Mixed Micelles of Fluorinated and Hydrogenated Surfactants

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Abstract: The model mixed surfactant system of sodium perfluorooctanoate and sodium decyl sulfate was carefully reexamined by a combination of nuclear magnetic resonance methods. Over a wide range of sample compositions, detailed ^{19}F and ^1H chemical shift data in combination with self-diffusion coefficients for the perfluorooctanoate and decyl sulfate ions are collected. All data are analyzed together in a framework that uses a minimal number of initial assumptions to extract the monomer concentrations of both surfactants and the micellar chemical shifts of ^{19}F and ^1H as a function of relative concentration. The main conclusion drawn from this analysis is that there exists neither complete demixing nor complete mixing on molecular or micellar levels. Instead, the experimental data favor a single type of micelles within which fluorinated surfactants are preferentially coordinated by fluorinated ones and hydrogenated surfactants by hydrogenated ones. The data are quantitatively interpreted in the framework of the first approximation of the regular solution theory (also called the quasi-chemical treatment) leading to an energy of mixing of $\omega = W/kT = 0.98$ between the constituting surfactant types. These findings may help to resolve a long controversy about micellar mixing−demixing in this particular mixture and in its relatives.

Introduction

Fluorocarbons have a strong hydrophobic character, and liquid perfluoroalkanes show a very low solubility in water. However, at room temperature fluoroalkanes are also immiscible with hydrogenated alkanes. This simultaneous hydro- and oleophobic character is unique and is exploited in a variety of applications, for instance, refrigeration, filtration, lubrication, foams, surface protection, and plastic manufacturing. The hydrophobicity of hydro- and fluorocarbons makes them both suitable as constituents in amphiphilic materials such as surfactants. The general features of the aqueous phase behavior of fluorinated and hydrogenated surfactants are similar, albeit with a few systematic differences. Hence, fluorinated surfactants reduce the surface tension of an aqueous solution more than a hydrogenated surfactant of comparable length, and the critical micelle concentration, CMC in water is generally lower for fluorosurfactants. For a given CMC value and a common headgroup, a hydrogenated surfactant contains roughly 1.5 times more carbon atoms compared to its fluorinated counterpart.[1] In the aggregated state, fluorosurfactants exhibit a lateral mobility[2] comparable to that of hydrogenated ones although the hydrocarbon tails are far more flexible and disordered than the fluorocarbon ones.[3,4] Many fluorosurfactants exhibit a high stability in extreme environments such as high temperatures and acidic conditions, largely due to the strongest single bond in organic chemistry, the C−F bond.

It has long been recognized that the mutual phobicity of fluorinated and hydrogenated surfactants can, together with the hydrophobicity of both species, lead to a nontrivial aqueous phase behavior.[5−8] Despite intensive research, this nontriviality seems to be of persistent character. From a theoretical perspective, there are several possible descriptions with often conflicting predictions. This situation is both based on and fuelled by apparently contradicting experimental investigations. To a large part, experimental discrepancy results from observational and instrumental limitations and interpretational problems of sparse data sets. Nothing illustrates these issues clearer than the substantial research effort invested in clarifying the microscopic pseudophase behavior of the aqueous mixtures of sodium perfluorooctanoate, SPFO, and sodium decyl sulfate, SDeS. The main and recurring question is whether SPFO and SDeS do form mixed micelles?

SPFO and SDeS are two common surfactants with approximately equal degrees of hydrophobicity. At 25 °C, their CMC values are close: 31 mM for SPFO[9] and 33 mM for SDeS.[10] Their degrees of counterion binding are somewhat different, 0.63−0.64 for SDeS[11,12] and 0.54−0.56 for SPFO.[13−15]

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In their influential study by equivalent conductance, Mukerjee and Yang[16] showed that the CMC for an aqueous mixture of SPFO and SDeS was higher than the CMCs of the individual components in water. The maximum CMC (roughly 40 mM at 25 °C) was found in the region of equimolar composition. On the basis of those data and inspired by the mutual phobicity between hydro- and fluorocarbon chains Mukerjee and Yang suggested the existence of two kinds of micelles, one rich in fluorosurfactants and one rich in hydrogenated surfactants. Their evidence was indirect: the measured CMC values were close to ones calculated for the case of complete demixing of SPFO and SDeS under the assumption of a logarithmic dependence between the CMCs and the concentration of counterions.[17,18] The idea of two distinct kinds of micelles has been subsequently supported by others. Among those, Zhu and Zhao[19,20] also relied on experimental CMC values (measured by surface tension) that coincided with values calculated under theoretical considerations similar to those of Mukerjee and Yang. In building perhaps the strongest case, Nagarajan claimed that within the framework of his sophisticated thermodynamic theory of micelle formation[21] the conductivity- and surface-tension-derived CMC data of Wada et al.[22] indicate micellar demixing. Two types of coexisting micelles were asserted: one rich in the fluorosurfactant with molar ratio $x_{SPFO} \geq 0.78$ and the other one rich in SDeS. In a similar analysis, Aratono et al.[23] reported the range $0.25 < x_{SDeS} < 0.72$ of sample compositions within which demixing occurred. Similar claims were sometimes based on partly contradicting experimental evidence: for example, Sugihara et al.[24] found two apparent CMC values by measuring the specific conductivity versus concentration, where the second one was independent of the composition. Since such a behavior is inconsistent with mixed micellization, the finding was interpreted as a sign of demixing.

Ever since the initial claim of demixing,[16] others stated the opposite: no demixing in the aqueous mixture of SPFO and SDeS. The opponents generally relied on the regular solution theory, which was first applied to the SPFO/SDeS system by Shinoda and Nomura.[25] Using the very CMC values of Mukerjee and Yang,[16] Shinoda pointed out that the energy of mixing $\omega = W/kT$ is below 2, and therefore complete mixing was expected. In this expression, W defines[26] the increase of energy of the system upon replacing one molecule A by one molecule B and vice versa in two fully phase-separated domains of A and B. From the experimental perspective, Harada and Sahara[27]

measured the mean partial molar volumes of a 1:1 mixture and arrived at only one CMC value, suggesting a completely mixed micelle with equal amounts of both surfactants. Reapplying the regular solution theory Kamogawa and Tajima[28] concluded that the CMC data derived from surface tension and conductance measurements are consistent with complete mixing over the whole compositional range. Those authors also presented supporting results from a molecular technique: electron spin resonance, ESR. Experiments monitored a nitrosyl radical incorporated into the micelles. The obtained probe rotational correlation times varied continuously over the entire composition range at 45 and 100 mM total surfactant concentration, which was interpreted as direct indication of complete mixing. Arguments for this finding and some indications of partial demixing (among micelles when 100 mM NaCl is added to the system, or into separate intramicellar regions) are weakened, though, by a serious drawback of the ESR method, namely the addition of and measurement on a third non-native molecular component. A third and also a fourth probe were added by Asakawa and Miyagishi[29] in a fluorescence quenching study. The fluorescence of alkyl- and perfluoroalkylpyridinium ions was monitored in 0−50 mM surfactant solutions with 200 mM NaCl added. The results suggested "a rather miscible mixed micelle".

