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Participation of Inclusion Complexes in the Surface Adsorbed Layer in Mixtures of α-Cyclodextrin and Cationic−Anionic Hydrogenated and Fluorinated Surfactants: A Surface Tension Proof

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S *Supporting Information*

ABSTRACT: It is generally considered that complexes of cyclodextrins (CDs) with ordinary surfactants are not surface-active in water. In this work, aqueous mixtures of α-CD, octyltriethylammonium bromide (OTEAB), and sodium perfluorooctanoate (SPFO) were studied by surface tension measurements. Comparison of the experimental results and the simulated ones in the premicellar region showed that the ability of the α-CD/OTEAB complexes to participate in the surface-adsorbed layer was dependent on the overall net charge of the surfactants: for the excess-SPFO system, the α-CD/OTEAB complexes did show a significant contribution to the surface activity of the mixture, but in the system with excess OTEAB, the α-CD/OTEAB complexes were not observed to influence the surface-adsorbed layer. We speculated that the surface-adsorbed layer in the premicellar region might also prefer an electroneutral state, as those cationic−anionic micelles did, and that the α-CD/OTEAB complexes were driven to the surface by electrostatic attractions from the excess oppositely charged SPFO. The calculated results for the surface area per molecule adsorbed at the air−water interface also supported our conclusion.

INTRODUCTION

Cyclodextrins (CDs) constitute a family of cyclic molecules built up from different numbers of glucopyranose units.[1] The special structure of CDs, involving a hydrophobic interior and a hydrophilic exterior, enables them to capture surfactants into their cavities to form host−guest inclusion complexes.[2] Since mixtures of CDs and surfactants are very useful in the areas of detergency, catalysis,[3] materials,[4] commodities, medicine,[5−7] and the food industry,[2] more and more works have been performed on the interactions between CDs and surfactants. However, most of the studies to date have focused on systems involving CD and a single surfactant;[8−20] works involving mixed surfactants are quite few. In the present work, we tried to study the surface tension of mixtures of CD with cationic−anionic hydrogenated and fluorinated surfactants. It is well-known that the surface-adsorbed layer at the air−water interface has many similarities to the micellar surface, when the responses of the surface tension and critical micelle concentration (cmc) to external factors such as electrolytes, alcohols, and cyclodextrins are taken into account. In this case, it is necessary to understand the equilibria of both micellization and complexation in CD/surfactant solutions reported in the literature.

Progress in Studies of CDs with Single Surfactants. The complexation of the surfactant monomers with CD is usually considered to be independent in most studies of CD/single-surfactant systems. For example, in mixtures of sodium perfluorooctanoate (SPFO) and β-CD, the kinetics of the monomer−micelle exchange process for the SPFO micelles is relatively unaffected by the presence of β-CD or the inclusion complex.[21] Recently, it has been shown that there is obvious competition between complexation and micellization in α-CD/single-surfactant systems whose complexation has a relatively small association constant, and a significant change in the ratio of complexes and micelles can be induced reversibly by temperature alternation.[22] Similarly, in mixtures of an imidazolium surfactant and α-CD, the process of micellar aggregation is the major process at high temperature while the formation of inclusion complexes is predominant only at room temperature.[23] Moreover, it has been reported that for very hydrophobic surfactants, a large amount of free CD exists in equilibrium with the micellar aggregates as a result of the competition between micellization and complexation. The percentage of uncomplexed β-CD increases as the hydrophobicity of the surfactant increases. The aggregation of surfactant monomers is more important than the complexation process in this mixed system. When the surfactant self-assembly structure is a vesicle, CD could even remain totally uncomplexed.[24]

In a word, recent studies have shown the equilibrium of micellization and its influence on the process of complexation to be more important than we used to think in systems involving CD and a single surfactant.

Progress in Studies of CDs with Hydrogenated Surfactant Mixtures. It is well-known that mixed surfactants are very

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important in industrial applications. In recent years, studies of the interactions between CDs and surfactant mixtures have attracted more and more attention. Some of them have shown rules similar to those of CD/single-surfactant systems. For example, it has been reported that the mixing behavior of cationic surfactant mixtures remains close to the ideal state in the presence of β-CD, except for mixtures of long-chain surfactants, which deviate from ideality because of the participation of inclusion complexes in the mixed-micelle formation.[25] It has also been confirmed that mixed-micelle formation in mixtures of nonionic and zwitterionic surfactants is close to ideal in nature in the presence of α-CD.[26]

The investigations have not been confined only to those micellar systems without synergistic interactions. It has been reported that β-CD can destroy aggregates of equimolar mixtures of cationic and anionic surfactants, which means that the complexation interactions between β-CD and the surfactants are stronger than the electrostatic/hydrophobic interactions between cationic and anionic surfactants.[27] Moreover, the host−guest inclusion between β-CD and surfactants can also destroy the self-aggregates of β-CD.[27] The interactions in 2:1 complexes of CD with cationic−anionic surfactants could induce precipitation because of the synergism of electrostatic attractions and intermolecular hydrogen bonding of CD.[28] β-CD can also cause the transition of an organized assembly of wormlike nanowires (prepared via the ionic self-assembly route from cationic organometal species and an anionic surfactant) into vesicles by including the organoiron blocks into β-CD to form complexes.[29]

In the above literature works, CD/surfactant complexation is a stronger process than micellization of the surfactants. However, mixtures of cationic and anionic surfactants in the presence of CD is expected to be more complicated. The equilibrium of micellization has played a more important role than previously thought. When the complexity of surfactant mixtures encounters the special nature of CDs, which have inherent selectivity due to their specific cavity size,[30] a new character of CD is revealed. At the same time, the equilibrium of micellization does not always play a passive role in the destruction of micelles by CD. It begins with the prelude that sodium dodecyl sulfate (SDS) has been found to be much more effective than β-CD when applied to decompacting condensates of complexes of DNA with cationic gemini surfactant, which shows that the attraction between the cationic and anionic surfactants is stronger than the interactions leading to complexation between β-CD and the gemini surfactant.[31]

The selectivity of CDs is another focus. It has been reported that β-CD forms 1:1 inclusion complexes with both cationic and anionic surfactants in equimolar mixtures of cationic and anionic surfactants without significant selectivity.[32] On the other hand, transitions from micelle to vesicle are controlled by adding due amounts of β-CD into aqueous solutions of nonequimolar mixtures of cationic and anionic surfactants; here the added β-CD is favored to include the "major" component in the cationic−anionic surfactant mixtures, and the aggregates consequently approach electroneutral mixing.[33] On the basis of this fact, modeling of the interplay between the equilibria of complexation and micellization has been discussed.[34] It is interesting that micellization could decide the selectivity of β-CD when the two surfactants have similar binding constants.

