volume V_{core} (in Å³) was calculated given the surfactant association number η using:

$$V_{core} = \eta V_{t, APFO} \tag{6}$$

where $V_{t,PFOA} = 333.6 \text{ Å}^3$ is the volume of a PFOA fluorocarbon chain.

Considering the volume contributions from the surfactant head-groups, counterions, ethanol molecules and associated water molecules, the micelle shell volume can be written as:

$$V_{shell} = \eta \left(V_{COO^{-}} + (1 - \alpha) V_{NH^{+}_{4}} + N_{H} V_{D_{2}O} \right) + \eta_{E} (V_{ethanol} + N_{HE} V_{D_{2}O})$$
(7)

where ${}^{V}coo^{-}$ is the volume of the PFOA head-group, ${}^{V}{}_{NH}{}^{+}_{4}$ the volume of the counterion ${}^{NH}{}^{+}_{4}$, ${}^{V}{}_{D_{2}}{}^{O}$ the volume of a D₂O molecule, V_{ethanol} the volume of an ethanol molecule, N_H and N_{HE} are the hydration numbers, i.e., the number of water molecules associated per surfactant molecule and alcohol molecule, respectively. $\alpha = Z/\eta$ is the fractional charge on a micelle. V_{ethanol} was obtained from the sum of the volumes of polar OD group and hydrocarbon tail V_{t,ethanol} given by:

$$V_{t,alcohol} = 27.4 + 26.9N_c$$
 (8)

where N_c is the number of carbon atoms in the hydrocarbon chain of the alcohol molecule (N_c for ethanol is 2, $V_{t,ethanol} = 81.2$ Å³). The molecular volume of ethanol calculated from the partial molar volume (58.6 cm³/mol) reported in the literature is 97.29 Å³. This value matches well with the ethanol volume (CD₃CD₂ volume (81.2 Å³) + polar –OD group volume (15.80 Å³)) we considered in this study. We fixed $N_{HE} = 2$ and $N_H = 12$, same as in scenario 1.

The scattering length density of the micelle core is calculated by equation (9)

$$\rho_{core} = \frac{\eta b_{CF_3(CF_2)_6}}{V_{core}} \tag{9}$$

where b_i is the coherent scattering length of molecule i. b_i values are reported in Table S1.

The scattering length density of the shell is calculated using equation (10), which includes the individual contributions to the scattering from surfactant hydrophilic head groups, counterions, ethanol and associated water molecules:

$$\rho_{shell} = \frac{\eta \left[b_{COO^{-}} + (1 - \alpha) b_{NH_{4}^{+}} + N_{H} b_{D_{2}O} \right] + \eta_{E} \left[b_{ethanol} + N_{HE} b_{D_{2}O} \right]}{V_{shell}}$$
(10)

The scattering length density of the solvent $\rho_{solvent}$ was calculated using the scattering lengths and concentrations of alcohol, surfactant, and heavy water. The concentration of PFOA present in the bulk solution was considered as its CMC.

SANS intensity data from PFOA + D₂O, corrected for solvent (D₂O) scattering, have been fitted by considering the ratio of micelle major to minor core axis (ϵ), shell thickness (δ), volume fraction of the micelles (ϕ), and total charge on a micelle (Z) as free parameters. We fixed the core minor radius (b) to be equal to the extended PFOA fluorocarbon chain length, and the ratio of micelle shell thickness at pole to equator equal to 1 (uniform shell thickness). The scattering length density of the solvent ($\rho_{solvent}$) and the core (ρ_{core}) have been fixed. We varied the shell thickness (δ) from 3 Å to 5 Å, and calculated the volume of the micelle core (V_{core}) and the shell (V_{shell}). From V_{core} and V_{shell}, using equations 6 and 7 ($\eta_E = 0$), we calculated the surfactant association number (η). During the fit, we adjusted the shell thickness ($\delta = 4.1$ Å) such that the association number (η) calculated from V_{core} (equation 6) equals the η value calculated from V_{shell} (equation 7). From the η , α , V_{shell} values thus obtained, we calculated the scattering length density of the shell (ρ_{shell}). SANS intensity data from PFOA + 10% d-ethanol D₂O, corrected for solvent (10% dethanol in D₂O) scattering, have been fitted by considering the ratio of micelle core major to minor axis (ε), shell thickness (δ), volume fraction of the micelles (ϕ), and total charge on a micelle (Z) as free parameters. We fixed the core minor radius (b) equal to the extended PFOA fluorocarbon chain length, and the ratio of micelle shell thickness at pole to equator equal to 1 (uniform shell thickness). The scattering length density of the solvent ($\rho_{solvent}$) and the core (ρ_{core}) have been fixed. If we vary the shell thickness and calculate the fitting parameters (η , η_E , α), then this model is giving realistic values for all shell thickness in the range 3.7 - 6.5 Å. Hence, it is difficult to choose a single shell thickness value like we did in scenario 1. Therefore, we considered the shell thickness as a free parameter. For the free parameter ε , we have given a lower limit constraint ($\varepsilon > 1$), otherwise the best fit would result in very low ε values ($\varepsilon \sim 0.3$) and large δ values ($\delta \sim 8$). The scattering length density of the shell (ρ_{shell}) depends on η , η_E , α , V_{shell} , (i.e., on ε , δ). We iteratively solved for the shell thickness and ε until the ρ_{shell} value resulting from the fit matches the ρ_{shell} value calculated from equation 10.