NMR spectroscopy is a prominent molecular technique that uses native molecular probes. In the first such study in this context, Carlfors and Stilbs[30] exploited ^{1}H and ^{19}F self-diffusion coefficients and spin relaxation data. Conclusions at that time were that demixing did occur, and that separate micelle types were formed in mixed alkanoate systems. Asakawa et al.[31] measured ^{19}F NMR chemical shifts and interpreted the data within the regular solution theory as signature of complete mixing. In contrast to the majority of previous studies, they also investigated the system at higher surfactant concentrations. Unfortunately, the extrapolative fashion they derived their micelle-specific chemical shifts remained unjustified. Guo et al.[32] instead used surface tension and ^{1}H and ^{19}F chemical shifts to obtain the CMC values for the mixed system. Within the regular solution theory, those results confirmed complete mixing. However, the chemical shifts did not give distinct CMC values at all compositions: both the ^{19}F shift at low SPFO content and the ^{1}H shift at low SDeS content resulted in curved intercept shapes. Unfortunately, this interesting point was ignored, and the conclusions were drawn from only a few reliable CMC values.

Some other weaknesses of thermodynamic approaches, such as uncertainties in experimental CMC values and the counterion effect have been pointed out by Kamrath and Frances.[33,34] Both have large impact on the decisive parameter—the energy of mixing. Kamrath pointed out that these effects may altogether render the results based on apparent CMCs inconclusive. De Lisi et al.[35] used the CMC values from the literature[23] and

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calculated the excess free energy for mixed micelle formation at all compositions. The work indicated no demixing region but instead a so-called critical point that is not in agreement with either of the two contrasting theories described above. Again, those results highlighted the extreme sensitivity of the obtained mixing scenario to the accuracy of CMC data.

Considering the wealth of investigations, it is not surprising that the SPFO/SDeS aqueous mixture is often presented as a prime and thoroughly reviewed[5] model system of surfactant mixing/demixing. The surprise is, indeed, that the basic question is still open—i.e., are the micelles mixed or demixed? In this paper, we try to resolve this long-debated issue. In a direct molecular (in contrast to thermodynamic) approach we exploit chemical shift and self-diffusion coefficient data by ^{1}H or ^{19}F NMR of the corresponding molecular species at varying concentrations. We want to point out that many other fluorinated– hydrogenated surfactant systems present interesting challenges to which the NMR approach outlined below could contribute positively.

Experimental Section

The total surfactant concentration (c) ranged from far below the CMCs up to 250 mM, and the mole fraction x_h of SDeS in the mixed system from 0 to 1. For all samples, both ^{19}F and ^{1}H NMR spectra were acquired and the peak positions recorded with the spectrometer frequency locked to the D$_2$O signal. All chemical shift data presented in Figure 1 are relative to the chemical shifts in the monomeric ($c = 10$ mM) SPFO and SDeS samples, with 0 ppm for ^{19}F assigned to the trifluoromethyl C(8)F$_3$ signal. The ^{1}H shift data instead refer to shift differences between the C(10)H$_3$ and the C(1)H$_2$ peaks, relative to the same shift difference in the monomer state. This approach is necessitated by the smaller value of the ^{1}H shift changes compared to those of ^{19}F. This condition makes the absolute chemical shift scale of ^{1}H more sensitive to minor (in the order of a Hz) errors in setting the external shift reference. Further experimental details are given as Supporting Information.

Results and Discussion

Chemical Shifts in Mixed Systems. The NMR chemical shift is a parameter that in part depends on the intermolecular surrounding of the nucleus in question. For a surfactant in a micellar solution, typically there are two such surroundings, an aqueous one in the monomer state and a hydrophobic one consisting of close-packed surfactant tails in the aggregated state. The exchange time between these two states is usually (with the exception of polymeric surfactants[36,37]) short with regard to the NMR time scale that is the inverse of the difference between the state-specific NMR frequencies. In that case, one can observe only the population average of the instantaneous chemical shifts

$$\delta^{obs} = \frac{c^{mon}}{c}\delta^{mon} + \left(1 - \frac{c^{mon}}{c}\right)\delta^{mic} \qquad (1)$$

where δ^{mon} represents the shift in the monomer state, δ^{mic} the shift of the aggregated state, c^{mon} the monomer concentration and c the total surfactant concentration.

Let us first consider the chemical shift of an atom in the hydrophobic surfactant tail. At low concentrations, the chemical
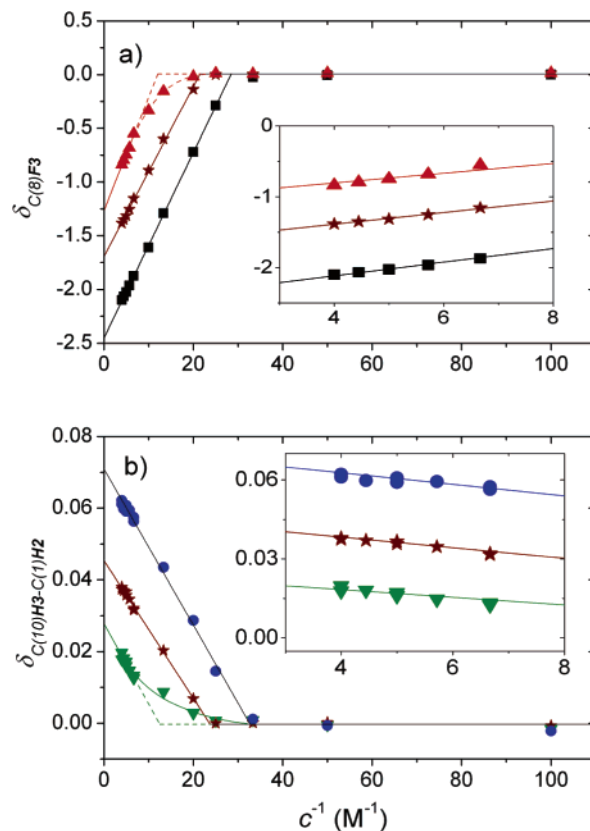
Figure 1. NMR chemical shifts in aqueous SPFO/SDeS mixtures at different molar fractions $x_h = 0$ (■), $x_h = 0.25$ (▼), $x_h = 0.50$ (★), $x_h = 0.75$ (▲), $x_h = 1$ (●) and as a function of the inverse total surfactant concentration. (a) The ^{19}F chemical shift of the trifluoromethyl group in SPFO. (b) The ^{1}H chemical shift difference between methyl and α-methylene groups of SDeS. (Inserts) Application of eq 2 to the shift data in the 150–250 mM concentration range.

