

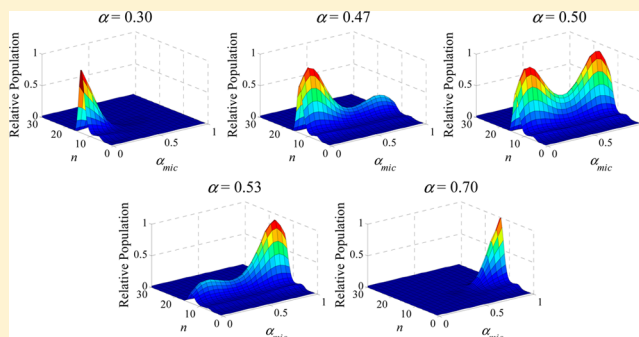
Molecular-Thermodynamic Framework to Predict the Micellization Behavior of Mixtures of Fluorocarbon-Based and Hydrocarbon-Based Surfactants

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S Supporting Information

ABSTRACT: We present a molecular-thermodynamic (MT) framework to predict the micellization properties of mixtures of fluorocarbon-based and hydrocarbon-based surfactants. Practically, this mixing reduces the use of fluorinated surfactants in the surfactant formulation, thereby addressing environmental concerns associated with the non-biodegradability and toxicity of fluorinated surfactants. The micellization properties of these mixtures are affected by the enthalpic interactions between the fluorocarbon and hydrocarbon surfactant tails. Consequently, the MT framework incorporates an enthalpy of mixing contribution estimated using regular solution theory (RST). The RST interaction parameter is estimated on the basis of phase equilibrium data. The MT framework also makes allowance for the coexistence of two types of micelles in solution to account for experimental findings which suggest that mixtures of fluorocarbon-based and hydrocarbon-based surfactants can form two types of micelles. Furthermore, the model used to calculate the packing free energy of binary mixtures of surfactant tails is generalized to incorporate the difference in the tail volumes, tail lengths, and conformational energies of the fluorocarbon and hydrocarbon tails. The MT framework is then used to predict micelle population distributions, critical micelle concentrations, and optimal micelle compositions for various mixtures of fluorocarbon-based and hydrocarbon-based surfactants, and the predictions are compared with the corresponding experimental values. While many of the predictions compare well with experiment, some of the experimentally observed trends are not reproduced by the MT framework. Ways to eliminate the discrepancy between theory and experiment are discussed. We also find that prediction of the micelle population distribution is very sensitive to the magnitude of the RST interaction parameter used to calculate the enthalpy of mixing, where an increase in the RST interaction parameter results in sharper peaks in the predicted bimodal micelle population distribution. In addition to the quantitative prediction of micellization properties, the MT framework provides useful physical insight about the reasons behind the differences in the micellization properties of various surfactant mixtures.



1. INTRODUCTION AND MOTIVATION

Owing to its position in the periodic table, the fluorine atom exhibits many extreme properties. It is the most electronegative element, making fluorinated molecules difficult to polarize.¹ This low polarizability leads to weak intermolecular interactions,¹ which results in the high surface activity of fluorocarbon-based surfactants. The low polarizability of fluorinated molecules is also responsible for their lipophobicity.² Another salient characteristic of fluorinated surfactants is the high strength of the C–F bond, which leads to their high thermal stability.² As a result, fluorocarbon-based surfactants are used in high temperature applications. In addition, the fluorine atom is just big enough to effectively cover the carbon skeleton in perfluorocarbons, which makes them chemically inert.³ Consequently, fluorocarbon-based surfactants can be used in highly corrosive environments.² These unique attributes of fluorocarbon-based surfactants make them far superior than their hydrocarbon counterparts, which

leads to their widespread use in paints, polishes, floor waxes, adhesives, fire-fighting foams,² and emulsion polymerization.²

The downside of using fluorinated surfactants is that, because of their chemical inertness and thermal stability, they are not biodegradable.² For example, perfluoro carboxylic acids and perfluoro sulfonates have been detected in the environment and in living beings including humans.^{4,5} Studies have shown that, at high concentrations, some fluorinated surfactants are toxic. For example, perfluorooctanoic acid and perfluorooctyl sulfonate are toxic at concentrations of 300 and 5 $\mu\text{g/L}$, respectively.⁴ Concerns about the bioaccumulation and toxicity of fluorinated surfactants have prompted a vigorous search for alternative surfactant formulations in which the use of fluorocarbon-based surfactants is minimized. To this end, an interesting strategy involves mixing fluorocarbon-based surfac-

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tants with other environmentally benign surfactants, such as hydrocarbon-based surfactants. In addition to reducing the fluorocarbon content of the surfactant formulation, mixing fluorocarbon-based and hydrocarbon-based surfactants lowers the cost of the surfactant formulation, because fluorocarbon-based surfactants are much more expensive than their hydrocarbon counterparts.²

It is well-known that fluorocarbons and hydrocarbons interact nonideally, with their mixtures exhibiting positive enthalpies of mixing.⁵ As a result, mixtures of fluorocarbon-based and hydrocarbon-based surfactants have received considerable attention, because they can exhibit significant deviations from the ideal-solution behavior. For example, for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium decyl sulfate (SDeS), Mukerjee and Yang found that the experimental critical micelle concentrations (CMCs), measured using electrical conductance, were not very different from the CMCs calculated by assuming complete demixing of micelles. This prompted Mukerjee and Yang to suggest that mixing of SPFO with SDeS leads to the coexistence of SPFO micelles and SDeS micelles.⁶ Aratono et al. concluded that, for certain solution compositions, mixing SPFO and SDeS leads to the coexistence of two types of mixed micelles: one rich in SPFO and the other rich in SDeS.⁷ Aratono et al. arrived at this conclusion on the basis of a thermodynamic treatment of their experimentally measured surface tension data.⁷ For the same system, Shinoda and Nomura⁸ used the regular solution theory (RST) to model the experimental data reported by Mukerjee and Yang⁶ and found that the RST interaction parameter was less than 2.0. Similar to the mixing in a conventional binary solution, Shinoda and Nomura showed that, for a binary mixture of surfactants, a RST interaction parameter which is smaller than 2.0 implies no demixing of micelles, that is, the existence of only one type of mixed micelle in solution.⁸ Accordingly, Shinoda and Nomura concluded that, in the SPFO–SDeS binary mixture, only a single type of SPFO–SDeS mixed micelle forms in solution. Kamogawa and Tajima also arrived at the same conclusion by measuring the electron-spin resonance (ESR) correlation times for certain spin probes in the mixed-micellar system consisting of SPFO and SDeS at 25 °C in the absence of salt.⁹ Interestingly, using nuclear-magnetic resonance spectroscopy, Nordstierna et al. concluded that the experimental measurements can be explained by assuming demixing within the mixed micelle.¹⁰ In other words, the experimental data can be rationalized by assuming that only a single type of mixed micelle, consisting of a fluorocarbon compartment and a hydrocarbon compartment, forms in solution. In view of the above, it is clear that, for the same binary surfactant mixture, use of different methods has led to very different conclusions, with some studies suggesting the existence of one type of mixed micelle and others suggesting the coexistence of two types of micelles. This follows because of the lack of a direct experimental method to verify the existence of two types of mixed micelles. Consequently, all the conclusions above were reached on the basis of indirect evidence.