Studies of CDs with Mixtures of Hydrogenated and Fluorinated Surfactants. Fluorinated surfactants are known to exhibit the lowest surface tensions among all kinds of surfactants.[35] Therefore, mixtures of hydrogenated and fluorinated surfactants are of particular interest. The volumes and heat capacities of mixtures of anionic hydrogenated and fluorinated surfactants in the presence of β-CD have been studied,[36] and hypotheses have been used for modeling. The complexity of the system has been discussed with respect to the deviations mainly present in the micellar region, where both the selectivity and the micellar composition are concerned.[36]

It has been reported that the 1:1 equilibrium binding constants of β-CD with fluorocarbon anionic surfactants are larger than those with hydrocarbon ones.[37] In our previous works, the selectivity of CDs in mixtures of anionic hydrogenated and fluorinated surfactants were studied. β-CD showed significant selectivity toward the fluorinated surfactant in equimolar and excess-hydrocarbon mixtures of SPFO and sodium alkyl sulfate,[38,39] while α-CD preferentially included the hydrogenated surfactant;[40] the size-match factor was found to be more important than the hydrophobicity of the surfactant.

Among the mixed-surfactant systems, mixtures of cationic and anionic hydrogenated and fluorinated surfactants have great industrial significance. They exhibit much higher efficiencies of surface activity than their individual components because of the strong electrostatic interactions between the oppositely charged headgroups, as conventional cationic−anionic surfactant mixtures do.[41] Moreover, the amount of the expensive fluorinated surfactant used can be greatly reduced.[35] The interactions between CD and an equimolar mixture of octyltriethylammonium bromide (OTEAB) and SPFO were studied in our previous work,[42] which showed that both α-CD and β-CD could destroy the mixed micelles of OTEAB and SPFO by selective inclusion. In contrast to the selectivity of β-CD for SPFO, α-CD showed selective inclusion of OTEAB. The demicellization ability of α-CD was found to be much smaller than that of β-CD. This shows that demicellization and selective complexation are two interactional aspects that can influence the composition of surfactants.[42]

We have also shown that the β-CD/SPFO or α-CD/OTEAB complexes might contribute to the surface-adsorbed layer in equimolar OTEAB−SPFO mixtures in the presence of CD.[42] In the previous work,[42] only the surface tension of the mixtures of β-CD and equimolar OTEAB−SPFO was investigated in detail, and weak participation of the β-CD/SPFO complexes at the surface was present. As for α-CD, there was only one experimental surface tension curve for the equimolar OTEAB−SPFO mixture (total surfactant concentration $C_t = 5\ \mathrm{mmol\cdot kg^{-1}}$) with the addition of α-CD.[42] Here the ternary aqueous mixtures of α-CD, OTEAB, and SPFO, in which inclusion complexes were expected to show a significant contribution to the surface activity, were given attention. In contrast to the previous work, nonequimolar systems (excess OTEAB or excess SPFO) were examined in the present study. The experiments were set directly to aim at the α-CD/OTEAB complexes. Two series of solutions were measured by surface tension: in the first series, the concentrations of the cationic species (free OTEAB and the α-CD/OTEAB complex) were kept almost constant in solution; in the second series, the concentration of anionic species (mainly free SPFO) was kept almost constant in solution. On the basis of the combination of our simulations and the calculation of surface area per molecule adsorbed at the surface, the mechanism of the interplay between surface adsorption and complexation is discussed with the assistance of the view of the interplay between micellization and complexation. It seems that whether the α-CD/OTEAB complex was present in the surface-adsorbed

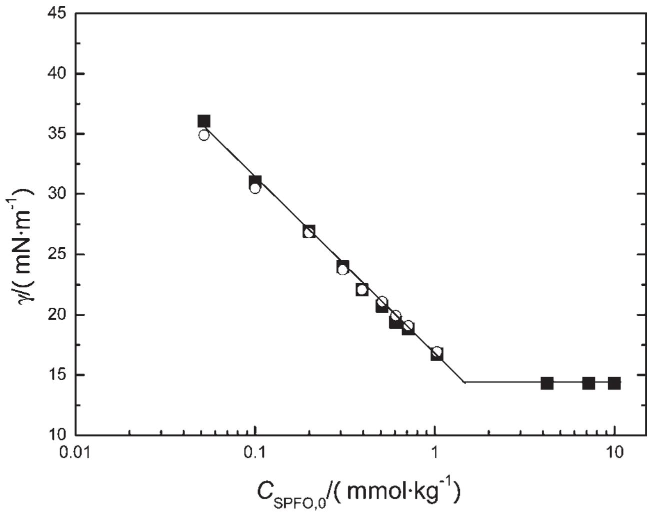

Figure 1. Surface tension (γ) for α-CD/OTEAB/SPFO mixtures vs the concentration of SPFO ($C_{\text{SPFO},0}$) with the OTEAB and α-CD concentrations held constant at C_0 = 1 mmol·kg^{-1}: ■, experimental points; ○, simulated points.

layer was closely related to the net charge of the composition of the surfactants.

EXPERIMENTAL SECTION

α-CD (CAS no. 10016-20-3, w = 0.98, ACROS; IUPAC name: (1*S*,3*R*,5*R*,6*S*,8*R*,10*R*,11*S*,13*R*,15*R*,16*S*,18*R*,20*R*,21*S*,23*R*,25*R*,26*S*,-28*R*,30*R*,31*R*,32*R*,33*R*,34*R*,35*R*,36*R*,37*R*,38*R*,39*R*,40*R*,41*R*,42*R*)-5,10,15,20,25,30-hexakis(hydroxymethyl)-2,4,7,9,12,14,17,19,22,-24,27,29-dodecaoxaheptacyclo[26.2.2.2^{3,6}.2^{8,11}.2^{13,16}.2^{18,21}.2^{23,26}]dotetracontane-31,32,33,34,35,36,37,38,-39,40,41,42-dodecol) and perfluorooctanoic acid monohydrate ($C_7F_{15}COOH\cdot H_2O$, CAS no. 335-67-1, w = 0.96, bp 192 °C, ACROS; IUPAC name: 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid) were used as received. SPFO (CAS no. 335-95-5; IUPAC name: sodium 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate) was prepared by neutralizing perfluorooctanoic acid with sodium hydroxide. OTEAB [n-$C_8H_{17}N(C_2H_5)_3$-Br; IUPAC name: triethyloctylazanium bromide] was prepared and purified by the procedure described in our previous work.[43] No minima were observed in plots of surface tension (γ) versus log c for these surfactants,[44,45] indicating the absence of surface-active impurities.[46]

The surface tension was measured by the drop volume method at (25 ± 0.01) °C.[46] The uncertainty in the drop volume method was ± 0.2 mN·m^{-1}. The measurements were made in a water bath maintained the desired temperature.

RESULTS

Experimental Surface Tension Results. The experiments were carried out by mixing SPFO with an equimolar mixture of α-CD and OTEAB. In the ternary aqueous mixtures, the total concentration of SPFO is $C_{\text{SPFO},0}$ and the total concentration of OTEAB (C_0) is identical with that of α-CD (C_0). To obtain information about the surface-adsorbed layer, the surface tensions (γ) of these aqueous mixed solutions were measured with either C_0 or $C_{\text{SPFO},0}$ kept constant. At first, the concentration of SPFO was fixed at $C_{\text{SPFO},0}$ = 2.496 mmol·kg^{-1} (γ = 51.41 mN·m^{-1}), however, it was observed that the surface tension immediately reached its minimum (γ = 14.33 mN·m^{-1}) in the presence of small amounts of the equimolar α-CD/OTEAB mixture (C_0 = 0.215 mmol·kg^{-1}). Because the cmc of an equimolar mixture of OTEAB and SPFO is 1.64 mmol·kg^{-1} (expressed by the total concentration of surfactants),[42] it was decided that C_0 and $C_{\text{SPFO},0}$ would be fixed at 1 mmol·kg^{-1} successively in the following experiments.