The fitting procedure for SANS intensity data from PFOA + 20% d-ethanol in D_2O corrected for solvent (20% d-ethanol in D_2O) scattering is the same as the procedure we followed for PFOA + 10% d-ethanol in D_2O , corrected for solvent (10% d-ethanol in D_2O) scattering, but without any constraints for ε .

Table S3 summarizes the important parameters obtained by fitting PFOA SANS data considering scenario 2.

Table S3. Parameters obtained by fitting PFOA SANS data considering scenario 2 corrected for solvent $(D_2O + d\text{-ethanol})$ scattering

C_{d-E} wt% η α ε b (Å) δ (Å) χ^2_R

0	30.0 (±0.3)	0.31 (±0.01)	1.74 (±0.007)	11.14	4.1	1.32
10	17.4 (±1.4)	0.76 (±0.06)	1 (±0.08)	11.14	5.4 (±0.6)	1.33
20	12.9 (±1.4)	0.78 (±0.09)	0.745 (±0.08)	11.14	3.7 (±0.7)	0.82
C _{d-E} wt%	$\eta_{\rm E}$	V _{et}	φ x 10 ³	d (Å)	I _{peak}	
0	0	0	27.2 (±0.3)	82.67	0.095	
10	38.2 (±8.0)	19.5 (±4.2)	38.4 (±2.4)	67.56	0.080	
20	9.1 (±6.9)	8.0 (±6.0)	34.5 (±3.2)	59.27	0.055	

The association number of PFOA micelles shown in Table S3 decreased by 43% and 57%, and the fractional charge on a micelle α increased by 145% and 152%, with the addition of 10% and 20% ethanol, respectively. The volume fraction of micelles φ increased in the presence of 10% ethanol and then decreased at 20% ethanol. As shown in Table S3, the number of ethanol molecules solubilizing in a micelle at 10% ethanol is 38, and at 20% ethanol is 9. The number of ethanol concentration increased from 10% to 20%, supporting a "cosurfactant" effect at 10% ethanol and a "cosolvent" effect at 20 % ethanol. The volume percent of ethanol in a micelle also decreased. The volume of a micelle (including bound counterions, hydration water, and ethanol in the shell) decreased by 17% and 51% with the addition of 10% and 20% ethanol, respectively.

The number of ethanol molecules solubilizing in a micelle at 10% ethanol in scenario 2 is double that of scenario 1. The micelle shell thickness at 20% ethanol in scenario 2 is much bigger than the micelle shell thickness in scenario 1.

Scenario 3: The micelle core consists of only fluorocarbon chains, and the shell consists of 1 or 2 CF_2 groups from PFOA, PFOA carboxylate head-groups, counterions, all d-ethanol molecules associated with the micelles, and associated water molecules (in this scenario, 1 or 2 CF_2 groups will be in close contact with ethanol molecules and water).

The major fitting parameters to describe the scattering from PFOA micelles in D₂O and in D₂O + 10% or 20% d-ethanol are the surfactant association number η , micelle volume fraction φ , charge on a micelle Z, and number of ethanol molecules per micelle η_E .

The micelle core radius (b) was obtained from the extended length of a fluorocarbon chain given by²⁴

$$l_{f,c}(in \text{ Å}) = 1.3n_c + 2.04 \tag{11}$$

where n_c is the number of carbon atoms in the fluorocarbon tail of the surfactant (n_c is 6 if 1 CF₂ group is located in the shell and b = 9.84 Å, n_c is 5 if 2 CF₂ groups are located in the shell and b = 8.54 Å, and n_c is 4 if 3 CF₂ groups are located in the shell and b = 7.24 Å). The core volume V_{core} (in Å³) was calculated given the surfactant association number η using:

$$V_{core} = \eta V_{t, PFOA} \tag{12}$$

where $V_{t,PFOA}$ is the volume of a PFOA fluorocarbon chain. $V_{t, PFOA}$ was obtained from the volumes of CF₃ (84 Å³) and CF₂ (41.6 Å³) groups:

$$V_{t, PFOA} = [41.6n_c + 42.4] \tag{13}$$

 n_c is 6 if 1 CF₂ group is in shell and $V_{t,PFOA} = 292$ Å³, n_c is 5 if 2 CF₂ groups are in shell and $V_{t,PFOA} = 250.4$ Å³, and n_c is 4 if 3 CF₂ groups are in shell and $V_{t,PFOA} = 208.8$ Å³.