Although there have been many experimental studies on the micellization behavior of mixtures of fluorocarbon-based and hydrocarbon-based surfactants, little effort has been devoted to theoretically understanding the micellization behavior of these interesting surfactant mixtures. To the best of our knowledge, Nagarajan's molecular-thermodynamic (MT) model is the only one that was developed to predict the micellization properties

of mixtures of fluorocarbon-based and hydrocarbon-based surfactants.¹¹ With this in mind, in this paper, we present a theoretical framework to model the micellization behavior of mixtures of fluorocarbon-based and hydrocarbon-based surfactants. Like Nagarajan's model, the model presented here is based on an MT description of the micellization process. The MT framework was chosen because it provides useful insight into the roles played by the surfactants comprising the mixture, including the surfactants' polar heads and nonpolar tails, as well as the effect of the solvent, the ions, and other solution conditions on the micellization process. In addition, the MT framework does not require experimental micellization data to make predictions of different micellization properties including CMCs, micelle shapes, sizes, and compositions.^{12,13}

In this paper, the original MT framework developed by Puvvada and Blankschtein,¹² and subsequently advanced by several others,^{13–18} is generalized to allow predictions of micellization properties of mixtures of fluorocarbon-based and hydrocarbon-based surfactants. Although the original MT framework developed by Blankschtein and coauthors is capable of modeling mixtures of hydrocarbon-based surfactants, it is not capable of modeling mixtures of fluorocarbon-based and hydrocarbon-based surfactants due to several assumptions made in the original framework which are described in detail in section 2. Accordingly, in this paper, the original MT framework^{12–18} has been generalized to model the coexistence of two types of micelles in solution. The resulting MT framework is then used to model several mixtures of fluorocarbon-based and hydrocarbon-based surfactants to predict mixture CMCs, micelle shapes, sizes, compositions, and degrees of counterion binding. Most importantly, the MT framework provides a theoretical basis to identify the conditions at which mixing fluorocarbon-based and hydrocarbon-based surfactants leads to the coexistence of two types of mixed micelles, an important capability that was lacking in the original MT framework developed by Blankschtein and coauthors.^{12–18} Beyond fundamental relevance, the ability to predict the coexistence of two types of micelles and other micellization properties of mixtures of fluorocarbon-based and hydrocarbon-based surfactants is very useful practically. For example, the ability to predict the shapes and sizes of the two types of coexisting micelles can aid in the design of surfactant formulations to generate materials with hierarchical or multimodal pore architectures for optimized transport and size selectivity.^{19,20} Similarly, the ability to predict micellization properties (CMCs, micelle shapes, micelle sizes, etc.) of mixtures of fluorocarbon-based and hydrocarbon-based surfactants enables the molecular-level design of surfactant formulations where the amount of fluorocarbon-based surfactant is minimized while exhibiting desirable performance properties.

The remainder of the paper is organized as follows. A brief overview of the original MT framework used here is presented in section 2.1. Generalization of the MT framework to enable modeling of mixtures of fluorocarbon-based and hydrocarbon-based surfactants is presented in section 2.2. This section also describes key improvements implemented in our MT framework relative to the MT model developed by Nagarajan.¹¹ The framework is then used to predict CMCs, micelle compositions, and micelle population distributions for several mixtures of fluorocarbon-based and hydrocarbon-based surfactants. The results, including comparisons with experimental data, are presented in section 3. Finally, our conclusions are summarized

in section 4. Additional useful information is provided in the Supporting Information.

2. THEORY

2.1. Review of the Original Molecular-Thermodynamic Framework for Mixtures of Surfactants. The original molecular-thermodynamic (MT) framework blends a thermodynamic description of a micellar solution with a molecular-level description of the free energy of micellization. The free energy of micellization is a quantitative measure of the tendency of a surfactant molecule to micellize in water, that is, to transfer from the monomeric state to the micellar state in water. Using thermodynamic concepts, the concentration of a micelle of aggregation number n , X_n , is given by^{16,21,22}

$$X_n = \frac{1}{e} \left(\frac{X_1}{\exp\left(\frac{g_{\text{mic}}}{kT} - 1 - \beta - \beta \ln X_{1c} - \sum_i \alpha_{n,i} \ln \alpha_{1,i}\right)} \right)^n \quad (1)$$

where X_n , X_1 , and X_{1c} denote the mole fractions of micelles of aggregation number n , surfactant monomers, and free surfactant counterions, respectively, g_{mic} is the free energy of micellization per surfactant molecule (a function of the characteristics of the micelle, including its shape, size, composition, and degree of counterion binding), k is the Boltzmann constant, T is the absolute temperature, β is the degree of counterion binding (defined as the number of counterions, per surfactant molecule, bound to the micelle), $\alpha_{n,i}$ is the micelle composition of surfactant i , and $\alpha_{1,i}$ is the monomer composition of surfactant i . Note that the concentration of micelles of aggregation number n , X_n , given in eq 1, depends on the micelle shape, size, composition, degree of counterion binding, surfactant monomer concentration, and free counterion concentration, and not just on the aggregation number, n , as the subscript suggests.

As stated above, the free energy of micellization is the free-energy change associated with a surfactant molecule as it transfers from the monomeric state to the micellar state. Since free energy is a state function, we can construct a convenient hypothetical path to calculate the free energy of micellization, g_{mic} . Specifically, g_{mic} can be decomposed as shown below:^{12,16}

$$g_{\text{mic}} = g_{\text{tr}} + g_{\text{int}} + g_{\text{pack}} + g_{\text{st}} + g_{\text{elec}} + g_{\text{mix}} \quad (2)$$

In eq 2, g_{tr} is the transfer free energy, g_{int} is the interfacial free energy, g_{pack} is the packing free energy, g_{st} is the steric free energy, g_{elec} is the electrostatic free energy, and g_{mix} is the mixing contribution to the micellization free energy. As indicated above, eq 2 can be obtained by conceiving a hypothetical path in which one first breaks the bonds between the surfactant heads and tails to separate the heads from the tails, and also discharges all the ionic species. Subsequently, one transfers the tails from an aqueous environment to a bulk tail-like (oil) phase. The free-energy change associated with this step is referred to as the transfer free energy, g_{tr} , and can be expressed in terms of the aqueous solubility of the surfactant tails.^{12,23} Following the transfer process, one re-establishes contact between the tail phase and water by forming a drop from the tail phase. The free-energy change associated with this step is known as the interfacial free energy, g_{int} , and is given by the product of the curvature-corrected interfacial tension between water and the oil drop and the surface area of the micelle core that is exposed to water.^{12,24} Note that we use

Tolman's correction to estimate the interfacial tension of a curved interface.²⁴

At this point, we recognize that the oil drop does not mimic the micelle core precisely, because the surfactant tails are subject to stricter conformational constraints in the micelle core than in the oil drop. The free-energy change associated with constraining the surfactant tails to mimic the micelle core is referred to as the packing free energy, g_{pack} . It is calculated on the basis of a mean-field, statistical-mechanical method pioneered by Ben Shaul et al.²⁵ For details, the interested reader is referred to the paper by Srinivasan and Blankschtein on the conformational characteristics of fluorocarbon-based surfactants.¹⁷

The packing step completes the formation of the micelle core. Next, one rejoins the surfactant heads and tails and places the discharged counterions in the micelle head region. The free energy associated with the localization of several finite-sized surfactant heads and counterions in a finite region is referred to as the steric free energy, g_{st} . The electrostatic free energy is the sum of the free energies associated with discharging the charged species at the beginning of the thought process and with charging the micelle at the end of the thought process. The discharge free energy is calculated using the Debye–Hückel expression for the self-energy of ionic species,²⁶ while the charging free energy is calculated using an approximate solution to the Poisson–Boltzmann equation. For details, the interested reader is referred to the paper by Srinivasan and Blankschtein.¹⁶

The contributions associated with mixing the different surfactant tails forming the mixed micelle, as well as with mixing the surfactant heads with the counterions, are not included in any of the free-energy contributions considered so far. Therefore, an additional mixing contribution, g_{mix} , is added. Note that g_{mix} includes only the entropic contribution to the mixing free energy because the original MT framework was designed only for mixtures of hydrocarbon-based surfactants where hydrocarbon tails are expected to mix ideally. Adding the free-energy contributions, g_{tr} , g_{int} , g_{pack} , g_{st} , g_{elec} , and g_{mix} yields g_{mic} as stated in eq 2.

There are several key differences between the MT framework described above and that developed by Nagarajan, referred to hereafter as the NR model (because it is based on the MT model developed by Nagarajan and Ruckenstein²⁷). First, the effect of curvature on the interfacial tension¹² is incorporated in the MT framework described above, while it is not in the NR model.^{11,27} We believe that this incorporation is necessary because micelles are small in size, which results in high curvatures, for which the interfacial tension is known to deviate from its value for flat interfaces.^{24,28}

Second, the method used to calculate the packing free energy in the context of the MT framework described above is very different from that used in the NR model. The equivalent of the packing free energy in the NR model is referred to as the deformation free energy of the surfactant tail.^{11,27} To calculate the deformation free energy, the NR model utilizes an approach which is similar to the theory developed by Semenov²⁹ for block copolymers by using a lattice representation. This approach yields convenient analytical expressions in terms of various parameters, including the lattice size and the chain length.^{11,27} As a result, the NR model is much simpler to implement than the model for g_{pack} used in our MT framework. However, it is not clear that the theory for polymeric chains is applicable to the shorter fluorocarbon and hydrocarbon surfactant tails considered here. Third, the NR model does

not account for the different energies associated with the different conformations of the surfactant tail. Specifically, while fluorocarbon chains are known to be more rigid than their hydrocarbon counterparts, this difference is not accounted for in the NR model when calculating the deformation free energy. Similarly, the differences in the geometrical properties of the fluorocarbon and hydrocarbon tails, including the tail volumes, are not accounted for in the NR model. As a result, the behavior of the deformation free energy as a function of the micelle size and composition in the NR model is very different from the behavior of the packing free energy used here. Fourth, unlike the MT framework described above, the NR model^{11,27} does not account for counterion binding. This neglect can greatly affect the calculation of the electrostatic and steric free energies, which can in turn severely affect the calculation of micellization properties like the CMC, and the micelle shape, size, and composition.