Table 1. Experimental Results for the Surface Tension (γ) of Mixtures of SPFO ($C_{\text{SPFO},0}$) with Equimolarly Mixed α-CD (C_0) and OTEAB (C_0) at 25 °C

system 1 (C_0 = 1 mmol·kg^{-1})		system 2 ($C_{\text{SPFO},0}$ = 1 mmol·kg^{-1})	
$C_{\text{SPFO},0}$/(mmol·kg^{-1})	γ/(mN·m^{-1})	C_0/(mmol·kg^{-1})	γ/(mN·m^{-1})
0	67.94	0	55.61
0.052	36.07	0.061	28.63
0.100	30.99	0.098	25.44
0.200	26.91	0.203	22.09
0.307	23.97	0.287	20.19
0.394	22.09	0.364	19.64
0.510	20.74	0.455	18.96
0.606	19.37	0.554	18.26
0.713	18.82	0.630	17.15
1.030	16.73	0.816	16.87
4.228	14.33	0.912	16.31
7.187	14.33	1.105	15.61
10.000	14.33	2.458	14.33
		6.381	14.33
		9.121	14.33

Figure 1 shows the surface tension (γ) of α-CD/OTEAB/SPFO mixtures obtained by adding SPFO to the equimolar mixture of OTEAB (C_0) and α-CD (C_0) with C_0 kept constant at 1 mmol·kg^{-1} (system 1). The surface tension of the blank OTEAB/α-CD solution (C_0 = 1 mmol·kg^{-1}) without SPFO was measured to be 67.94 mN·m^{-1}. The experimental surface tension data for system 1 are listed in Table 1. As shown in Figure 1, the break point corresponding to the apparent critical micelle concentration (cmc*) appeared at approximately $C_{\text{SPFO},0}$ = 1.46 mmol·kg^{-1} for C_0 = 1 mmol·kg^{-1}.

Figure 2 shows the surface tension (γ) of α-CD/OTEAB/SPFO mixtures obtained by adding the equimolar OTEAB/α-CD mixture (each with concentration C_0) into SPFO with the concentration of SPFO ($C_{\text{SPFO},0}$) kept constant at 1 mmol·kg^{-1} (system 2). The surface tension of the blank solution containing only 1 mmol·kg^{-1} SPFO was measured to be 55.61 mN·m^{-1}. The experimental surface tension data for system 2 are listed in Table 1. As shown in Figure 2, the break point corresponding to the cmc* appears at approximately C_0 = 1.43 mmol·kg^{-1} when $C_{\text{SPFO},0}$ = 1 mmol·kg^{-1}.

The surface tensions of solutions containing 5 mmol·kg^{-1} OTEAB at various concentrations of α-CD were measured and are shown in Table 2. The surface tension values are quite large, showing that the mixtures of α-CD and OTEAB were not surface-active.

Calculation of the Solution Composition in the Premicellar Region and Simulation of the Surface Tension. The surface tension curve in the premicellar region is usually applied to calculate the binding constants for CD/single-surfactant systems.[47−50] In our previous work, we calculated the compositions

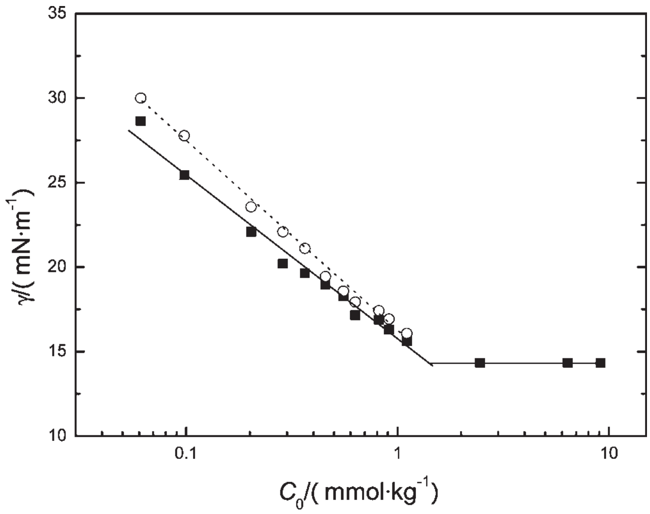

Figure 2. Surface tension (γ) of α-CD/OTEAB/SPFO mixtures vs the concentration of equimolarly mixed OTEAB/α-CD (C_0) with the concentration of SPFO held constant at 1 mmol·kg^{-1}: ■, experimental points; ○, simulated points.

of solutions of equimolarly mixed surfactants with added CD in which the two surfactants formed CD/surfactant complexes with 1:1 and 1:1/2:1 stoichiometries (e.g., β-CD + equimolar OTEAB/SPFO[42] and α-CD + equimolar sodium decyl sulfate/SPFO[40]). However, for the present α-CD/OTEAB/SPFO system, both of the binding compounds had 1:1 stoichiometry. In the present system, we tried to utilize the binding equilibrium constants of α-CD/SPFO and α-CD/OTEAB obtained in our previous work [K_F = (11.5 ± 4.8) mol^{-1}·kg and K_H = (2.14 ± 0.62) · 10^3 mol^{-1}·kg, respectively[42]]. Notably, the cavity of α-CD could not accommodate fluorocarbon chains, and only weak associates with small binding constants were formed.[40,51] The specific selectivity of α-CD for OTEAB will be helpful in the discussion of the calculation results later.

The equilibrium constants for the 1:1 binding of OTEAB and SPFO with α-CD (K_H and K_F, respectively) are defined by following equations:

$$\mathrm{CD} + \mathrm{OTEAB} \rightleftarrows \mathrm{CD}\cdot\mathrm{OTEAB}$$

$$K_H = \frac{C_{\mathrm{CD}\cdot\mathrm{OTEAB}}}{C_{\mathrm{CD}}\cdot C_{\mathrm{OTEAB}}} \tag{1}$$

$$\mathrm{CD} + \mathrm{SPFO} \rightleftarrows \mathrm{CD}\cdot\mathrm{SPFO}$$

$$K_F = \frac{C_{\mathrm{CD}\cdot\mathrm{SPFO}}}{C_{\mathrm{CD}}\cdot C_{\mathrm{SPFO}}} \tag{2}$$

where C_{CD}, C_{OTEAB}, C_{SPFO}, $C_{\mathrm{CD}\cdot\mathrm{OTEAB}}$, and $C_{\mathrm{CD}\cdot\mathrm{SPFO}}$ are the concentrations of free α-CD, OTEAB monomers, SPFO monomers, 1:1 α-CD/OTEAB complexes, and α-CD/SPFO associates, respectively.