Considering the volume contributions from CF_2 groups, surfactant head-groups, counterions, ethanol, and associated water molecules, the micelle shell volume can be written as:

$$V_{shell} = \eta \Big(nV_{CF_2} + V_{COO^-} + (1 - \alpha)V_{NH_4^+} + N_H V_{D_2O} \Big) + \eta_E (V_{ethanol} + N_{HE} V_{D_2O})$$
(14)

where V_{CF_2} is the volume of the CF₂ group, n the number of CF₂ groups inside the shell in association with ethanol molecules, V_{COO}^- the volume of the PFOA head-group, V_{NH}^+ the volume of the counterion NH_4^+ , V_{D_2O} the volume of a D₂O molecule, V_{ethanol} the volume of an ethanol molecule, N_H and N_{HE} are the hydration numbers, i.e., number of water molecules associated per surfactant molecule and alcohol molecule, respectively. $\alpha = Z/\eta$ is the fractional charge on a micelle. V_{ethanol} was obtained from the sum of the volumes of polar OD group and hydrocarbon tail V_{tethanol} :

$$V_{t,alcohol} = 27.4 + 26.9N_c \tag{15}$$

where N_c is the number of carbon atoms in the hydrocarbon chain of the alcohol molecule (for ethanol $N_c = 2$, $V_{t,ethanol} = 81.2$ Å³). The molecular volume of ethanol calculated from the partial molar volume (58.6 cm³/mol) reported in the literature is 97.29 Å³. This value matches well with the ethanol volume (CD₃CD₂ volume (81.2 Å³) + polar –OD group volume (15.80 Å³)) that we considered in this study. We fixed $N_{HE} = 2$ and $N_H = 12$, same as scenario 1.

The scattering length density of the core is calculated by equation (16):

$$\rho_{core} = \frac{\eta b_{CF_3(CF_2)_{6-n}}}{V_{core}} \tag{16}$$

where n is the number of CF_2 groups in the shell in association with ethanol molecules, b_i is the coherent scattering length of molecule i. b_i values are reported in Table S1.

The scattering length density of the shell is calculated using equation (17), which includes the individual contributions to the scattering from surfactant CF_2 groups in the shell, hydrophilic head-groups, counterions, ethanol, and associated water molecules.

$$\rho_{shell} = \frac{\eta \left[nb_{CF_2} + b_{COO^-} + (1 - \alpha)b_{NH_4^+} + N_H b_{D_2 O} \right] + \eta_E \left[b_{ethanol} + N_{HE} b_{D_2 O} \right]}{V_{shell}}$$
(17)

The scattering length density of the solvent $\rho_{solvent}$ was calculated using the scattering lengths and concentrations of alcohol, surfactant, and heavy water. The concentration of PFOA present in the bulk solution was considered as its CMC.

SANS intensity data from PFOA + D₂O corrected for solvent (D₂O) scattering have been fitted by considering the ratio of micelle core major to minor axis (ϵ), shell thickness (δ), volume fraction of the micelles (ϕ), and total charge on a micelle (Z) as free parameters. We fixed the core minor radius (b) to be equal to the extended PFOA fluorocarbon chain length, and the ratio of micelle shell thickness at pole to equator equal to 1 (uniform shell thickness). The scattering length density of the solvent ($\rho_{solvent}$) and the core (ρ_{core}) have been fixed. We varied the shell thickness (δ) and calculated the volume of the micelle core (V_{core}) and the shell (V_{shell}). From V_{core} and V_{shell} , using equations 12 and 14 ($\eta_E = 0$), we calculated the surfactant association number (η). During the fit, we adjusted the shell thickness (δ) such that the association number (η) calculated from V_{core} (equation 12) equals to the η value calculated from V_{shell} (equation 14). From η , α , V_{shell} values obtained, we calculated the scattering length density of the shell (ρ_{shell}).

SANS intensity data from PFOA + 10% d-ethanol D_2O corrected for solvent (10% dethanol in D_2O) scattering have been fitted by considering the ratio of micelle core major to minor axis (ε), shell thickness (δ), volume fraction of the micelles (φ), and total charge on a micelle (Z) as free parameters. We fixed the core minor radius (b) equal to the extended PFOA fluorocarbon chain length, and the ratio of micelle shell thickness at pole to equator equal to 1 (uniform shell thickness). The scattering length density of the solvent ($\rho_{solvent}$) and the core (ρ_{core}) have been fixed. The scattering length density of the shell (ρ_{shell}) depends on η , η_{E} , α , V_{shell} , (i.e., on ε , δ). We iteratively solved for shell thickness and ε until the ρ_{shell} given by the fitting software matches with the ρ_{shell} value calculated from equation 17.

The fitting procedure for SANS intensity data from PFOA + 20% d-ethanol D_2O corrected for solvent (20% d-ethanol in D_2O) scattering is the same as the procedure we followed for PFOA + 10% d-ethanol D_2O corrected for solvent (10% d-ethanol in D_2O) scattering.

Table S4 summarizes the important parameters obtained by fitting PFOA SANS data considering scenario 3.

Table S4. Parameters obtained by fitting SANS data of 110 mM PFOA in D_2O + d-ethanol solutions corrected for solvent (D_2O + d-ethanol) scattering using core-shell ellipsoid form factor and Hayter rescaled MSA structure factor considering scenario 3.