2.2. MT Framework for Mixtures of Fluorocarbon-Based and Hydrocarbon-Based Surfactants. The original MT framework developed by Blankshtein and coauthors,^{12–18} described in section 2.1, cannot model mixtures of fluorocarbon-based and hydrocarbon-based surfactants. This inability is due to two main assumptions underlying the original framework: (i) The mixing free energy model used is not applicable to mixtures of fluorocarbon-based and hydrocarbon-based surfactants because it does not include the enthalpic contribution to the free energy of mixing. Indeed, it is well-known that mixtures of fluorocarbons and hydrocarbons exhibit a positive enthalpy of mixing, and (ii) prediction of micellization properties, including CMC, micelle shape, size, composition, and degree of counterion binding, are made by assuming that only one type of micelle exists in solution. Assumption ii is not valid for mixtures of fluorocarbon-based and hydrocarbon-based surfactants because there is experimental evidence which suggests that these mixtures can form two types of micelles. In addition, one needs to model the packing free energy of mixtures of fluorocarbon tails and hydrocarbon tails in a manner that accounts for the difference in the tail volumes, tail lengths, and energies associated with the chain conformations. In the following sections, we provide details of the modifications made to the original MT framework^{12–18} to extend its ability to model mixtures of fluorocarbon-based and hydrocarbon-based surfactants.

2.2.1. Enthalpy of Mixing. The primary reason for the coexistence of two types of micelles in mixtures of fluorocarbon-based and hydrocarbon-based surfactants is the positive enthalpy of mixing exhibited by mixtures of fluorocarbons and hydrocarbons. As discussed above, the enthalpic contribution to the free energy of mixing was neglected in the original MT framework.^{12–18} However, for mixtures of fluorocarbon-based and hydrocarbon-based surfactants, it is essential to accurately model the enthalpy of mixing associated with the fluorocarbon and the hydrocarbon tails because they are known to mix nonideally. Early attempts to model mixtures of fluorocarbons and hydrocarbons utilized the regular solution theory (RST), along with the commonly used mixing rules, to model the interaction parameter quantifying the interactions between two different types of molecules. Unfortunately, this did not yield satisfactory results.⁵ Specifically, it was found that the geometric-mean mixing rule used to estimate the unlike interaction parameter yielded values which are higher than those required to accurately predict the fluorocarbon–hydrocarbon mixture properties.⁵ More sophis-

ticated models, based on the statistical associating fluid theory (SAFT),³⁰ were also utilized to predict the phase behavior of mixtures of fluorocarbons and hydrocarbons.^{31–33} These models confirmed the findings by other researchers that the unlike interaction energy has to be about 10% smaller than that predicted by the geometric-mean mixing rule for the SAFT-based model to accurately predict the experimental data. It then follows that the departure from the geometric-mean mixing rule needs to be accounted for in any model used to properly quantify the enthalpic interactions between fluorocarbons and hydrocarbons.

With the above in mind, because of its simple mathematical form and broad applicability to nonpolar mixtures, we have used RST to model the nonideal interactions between the fluorocarbon and hydrocarbon tails. However, in view of the challenge associated with the estimation of the interaction parameter discussed above, we estimated this parameter on the basis of experimental phase equilibrium data for mixtures of fluorocarbons and hydrocarbons, instead of implementing commonly used mixing rules. Recall that, in the RST, the enthalpy of mixing, ΔH_{mix} , of a binary solution is given by

$$\Delta H_{\text{mix}} = A_{\text{mix}} \phi_1 \phi_2 V \quad (3)$$

where A_{mix} is the interaction parameter between components 1 and 2, ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively, and V is the solution volume. Using eq 3, the free energy of mixing per molecule, g_{mix} , for mixtures of fluorocarbon-based and hydrocarbon-based surfactants can be written as follows:

$$g_{\text{mix}} = kT \left(\sum_i \alpha_{n,i} \ln \left(\frac{\alpha_{n,i}}{1 + \beta} \right) + \beta \ln \left(\frac{\beta}{1 + \beta} \right) \right) + A_{\text{mix}} \phi_1 \phi_2 \left(\sum_i \alpha_{n,i} v_{\text{tail},i} \right) \quad (4)$$

where the extensive solution volume, V , in eq 3 has been replaced by the intensive average tail volume, which is the volume of the micelle core on a per molecule basis, to obtain the mixing free energy per molecule. The value of A_{mix} was calculated on the basis of the values reported in several experimental studies involving mixtures of fluorocarbons and hydrocarbons.^{5,34–38} In these studies, values of A_{mix} for mixtures of fluorocarbons and hydrocarbons having 5–8 carbon atoms were calculated on the basis of measurements of vapor–liquid equilibrium,³⁶ liquid–liquid equilibrium,^{34,36} calorimetry data,³⁵ consolute temperatures,³⁴ and infinite-dilution activity coefficients.³⁸ The value of A_{mix} was found to vary as a function of temperature and of the number of carbon atoms in the fluorocarbon and hydrocarbon constituents. Specifically, the calculated A_{mix} values were found to vary between 6.6 and 9.8 cal/cm³ for temperatures varying between 10 and 50 °C and the number of carbon atoms in the fluorocarbon and hydrocarbon chains varying between 5 and 8. Note that this variation in A_{mix} is indeed significant. However, in the absence of quality data characterizing the effect of the hydrocarbon chain length, the fluorocarbon chain length, and the temperature, we used the average of all the experimental A_{mix} values,^{5,34–36,38} namely, $A_{\text{mix}} = 8.21$ cal/cm³, in the calculations reported here.

2.2.2. Packing Free Energy of Mixtures of Fluorocarbon and Hydrocarbon Tails. The packing free energy per molecule, g_{pack} , is the free-energy penalty associated with the restructuring

of an oil drop such that it mimics the micelle core (with the surfactant head–tail connection tethered at the interface). As discussed in section 2.1, g_{pack} for a micelle of a given shape and size is calculated on the basis of the mean-field, statistical-mechanical method pioneered by Ben-Shaul et al.²⁵ The method advanced by Ben-Shaul et al.²⁵ has been modified by several authors to utilize them for specific applications. For example, Szleifer et al. developed the original method to calculate the packing characteristics, including bond order parameters and density profiles of chain segments in micelles of different shapes formed by mixtures of surfactants.³⁹ The packing characteristics of lipids packed in a bilayer were calculated by Fattal and Ben-Shaul by extending the method presented in ref 25.⁴⁰ Longo et al. developed the original method (presented in ref 25) to predict the stability of bilayers composed of saturated lipids⁴¹ and bolalipids,⁴² while Fattal and Ben-Shaul extended the original method to model the packing characteristics of proteins embedded in lipid bilayers.^{43,44} Other packing models include those developed by Elliott et al. to predict the phase diagram of mixtures of lipids.^{45,46} The models in refs 45 and 46 add a potential function to the expression for g_{pack} . The potential function is assumed to depend on the orientation of the lipid chains, and is necessary to predict liquid-to-gel phase transitions. The method developed by Elliott et al.^{45,46} has been extended by several authors, including Khelashvili et al.,⁴⁷ Tumaneng et al.,⁴⁸ and Pandit et al.⁴⁹ These models use molecular dynamics simulations to determine the parameters associated with the potential function in order to predict lipid bilayer properties.