In the concentration range below the cmc*, the equilibrium of micellization was neglected. Here the interactions between cationic and anionic species might induce the presence of ion pairs, although no micelles were formed in the aqueous solution. However, on the basis of the fact that α-CD can destroy mixed micelles of equimolar OTEAB/SPFO mixtures,[42] the equilibrium constant for formation of ion pairs could be expected to be relatively small in the premicellar region. Thus, in the calculation process only the equilibria mentioned above (eqs 1 and 2) were taken into consideration at concentrations below the cmc*.

Table 2. Surface Tensions (γ) of Solutions Containing 5 mmol·kg^{-1} OTEAB and Various Concentrations of α-CD ($C_{\alpha\text{-CD}}$) at 25 °C

$C_{\alpha\text{-CD}}$/(mmol·kg^{-1})	γ/(mN·m^{-1})
0	67.10
1.176	66.97
3.096	67.10
5.042	67.23
7.024	67.50
11.973	66.00
15.007	68.07

According to the law of conservation of mass, the following equations can be obtained:

$$C_{\mathrm{CD},0} = C_{\mathrm{CD}} + C_{\mathrm{CD}\cdot\mathrm{OTEAB}} + C_{\mathrm{CD}\cdot\mathrm{SPFO}} \tag{3}$$

$$C_{\mathrm{OTEAB},0} = C_{\mathrm{OTEAB}} + C_{\mathrm{CD}\cdot\mathrm{OTEAB}} \tag{4}$$

$$C_{\mathrm{SPFO},0} = C_{\mathrm{SPFO}} + C_{\mathrm{CD}\cdot\mathrm{SPFO}} \tag{5}$$

Because OTEAB and α-CD were equimolarly premixed, their initial concentrations had the following relationship:

$$C_{\mathrm{CD},0} = C_{\mathrm{OTEAB},0} = C_0 \tag{6}$$

Introducing eqs 1 and 2 into eqs 3, 4, and 5 gives

$$C_0 = C_{\mathrm{CD}} + K_H\cdot C_{\mathrm{CD}}\cdot C_{\mathrm{OTEAB}} + K_F\cdot C_{\mathrm{CD}}\cdot C_{\mathrm{SPFO}} \tag{7}$$

$$C_0 = C_{\mathrm{OTEAB}} + K_H\cdot C_{\mathrm{CD}}\cdot C_{\mathrm{OTEAB}} \tag{8}$$

$$C_{\mathrm{SPFO},0} = C_{\mathrm{SPFO}} + K_F\cdot C_{\mathrm{CD}}\cdot C_{\mathrm{SPFO}} \tag{9}$$

From eqs 8 and 9, the equilibrium concentrations of OTEAB and SPFO, can be expressed by eqs 10 and 11, respectively:

$$C_{\mathrm{OTEAB}} = \frac{C_0}{1 + K_H\cdot C_{\mathrm{CD}}} \tag{10}$$

$$C_{\mathrm{SPFO}} = \frac{C_{\mathrm{SPFO},0}}{1 + K_F\cdot C_{\mathrm{CD}}} \tag{11}$$

Therefore, from the combination of eqs 10 and 11 with eq 7, the initial concentration of α-CD can also be expressed as

$$C_0 = C_{\mathrm{CD}} + K_H\cdot C_{\mathrm{CD}}\cdot\frac{C_0}{1 + K_H\cdot C_{\mathrm{CD}}} + K_F\cdot C_{\mathrm{CD}}\cdot\frac{C_{\mathrm{SPFO},0}}{1 + K_F\cdot C_{\mathrm{CD}}} \tag{12}$$

which can be rewritten in the following form:

$$\begin{aligned} &K_HK_F\cdot C_{\mathrm{CD}}{}^3 + (K_H + K_F + K_HK_F\cdot C_{\mathrm{SPFO},0})\cdot C_{\mathrm{CD}}{}^2 \\ &\quad + (1 + K_F\cdot C_{\mathrm{SPFO},0} - K_FC_0)\cdot C_{\mathrm{CD}} - C_0 = 0 \end{aligned} \tag{13}$$

The value of C_{CD} in eq 13 was obtained using the Newton–Raphson method[52] for given values of $C_{\mathrm{SPFO},0}$ and C_0. Next,

Table 3. Calculated Compositions of Mixtures of SPFO ($C_{\mathrm{SPFO},0}$) with Equimolarly Mixed α-CD (C_0) and OTEAB (C_0) in the Premicellar Region

$C_{\mathrm{SPFO},0}$	C_0	C_{CD}	C_{SPFO}	C_{OTEAB}	$C_{\mathrm{CD\cdot SPFO}}$	$C_{\mathrm{CD\cdot OTEAB}}$
$\mathrm{mmol\cdot kg^{-1}}$	$\mathrm{mmol\cdot kg^{-1}}$	$\mathrm{mmol\cdot kg^{-1}}$	$\mathrm{mmol\cdot kg^{-1}}$	$\mathrm{mmol\cdot kg^{-1}}$	$\mathrm{mmol\cdot kg^{-1}}$	$\mathrm{mmol\cdot kg^{-1}}$
0.052	1.000	0.488575	0.0517095	0.488866	0.000290535	0.511134
0.100	1.000	0.488398	0.0994415	0.488956	0.000558521	0.511044
0.200	1.000	0.488029	0.198884	0.489145	0.00111620	0.510855
0.307	1.000	0.487635	0.305288	0.489347	0.00171199	0.510653
0.394	1.000	0.487315	0.391804	0.489511	0.00219572	0.510489
0.510	1.000	0.486890	0.507160	0.489729	0.00283971	0.510271
0.606	1.000	0.486538	0.602628	0.489910	0.00337182	0.510090
0.713	1.000	0.486147	0.709036	0.490111	0.00396400	0.509889
1.030	1.000	0.484992	1.024287	0.490705	0.00571287	0.509295
1.000	0.061	0.0540541	0.999379	0.0546754	0.000621236	0.00632462
1.000	0.098	0.0823680	0.999054	0.0833144	0.000946336	0.0146856
1.000	0.203	0.151547	0.998260	0.153287	0.00173976	0.0497127
1.000	0.287	0.198999	0.997717	0.201282	0.00228326	0.0857177
1.000	0.364	0.238324	0.997267	0.241057	0.00273323	0.122943
1.000	0.455	0.280940	0.996780	0.284160	0.00322041	0.170840
1.000	0.554	0.323613	0.996292	0.327320	0.00370775	0.226680
1.000	0.630	0.354274	0.995942	0.358332	0.00405762	0.271668
1.000	0.816	0.423306	0.995156	0.428150	0.00484444	0.387850
1.000	0.912	0.456238	0.994781	0.461457	0.00521935	0.450543
1.000	1.105	0.518092	0.994077	0.524015	0.00592277	0.580985

C_{SPFO}, C_{OTEAB}, $C_{\mathrm{CD\cdot SPFO}}$, and $C_{\mathrm{CD\cdot OTEAB}}$ were obtained successively using eqs 11, 10, 5, and eq 4. The calculated equilibrium concentrations of the species in the α-CD/OTEAB/SPFO mixtures are shown in Table 3.