C _{d-E} wt%	η	α	φ x 10 ³	$\eta_{\rm E}$	v _{et}	b (Å)	3	δ (Å)	d (Å)	I _{peak}	red $\cdot \chi^2$
1 CF ₂ group in shell in association with ethanol molecules											
0	27.4 (±0.3)	0.35 ±0.01	24.6 (±0.6)	0	0	9.84	2.00 (±0.02)	4.46	82.7	0.095	1.2
10	14.6 (±1.9)	0.86 (±0.1)	44.2 (±1.3)	67.5 (±9.6)	30.5 (±4.7)	9.84	1.06 (±0.14)	7.19 (±0.5)	67.6	0.080	1.3
20	12.6 (±2.1)	0.80 (±0.1)	34.9 (±2.5)	12.1 (±8.7)	10.4 (±7.6)	9.84	0.923 (±0.15)	4.35 (±0.8)	59.3	0.055	0.8
		2 CF	₂ groups	in shell	in associ	ation w	ith ethanol	molecu	les		
0	25.8 (±0.4)	0.37 ±0.01	24.9 (±0.7)	0	0	8.54	2.47 (±0.03)	4.84	82.7	0.095	1.5
10	13.2 (±6.5)	0.95 (±0.5)	41.5 (±1.1)	64.9 ±31.0	31.5 ±16.6	8.54	1.26 (±0.62)	7.58 (±1.6)	67.6	0.080	1.3

20	12.3	0.83	32.6	8.8	8.13	051	1.18	4.58	50.2	0.055	0.0
20	(±8.5)	(±0.6)	(±4.5)	±32.1	±29.7	8.34	(±0.81)	(±2.8)	59.5	0.055	0.0

If we consider 3 or more CF₂ groups in the shell in close contact with ethanol molecules, then the obtained fractional charge or charge per surfactant molecule in a micelle (α) becomes greater than 1, which is unrealistic. Therefore, it is not reasonable to consider 3 CF_2 groups in the shell. The PFOA micelle association number shown in Table S4 decreased by 47% when considering 1 CF₂ group in shell or 49% when considering 2 CF₂ groups in shell, and by 54% when considering 1 CF₂ group in shell or 52% when considering 2 CF₂ groups in shell with the addition of 10% and 20% ethanol, respectively. The fractional charge on a micelle α and volume fraction φ increased with 10% ethanol addition, and then decreased with 20% ethanol addition. As shown in Table S4, the number of ethanol molecules solubilizing in a micelle considering 1 CF₂ group in the shell at 10% ethanol is 67, and at 20% ethanol is 12, and when considering 2 CF₂ groups in shell at 10% ethanol is 65, and at 20% ethanol is 9, respectively. We can conclude that 1 or 2 CF₂ groups in the shell do not make a significant difference in the association number and number of ethanol molecules per micelle. The number of ethanol molecules solubilized in PFOA micelles decreased when ethanol concentration increased from 10% to 20%, supporting a "cosurfactant" effect at 10% ethanol and a "cosolvent" effect at 20 % ethanol. The volume percent of ethanol in a micelle also decreased. The volume of a micelle (including bound counterions, hydration water, and ethanol in the shell) remained approximately the same in the presence of 10% ethanol, whereas it decreased by 45% with the addition of 20% ethanol. The number of ethanol molecules solubilizing in a micelle at 10% ethanol in scenario 3 is double that of scenario 2.

Viscosity

Viscosity measurements of surfactant solutions can help us in determining surfactant micelle size, possible shape changes, micelle volume fraction and hydration.^{25,26} We performed viscosity measurements of surfactant solutions using Cannon-Fenske capillary viscometer of sizes 50 and 100 depending on the viscosity range of the sample solutions. The efflux time for each sample concentration was measured, and two consecutive readings with the same sample concentration inside with time difference less than 0.50 seconds were considered. The kinematic viscosity (η) is calculated by multiplying the efflux time with the viscometer calibration constant provided by the manufacturer, Cannon Instrument Co.

The ratio of kinematic viscosity of solution (η) and kinematic viscosity of pure solvent (η_0) gives the relative viscosity ($\eta_r = \eta/\eta_0$) of solution. The relative viscosity can be expressed in terms of the volume fraction of micelles (ϕ) as follows^{27,28}

$$\eta_r = 1 + \nu \phi + k_1 (\nu \phi)^2 + O(\phi)^3$$
(18)

where v is a shape factor representing the micelle shape and k₁ is a coefficient corresponding to pair-wise hydrodynamic interactions between the micelles.²⁸ The volume fraction of micelles (ϕ) is given by $\phi = V_{s}^{hyd}(c_{s} - c_{1})$, where V_{s}^{hyd} is the hydrated volume of a surfactant molecule, c_s is the total surfactant concentration, and c₁ is the concentration of unassociated surfactant (taken to be the CMC).²⁸

For spherical micelles, the shape factor v is considered to be 2.5. 27,28 For cylindrical micelles, the shape factor v is given by 27

$$\nu = 2.5 + 0.407(J-1)^{1.508}$$
, for $1 < J < 15$ (19)

$$\nu = 1.6 + \frac{J^2}{15} \left[\frac{1}{(\ln(2J) - 1.5)} + \frac{3}{(\ln(2J) - 0.5)} \right], \text{ for } J > 15$$
(20)

where $J = \left(\frac{L}{d}\right) \left[\frac{2}{3 - (d/L)}\right]^{1/2}$, (L/d) is the axial ratio of a cylindrical micelle, L is the length of a cylindrical micelle including contribution from hemispherical ends, and d is the diameter.²⁷