In this paper, we have used the original mean-field, statistical-mechanical method developed by Ben-Shaul et al.²⁵ to calculate the packing free energy of mixtures of surfactant tails. The details of the method in the context of the MT model developed by Blankschtein and coauthors were discussed by Shiloach and Blankschtein in their study of binary mixtures of surfactants.²² This method is computationally very expensive. Accordingly, the packing data for each shape is converted into polynomials that relate the packing free energy to the micelle size and the micelle composition. These polynomial functions are subsequently used to calculate the free energy of micellization, g_{mic} , the CMC, and other micellization properties.²² The packing polynomials for the mixtures of fluorocarbon and hydrocarbon tails considered in this paper are reported in section 1 in the Supporting Information.

In the context of the packing free energy, the size of the micelle core (that is, the radius for spheres and infinite cylinders and the half-thickness for infinite bilayers) is limited by the maximum length of the surfactant tail, because the micelle core cannot have voids. However, in the case of a mixed-micelle core formed by surfactants having different tail lengths, the maximum size of the micelle core becomes a function of the micelle composition as well. In the NR model, the maximum micelle size of a mixed-micelle core, r_{max} , was assumed to be equal to a volume-fraction-based weighted average of the maximum lengths of the constituent surfactant tails. Specifically, the NR model assumes that¹¹

$$r_{\text{max}} = \phi_1 l_{\text{tail},1} + \phi_2 l_{\text{tail},2} \quad (5)$$

where ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2 and $l_{\text{tail},1}$ and $l_{\text{tail},2}$ are the maximum tail lengths of surfactants 1 and 2, respectively. Since our approach explicitly involves calculating the packing free energy at different micelle compositions, shapes, and sizes, one can actually determine

the functional dependence of the maximum micelle-core size on the micelle composition without making the simplifying assumption made in the NR model. Plots showing the variation of r_{max} as a function of the composition of the longer tail in binary mixtures are shown in Figures S1 and S2 in section 1 in the Supporting Information. Figures S1 and S2 (Supporting Information) show that, for cylindrical and spherical shapes, as well as for cases when the difference between r_{max} for the longer tail, $r_{\text{max,long}}$, and r_{max} for the shorter tail, $r_{\text{max,short}}$, is large, r_{max} starts at $r_{\text{max,short}}$ when the composition of the longer tail is 0.0 and quickly rises to $r_{\text{max,long}}$ well before the composition of the longer tail is 1.0. On the basis of this observation, we propose the following expression for r_{max} :

$$r_{\text{max}} = r_{\text{max,short}} + (r_{\text{max,long}} - r_{\text{max,short}})(1 - e^{-\alpha_{\text{long}}/\alpha_0}) \quad (6)$$

where α_{long} is the composition of the longer tail and α_0 is a parameter used to fit the data. The functional form in eq 6 works best for cylindrical and spherical micelle cores, and for cases when the difference between $r_{\text{max,long}}$ and $r_{\text{max,short}}$ is large. On the other hand, eq 5 systematically underpredicts the maximum micelle-core size for these cases. For bilayers, as well as for cases when the difference between $r_{\text{max,long}}$ and $r_{\text{max,short}}$ is small, eq 6 does not work as well, while eq 5 works better. This difference in the behavior of r_{max} for the different micelle-core shapes is due to the difference in the volume distribution in the three micelle-core shapes. Indeed, bilayers have a uniform distribution of volume, while cylinders and spheres have more volume near the periphery than in the center. Compared to cylindrical and spherical micelles, bilayer-like micelles are not that commonly encountered micelle shapes. Consequently, we have used eq 6 to determine the maximum micelle-core size.

2.2.3. Prediction of Micellization Properties. The critical micelle concentration (CMC) is defined as the surfactant concentration that marks the onset of aggregate formation. In the context of the MT framework, we adopted Tanford's definition of the CMC. Specifically, Tanford defined the CMC as the surfactant concentration at which 5% of the surfactant molecules are in micellar form and the remaining 95% are in monomeric form.⁵⁰ The number of molecules in micellar form is equal to $\sum_{\text{micelles}} nX_n$, where n is the aggregation number of the micelle and X_n is the concentration of the micelle, which is given in eq 1. Note that other micelle characteristics, including micelle shapes, sizes, compositions, and degrees of counterion binding, can be predicted by first determining whether the micelle population distribution is unimodal or bimodal. Specifically, if the micelle population distribution is found to be unimodal, then the optimal micelle corresponds to the micelle with the highest population. On the other hand, if the micelle population distribution is found to be bimodal, then the characteristics of the two types of micelles correspond to the two peaks in the micelle population distribution.

The micelle population distribution is computed by calculating the concentration of each type of micelle that can exist in solution. For each aggregation number, the concentrations of various micelles spanning micelle compositions between 0.0 and 1.0 and degrees of counterion binding between 0.0 and 1.0 are calculated. In the case of spherical micelles, the aggregation number uniquely determines the size of the micelle. However, in the case of spherocylindrical and discoidal micelles, the aggregation number alone is not sufficient to determine the size of these micelles. For example, in the case of a spherocylindrical micelle, each micelle

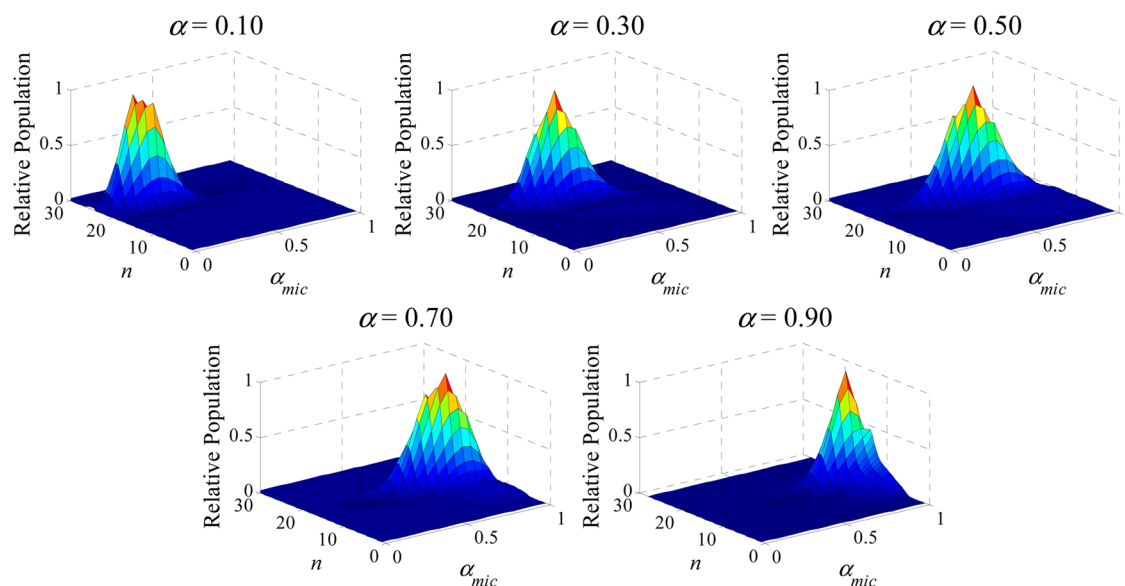


Figure 1. Relative micelle population distribution for the binary mixture of lithium perfluorooctyl sulfonate (LiPFOS) and octyl glucoside (OG). Note that the micelle composition, α_{mic} , and the solution composition, α , correspond to the composition of LiPFOS.

aggregation number corresponds to a set of infinitely many combinations of the cylinder radii and lengths.

The population of all possible types of micelles is calculated to determine what fraction of the added surfactant remains in micellar form. Specifically, for each aggregation number, the population of micelles is integrated over three independent variables: (i) the micelle composition, (ii) the degree of counterion binding, and (iii) the micelle radius or width for spherocylinders and discs, respectively. The integration is carried out numerically using the trapezoidal rule. Note that the integrals over all three variables are finite, because the micelle composition and the degree of counterion binding vary between 0.0 and 1.0, and the micelle radius and thickness in the case of spherocylinders and discs, respectively, are limited by r_{max} (see eq 6).