According to the calculated compositions of the ternary aqueous mixtures of α-CD, OTEAB, and SPFO, "simulated" solutions containing only OTEAB and SPFO were prepared (the concentrations of OTEAB and SPFO were equal to the values of C_{OTEAB} and C_{SPFO}, respectively, in Table 3). The simulation was based on the hypothesis that if the effective components responsible for the surface activity of the mixture were uncomplexed OTEAB and SPFO only, then free α-CD, the α-CD/OTEAB complexes, and the α-CD/SPFO associates could be ignored. The surface tensions of these "simulated" solutions were measured and are compared with the experimental points in Figures 1 and 2. Good agreement between the simulated points and the experimental points can be seen in Figure 1; however, in Figure 2 the simulated points show a positive deviation from the experimental points.

Estimation of the Maximum Surface Amount Adsorbed in Ternary α-CD/OTEAB/SPFO Mixtures. For the surface adsorption of an aqueous mixture, on the basis of the Gibbs adsorption equation,[53] the following equation can be obtained for ternary α-CD/OTEAB/SPFO mixtures:

$$-\mathrm{d}\gamma = RT\sum_i \Gamma_i\,\mathrm{d}(\ln C_i) = RT\Big[\Gamma_{\mathrm{PFO^-}}\,\mathrm{d}(\ln C_{\mathrm{PFO^-}}) + \Gamma_{\mathrm{OTEA^+}}\,\mathrm{d}(\ln C_{\mathrm{OTEA^+}}) + \Gamma_{\mathrm{Na^+}}\,\mathrm{d}(\ln C_{\mathrm{Na^+}}) + \Gamma_{\mathrm{Br^-}}\,\mathrm{d}(\ln C_{\mathrm{Br^-}}) + \Gamma_{\mathrm{CD}}\,\mathrm{d}(\ln C_{\mathrm{CD}}) + \Gamma_{\mathrm{CD\cdot OTEA^+}}\,\mathrm{d}(\ln C_{\mathrm{CD\cdot OTEA^+}}) + \Gamma_{\mathrm{CD\cdot PFO^-}}\,\mathrm{d}(\ln C_{\mathrm{CD\cdot PFO^-}})\Big] \tag{14}$$

In eq 14, Γ_i is the maximum surface amount of adsorbed species i, C_i is the concentration of species i, R is the gas constant, and T is the thermodynamic temperature. For the present system, $C_{\mathrm{Na^+}} = C_{\mathrm{SPFO},0}$ and $C_{\mathrm{Br^-}} = C_0$. It can be seen that the system is very complicated. Therefore, the following hypotheses were used to simplify the analysis in order to obtain the maximum surface amount adsorbed (Γ) and minimum surface area per molecule ($A_{\min}$) from surface tension curves: (1) The interactions between α-CD and SPFO were neglected. It can be seen that the binding equilibrium constant of the α-CD/SPFO associates is much smaller than that of the α-CD/OTEAB complexes [$K_F = (11.5 \pm 4.8)\ \mathrm{mol^{-1}\cdot kg} \ll K_H = (2.14 \pm 0.62)\cdot 10^3\ \mathrm{mol^{-1}\cdot kg}$].[42] It is known that the cavity of α-CD cannot accommodate fluorocarbon chains and that α-CD shows only weak association with the terminal CF_3 group.[40,51] In the mixed solution, the inclusion of α-CD was supposed to be specific to OTEAB. This hypothesis was supported by the calculated composition as shown in Table 3, in which the concentration of α-CD/SPFO associates ($C_{\mathrm{CD\cdot SPFO}}$) was extremely low in comparison with the concentrations of the other components. On the other hand, in comparison with the anionic SPFO monomers, the amount of α-CD/SPFO associates was too small and the α-CD/SPFO associates had less adsorption ability, so the presence of α-CD/SPFO associates in the surface-adsorbed layer could be neglected. (2) The adsorption of α-CD was neglected. It is known that α-CD is non-surface-active. The surface tension of the 5 $\mathrm{mmol\cdot kg^{-1}}$ α-CD solution was measured to be 68.91 $\mathrm{mN\cdot m^{-1}}$ at 25 °C. When the concentration of α-CD was relatively small, there were no 2:1 complexes, and the self-aggregates of α-CD formed by intermolecular hydrogen bonding (if any) could be destroyed by surfactants. Moreover, no electrostatic synergism of free α-CD existed. Therefore, the free α-CD should not have been present in the surface-adsorbed layer.[27,54−57]

With these two hypotheses, eq 14 can be expressed in the following form:

$$\begin{aligned}-\mathrm{d}\gamma = RT\Big[&\Gamma_{\mathrm{PFO}^-}\,\mathrm{d}(\ln C_{\mathrm{PFO}^-}) + \Gamma_{\mathrm{OTEA}^+}\,\mathrm{d}(\ln C_{\mathrm{OTEA}^+})\\ &+ \Gamma_{\mathrm{Na}^+}\,\mathrm{d}(\ln C_{\mathrm{Na}^+}) + \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_{\mathrm{Br}^-})\\ &+ \Gamma_{\mathrm{CD\cdot OTEA}^+}\,\mathrm{d}(\ln C_{\mathrm{CD\cdot OTEA}^+})\Big]\end{aligned} \tag{15a}$$

which can also be written as

$$\begin{aligned}-\mathrm{d}\gamma = RT\Big[&\Gamma_{\mathrm{PFO}^-}\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}}) + \Gamma_{\mathrm{OTEA}^+}\,\mathrm{d}(\ln C_{\mathrm{OTEA}^+}) + \Gamma_{\mathrm{Na}^+}\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}})\\ &+ \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_0) + \Gamma_{\mathrm{CD\cdot OTEA}^+}\,\mathrm{d}(\ln C_{\mathrm{CD\cdot OTEA}^+})\Big]\end{aligned} \tag{15b}$$

It was noted that α-CD and OTEAB were equimolarly mixed, so according to mass conservation,

$$C_0 = C_{\mathrm{CD}} + C_{\mathrm{CD\cdot OTEA}^+} = C_{\mathrm{OTEA}^+} + C_{\mathrm{CD\cdot OTEA}^+} \tag{16}$$

It follows from eq 16 that

$$C_{\mathrm{CD}} = C_{\mathrm{OTEA}^+} \tag{17}$$

which is consistent with the calculated data in Table 3 and also shows that neglecting the association between α-CD and SPFO was reasonable. Next, combining eqs 16, 17, and 1 affords the following result:

$$C_{\mathrm{OTEA}^+} = \frac{-1 + \sqrt{1 + 4K_{\mathrm{H}}C_0}}{2K_{\mathrm{H}}} \tag{18}$$