shift is independent of concentration up to the CMC, as a consequence of the unaffected aqueous chemical environment. At CMC, micelles start to form, and the atom may become embedded in the micellar core, with the surrounding there significantly different from that in water. Upon increasing concentration, more and more surfactants form micelles while the monomer concentration remains close to the CMC value, yielding the functional dependence of eq 1. The further the atom from the headgroup, the larger the change of environment. Hence, the end of the hydrophobic tail should be most sensitive to micellar aggregation. Under the assumption of a constant c^{mon} above CMC and concentration-independent micellar interior, δ^{obs} becomes a linear function of c^{-1} and the intercept of this dependence and the constant δ^{mon} line defines the CMC. The method outlined above has been used countless times for measuring CMCs by NMR. However, the validity of assumptions underlying eq 1 is limited even in simple surfactant systems:[38,39] for example, above the CMC, c_{mon} is not independent of concentration.[40–42]

For a variety of reasons, the chemical shift of ^{19}F nuclei is more than 1 order of magnitude more sensitive to the intermo-

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lecular environment than that for ^1H nuclei. Hence, the ^{19}F chemical shift difference between aqueous and dense fluorocarbon environments is roughly 2–3 ppm, while the ^1H chemical shift difference between aqueous and hydrocarbon environments is <0.1 ppm. Furthermore, there is a well-documented difference[43] between ^{19}F chemical shifts in dense *fluorocarbon and hydrocarbon* environments. Hence, one can expect the chemical shift to be a suitable tool for investigating the composition of micelles in mixed fluorosurfactant−hydrogenated surfactant system. This remains true even if it is known that conformational changes may also slightly affect the chemical shift in the different surfactant states. If at all significant, this effect should be present in the more flexible hydrogenated surfactants.

In a mixed solution of fluorosurfactant (f) and hydrogenated surfactant (h) the chemical shift of the fluorosurfactant f is given by

$$\delta_f{}^{obs} = \frac{c_f{}^{mon}}{c_f}\delta_f{}^{mon} + \left(1 - \frac{c_f{}^{mon}}{c_f}\right)\delta_f{}^{mic} \qquad (2)$$

where c_f represents its total concentration and $c_f{}^{mon}$ its monomer concentration; an analogous expression is valid for surfactant h. Even though eq 2 is *formally* equivalent to eq 1, there are two crucial differences. First, in eq 1 the assumption of constancy of δ^{mic} is both physically plausible (in case of constant micellar size) and experimentally verified in many systems. On the other hand, $\delta_f{}^{mic}$ and $\delta_h{}^{mic}$ should, indeed, be dependent upon the nature−molecularly mixed or not−of the formed aggregates. Second, the amount of monomeric surfactant $c_f{}^{mon}$ is *essentially* unknown. For these reasons, evaluation of the dependence of the chemical shift on the total and relative concentrations cannot alone be informative on the nature of the formed aggregates in mixed systems. Any result[31,32,44,45] derived on that basis must inevitably be dependent on simplifying assumptions that have to be made to reduce the number of unknowns (two for each molecular species, $c_f{}^{mon}$, $c_h{}^{mon}$, $\delta_f{}^{mic}$, $\delta_h{}^{mic}$) to the number of independent experimental parameters (one for each molecular species, $\delta_f{}^{obs}$ and $\delta_h{}^{obs}$). Hence, complementary experimental information is required to perform a less biased analysis of the shift data.

Self-Diffusion Coefficients in Mixed Systems. The self-diffusion coefficient in solution (*D*) depends on the temperature, the viscosity of the solvent, and the size of the species in question. For the latter reason, *D* is sensitive to molecular aggregation. For a fast exchange of surfactant molecules between the monomer and micellar aggregate states the experimental self-diffusion coefficient becomes the population average

$$D^{obs} = \frac{c^{mon}}{c}D^{mon} + \left(1 - \frac{c^{mon}}{c}\right)D^{mic}, \qquad (3)$$

where D^{mon} represents the diffusion coefficient of the monomer and D^{mic} the diffusion coefficient of the micelle. Functionally, eq 3 is akin to eq 1. At high surfactant concentrations, obstruction effects caused by micellar aggregates can be

explicitly taken into account as[46]

$$D^{obs} = \frac{c^{mon}}{c}\frac{D^{mon}}{1 + \dfrac{\Phi}{2}} + \left(1 - \frac{c^{mon}}{c_i}\right)\frac{D^{mic}}{1 + 2\Phi}, \qquad (4)$$

where Φ represents the micellar volume fraction.

In a mixed solution with two types of surfactants, f and h, the observed self-diffusion coefficient for surfactant f is given instead as

$$D_f{}^{obs} = \frac{c_f{}^{mon}}{c_f}\frac{D_f{}^{mon}}{1 + \dfrac{\Phi}{2}} + \left(1 - \frac{c_f{}^{mon}}{c_f}\right)\frac{D_f{}^{mic}}{1 + 2\Phi} \qquad (5)$$

with an analogous expression for surfactant h. Two important issues should be pointed out. First, it is the total micellar volume that obstructs diffusion and therefore Φ becomes

$$\Phi = (c_f - c_f{}^{mon}){\cdot}V_f{}^{mic} + (c_h - c_h{}^{mon}){\cdot}V_h{}^{mic} \qquad (6)$$

where $V_i{}^{mic}$ is the molar volume of the micellized surfactant anion *i*. Second, just as in the case of chemical shifts, the concentration dependence of the observed surfactant self-diffusion coefficients[30,47,48] cannot be properly evaluated in terms of mixed aggregates without making some simplifying and, in principle, unverifiable assumptions. Note that the straightforward combination of the diffusion and chemical shift data is not of any help since the number of unknowns (six, $c_f{}^{mon}$, $c_h{}^{mon}$, $\delta_f{}^{mic}$, $\delta_h{}^{mic}$, $D_f{}^{mic}$, $D_h{}^{mic}$) still exceeds the number of independent experimental parameters (four, $\delta_f{}^{obs}$, $\delta_h{}^{obs}$, $D_f{}^{obs}$, $D_h{}^{obs}$).