Another important consideration in calculating the micelle population distribution involves determining the upper limit on the aggregation number. For spherical micelles, the aggregation number is limited by r_{max} (see eq 6). However, spherocylindrical and discoidal micelles can theoretically grow indefinitely in one and two dimensions, respectively. Nevertheless, from an entropic standpoint, the micelles cannot grow indefinitely. As a result, the population of micelles will eventually become negligible beyond some threshold aggregation number. Because there is no theoretical way to a priori estimate this threshold aggregation number, we estimated it in the process of calculating the population of micelles of different aggregation numbers. Specifically, starting from the lowest aggregation number, set at 6 here, the contribution of micelles of each aggregation number, in increasing order, was calculated and added to compute the concentration of surfactant molecules in micellar form. Note that setting the lowest aggregation number at 6 does not significantly affect the model predictions. Nevertheless, it should be noted that the maximum aggregation number of a spherical micelle formed by a surfactant having a 6-carbon fluorocarbon tail, based on the tail volume and the maximum tail length, is 13.7. Therefore, the lowest aggregation number cannot be higher than 13, and we chose 6 which is close to one-half of 13. This addition is terminated when the following criterion is met: the contribution of micelles of the 10

largest aggregation numbers, toward the population of micelles, is less than 1% of the maximum contribution by any aggregation number. In other words, if the sum of the population of micelles with aggregation numbers $n, n + 1, n + 2, \dots, n + 9$ is less than 1% of the population of micelles with aggregation number m , where m is the aggregation number with the largest population of micelles, then the population of micelles with an aggregation number higher than $n + 9$ is ignored. Note that the motivation for choosing the 10 largest aggregation numbers is to select a sufficiently large number such that no significant portion of the micelle population distribution is neglected.

Implementation of the method described above to calculate micellization properties for various mixtures of fluorocarbon-based and hydrocarbon-based surfactants requires knowledge of several molecular descriptors. The values of these descriptors for all the surfactants considered in this paper are listed in section 1 of the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. MT Framework Predictions for Hypothetical Binary Mixtures of Fluorocarbon-Based and Hydrocarbon-Based Surfactants. The MT framework presented above was first used to predict the critical micelle concentrations (CMCs) and micelle population distributions of three hypothetical binary surfactant mixtures to test the ability of the framework to predict bimodal micelle population distributions. The three hypothetical mixtures include

- (1) A binary mixture consisting of two identical 7-carbon fluorocarbon-based nonionic surfactants having a head area of 60 \AA^2 (typical of a glucamide head).
- (2) The binary mixture in 1 above with added hypothetical antagonistic enthalpic interactions between the surfactant tails. The enthalpic interactions are calculated using eq 3 with $A_{mix} = 8.21 \text{ cal/cm}^3$.
- (3) The binary mixture in 2 above but with the nonionic head of one of the two surfactants replaced by an ionic sulfonate head.

The results for the three hypothetical surfactant mixtures considered are presented in section 2 in the Supporting Information, and clearly show that the MT framework presented above is capable of predicting the coexistence of two types of micelles in solution. These results also illustrate how the choice of surfactant head and tail can affect the behavior of the micelle population distribution and the mixture CMC.

3.2. MT Framework Predictions for Real Binary Mixtures of Fluorocarbon-Based and Hydrocarbon-Based Surfactants. To demonstrate the ability of the MT framework to predict the behavior of mixtures of fluorocarbon-based and hydrocarbon-based surfactants, in this section, predictions of CMCs, micelle compositions, and micelle population distributions are compared with available experimental data for several real mixtures of fluorocarbon-based and hydrocarbon-based surfactants. The four mixtures considered below include: (i) a mixture of an ionic surfactant and a nonionic surfactant, (ii) a mixture of two ionic surfactants having similar sized head groups and similar CMCs, (iii) a mixture of two ionic surfactants having similar sized head groups but different CMCs, and (iv) a mixture of two ionic surfactants having different sized head groups. Mixtures i–iv above were chosen to illustrate the effect of the constituent surfactant heads and tails on the micellization properties of the surfactant mixture.

3.2.1. Binary Mixture of Lithium Perfluorooctyl Sulfonate (LiPFOS) and Octyl Glucoside (OG). Figure 1 shows the micelle population distribution for the binary mixture of lithium perfluorooctyl sulfonate (LiPFOS) and octyl glucoside (OG) at various solution compositions. Note that all micelle population distribution plots shown in this section correspond to $A_{\text{mix}} = 8.21 \text{ cal/cm}^3$ (see section 2.2.1), unless otherwise specified. Figure 1 shows that the micelle population distribution remains unimodal over the entire solution composition range, in spite of the fact that, upon mixing, the surfactant tails exhibit a positive enthalpy of mixing, and therefore do not like to mix with each other. This interesting finding reflects the fact that mixing of the ionic sulfonate heads and nonionic glucoside heads is encouraged because it reduces the net charge of the surfactant micelle, thereby reducing the electrostatic free energy. In this surfactant mixture, the increase in the free energy of micellization due to the enthalpy of mixing of the surfactant tails is lower than the decrease in the free energy of micellization due to the decrease in the charge of the micelle. As a result, the micelle population distribution remains unimodal throughout the entire solution composition range.

Figures 2 and 3 compare the predicted CMCs and the predicted micelle compositions for the binary mixture of LiPFOS and OG with the available experimental values, respectively.⁵¹ The MT framework accurately predicts the qualitative trends for both the mixture CMC and the micelle composition. Quantitatively, the predicted CMCs are within a factor of 1.5 of the experimental CMCs, which is viewed as excellent agreement. This follows because the CMC has an exponential dependence on the free energy of micellization, g_{mic} , which is the quantity that is actually modeled in the MT framework. As a result, a small error in g_{mic} can result in a significant error in the CMC. The MT framework predictions of the composition of LiPFOS in the micelle are systematically lower than the experimental values (see Figure 3). To understand this trend, consider Figure 2, which shows that the CMC of LiPFOS (at $\alpha = 1.0$) is lower than that of OG (at

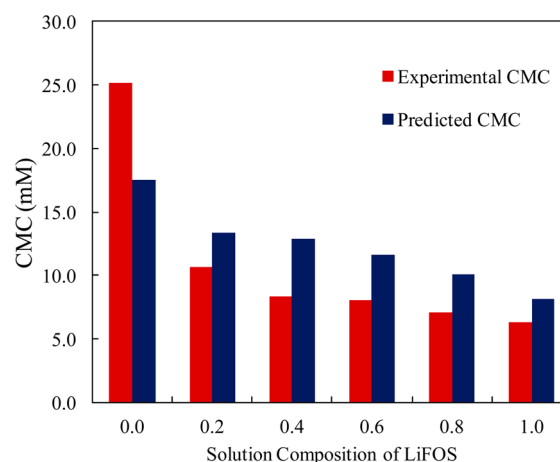


Figure 2. Predicted and experimental CMCs vs solution composition for a binary mixture of lithium perfluorooctyl sulfonate (LiPFOS) and octyl glucoside (OG).

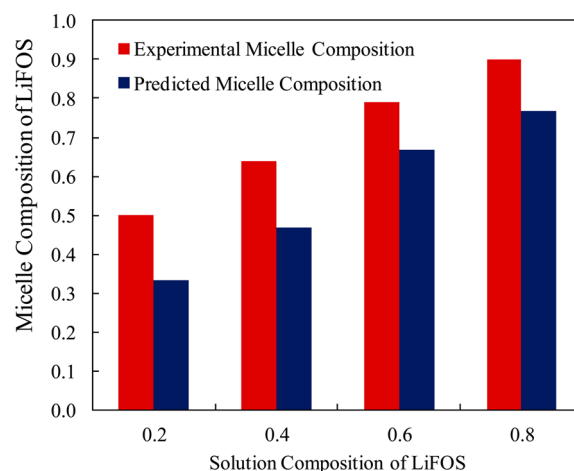


Figure 3. Predicted and experimental micelle compositions vs solution composition for a binary mixture of lithium perfluorooctyl sulfonate (LiPFOS) and octyl glucoside (OG).

$\alpha = 0.0$). This indicates that LiPFOS has a higher tendency to micellize than OG. As a result, the micelles are richer in LiPFOS, while the monomers are richer in OG. This behavior is reflected in both the experimental and predicted values of the optimal micelle composition of LiPFOS which is always higher than, or equal to, the solution composition of LiPFOS (see Figure 3). In Figure 2, the MT framework underpredicts the CMC of OG (at $\alpha = 0.0$) while it overpredicts the CMC of LiPFOS (at $\alpha = 1.0$). As a result, the difference between the predicted CMCs of OG and LiPFOS is lower than the difference between the experimental CMCs of OG and LiPFOS. Accordingly, the tendency of LiPFOS to micellize relative to OG predicted by the MT framework is not as high as that based on the experimental data. This is the reason behind the systematic underprediction of the micelle composition of LiPFOS shown in Figure 3.