This allows eq 15b to be rewritten as follows:

$$\begin{aligned}-\mathrm{d}\gamma = RT\Big[&\Gamma_{\mathrm{PFO}^-}\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}}) + \Gamma_{\mathrm{OTEA}^+}\,\mathrm{d}(\ln C_{\mathrm{OTEA}^+}) + \Gamma_{\mathrm{Na}^+}\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}})\\ &+ \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_0) + 2\Gamma_{\mathrm{CD\cdot OTEA}^+}\,\mathrm{d}(\ln C_{\mathrm{OTEA}^+})\Big]\\ -\mathrm{d}\gamma = RT\Big[&(\Gamma_{\mathrm{PFO}^-} + \Gamma_{\mathrm{Na}^+})\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}}) + (\Gamma_{\mathrm{OTEA}^+}\\ &+ 2\Gamma_{\mathrm{CD\cdot OTEA}^+})\,\mathrm{d}(\ln C_{\mathrm{OTEA}^+}) + \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_0)\Big]\\ -\mathrm{d}\gamma = RT\Bigg[&(\Gamma_{\mathrm{PFO}^-} + \Gamma_{\mathrm{Na}^+})\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}}) + (\Gamma_{\mathrm{OTEA}^+}\\ &+ 2\Gamma_{\mathrm{CD\cdot OTEA}^+})\,\mathrm{d}\left(\ln \frac{-1 + \sqrt{1 + 4K_{\mathrm{H}}C_0}}{2K_{\mathrm{H}}}\right) + \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_0)\Bigg]\\ -\mathrm{d}\gamma = RT\Big\{&(\Gamma_{\mathrm{PFO}^-} + \Gamma_{\mathrm{Na}^+})\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}}) + (\Gamma_{\mathrm{OTEA}^+}\\ &+ 2\Gamma_{\mathrm{CD\cdot OTEA}^+})\,\mathrm{d}\left[\ln(-1 + \sqrt{1 + 4K_{\mathrm{H}}C_0})\right] + \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_0)\Big\}\end{aligned} \tag{19}$$

For system 1 in Table 1 (see Figure 1), C_0 was kept constant, for which case eq 19 reduces to

$$-\mathrm{d}\gamma = RT(\Gamma_{\mathrm{PFO}^-} + \Gamma_{\mathrm{Na}^+})\,\mathrm{d}(\ln C_{\mathrm{SPFO,0}}) \tag{20}$$

On the basis of the principle of charge neutralization in the surface-adsorbed layer, it follows that

$$\Gamma_{\mathrm{OTEA}^+} + \Gamma_{\mathrm{CD\cdot OTEA}^+} + \Gamma_{\mathrm{Na}^+} = \Gamma_{\mathrm{PFO}^-} + \Gamma_{\mathrm{CD\cdot PFO}^-} + \Gamma_{\mathrm{Br}^-} \tag{21}$$

Because the OTEAB ions in solution are in excess for system 1 and more hydrophobic than Na^+ ions, and because the α-CD/SPFO associates are hypothesized to be absent, it can be deduced from eq 21 that $\Gamma_{\mathrm{PFO}^-} \gg \Gamma_{\mathrm{Na}^+}$; thus, the maximum surface amount of adsorbed perfluorooctanoate ions (PFO^-) can be estimated from the surface tension results in Figure 1 using eq 22:

$$\Gamma_{\mathrm{PFO}^-} = -\frac{1}{RT}\cdot\frac{\mathrm{d}\gamma}{\mathrm{d}(\ln C_{\mathrm{SPFO,0}})} = -\frac{1}{2.303RT}\cdot\frac{\mathrm{d}\gamma}{\mathrm{d}(\log C_{\mathrm{SPFO,0}})} \tag{22}$$

From the linear fit of the experimental points (γ vs $\log C_{\mathrm{SPFO,0}}$), the slope was obtained as −14.93285 ± 0.29971, and Γ_{PFO^-} was calculated to be $(2.616 \pm 0.053)\cdot 10^{-10}\ \mathrm{mol\cdot cm^{-2}}$ according to eq 22.

For system 2 in Table 1 (see Figure 2), $C_{\mathrm{SPFO,0}}$ was kept constant, so eq 19 takes the following form:

$$\begin{aligned}-\mathrm{d}\gamma = RT\Big\{&(\Gamma_{\mathrm{OTEA}^+} + 2\Gamma_{\mathrm{CD\cdot OTEA}^+})\,\mathrm{d}\left[\ln(-1 + \sqrt{1 + 4K_{\mathrm{H}}C_0})\right]\\ &+ \Gamma_{\mathrm{Br}^-}\,\mathrm{d}(\ln C_0)\Big\}\end{aligned} \tag{23}$$

Because the SPFO in solution is in excess for system 2, the adsorption of Br^- ions can be ignored. Therefore,

$$\Gamma_{\mathrm{OTEA}^+} + 2\Gamma_{\mathrm{CD\cdot OTEA}^+} = -\frac{1}{2.303RT}\cdot\frac{\mathrm{d}\gamma}{\mathrm{d}\left[\log(-1 + \sqrt{1 + 4K_{\mathrm{H}}C_0})\right]} \tag{24}$$

From the linear fit of the experimental points (γ vs $\log[-1 + (1 + 4K_{\mathrm{H}}C_0)^{1/2}]$), the slope was obtained as −12.89124 ± 0.36521, and $\Gamma_{\mathrm{OTEA}^+} + 2\Gamma_{\mathrm{CD\cdot OTEA}^+}$ was calculated to be $(2.258 \pm 0.064)\cdot 10^{-10}\ \mathrm{mol\cdot cm^{-2}}$ according to eq 24.

Estimation of the Minimum Surface Area per Molecule Adsorbed at the Air−Water Interface in Ternary α-CD/OTEAB/SPFO Mixtures and Simulated OTEAB/SPFO Solutions. The surface area per molecule can be obtained from corresponding maximum surface amount adsorbed (Γ) using eq 25:[53]

$$A_{\mathrm{min}} = \frac{1}{N_0\Gamma} \tag{25}$$

in which N_0 is the Avogadro constant. For system 1, A_{PFO^-} was calculated to be (0.635 ± 0.013) nm². Thus, in the α-CD/OTEAB/SPFO ternary mixtures, the minimum surface area per molecule for the anionic surfactant (PFO^- ions) was estimated to be approximately 0.635 nm².

For system 2, the estimation was complicated. However, we obtained a limit for the average surface area per molecule of adsorbed OTEA^+ (complexed and uncomplexed) as follows:

$$\bar{A}_{\mathrm{OTEA\text{-}all\text{-}state}} = \frac{1}{N_0(\Gamma_{\mathrm{OTEA}^+} + \Gamma_{\mathrm{CD\cdot OTEA}^+})} > \frac{1}{N_0(\Gamma_{\mathrm{OTEA}^+} + 2\Gamma_{\mathrm{CD\cdot OTEA}^+})} \tag{26}$$

From eq 24, $\Gamma_{\mathrm{OTEA}^+} + 2\Gamma_{\mathrm{CD\cdot OTEA}^+}$ was calculated to be $(2.258 \pm 0.064)\cdot 10^{-10}\ \mathrm{mol\cdot cm^{-2}}$. Therefore, the limit of $\bar{A}_{\mathrm{OTEA\text{-}all\text{-}state}}$ was calculated to be (0.736 ± 0.021) nm².