The relative viscosity of PFOA in both 10 wt% and 20 wt% ethanol in water mixtures increased with an increase in surfactant concentration. Viscosity data of PFOA in ethanol+water mixtures have not been previously reported in the literature. To estimate the hydrated volume of a surfactant molecule $\binom{V^{hyd}}{s}$, we plotted (Figure S2) the relative viscosity of PFOA in ethanol + water mixtures as a function of micellized surfactant concentration ($C_m = C_s - CMC$), where C_s is the total surfactant concentration. The shape factor v for PFOA in pure water is estimated using equations (19) or (20) and the axial ratio (L/d) of PFOA micelles is obtained from our SANS results. The estimated shape factor v for PFOA in pure water is 2.61, in 10% ethanolwater is 2.51 and in 20% ethanol-water is 2.52. From equation (18) fitted to the relative viscosity data in Figure S2, the hydrated volume of a PFOA molecule $\binom{V^{hyd}}{s}$ in pure water is estimated to be 806 Å³, V^{hyd}_{s} in 10% ethanol in water mixture is estimated 526 Å³ and in 20% ethanol in water mixture 720 Å³. The hydrated volume of PFOA $\binom{V^{hyd}}{s}$ decreased by ~35% and ~11% for 10% and 20% ethanol addition, respectively. The hydrated volume also includes the ethanol molecules solubilized. In the case of SDS, from the shape factor v = 2.5 (spherical micelles) and the parameters of the equation (18) fitted to surfactant relative viscosity data in Figure S2, the hydrated volume of a SDS molecule $\binom{V^{hyd}}{s}$ in pure water, 10% and 20% ethanol – water mixtures are estimated to 1628 Å³, 1124 Å³ and 1085 Å³ respectively. The hydrated volume of SDS molecule $\binom{V^{hyd}}{s}$ decreased by 31% and 33% with 10% and 20% ethanol addition, respectively.



Figure S2. Relative viscosity of (a) PFOA and (b) SDS aqueous solutions in the absence and in the presence of 10% or 20% ethanol plotted as a function of micellized PFOA or SDS concentrations (20 °C). The lines through the viscosity data are fits to equation (18).

2. SIMULATIONS: METHODS AND MODELS

The force field for molecular dynamics (MD) simulations of PFOA-ammonium salt dissolved in water has been developed following the standard procedure for the atomistic polarizable force field APPLE&P.²⁹ The atomic charges of ammonium ion were obtained by fitting to the electrostatic potential around the ion, which was obtained using high-level quantum chemistry calculations, i.e., MP2/aug-cc-pVTZ in Gaussian 09 package.^{30,31} The van der Waals (VDW) interactions between cationic nitrogen and water were directly transferred from the model of tetraalkylammonium bromide in water.³² In the simulation, each system was comprised of 32 PFO-NH₄ ion pairs and about 4000 water/ethanol molecules.

Interaction potentials

$$U^{tot}(r) = U^{NB}(r) + \sum_{bends} U^{BENDS}(\theta_{ijk}) + \sum_{dihedrals} U^{DIHEDRALS}(\phi_{ijkl}) + \sum_{deformation} U^{DEFORMATION}(\phi_{ijkl})$$
(18)

In Eq 18, U^{tot} stands for total potential energy, U^{NB} for non-bonded potential energy. The equation for U^{NB} is given in Eq 19.

$$U^{NB}(r) = U^{RD}(r) + U^{coul}(r) =$$

$$\sum_{i>j} \left(A_{\alpha\beta} \exp\left(-B_{\alpha\beta}r_{ij}\right) - C_{\alpha\beta}r_{ij}^{6}\right) +$$

$$\sum_{i>j} \left(\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}\right) \quad (19)$$

where $A_{\alpha\beta}$, $B_{\alpha\beta}$ and $C_{\alpha\beta}$ describe the pairwise VDW interactions, q_i and q_j are the atomic charges for atoms *i* and *j*, ϵ_0 denotes permittivity in vacuum.

The bond-based potential energy is comprised of two contributions: harmonic bends and dihedrals, while all the chemical bonds were constrained using the SHAKE algorithm.³³ U^{BENDS} is the three-body angle potential, $U^{DIHEDRALS}$ for dihedral potentials and $U^{DEFORMATION}$ for out-of-plane deforamtion, with the detailed equations given in Eq 20 and Eq 21, respectively.

$$U^{BEND}(\theta_{ijk}) = 0.5 \times k^{BEND}_{\alpha\beta\gamma} (\theta_{ijk} - \theta^{\ 0}_{ijk})^2 \quad (20)$$

$$U^{DIHEDRALS}(\phi_{ijkl}) = \sum_{n} 0.5 \times k^{DIHEDRAL}_{\alpha\beta\gamma\delta n} (1 - \cos(n\phi_{ijkl})) \quad (21)$$

$$U^{DEFORMATION}(\phi_{iJkl}) = \sum_{n} \frac{K^{DEFORMATION}_{iJkl}}{2} \left(\phi_{ijkl} - \frac{\pi}{2}\right)^2 \quad (22)$$

 θ_{ijk}^{0} stands for angle at equilibrium, θ_{ijk} for instantaneous bend angle, and $k_{\alpha\beta\gamma}^{BEND}$ for strength of bend angle. The meaning of parameters in the definitions of various equations can be interpreted accordingly. In all equations, subscripts α , β , $\gamma \delta$ are used to indicate the types of atoms *i*, *j*, *k*, *l* and n is the order of cosine functions.