3.2.2. Binary Mixture of Sodium Perfluorooctanoate (SPFO) and Sodium Decyl Sulfate (SDeS). Figure 4 shows the micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium decyl sulfate (SDeS) at various solution compositions, α . Figure 4 shows that the micelle population distribution becomes bimodal at $0.4 \leq \alpha \leq 0.5$. This is because SPFO and SDeS have similar

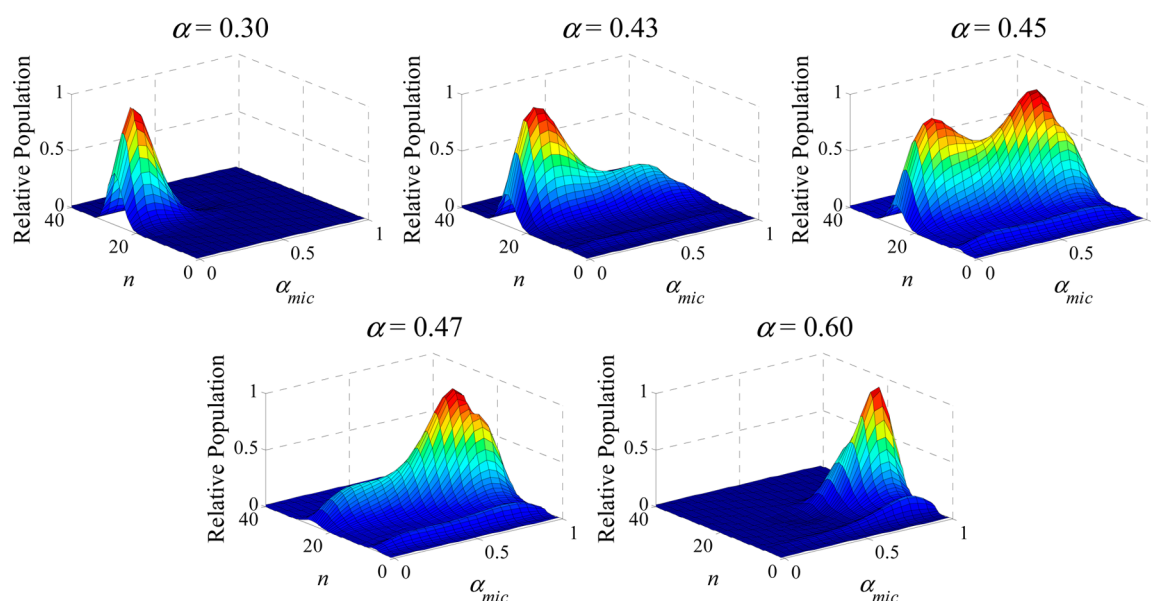


Figure 4. Relative micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium decyl sulfate (SDeS). Note that the micelle composition, α_{mic} , and the solution composition, α , correspond to the composition of SPFO.

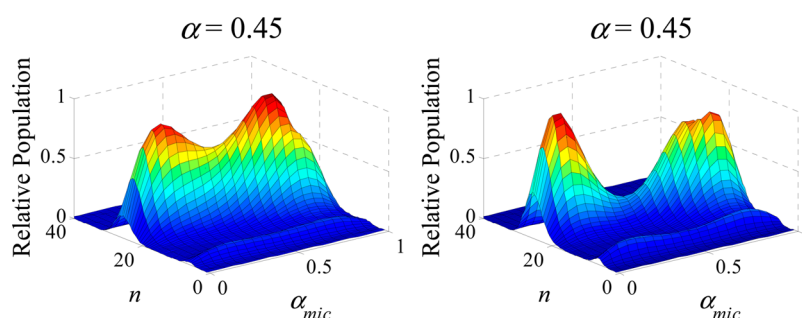


Figure 5. Relative micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium decyl sulfate (SDeS). The plot on the left corresponds to $A_{mix} = 8.21 \text{ cal/cm}^3$, and the plot on the right corresponds to $A_{mix} = 9.89 \text{ cal/cm}^3$.

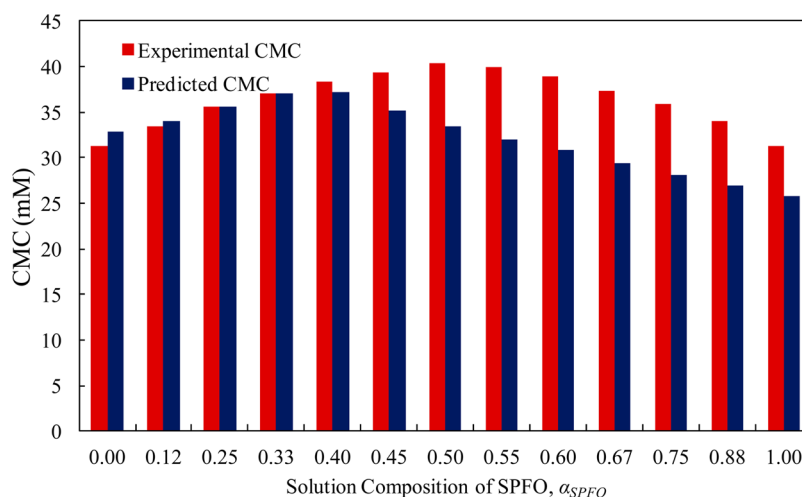


Figure 6. Predicted and experimental CMCs vs solution composition of SPFO, α_{SPFO} , for a binary mixture of sodium perfluorooctanoate (SPFO) and sodium decyl sulfate (SDeS).

volumes, and therefore, close to $\alpha = 0.45$, the free energy of mixing is largest. Accordingly, from a free energy viewpoint, it is more favorable to form two types of mixed micelles (one rich in fluorocarbon-based surfactant and the other rich in hydrocarbon-based surfactant) to reduce the free energy of mixing,

instead of forming a single type of mixed micelle with a higher free energy of mixing.

The results shown in Figure 4 agree with those reached by Mukerjee and Yang⁶ and by Aratono et al.⁷ However, they do not agree with the conclusions reached by Shinoda and

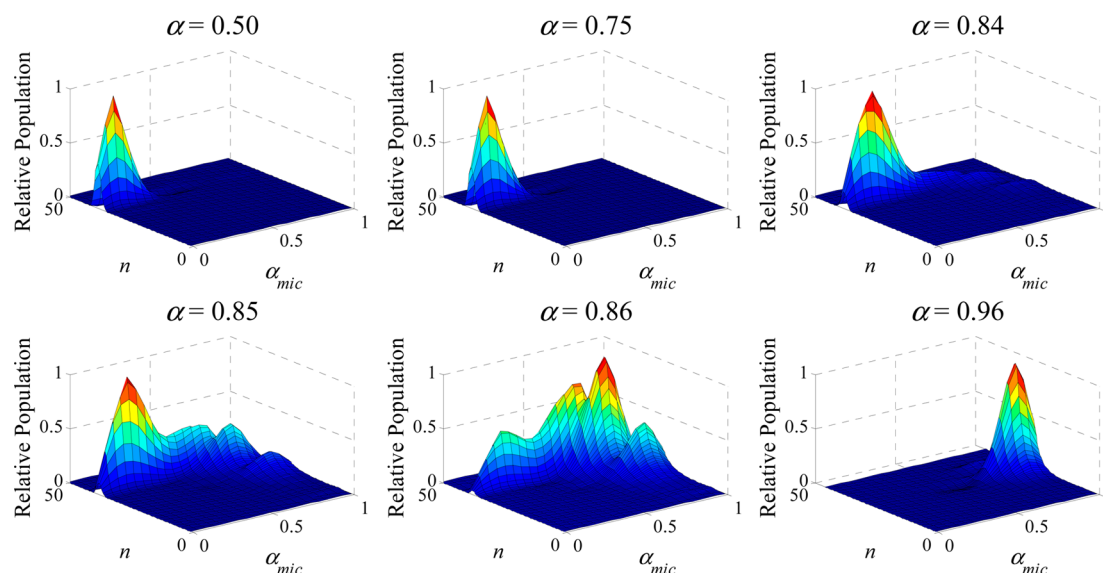


Figure 7. Relative micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecyl sulfate (SDS). Note that the micelle composition, α_{mic} , and the solution composition, α , correspond to the composition of SPFO.