On the other hand, from the "simulated" solutions prepared by mixing only OTEAB and SPFO (whose concentrations were equal to the calculated C_{OTEAB} and C_{SPFO} values in Table 3), the maximum surface amount adsorbed and minimum surface area per molecule of adsorbed surfactants in the absence of α-CD could also be obtained. The surface tensions of these simulated solutions (γ_{sim}) of cationic−anionic surfactant mixtures were also measured, as shown in Figures 1 and 2. Both of the simulated series could be simply treated as follows:[53]

$$\Gamma_{\text{surf-ion}} = -\frac{1}{2.303RT} \cdot \frac{d\gamma}{d(\log C_{\text{surf-ion}})} \tag{27}$$

where "surf-ion" stands for either PFO^- or $OTEA^+$. Equation 27 means that for cationic−anionic surfactant mixtures, the value of Γ for one surfactant ion can be obtained using eq 27 when the concentration of the other oppositely charged surfactant ion is kept constant.[53]

For the first series of simulated solutions, the concentration of OTEAB was constant [(0.489 to 0.491) $mmol \cdot kg^{-1}$] while the concentration of SPFO was varied (see Table 3). The linear fit of γ_{sim} versus log C_{SPFO} showed a slope of -13.79608 ± 0.22333, and the simulated Γ_{PFO^-} value was calculated to be $(2.417 \pm 0.039) \cdot 10^{-10}$ $mol \cdot cm^{-2}$ according to eq 27. From this, the simulated A_{PFO^-} value was calculated to be (0.687 ± 0.012) nm^2 using eq 25. Thus, in the simulated mixtures containing only OTEAB and SPFO, the minimum surface area per molecule for anionic surfactant (PFO^-) ions was estimated to be approximately 0.687 nm^2.

For the second series of simulated solutions, the concentration of SPFO was constant [(0.994 to 0.999) $mmol \cdot kg^{-1}$] while the concentration of OTEAB was varied (see Table 3). The linear fit of γ_{sim} versus log C_{OTEAB} showed a slope of -14.48560 ± 0.27900, and the simulated Γ_{OTEA^+} value was calculated to be $(2.537 \pm 0.049) \cdot 10^{-10}$ $mol \cdot cm^{-2}$ according to eq 27. From this, the simulated A_{OTEA^+} value was calculated to be (0.655 ± 0.013) nm^2 using eq 25. Therefore, in the simulated mixtures containing only OTEAB and SPFO, the minimum surface area per molecule for cationic surfactant ($OTEA^+$) ions was estimated to be approximately 0.655 nm^2.

DISCUSSION

The Ability of α-CD/OTEAB Complexes To Participate in the Surface-Adsorbed Layer. It is well-known that in an aqueous system of a conventional surfactant with CD, the equilibria are complexation, formation of micelles, and surface adsorption, as shown in the picture drawn by Funasaki et al.,[58] in which the inclusion complexes are considered to stay in the aqueous phase and not to be present at the air−water interface. In the present work, as shown in Table 2, the solution containing 5 $mmol \cdot kg^{-1}$ OTEAB in the presence of α-CD showed no surface activity. Thus, it could be confirmed that the α-CD/OTEAB complexes were not surface-active and that they should not be present in the surface-adsorbed layer.

In this work, some specialties were found to facilitate the investigation of the nonequimolar cationic−anionic surfactant mixtures to some extent: α-CD selectively includes one of the two surfactants, with only 1:1 stoichiometry for the complexation. The two series of ternary aqueous mixtures were prepared by mixing SPFO ($C_{SPFO,0}$) with equimolar α-CD(C_0)/OTEAB (C_0) mixtures. For the first series (system 1 in Table 1), C_0 was kept constant and SPFO was added (black squares in Figure 1), while for the second series (system 2 in Table 1), $C_{SPFO,0}$ was kept constant and C_0 was increased (black squares in Figure 2). The solution compositions of the two series in the premicellar region were calculated as shown in Table 3. It was seen that the amount of α-CD/SPFO associates was very small in comparison with other components in solution, so the association between α-CD and SPFO could be neglected. For system 1, the concentrations of free α-CD, OTEAB monomers, and the α-CD/OTEAB complexes (C_{CD}, C_{OTEAB}, and $C_{CD \cdot OTEAB}$ in Table 3) were almost unchanged upon addition of SPFO. In other words, when both α-CD and OTEAB were in excess, the complexation of α-CD with OTEAB was unaffected in the premicellar region. The experimental data in Figures 1 and 2 presented the systems with excess OTEAB and excess SPFO, respectively.

By comparing the experimental data for the ternary solutions with the surface tensions of the corresponding simulated solutions, we found that the α-CD/OTEAB complexes could participate in surface adsorption and contribute to the surface activity of solutions, depending on the sign of the charge of the excess ionic surfactant. The simulated solutions contained the same concentrations of free OTEAB and SPFO surfactants as the ternary mixtures but contained only OTEAB and SPFO. Because it is generally considered that neither the CDs nor the complexes were surface-active, this simulation in the premicellar region might be reasonable. In Figure 1, the experimental data for the ternary solutions and the surface tensions of the simulated solutions were almost identical with each other, showing that in the excess-OTEAB system, the surface tension of the α-CD/OTEAB/SPFO mixtures was totally unaffected by the α-CD/OTEAB complexes. However, in Figure 2, the experimental surface tension points were significantly lower than the surface tensions of the simulated solutions, showing that in the excess-SPFO system, the existence of α-CD/OTEAB complexes might make a contribution to lowering the surface tension of the α-CD/OTEAB/SPFO mixtures.

Surface Area per Molecule at the Air−Water Interface. For the excess-OTEAB series of ternary mixtures of α-CD, OTEAB, and SPFO (system 1), the surface area per molecule of the anionic surfactant (PFO^-) ions, A_{PFO^-}, was estimated as (0.635 ± 0.013) nm^2. Meanwhile, the simulated A_{PFO^-} was calculated to be (0.687 ± 0.012) nm^2. The two results were well-consistent with each other.

For the excess-SPFO series (system 2), the estimation was complicated, but it could be shown that the average surface area per molecule of $OTEA^+$ (both complexed and uncomplexed), $\bar{A}_{\text{OTEA-all-state}}$, was larger than 0.736 nm^2. As shown by eq 26, the larger extent of $\bar{A}_{\text{OTEA-all-state}}$ was dependent on the adsorption of the α-CD/OTEAB complexes: the more α-CD/OTEAB complexes were adsorbed in the surface layer, the larger value of $\bar{A}_{\text{OTEA-all-state}}$ was. This is consistent with the steric effect of introducing α-CD rings in the surface-adsorbed layer. However, the simulated solution containing OTEAB and SPFO showed a simulated A_{OTEA^+} of (0.655 ± 0.013) nm^2, showing that the simulated A_{OTEA^+} in OTEAB/SPFO mixtures was smaller than $\bar{A}_{\text{OTEA-all-state}}$ in ternary mixtures. Combining the surface tension comparisons in Figure 2 with the comparisons of the surface areas per molecule leads to the conclusion that in the excess-SPFO system, the existence of additional α-CD/OTEAB complexes could facilitate reducing the surface tension but the participation of α-CD/OTEAB complexes in surface adsorption would affect the compactness of the surface-adsorbed layer.