Force field parameters

The molecular representation and atom labels can be seen in Figure S3. The detailed parameters of force field are given in Table S5. Since very small polarizability has been observed

in F atoms, the non-polarizable version of the force field was parameterized and utilized for the efficiency of computations.



Figure S3. Molecular representations and atom labels of simulated species.

Table S5. Force field parameters: definition of atoms and partial atomic charges.

	А	В	С	Partial				
Label	[Kcal*mol ⁻¹]	[Å-1]	[Kcal*mol ⁻¹ *Å ⁻⁶]	charge (e)		Bonded atoms		
На	5352.3	6	0	0.4100	0			
Hw	0	0	0	0.5564	Ow	Hw		
С	97431	3.6222	519.87	-0.3151	С	F	F	Cc
C	97431	3.6222	519.87	-0.0430	Cm	0	Н	Н
С	97431	3.6222	519.87	0.1200	Cm	F	F	С

Cc	33749.8	3.2995	618.32	0.8235	C	0	0	
Cm	108283	3.6405	560.53	-0.0466	C	Н	Н	Н
Cm	108283	3.6405	560.53	0.1800	F	F	F	С
N+	39091.8	4.5672	122.04	-0.8276	Н	Н	Н	Н
0	15923.1	3.6446	239.07	-0.6989	Cc			
0	15923.1	3.6446	239.07	-0.5422	C	На	Lp	Lp
Ow	880783.4	0	851.26	0.0000	Hw	Hw	Lp	
F	7117.9	3.4174	150.72	-0.0600	Cm			
F	7117.9	3.4174	150.72	-0.0553	C			
Lp	0	0	0	-1.1128	Ow			
Lp	0	0	0	-0.0217	0			

Table S6. Force field parameters for cross-terms of repulsion-dispersion interactions.

		А	В	С
Atom i	Atom j	[Kcal*mol ⁻¹]	[Å ⁻¹]	[Kcal*mol ⁻¹ *Å ⁻⁶]
Н	Hw	5501.88	4.89892	0
Н	С	19676.84	3.87866	108.37
Н	Cc	9786.45	3.59942	118.19
Н	Cm	20901.72	3.89336	112.53
Н	N+	14331.84	4.45788	52.51
Н	0	4826.183	3.89	26.903
Н	Ow	4480.399	3.603	112.593
Н	F	4815.92	3.7056	58.35
Н	Lp	0	0	0
Hw	C	13419.48	4.06573	0
Hw	Cc	5969.84	3.70354	0
Hw	Cm	14362.57	4.08627	0
Hw	N+	17036.14	5.12627	0
Hw	0	5526.27	4.09088	0
Hw	Ow	0	0	0
Hw	F	3046.09	3.83587	0
Hw	Lp	0	0	0
С	Cc	55167.82	3.43487	566.96
С	Cm	102702	3.63127	539.82
С	N+	49303.64	3.91795	251.88

С	0	39381.12	3.63328	352.54
С	Ow	38418.21	3.4042	728.04
С	F	25938.08	3.50943	279.92
С	Lp	0	0	0
Cc	Cm	57913.54	3.44111	588.72
Cc	N+	306620.8	3.5009	1900.68
Cc	0	22186.61	3.44249	384.48
Cc	Ow	23769.94	3.2762	793.99
Cc	F	15413.7	3.35484	305.28
Cc	Lp	0	0	0
Cm	N+	52447.87	3.93375	261.55
Cm	0	41523.26	3.64255	366.07
Cm	Ow	40307.17	3.41006	755.97
Cm	F	27270.08	3.51669	290.66
Cm	Lp	0	0	0
N+	0	20152.44	3.93727	170.81
N+	Ow	30864.47	3.3604	1092.74
N+	F	11889.51	3.73391	135.62
N+	Lp	0	0	0
0	Ow	15439.67	3.41135	493.71
0	F	10450.64	3.51829	189.82
0	Lp	0	0	0
Ow	F	10808.63	3.3872	302.01
Ow	Lp	0	0	0
F	Lp	0	0	0

Table S7. Constrained distances for bonds.

Atom i	Atom j	r0 [Å]
Cm	F	1.33
С	Cm	1.55
С	F	1.33
С	C	1.55
С	F	1.33
С	Cc	1.568
Cc	0	1.248
Н	N+	1.02
Hw	Ow	0.957
Hw	Hw	1.514
Ow	Lp	0.1546

Table S8. Force field parameters for bends.

			K0	
Atom i	Atom j	Atom k	[Kcal/mol/rad ²]	θ_0

F	Cm	F	240	109.6
С	Cm	F	180	109.1
Cm	C	F	180	108.4
С	С	Cm	160.6	113.7
F	С	F	240	110.2
С	C	F	180	109
С	C	С	160.6	111.7
Cc	C	С	140	112
F	C	F	240	110.2
F	C	Cc	180	111.1
С	Cc	0	172	113.5
0	Cc	0	280	133
Н	N+	Н	95	109.5
Hw	Ow	Hw	0	104.52

Table S9. Force field parameters for torsions.