Although the functional dependencies in eqs 2 and 5 are the same, the parameters involved are rather different. As demonstrated below, one can conservatively exploit the self-diffusion data to get *accurate and model-independent* estimates of $c_f{}^{mon}$ and $c_h{}^{mon}$. In doing so, we gain access to *model-independent* information about the mixed micelles in the form of the extracted $\delta_f{}^{mic}$ and $\delta_h{}^{mic}$ values.

Consistent Analysis of Experimental Chemical Shifts and Self-Diffusion Coefficients. The self-diffusion coefficients of the two surfactant species were measured in the range of total concentrations $c = 150-250$ mM and mole fractions $x_h = 0-1$, and in 10 and 20 mM monomeric solutions of single surfactants (see a selected set of data in Figure 2, all other data are given as Supporting Information). Monomeric diffusion coefficients (see Table 1) were identical (within the approximately 2% experimental error) at 10 and 20 mM for both SPFO and SDeS.

The volume fraction of micelles required for the evaluation can be obtained from scattering experiments. The data of Berr and Jones[15] provide an estimate of 0.4 L/mol for the volume of the micellized PFO$^-$ anion. However, their estimate includes hydration water; subtracting the volume of six hydration water molecules per micellar surfactant gives a volume estimate of ca. 0.3 L/mol. Griffiths et al.[49] arrived at the volume of the micellized dodecyl sulfate anion by an analysis of SANS data.

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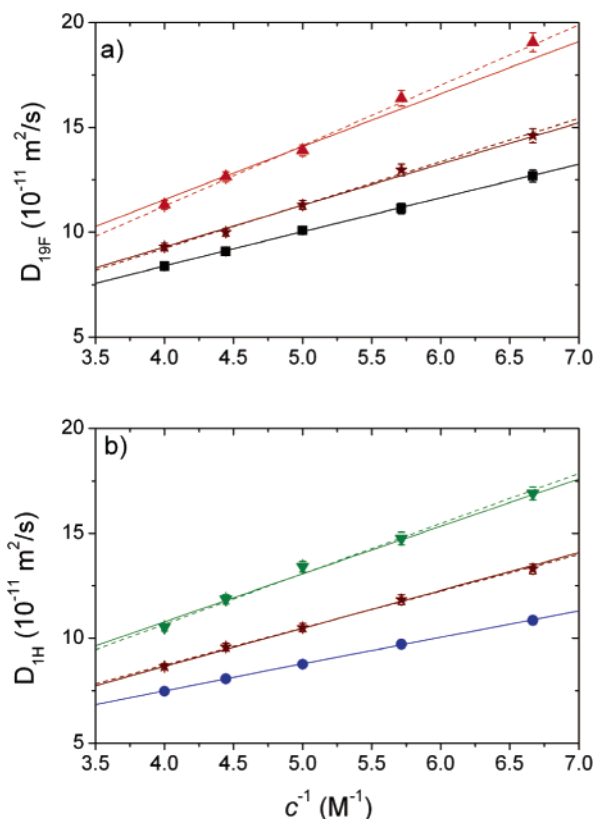
Figure 2. NMR self-diffusion coefficients in aqueous SPFO/SDeS mixtures at different molar fractions $x_h = 0$ (■), $x_h = 0.25$ (▼), $x_h = 0.50$ (★), $x_h = 0.75$ (▲), $x_h = 1$ (●) and as a function of the inverse total surfactant concentration. (a) SPFO. (b) SDeS. The lines represent fits of eq 5 to the data under the assumption of complete mixing (solid) or complete demixing (dashed) of SPFO and SDeS.

Table 1. Self-Diffusion Coefficients of Monomeric Perfluorooctanoate (D_f^{mon}) and Decyl Sulfate (D_h^{mon}) Surfactant Ions at 10 and 20 mM Concentrations, Respectively

c (mM)	D_f^{mon} (10^{-11} m² s⁻¹)	D_h^{mon} (10^{-11} m² s⁻¹)
10	43.7 ± 0.9	43.2 ± 0.7
20	43.3 ± 0.8	44.3 ± 0.7

A recalculation of their information for the decyl sulfate ion sets the latter volume to approximately 0.3 l/mol. Therefore, in our evaluation below we set $V_f^{mic} = V_h^{mic} = 0.3$ L/mol; since the micellar volume fractions are still low (<8%) at any of the concentrations, even a 20% error in estimating the micellar volume fractions modifies the final obtained monomer concentrations by less than 1%.