Mechanism of Participation of the CD/Surfactant Complexes in the Surface-Adsorbed Layer. It is well-known that CD/surfactant inclusion complexes have no surface activity, so the participation of complexes at the surface has rarely been seen. It has been reported that at aqueous solution/air interfaces, native α-CD spontaneously forms films constructed by CD−CD hydrogen bonding.[54] Both the temperature and SDS concentration strongly modify the viscoelastic properties of such films. It has been shown that the films consist of self-assembled nanotubes whose

Table 4. Calculated Critical Compositions of Mixtures of SPFO ($C_{\mathrm{SPFO},0}$) with Equimolarly Mixed α-CD (C_0) and OTEAB (C_0) at the Apparent Critical Micelle Concentration

$C_{\mathrm{SPFO},0}$ mmol·kg^{-1}	C_0 mmol·kg^{-1}	C_{CD} mmol·kg^{-1}	C_{SPFO} mmol·kg^{-1}	C_{OTEAB} mmol·kg^{-1}	$C_{\mathrm{CD\cdot SPFO}}$ mmol·kg^{-1}	$C_{\mathrm{CD\cdot OTEAB}}$ mmol·kg^{-1}
1.460	1.000	0.483436	1.451928	0.491508	0.00807201	0.508492
1.000	1.430	0.612091	0.993010	0.619081	0.00698984	0.810919

building blocks are cyclodextrin dimers (α-CD$_2$) and α-CD$_2$/SDS$_1$ complexes.[54,55]

However, in those works, the presence of the α-CD/surfactant complexes at the surface were induced by hydrogen bonding and did not make a contribution to the surface activity of the solution.[57] In the present work, we report that the inclusion complexes did show an important contribution to the surface-adsorbed layer. The simulation of surface tension curves and the calculation of surface area per adsorbed molecule revealed that the α-CD/OTEAB complexes made a contribution to surface adsorption only when the anionic surfactants were in excess.

The critical micelle concentration (cmc) is theoretically defined as the concentration of monomers at a critical state of formation of micelles. When the calculation method of solution composition in the premicellar region was utilized to estimate the micellar composition at the apparent cmc (cmc*), the concentrations of all the species in solution could be obtained, and the results are shown in Table 4. Here, the calculation method used to obtain the solution compositions at the cmc*'s (the break points in Figures 1 and 2) for the two series was the same as that applied in Table 3, with only the given C_0 and $C_{\mathrm{SPFO},0}$ changing to the corresponding values at the cmc*. Although CD (free and complexed) might show affinity toward the micelles because of ion−dipole interactions between the carboxylate headgroups in the hydrophilic shell and the hydroxyl groups of the CD,[10,59,60] this kind of interaction between CD and micelles might be weak because the cationic−anionic surfactant headgroups in micelles strongly interact with each other. Generally it is concluded that the presence of CD has no effect on existing strong micelles but increases the cmc.[24] Here, with the assumptions that α-CD included only surfactant monomers in solution and that the complexes did not participate in the micelles,[61] the concentrations of SPFO and OTEAB in Table 4 could be regarded as the critical composition of micelles: the sums of C_{SPFO} and C_{OTEAB} were 1.94 mmol·kg^{-1} (critical composition of micelles SPFO:OTEAB = 2.95) and 1.61 mmol·kg^{-1} (critical composition of micelles SPFO:OTEAB = 1.60) for systems 1 and 2, respectively, which was consistent with the discussion in our previous work that SPFO might be the much more contributive component in mixed OTEAB/SPFO micelles.[42] Because this SPFO:OTEAB composition ratio was not very far from 1:1, although the cmc*'s were obviously increased [(2.46 and 2.43) mmol·kg^{-1}, respectively] in comparison with the cmc of equimolar OTEAB/SPFO (1.64 mmol·kg^{-1}),[42] the total concentrations of surfactant monomers [(1.94 and 1.61) mmol·kg^{-1}, respectively] were close to the cmc of equimolar OTEAB/SPFO. It was also consistent with the general situation that the presence of CD has no effect on existing strong micelles but raises the cmc.[24]

However, in contrast to the situation at the critical point of micelle formation, the α-CD/OTEAB complexes showed an influence on the surface-adsorbed layer in the premicellar region. The difference between the optimum compositions of micelles and the surface-adsorbed layer in the OTEAB/SPFO mixture might be the reason. This showed that SPFO was preferred in the critical micellar composition as discussed above. However, the ratio of cationic to anionic surfactant in the surface layer in the OTEAB/SPFO mixture ($\Gamma_{\mathrm{OTEA^+}}/\Gamma_{\mathrm{PFO^-}}$), which could be obtained from the maximum amounts adsorbed for the simulated solutions, was calculated to be (2.537/2.417 = 1.05); this implies that if no α-CD exists to interfere with the OTEAB/SPFO mixture, the surface-adsorbed layer in OTEAB/SPFO mixtures would prefer a nearly electroneutral state with cationic and anionic surfactants equimolarly adsorbed.

When SPFO monomers were present in large excess, the α-CD/OTEAB complexes were driven to the surface-adsorbed layer by the excess oppositely charged SPFO monomers and played an important role for the surface activity of the solution. We proved that this kind of driving process of the α-CD/OTEAB complexes by SPFO would not occur when OTEAB was in excess. In other words, the surface-adsorbed layer also prefers an electroneutral state. When the number of OTEAB monomers was very small in comparison with the number of SPFO monomers, the α-CD/OTEAB complexes could lend a hand to some extent. In this work, the estimation of surface area per molecule adsorbed at the air−water interface also supported our conclusion. The special behavior of α-CD/OTEAB complexes might be attributed to the structural character of the inclusion complex, as discussed in our previous work,[42] where the headgroup of the surfactant is totally exposed outside the cavity of α-CD. The synergism between the α-CD/OTEAB complexes and SPFO showed a significant effect on lowering the surface tension. This is similar to the literature report that complexes of *β*-CD with cationic alkylimidazolium surfactant can also interact with small anionic fluorinated species in solutions as ion pairs.[62]

■ SUMMARY

The surface tension of α-CD/OTEAB/SPFO ternary mixtures was measured and simulated. It was found that the α-CD/OTEAB complexes could participate in surface adsorption and contribute to the surface activity of the solution, but this contribution to the surface adsorption existed only when the anionic SPFO surfactants were excess. In the excess-OTEAB system, the α-CD/OTEAB complexes had no effect on the surface tension of the α-CD/OTEAB/SPFO mixture. With the calculation of the critical composition at the cmc*, this showed that SPFO might be the more contributive component in mixed OTEAB/SPFO micelles and that the presence of α-CD had no effect on existing micelles but only raised the cmc. The surface-adsorbed layer preferred a state of electroneutralization, and when the number of OTEAB monomers was very small in comparison with the number of SPFO monomers, the α-CD/OTEAB complexes could lend a hand to some extent through electrostatic interactions. The conclusions were also well-supported by the calculated results for surface area per molecule at the air−water interface.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional surface tension data (XLS). This material is available free of charge via the Internet at http://pubs.acs.org.

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