Nomura⁸ and by Kamogawa and Tajima,⁹ who concluded that this binary mixture leads to only a single type of mixed micelle. It is interesting to note that the two peaks in the micelle population distribution are not very sharp and have significant overlap. By increasing the enthalpic interaction parameter A_{mix} by 20% from 8.21 to 9.85 cal/cm³, which is close to the maximum value of A_{mix} observed experimentally for mixtures of hydrocarbons and fluorocarbons, as described in section 2.2.1, two peaks clearly emerge in the micelle population distribution, as illustrated in Figure 5, and as suggested by Aratono et al.⁷

Figure 5 above and Figure S6 in the Supporting Information clearly indicate that the predicted micelle population distribution strongly depends on the magnitude of the enthalpic interaction parameter used. In the predictions shown, the value of A_{mix} used is an average calculated on the basis of the available experimental data for mixtures of fluoroalkanes and alkanes of various lengths and measured at various temperatures, as discussed in section 2.2.1. On the basis of the results in Figure 5, it is clear that the ability of the MT framework to accurately predict micelle population distributions will benefit greatly from a more accurate estimation of the enthalpic interaction parameter, A_{mix} .

Figure 6 compares the predicted and experimental CMCs as a function of the solution composition of SPFO, α_{SPFO} , for the binary mixture of SPFO and SDeS.⁷ The MT framework accurately predicts the qualitative mixture CMC trends. Quantitatively, the predicted CMCs are within a factor of 1.3 of the experimental CMCs, which is viewed as excellent agreement, as discussed in section 3.2.1. It also predicts a maximum in the CMC at $\alpha_{SPFO} = 0.40$, while the experimental maximum is observed at $\alpha_{SPFO} = 0.50$. Note that the experimental CMCs of SPFO (31.2 mM) and SDeS (31.3 mM) are very close to each other, which results in the experimentally observed maximum at 0.50. On the other hand, the MT framework predicts that the CMC of SPFO (25.7 mM) is lower than that of SDeS (32.8 mM). As a result, the predicted maximum in the CMC occurs at a solution composition that is richer in SPFO, rather than at the equimolar solution composition.

3.2.3. Binary Mixture of Sodium Perfluorooctanoate (SPFO) and Sodium Dodecyl Sulfate (SDS). Figure 7 shows the micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecyl sulfate (SDS) for various solution compositions, α . The micelle population distribution in Figure 7 shows bimodality for $0.84 \leq \alpha \leq 0.91$. On the basis of the micelle population distribution for the binary mixture of SPFO and SDeS in Figure 4, we can a priori expect that the binary mixture of SPFO and SDS will show bimodality. This follows because SDS has two more carbon atoms in the tail compared to SDeS. As a result, for the same micelle composition, the SPFO–SDS mixed micelle has a higher average tail volume compared to the SPFO–SDeS mixed micelle that results in an increase in the enthalpy of mixing (see eqs 3 and 4) which is the primary driving force behind the bimodality in the micelle population distribution.

Figure 8 compares the predicted and experimental CMCs as a function of α_{SPFO} for the binary mixture of SPFO and SDS.⁵² Quantitatively, the predicted CMCs are within a factor of 2.0 of the experimental CMCs, which is viewed as very good agreement, as discussed in section 3.2.1. However, Figure 8 shows that qualitatively the MT framework does not predict the

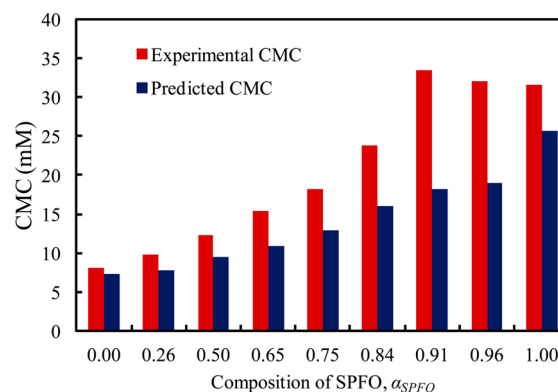


Figure 8. Predicted and experimental CMCs vs the solution composition of SPFO, α_{SPFO} , for a binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecyl sulfate (SDS).

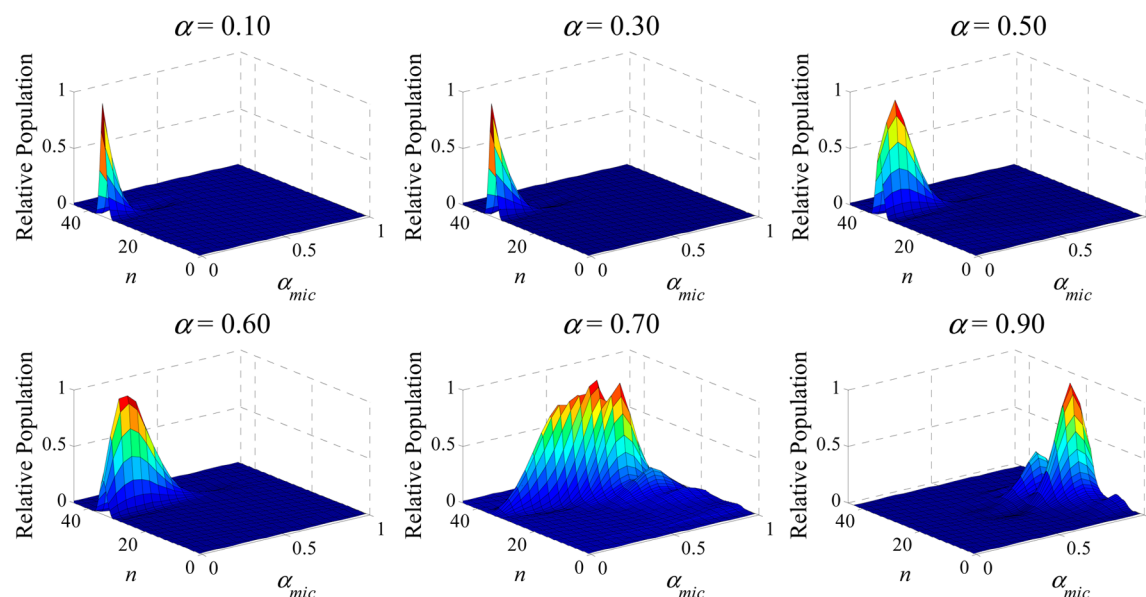


Figure 9. Relative micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecanoate (SDO). Note that the micelle composition, α_{mic} , and the solution composition, α , correspond to the composition of SPFO.

maximum observed in the experimental CMC data at $\alpha_{SPFO} = 0.91$. Instead, the CMC is predicted to plateau at $0.84 \leq \alpha \leq 0.96$, and then to increase again. The maximum in the CMC observed by Sugihara et al.⁵² is absent in the mixture CMCs calculated by Kamrath and Franses⁵³ using the differential conductance data of Mukerjee and Yang.⁶ However, the absence of the maximum may be attributed to a fewer number of solution compositions at which the CMC was calculated. Note that, although the MT framework predicts bimodality in the micelle population distribution, the predicted mixture CMC does not show a maximum even when A_{mix} is increased by 20%, from 8.21 to 9.85 cal/cm³ (not shown). This indicates that A_{mix} would have to be increased significantly to predict a maximum in the CMC for this mixture. This is probably because SDS has a CMC that is much lower than that of SPFO due to a lower transfer free energy. Upon adding a little bit of SDS to SPFO, while the mixing free energy increases, the decrease in the transfer free energy is higher, thereby reducing the CMC.

3.2.4. Binary Mixture of Sodium Perfluorooctanoate (SPFO) and Sodium Dodecanoate (SDO). Figure 9 shows the micelle population distribution for the binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecanoate (SDO) at various solution compositions, α . The micelle population distribution in Figure 9 remains unimodal throughout the entire solution composition range, becoming very broad at $\alpha = 0.70$. This indicates that the antagonism between the surfactant tails is not sufficiently high to result in the coexistence of two types of micelles. This can be understood on the basis of the difference in the size of the heads of the two surfactants. Compared to SPFO, SDO has a very small head area (see the Supporting Information). One can show that, for the same area per molecule (which would correspond to micelles of the same size because SDO and SPFO have similar tail volumes), the steric free energy associated with forming a single type of mixed micelle with the two different sized heads is lower than the steric free energy associated with forming two types of mixed micelles: one formed by surfactants having a smaller head and the other formed by surfactants having a bigger head.⁵⁴ In this case, the

reduction in the steric free energy resulting from mixing the different sized surfactant heads is slightly higher than the increase in the mixing free energy resulting from the enthalpy of mixing associated with mixing of the surfactant tails. As a result, we observe a broadening of the micelle population distribution close to $\alpha = 0.70$ and no bimodality.