Since we do not *a priori* know the state of aggregates in the mixed system, we evaluate our concentration-dependent diffusion data for the two extreme cases: (i) complete mixing and (ii) complete demixing of SPFO and SDeS. In case (i) we set $D^{mic} = D_f^{mic} = D_h^{mic}$ while fitting eq 5 and its analogue for D_h^{obs} to the experimental data. In the opposite case (ii) we allow two independent values for D_f^{mic} and D_h^{mic} while fitting the two equations to their respective data sets. Irrespective of the model, the monomer diffusion coefficients were set to the values (see Table. 1) obtained in the corresponding monomeric solutions. Typical fits to some selected data sets are shown in Figure 2. The first conclusion is that there are no systematic deviations between the experimental data and the theoretical fits, irrespective of the chosen model of mixing. The obtained concentrations
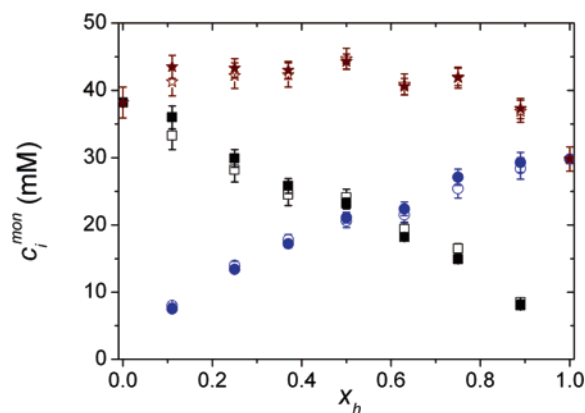
Figure 3. Individual monomer concentrations of SPFO (■) and SDeS (●) and the total monomer concentration (★) in the range of total surfactant concentrations of 150−250 mM as obtained from fits illustrated in Figure 2. Data represented by open and full symbols were obtained under the assumption of complete mixing or complete demixing, respectively.
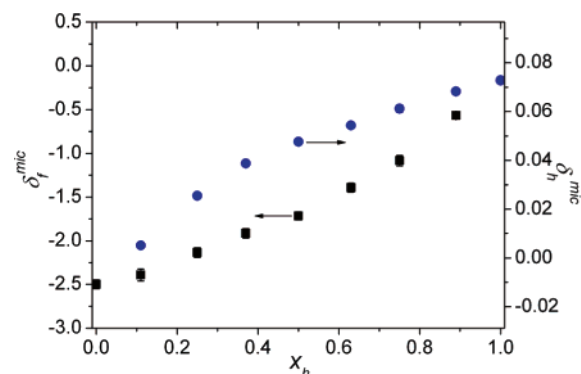

Figure 4. Micellar ^{19}F chemical shifts of the trifluoromethyl group in SPFO (■) and the micellar ^{1}H chemical shift difference between the methyl and α-methylene groups in SDeS (●) presented as a function of the surfactant molar fraction. The error bars (visible only for a few data points) predominantly propagated from the monomer concentration uncertainties taken as differences between extremes of possible values in Figure 3.

of monomeric surfactants at different mole fractions x_h are shown in Figure 3. Clearly, monomer concentration is by good approximation (within a few percent) independent of the selected model in the range $c = 150−250$ mM. The ultimate reason behind this favorable outcome is the order-of-magnitude difference between the large monomer and the much lower micellar self-diffusion coefficients. For the same reason, the error of the obtained *micellar* diffusion coefficients is large, of the order of 50%. Moreover, since those data are model-dependent they have no intrinsic value.

Returning now to eq 2 and its analogue for δ_h^{obs}, the chemical shift characteristic for the micelles can be obtained by fitting to the concentration dependence of the respective chemical shift in the $c = 150−250$ mM range with one free parameter in each fit: δ_f^{mic} and δ_h^{mic}. The quality of the obtained fits is illustrated in Figure 1 (see all data in Supporting Information) while the so-obtained micellar chemical shifts are displayed in Figure 4. The apparent symmetry of the ^{1}H and ^{19}F chemical shift data (with respect to a linear dependence) indicates that conformational effects cannot have a major influence on the observed chemical shifts, which are instead predominantly defined by intermolecular effects.

The data and the fits in Figure 1 also illustrate that the CMC is well defined (by a precision of less than 10%) by a
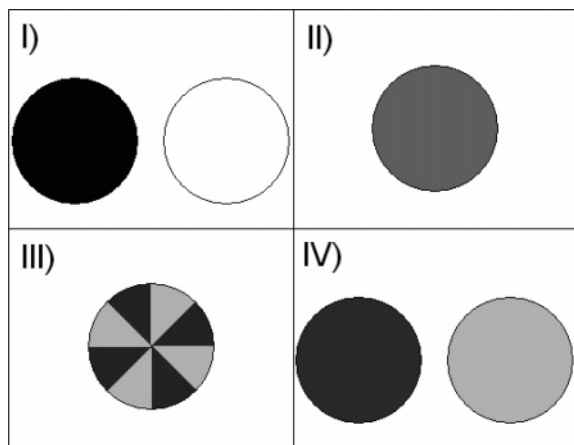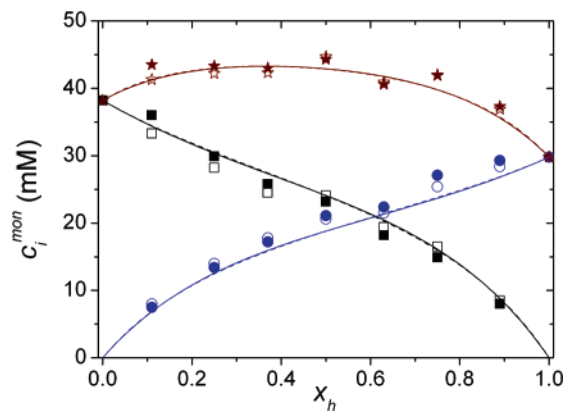
Figure 5. Schematic illustration of the four models of aggregation for mixed aqueous solutions of SPFO and SDeS. (I) Complete demixing. (II) Complete mixing. (III) Nonrandom molecular mixing in a single type of micelles. (IV) Partially demixed micelles.

Figure 6. Application of the regular solution theory to individual monomer concentrations of SPFO (■) and SDeS (●) and the total monomer concentration (★) in the 150−250 mM range of total surfactant concentration. The fits of the zeroth (solid line, yielding $\omega = 0.93$ for the energy of mixing) and the first approximation (dashed line, $\omega = 0.98$) of the regular solution theory virtually coincide.

conventional NMR analysis only at mole fractions $0.3 < x_h < 0.7$. In that region, the slope of the chemical shift changes abruptly for both surfactant species. At other mole fractions, there is a smooth transition region between "monomer" and "micellar" regimes of the concentration dependence of the chemical shifts. First, this finding directly questions the reliability of previous CMC determinations by NMR in this mixed surfactant system (and, perhaps, also in other ones). Second, it points to a strong variation of the monomer concentration of the minor surfactant component at the onset of micellar aggregation. This can be explained by the nonideality of mixing that may favor separating the minor component from the initial pure aggregates of the major component. If so, this finding also casts doubt on the interpretation of other data for this system, primarily those based on conductivity

Irrespective of the behavior in the vicinity of CMC, we have two sets of *consistent and model-independent* data that convey information on the state of micelles in the $c = 150-250$ mM range. One data set, i.e., the variation of the monomer concentrations with the mole fraction in Figure 3, is indirect and may provide further insight through a thermodynamic analysis (see below). The other data set, the micellar chemical shifts in Figure 4, can provide direct molecular information on the state of micelles in our mixed system. Below, we investigate which of the possible micellar structures are consistent with this molecular information.