Atom	Atom	Atom	Atom		k1	k2	k3	k4	k5	k6
i	j	k	1	Ν	[Kcal/mol]	[Kcal/mol]	[Kcal/mol]	[Kcal/mol]	[Kcal/mol]	[Kcal/mol]
F	C	Cm	F	3	0	0	-0.36			
C	C	Cm	F	4	0	0	-0.36			
Cm	C	C	F	4	0	0	-0.36			
C	C	C	Cm	6	-0.346	0	3.026	-1.553	-0.566	-0.734
F	C	C	F	3	0	0	-0.36			
С	C	C	F	3	0	0	-0.36			
С	C	C	C	6	-0.346	0	3.026	-1.553	-0.566	-0.734
С	C	C	C	4	-0.271	0.152	-0.187	-0.5		
С	C	C	Cc	2	0	0.15				
Cc	C	C	F	3	0	0	-0.36			
0	Cc	C	C	6	-1.225	0.316	-0.099	-0.081	0.096	0.063

Table S10. Force field parameters for out-of-plane deformations.

Atom i	Atom j	n j Atom k		K _{iJkl} [Kcal/mol*rad ²]	
0	Сс	0	С	36.5	

Simulated systems

The compositions of simulated systems are given in Table S6. Considering the very low CMC for PFOA in water, we conduct simulations at a concentration higher than experimental CMC, yet the number of PFOA was chosen such that only one well-defined PFOA micelle can be expected in the simulation box. Additionally, the number of water molecules was adjusted to

ensure that the size of the formed micelle is not larger than half of the simulation cell in order to avoid interaction of the micelle with its own image due to periodic boundary conditions.

	N _{pfoa}	N _{NH4}	N _{H2O}	N ethanol	C _{PFOA} (M/L)	wt ethanol
1	32	32	4032	0	0.39	0
2	32	32	4032	100	0.36	6%
2	32	32	4032	200	0.34	13%
3	32	32	4032	400	0.30	25%

Table S11. Composition of simulated systems.

Density profiles of F atoms and COO groups of PFO⁻ relative to PFOA micelle center of mass in pure water.



Figure S4. Number density profiles of F and COO groups of PFO- relative to PFOA micelle center of mass obtained from simulations of systems with no and 25% of ethanol.

Representative micelle morphologies of all simulated systems are shown in Figure S4.



Figure S5. Structures of micelles obtained from MD simulations with different polarity and concentration of additive molecules.



Figure S6. Principal components of the radius of gyration tensor of PFO⁻ micelle as a function of ethanol concentration as obtained from MD simulations.

References

¹ Xing, H.; Yan, P.; Xiao, J.-X., Unusual Location of The Pyrene Probe Solubilized in The Micellar Solutions of Tetraalkylammonium Perfluorooctanoates. *Soft Matter* **2013**, *9* (4), 1164-1171.

² Nivaggioli, T.; Alexandridis, P.; Hatton, T. A.; Yekta, A.; Winnik, M. A., Fluorescence Probe Studies of Pluronic Copolymer Solutions as a Function of Temperature. *Langmuir* **1995**, *11* (3), 730-737.

³ Lin, Y.; Alexandridis, P., Cosolvent Effects on the Micellization of an Amphiphilic Siloxane Graft Copolymer in Aqueous Solutions. *Langmuir* **2002**, *18* (11), 4220-4231.

⁴ An, Y.-J.; Jeong, S.-W., Interactions of Perfluorinated Surfactant with Polycyclic Aromatic Hydrocarbons: Critical Micelle Concentration and Solubility Enhancement Measurements. *J. Colloid Interface Sci.* **2001**, *242* (2), 419-424.

⁵ Damas, C.; Naejus, R.; Coudert, R.; Frochot, C.; Brembilla, A.; Viriot, M. L., Fluorocarbon and Hydrocarbon Short-Chain Nonionic Amphiphiles: a Comparative Study of Their Behavior In Aqueous Medium. *J. Phys. Chem. B* **1998**, *102* (52), 10917-10924.

⁶ Kancharla, S.; Canales, E.; Alexandridis, P., Perfluorooctanoate in Aqueous Urea Solutions: Micelle Formation, Structure, and Microenvironment. *Int. J. Mol. Sci.* **2019**, *20* (22), 5761. ⁷ Kronberg, B.; Holmberg, K.; Lindman, B., *Surface Chemistry of Surfactants and Polymers*. John Wiley & Sons, Incorporated: Somerset, 2014.

⁸ Kronberg, B.; Holmberg, K.; Lindman, B., *Surface Chemistry of Surfactants and Polymers*. John Wiley & Sons, Incorporated: Somerset, 2014.

⁹ Caponetti, E.; Martino, D. C.; Floriano, M. A.; Triolo, R., Localization of n-Alcohols and Structural Effects in Aqueous Solutions of Sodium Dodecyl Sulfate. *Langmuir* **1997**, *13* (13), 3277-3283.

¹⁰ Duvoisin, S.; Kuhnen, C. A.; Ouriques, G. R., Theoretical Study of The Ammonium Perfluorooctanoate/Water System. *J. Mol. Struct.: THEOCHEM* **2002**, *617* (1), 201-207.

¹¹ Ohtaki, H.; Radnai, T., Structure and Dynamics of Hydrated Ions. *Chem. Rev.* **1993**, *93* (3), 1157-1204.