The results shown in Figure 9 agree with those reached by Pedone et al.⁵⁵ and Caponetti et al.⁵⁶ that the binary mixture of SPFO and SDO does not demix. However, it does not agree with the conclusions reached by Mukerjee and Yang,⁶ who claimed that the binary mixture of SPFO and SDO leads to the coexistence of two types of micelles. Figure 10 compares the

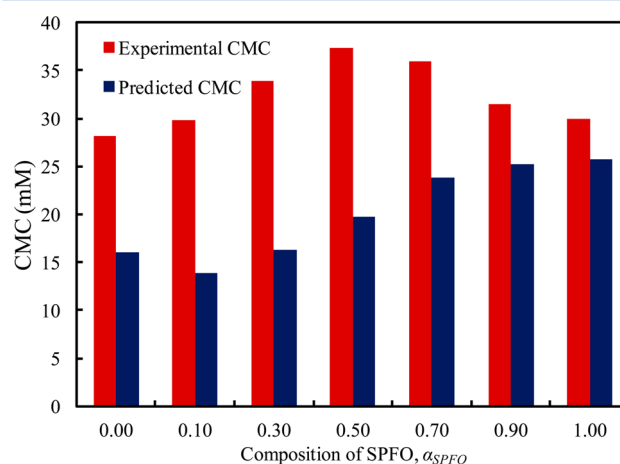


Figure 10. Predicted and experimental CMCs vs the solution composition of SPFO, α_{SPFO} , for a binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecanoate (SDO).

predicted and experimental CMCs⁵⁷ for the binary mixture of SPFO and SDO. Quantitatively, the predicted CMCs are within a factor of 2.2 of the experimental CMCs, which is viewed as very good agreement, as discussed in section 3.2.1. However, qualitatively, the MT framework does not predict the maximum in the CMC observed in the experimental data at $\alpha_{SPFO} = 0.5$

(see Figure 10). The primary reason behind the absence of the maximum in the predicted mixture CMCs is the underprediction of the CMC of SDO by the MT framework.⁵⁷ On the basis of the experimental CMC data shown in Figure 10, SPFO and SDO have similar CMCs, and therefore exhibit similar tendencies to micellize. However, in the context of the MT framework predictions, SDO exhibits a higher tendency to micellize than SPFO. Note that, although the predicted CMC of SDO is within a factor of 1.75 of the experimental value, which is viewed as very good agreement (see section 3.2.1), to accurately predict qualitative trends of surfactant mixtures, it is necessary to accurately predict the qualitative behavior of the CMCs of the pure components. To prove this, we assumed that SDO possesses a 9-carbon tail instead of its traditional 10-carbon tail to increase its CMC. Indeed, by decreasing the number of carbon atoms in the surfactant tail to 9, the CMC of SDO increased from 16.1 to 29.5 mM, which is closer to the experimental CMC of SDO (28.1 mM). As a result, the MT predictions of the mixture CMCs show a maximum at $\alpha_{\text{SPFO}} = 0.5$ which is also in agreement with the experimental values (see Figure 11). This example clearly shows that the qualitative

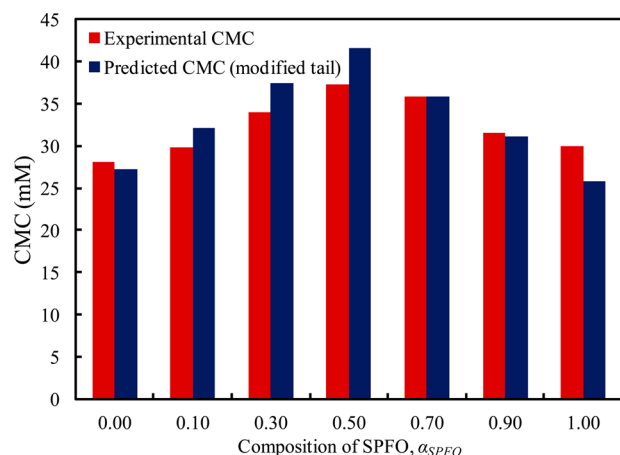


Figure 11. Predicted and experimental CMCs vs the solution composition of SPFO, α_{SPFO} , for a binary mixture of sodium perfluorooctanoate (SPFO) and sodium dodecanoate (SDO). Note that the predictions are made by assuming that SDO has a 9-carbon tail instead of a 10-carbon tail.

discrepancy between the MT framework CMC predictions and the experimental CMC data is due to the underprediction of the CMC of SDO, and not due to any inherent theoretical limitations of the modeling framework presented here as it applies to mixtures of fluorocarbon-based and hydrocarbon-based surfactants.

4. CONCLUSIONS

In summary, in this paper, we presented a molecular-thermodynamic (MT) framework to predict the micellization behavior of mixtures of fluorocarbon-based and hydrocarbon-based surfactants. This mixing reduces the use of fluorinated surfactants in the surfactant formulation, thereby addressing the non-biodegradability and environmental toxicity concerns associated with fluorinated surfactants, as well as lowering the cost of the surfactant formulation. The theoretical framework presented here is based on the original MT framework developed by Blankschtein and coauthors,^{12–18} which was not able to predict the micellization properties of mixtures of

fluorocarbon-based surfactants and hydrocarbon-based surfactants due to several modeling assumptions. The micellization properties of these mixtures are affected by the enthalpic interactions between the fluorocarbon and hydrocarbon surfactant tails. Therefore, an enthalpy of mixing contribution modeled using the regular solution theory (RST) was included in the mixing free energy. The RST interaction parameter was estimated on the basis of phase equilibrium data. Allowance for the coexistence of two types of micelles in solution was also made in the theoretical framework developed here because there is experimental evidence which suggests that mixtures of fluorocarbon-based and hydrocarbon-based surfactants form two types of micelles. Additionally, the model used to calculate the packing free energy of mixtures of hydrocarbon tails and fluorocarbon tails was generalized to incorporate the difference in tail volumes, tail lengths, and conformational energies.

Depending on the interactions between the constituent surfactants, the MT framework is able to predict the coexistence of two types of mixed micelles in solution, one rich in the fluorocarbon-based surfactant and the other rich in the hydrocarbon-based surfactant. While the antagonistic enthalpic interactions between the fluorocarbon and hydrocarbon tails encourage the formation of two types of micelles, the synergistic contribution resulting from the interactions between charged and uncharged, as well as between small and big, surfactant heads encourages the formation of a single type of mixed micelle. The delicate balance between the antagonistic and synergistic interactions determines the micellization behavior of the surfactant mixtures.

In addition, the MT framework is able to predict micelle population distributions, CMCs, and optimal micelle compositions for various binary mixtures of fluorocarbon-based and hydrocarbon-based surfactants. The CMCs predicted by our MT framework compare well with the experimental CMCs for the binary mixtures of LiPFOS and OG and SPFO and SDeS. On the other hand, the MT framework was unable to fully predict some aspects of the experimental mixture CMC data for the binary mixtures of SPFO and SDS and SPFO and SDO. It was shown that the discrepancy between the experimental data and the modeling results for the binary mixture of SPFO and SDO is due to an underprediction of the CMC of SDO. The discrepancy was eliminated by artificially forcing the predicted CMC of SDO to match the experimental value. The discrepancy between the experimental data and the modeling results for the binary mixture of SPFO and SDS may be due to the inaccurate estimation of the RST interaction parameter due to the absence of phase equilibrium data. We have shown that the ability to accurately predict micelle population distributions is affected greatly by the chosen value of A_{mix} . Indeed, the predictions of the MT framework may be further improved if more accurate estimates of A_{mix} could be obtained.

■ ASSOCIATED CONTENT

Supporting Information

Details of the molecular descriptors corresponding to all the surfactants considered in this paper and results for the hypothetical binary surfactant mixtures introduced in section 3.1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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