Tests of the Aggregation Models: Completely Immiscible Surfactants. In this extreme, the system contains two different kinds of micelles, one purely built by SPFO and the other one by SDeS, as illustrated by Scheme I in Figure 5. There, the micellar shifts δ_f^{mic} and δ_h^{mic} would be expected to be roughly constant upon altering the mole fraction, since the intermolecular environment would remain constant for both the ^{19}F and ^{1}H nuclei. Regarding the data of Figure 4, the continuous change of δ_f^{mic} and δ_h^{mic} with composition excludes this model.

This conclusion is in accordance with the obtained monomer concentrations in Figure 3. Regular solution theory (in the zeroth approximation) applied to experimental CMC values[25,31] previously yielded $\omega = 1.8$ for the energy of mixing in our systems. Considering the large impact[33,34] of experimental uncertainties on those findings and that $\omega = 2$ is the division line within that theory between mixing and demixing, that value could not

convincingly clarify the nature of SPFO−SDeS mixing. Furthermore, previous such evaluations of NMR data[31] depended on strong simplifying assumptions (see discussion above concerning chemical shifts). Instead, fitting the regular solution theory in the zeroth approximation to our experimental monomer data (see Figure 6) yields $\omega = 0.93 \pm 0.02$, a number that is clearly inconsistent with immiscible behavior of SPFO and SDeS.

Tests of the Aggregation Models: Completely Miscible Surfactants. If complete mixing occurs (Scheme II in Figure 5), the micelle has a spatially uniform distribution of fluorinated and hydrogenated surfactants. The chemical shift of micellar species f, δ_f^{mic} depends then on its relative molar volume in the micelle as

$$\delta_f^{mic} = \phi_h^{\ 0}\delta_f^{\ H} + \phi_f^{\ 0}\delta_f^{\ F} = \delta_f^{\ H} + \phi_f^{\ 0}(\delta_f^{\ F} - \delta_f^{\ H}) \qquad (7)$$

where ϕ_f^0 and $\phi_h^0 = 1 - \phi_f^0$ represent the molar volume fractions of the tails of surfactant f and h, respectively, in the micellar state. δ_f^F stands for the ^{19}F shift of surfactant f in a *fluorinated* environment and δ_f^H for the ^{19}F shift in a *hydrogenated* environment. On the basis of eq 7, one would then naively expect a linear variation of chemical shifts by the mole fraction x_h. This is clearly not the case. However, there are two reasons why the theoretical curve should not be linear.

First, the volumes of the two surfactant tails are not identical. The best estimates for their ideal molar volumes can be derived from densities of alkanes and perfluoroalkanes[50−52] which yield $V_{ideal}^{PFO} = 202$ mL/mol and $V_{ideal}^{DeS} = 177$ mL/mol. In Figure 7 we plot the expected chemical shift variation corresponding to these molar volumes and two other simulations where the relative molar volumes are set 10% higher (1.25) and 10% lower (1.03) than the best estimate above (1.14). Through this procedure we investigate the effect of uncertainties in our volume estimates. Clearly, the figure shows that this effect is small and cannot account for the experimental behavior of the chemical shifts.

(50) *CRC Handbook of Chemistry and Physics*; Electronic Edition Version, 2004.
(51) *CrossFire Beilstein Database*, 2006.
(52) *Chemfinder CambridgeSoft Corporation*, http://chemfinder.cambridgesoft-.com/, 2006.
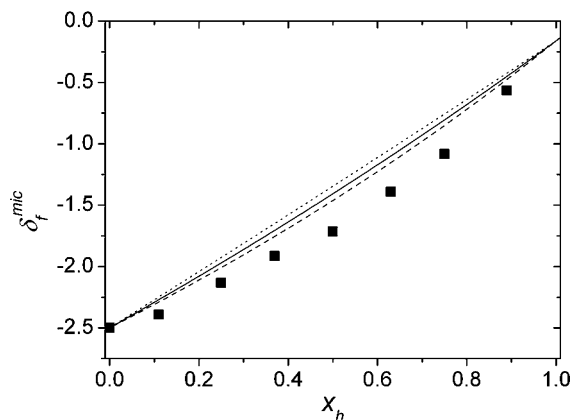
Figure 7. Micellar ^{19}F chemical shift of the SPFO trifluoromethyl group (■) as a function of the molar fraction. Complete mixing with ideal volume effect and with $V_{ideal}^{PFO} = 202$ mL/mol and $V_{ideal}^{DeS} = 177$ mL/mol yields the solid line. The shift variation with the relative molar volumes set 10% higher (dashed line) and 10% lower (dotted line) is also displayed.

Second, there is no reason to assume that *within the micelle* any mixing of alkane and perfluoroalkane moieties is ideal. Even if that did not lead to separation of different surfactants into distinct regions within the aggregate (see also model III), one should obtain slightly larger micellar volume akin to the case of the volume change upon mixing perfluoroalkane with an alkane. Hence, nonideal mixing leads to

$$\phi_f = \phi_f^{\,0}\frac{\rho}{\rho^0}, \qquad (8a)$$

$$\phi_h = \phi_h^{\,0}\frac{\rho}{\rho^0}, \qquad (8b)$$

where ρ_0 represents the density of an ideal solution and ρ the actual density. Since the chemical shift is a sensitive function of density, this effect cannot be neglected.

To properly account for such a nonideality, we must return to the full expression of intermolecular shielding effects[53] from which the conventional relation eq 7 can be derived in case of ideal mixing. Hence, the chemical shift generally becomes

$$\delta_f^{\,mic} = \delta_f^{\,GAS} - \phi_f(\delta_f^{\,GAS} - \delta_f^{\,F}) - \phi_h(\delta_f^{\,GAS} - \delta_f^{\,H}), \quad (9)$$

where $\delta_f^{\,GAS}$ represents the ^{19}F shift in the gaseous state, i.e., without contributions from intermolecular effects. Combining this with eqs 8 and 9 finally leads to

$$\delta_f^{\,mic} = \delta_f^{\,GAS} - \frac{\rho}{\rho^0}\{\phi_f^{\,0}(\delta_f^{\,GAS} - \delta_f^{\,F}) - \phi_h^{\,0}(\delta_f^{\,GAS} - \delta_f^{\,H})\}. \qquad (10)$$

In an ideal solution, $\rho = \rho_0$, and we thus return to eq 7.