¹² Singh, G.; Verma, R.; Wagle, S.; Gadre, S. R., Explicit Hydration of Ammonium Ion By Correlated Methods Employing Molecular Tailoring Approach. *Mol. Phys.* **2017**, *115* (21-22), 2708-2720.

¹³ Ohtaki, H.; Radnai, T. Structure and Dynamics of Hydrated Ions. *Chem. Rev.* 1993, 93 (3), 1157–1204.

¹⁴ Marcus, Y. Ionic Radii in Aqueous Solutions. Chem. Rev. **1988**, 88 (8), 1475–1498.

¹⁵ Singh, G.; Verma, R.; Wagle, S.; Gadre, S. R. Explicit Hydration of Ammonium Ion by Correlated Methods Employing Molecular Tailoring Approach. *Mol. Phys.* **2017**, *115* (21–22), 2708–2720.

¹⁶ Hayter, B.; Frame, G. C.; Rcccwcd, I.; August, I.; Jt, I.; Introduction, I. Concentration-Dependent Structure of Sodium Octanoate Micelles. *Chem. Phys. Lett.* **1982**, *93* (I), 91–94.

¹⁷ Berr, S. S.; Jones, R. R. M. Small-Angle Neutron Scattering from Aqueous Solutions of Sodium Perfluorooctanoate above the Critical Micelle Concentration. *J. Phys. Chem.* **1989**, *93* (6), 2555–2558.

¹⁸ Rutgers, A. J.; Hendrikx, Y. Ionic Hydration. *Trans. Faraday Soc.* **1962**, *58*, 2184–2191.

¹⁹ Duvoisin, S.; Kuhnen, C. A.; Ouriques, G. R. Theoretical Study of the Ammonium Perfluorooctanoate/Water System. *J. Mol. Struct. THEOCHEM* **2002**, *617* (1), 201–207.

²⁰ Caponetti, E.; Chillura Martino, D.; Floriano, M. A.; Triolo, R. Localization of N-Alcohols and Structural Effects in Aqueous Solutions of Sodium Dodecyl Sulfate. *Langmuir* **1997**, *13* (13), 3277–3283.

²¹ Ritscher, A.; Wang, Z.; Scheringer, M.; Boucher, J. M.; Ahrens, L.; Berger, U.; Bintein, S.; Bopp, S. K.; Borg, D.; Buser, A. M.; et al. Zürich Statement on Future Actions on Per- and Polyfluoroalkyl Substances. *Environ. Health Perspect.* **2018**, *126* (8), 084502.

²² Wyman, J., The Dielectric Constant of Mixtures of Ethyl Alcohol and Water From -5 to 40. *J. Am. Chem. Soc.* **1931**, *53* (9), 3292-3301.

²³ Bodratti, A. M.; Cheng, J.; Kong, S. M.; Chow, M. R.; Tsianou, M.; Alexandridis, P., Self-Assembly of Polyethylene Glycol Ether Surfactants in Aqueous Solutions: The Effect of Linker between Alkyl and Ethoxylate. *Journal of Surfactants and Detergents* **2019**, *22* (5), 1147-1161

²⁴ Srinivasan, V.; Blankschtein, D., Prediction of Conformational Characteristics and Micellar Solution Properties of Fluorocarbon Surfactants. *Langmuir* **2005**, *21* (4), 1647-1660.

25 López-Fontán, J. L.; Sarmiento, F.; Schulz, P. C., The aggregation of sodium perfluorooctanoate in water. *Colloid Polym. Sci.* 2005, 283 (8), 862-871.

26 Antoniou, E.; Alexandridis, P., Polymer conformation in mixed aqueous-polar organic solvents. *Eur. Polym. J.* **2010**, 46 (2), 324-335.

27 Nagarajan, R., Are large micelles rigid or flexible? A reinterpretation of viscosity data for micellar solutions. *J. Colloid Interface Sci.* **1982**, 90 (2), 477-486.

28 Zoeller, N.; Blankschtein, D., Experimental determination of micelle shape and size in aqueous solutions of dodecyl ethoxy sulfates. *Langmuir* **1998**, 14 (25), 7155-7165.

²⁹ Borodin, O. Polarizable Force Field Development and Molecular Dynamics Simulations of Ionic Liquids. *J. Phys. Chem. B* **2009**, 113, 11463–11478.

³⁰ Head-Gordon, M., Pople, J. A., Frisch, M. J. MP2 Energy Evaluation by Direct Methods. *Chem. Phys. Lett.* **1988**, *153*, 503-506.

³¹ Kendall, R. A., Dunning Jr, T. H., Harrison, R. J. Electron Affinities of The First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. *J. Chem. Phys.* **1992**, *96*, 6796-6806.

³² Dong, D.; Hooper, J. B.; Bedrov, D. Structural and Dynamical Properties of Tetraalkylammonium Bromide Aqueous Solutions: A Molecular Dynamics Simulation Study Using a Polarizable Force Field. *J. Phys. Chem. B* **2017**, *121*, 4853-4863.

³³ Palmer, B. J. Direct Application of Shake to the Velocity Verlet Algorithm. *J. Comput. Phys.* **1993**, 104(2), 470–472.