To explore the effect of nonideal mixing upon the chemical shifts, the numerical values of $\delta_f^{\,GAS}$, $\delta_f^{\,F}$, $\delta_f^{\,H}$, and ρ must be at hand. The first three are listed by Abraham et al.;[43] for the C(8)-F$_3$ group of perfluorohexane in mixtures with hydrogenated alkanes of different lengths or in the gaseous phase, see the summarized values in Table 2. One could well argue that these literature values for $\delta_f^{\,F}$ and $\delta_f^{\,H}$ are not fully applicable for a surfactant methyl group in a micelle. However, they are in very good agreement with the micellar shifts at $x_h = 0$ and $x_h = 1$ in

(53) Muller, N. *J. Magn. Reson.* **1977**, *28*, 203-216.

Table 2. ^{19}F Chemical Shift of the Trifluoromethyl Group in Different Chemical Environments[43]

environment	δ_t (ppm)[a]
gas	−6.336
fluorocarbon	−2.499
hydrocarbon	−0.161[b]

[a] The shift values are given with respect to the trifluoromethyl shift in its aqueous monomeric state (0 ppm). [b] Extrapolated chemical shift in $C_{10}H_{20}$ from chemical shifts at $x_h \approx 1$ measured in alkanes of different lengths.
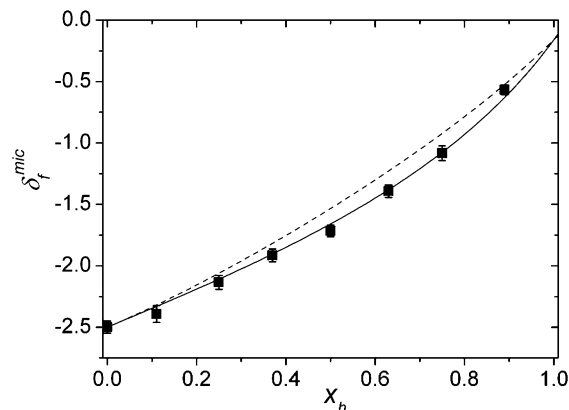
Figure 8. Micellar ^{19}F chemical shift of the SPFO trifluoromethyl group (■) as a function of the molar fraction. The chemical shift variation calculated under the assumption of nonideal volume excess for a spatially homogeneous SPFO/SDeS mixture within a micelle is shown as a dashed line. The solid line was obtained by fitting eqs 13−15 derived by the first approximation of the regular solution theory and nonideal excess volume to the chemical shift data. The fit yields $\omega = 0.98 \pm 0.02$ for the energy of mixing of SPFO and SDeS and a molecularly nonrandom mixing characterized by approximately 20% preference of the same surfactant type as nearest neighbors within the micelle.

Figure 4 (where the last one is extrapolated). Since we cannot find sufficiently good reference values for comparable ^1H chemical shifts, $\delta_h^{\,mic}$ is left without further analysis.

Concerning the density of alkane-perfluoroalkane mixtures, Bedford and Dunlap[54] and more recently Lepori et al.[55] investigated the volume effect for various chain lengths, compositions, and temperatures. If we assume that the interior of a micelle can be by a good approximation described as a liquid alkane−perfluoroalkane mixture, those data for miscible pairs (such as hexane and perfluorohexane) can be exploited. Hence, the excess volume, V_{exc} is approximated by a polynomial equation

$$V_{exc} = x_f x_h[A_0 + A_1(x_f - x_h) + A_2(x_f - x_h)^2] \qquad (11)$$

with $A_0 = 19.94$ cm^3/mol, $A_1 = 0.77$ cm^3/mol, and $A_2 = 6.15$ cm^3/mol.[55] The true density of the micellar interior is then obtained from the excess volume as

$$\frac{\rho}{\rho_0} = \frac{V_{ideal}}{V_{ideal} + V_{exc}} \qquad (12)$$

with the ideal molar volumes of the chains set to values given above. The dotted line in Figure 8 represents the chemical shift calculated via eq 10, using shift data from Table 2 and densities from eqs 11−12. Clearly, the result is not in good agreement

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(55) Lepori, L.; Matteoli, E.; Spanedda, A.; Duce, C.; Tine, M. R. *Fluid Phase Equilib.* **2002**, *201*, 119−134.

with the experimental micellar chemical shifts δ_f^{mic}. Therefore, we suggest that a single type of micelles with a spatially homogeneous micellar interior is not the state of the PFO-DeS mixture.

Tests of the Aggregation Models: Micelles with Partial Separation of the Constituting Surfactants. Qualitatively, the experimental micellar shifts seem to lie between the two extreme cases, (i) complete demixing and (ii) complete and within the aggregate spatially homogeneous mixing of the two surfactants types. Hence, a qualitative explanation that allows for a spatial inhomogeneity of surfactant distribution seems plausible. There are two possibilities: either there are regions with different tail concentrations within a single sort of micelle or there are two micellar populations with different concentrations of the surfactants. These models are depicted as Schemes III and IV in Figure 5. It is important to realize that because of fast exchange of individual surfactants between micelles on the NMR time scale these two possibilities cannot be distinguished on the basis of the measured average chemical shifts. Instead, in the simplest case both models can be characterized by local volume fractions $\phi_f^{loc} > \phi_f^0$ and $\phi_h^{loc} = \phi_h^0 - (\phi_f^{loc} - \phi_f^0)$ that describe the time average of the excess of surfactant f and the deficit of surfactant h as nearest neighbors for surfactant f. It is also clear from our data that this local excess, that we try to characterize below, must be rather small. In this model,[56] the average micellar chemical shift becomes

$$\delta_f^{mic} = \delta_f^{GAS} - \left\langle\frac{\rho}{\rho^0}\right\rangle\{\phi_f^{loc}(\delta_f^{GAS} - \delta_f^F) - \phi_h^{loc}(\delta_f^{GAS} - \delta_f^H)\} \tag{13}$$

where $\langle\rho/\rho^0\rangle$ represents an average over the different local environments.

For a single type of micelles we can explore this model within the framework of the quasi-chemical treatment, or *the first approximation* of regular solution theory[26] which describes a molecularly *nonrandom* mixing in a binary solution. The treatment in its original form is only valid for mixtures where the molecules are of equal size and where there are no excess volume effects upon mixing. However, these restrictions are minor since $V_{ideal}^{PFO}/V_{ideal}^{DeS} = 1.14$ (that is, close to 1) and excess volume effects are rather small, too ($\rho/\rho_0 = 0.974$ at $x_h = 0.5$).[55] Using this approach, we describe the local volume fractions through

$$\phi_f^{loc} = \frac{\phi_f^0}{x_f}\left\{1 - \frac{2x_h}{1 + (1 + 4x_h x_f \gamma)^{1/2}}\right\} \tag{14}$$

where

$$\gamma = \exp\left(\frac{2w}{zkT}\right) - 1. \tag{15}$$

For a small local surfactant excess/deficit, $\langle\rho/\rho^0\rangle$ is by good approximation [the effects are of higher order in $(\phi_f^{loc} - \phi_f^0)$] the same as ρ/ρ_0 for the spatially homogeneous case; we shall use this approximation below.

One important difference between the zeroth and the first approximations of the regular solution theory is the number of nearest neighbors z specified in the latter. An interesting feature

of the first approximation applied to aggregated systems is the insensitivity of the monomer concentration to the number of nearest neighbors z. On the other hand, ϕ_f^{loc} is very sensitive to this particular parameter. Hence, as a test of our whole experimental and evaluation procedure we simultaneously fit all of the obtained monomer concentrations[25,26] (Figure 6) and micellar chemical shifts (via eq 13, see Figure 8) within the framework of the first approximation of the regular solution theory. This yields parameter values $\omega = 0.98 \pm 0.02$ and $z = 4.7 \pm 0.7$. The latter number coincides with sound expectations based on generally accepted ideas on micellar structures. Moreover, the ω values obtained in the first and zeroth approximations are close to each other. Note that, with an energy of mixing of $\omega = 0.98$ that is clearly below its limiting value[26] $\omega \geq 2$, there is no micellar-level demixing predicted by the regular solution theory.

From the data above the average local excess of fluorinated neighbors to the fluorosurfactants becomes $\phi_f^{loc}/\phi_f^0 = 1.10$. In other words, a fluorinated surfactant has approximately 20% more fluorinated than hydrogenated neighbors. We stress that from the chemical shifts alone we cannot decisively establish whether the molecular demixing is on the molecular (see Scheme III) or on the aggregate (Scheme IV, with two micellar sorts with 20% difference in relative compositions) level or is in an intermediate state between those two limiting situations. Selection among these models is permitted instead by the monomer concentration data that, interpreted above within framework of the regular solution theory, favor Scheme III.

Conclusions

We have reinvestigated the mixed surfactant system of SPFO and SDeS in aqueous solution. As outlined in the Introduction, the system is a classical example among surfactant scientists albeit without an agreement about its actual molecular structure. This awkward situation reflects the inherent complexities with investigating fluorinated−hydrogenated mixed surfactant systems. These complexities that make the investigations prone to experimental and interpretational artifacts can be crudely grouped in three broad classes. Note that in some particular systems with clear and divergent molecular scenarios[57] experiments can provide a clear preference for either particular structural model.

All experiment types that rely on non-native probe molecules[28,29,58,59] (or non-native environments[60]) suffer from inherent problems related to uncertainties concerning partition coefficients. Note that exploiting different (i.e., fluorinated and hydrogenated) probe molecules with known partition coefficients in distinct pure environments will not necessarily aid the interpretation of data obtained in a complex molecular environment. This is amply indicated by the present study. Drawing conclusions about micellar aggregates from data recorded at dividing interfaces[60] suffers from similar limitations.

The scarcity of data is the common element in the second group. We dealt with a system that has not only different molecular components but also different and delicately balanced

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(and, hence, often strongly dependent on the counterions[61,62]) physical states. Hence, a meaningful characterization of the structure on all levels may involve several (in our present case, four to five) numerical parameters. Typically, one has no access to (i) equally many or more experimental variables, (ii) all of which are sensitive to those structural parameters. As concerning NMR, corresponding implications have been discussed above. Here, it is the fortuitously different dynamic ranges of two experimental parameters (chemical shift and diffusion) to concentration change that aids the analysis. Previous NMR studies[30,31,44,45,48,63] had to rely on some assumptions to reduce the number of structural parameters. Even when done with care and insight, one cannot remain certain about the validity of the assumptions. Indeed, the contrasting result of the earlier study of Carlfors and Stilbs[30] can, to a large extent, be traced back to the invalidity of low-concentration partition coefficients for the high-concentration range. Other NMR studies used other types of assumptions to reduce the number of structural parameters. In our opinion, some outcomes of those studies depend strongly on the assumption made. In the ultimate limit, conductivity and surface tension experiments [16,19,20,24] each measure only a single experimental parameter and thereby can only perform model-dependent structural consistency tests in favorable cases. Scattering experiments in bulk phases[64] provide a numerically large array of experimental parameters, although some of those may have limited structural sensitivity.

The third and perhaps the least severe complexity factor is limitations of our molecular theories[21,23,25,33,34,65] both as concerning permitted range of application and predictive power. Before recapitulating our own findings, we want to note that our analysis is not free from several of the deficiencies listed above. In particular, we want to stress that our results are valid for total concentrations of 150−250 mM, that is, far above the cmc values of either surfactant. Some observations made at lower concentrations such as the curiously continuous variation of chemical shift at low and high volume fractions (see Figure 1) are not explained here.

Our combined set of experimental shift and diffusion data clearly exclude complete demixing and complete and spatially homogeneous mixing of the two surfactants that make up the solution. In the investigated range 150−250 mM of total concentration, this conclusion is valid for the whole range of molar fractions. The molecular data in form of micellar chemical shifts permit both (i) partial demixing into two distinct micelle types, one rich in fluorinated surfactants and the other in hydrogenated surfactants, or (ii) no micellar level demixing but local chemically selective coordination within a single micelle type. In both cases, the average excess/deficit of the same/different surfactant, respectively, as nearest molecular neighbor is small, in the order of 20%. We note that phase separation on the molecular level was indicated, although without quantitative conclusions in other fluorinated−hydrogenated mixed surfactant solutions.[28,66] If we invoke the regular solution theory, the low obtained value of the energy of mixing is indirect evidence that favors the one-micelle-type scenario.

Supporting Information Available: Experimental material and sample properties, NMR pulse sequences and parameters. NMR chemical shifts in an aqueous SPFO/SDeS mixture at different compositions (Figure S1). Surfactant self-diffusion coefficients in an aqueous SPFO/SDeS mixture at different compositions (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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