A Study of the Behavior of α-Cyclodextrin with Single Solutions of Hydrogenated and Fluorinated Surfactants and Their Mixtures†

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The interactions between α-cyclodextrin (α-CD) and an equimolar mixture of the anionic hydrogenated and fluorinated surfactants sodium decyl sulfate (SDeS) and sodium perfluorooctanoate (SPFO), respectively, were studied by ^{1}H and ^{19}F NMR spectroscopy. It was directly proved that α-CD preferentially included the hydrogenated surfactant in such a surfactant mixture, although SDeS and SPFO showed almost the same hydrophobicity. The added α-CD formed 1:1 and 2:1 complexes with SDeS, but SPFO showed only a weak association with α-CD after the near saturation of inclusion of SDeS. Such selectivity of α-CD is contrary to that of *β*-CD, as shown in our previous work in which *β*-CD preferentially included the fluorinated surfactant in an SDeS/SPFO mixture. This selectivity of α-CD could be ascribed to the better fit between the cavity of α-CD and the hydrocarbon chain. It is consistent with the equilibrium constants (*K*) for the inclusion complexes in the solution. A peculiar trend of chemical shift variation was noted in mixtures of α-CD with the single surfactant SDeS: the chemical shift of *β*-CH_2 increased rapidly while *ω*-CH_3 showed a smaller ascent to declivity, until both of them reached a plateau. The binding constant for the formation of the 2:1 α-CD/SDeS complex (K_2) was found to be relatively large, as determined by the NMR investigation.

Introduction

Cyclodextrins (CDs) constitute a family of cyclic molecules built up from different numbers of glucopyranose units.[1] The most common CDs are α, *β*, and *γ*, which consist of six, seven, and eight units, respectively.[1] The special structure of CDs enables them to capture surfactants in their cavities to form host−guest inclusion complexes. The interactions between CDs and surfactants have been widely investigated. However, most studies have focused on systems containing CD and a single surfactant,[2−9] and investigations of CDs and mixed surfactants are quite few.[10−14]

In previous work, we found that in mixtures of hydrogenated and fluorinated surfactants, *β*-CD showed significant selectivity for complex formation with the fluorinated surfactants.[12] In this work, α-CD was used, and its interactions with a mixture of hydrogenated and fluorinated surfactants were studied. We tried to find whether there is any difference between the behaviors of CDs for the same surfactant system. ^{1}H and ^{19}F NMR spectroscopies were applied to obtain information on the hydrogenated and fluorinated surfactants, respectively. The surfactants sodium decyl sulfate (SDeS) and sodium perfluorooctanoate (SPFO) were chosen because of their similar critical micelle concentrations (cmc's), which are 30 mM and 31 mM, respectively.[12] Therefore, comparisons were reasonable on the basis that the two surfactants had similar hydrophobicities.

Experimental Procedures

Materials. α-CD (98 %, ACROS), perfluorooctanoic acid monohydrate (ACROS), D_2O (atom percentage of deuterium = 99.8 %, ACROS), and SDeS (HPLC, ACROS) were used as received. SPFO was prepared by neutralizing perfluorooctanoic acid with sodium hydroxide. The solid product was obtained by freeze-drying under vacuum.

Equipment and Methods. Both the ^{1}H and ^{19}F NMR experiments were performed on a Varian Mercury Plus 300 spectrometer (^{1}H, 300.07 MHz; ^{19}F, 282.31 MHz) with D_2O as the solvent at 25 °C. Methanol ($3\cdot10^{-4}$ M) was used as the internal reference (3.343 ppm) for chemical shifts of protons.[15,16] All fluorine chemical shifts were referenced to the external standard trifluoroacetic acid (−79.46 ppm), with the field frequency locked.

The steady-state pyrene fluorescence measurements were performed on a Hitachi 4500 fluorescence spectrophotometer. The concentration of pyrene used was approximately $5\cdot10^{-7}$ M. The excitation wavelength was 337 nm. The ratio of the intensities of the first (I_1, 374 nm) and third (I_3, 384 nm) vibrational peaks of the emission spectrum of pyrene was used in evaluating the polarity of the local microenvironment.[17]

The experiments were carried out by addition of α-CD into an equimolar mixture of SDeS and SPFO. The changes in the chemical shifts of ^{1}H and ^{19}F ($\Delta\delta_H$ and $\Delta\delta_F$, respectively) were analyzed at different concentrations of α-CD. Here $\Delta\delta$ is defined as $\delta_{obsd} - \delta_{mono}$, where δ_{obsd} is the chemical shift observed in the SDeS/SPFO/α-CD mixture and δ_{mono} is the chemical shift of monomers of SDeS or SPFO in the respective single-surfactant solution.

The variation of chemical shifts of single surfactants with the addition of α-CD was also studied by ^{1}H and ^{19}F NMR spectroscopy. For α-CD/single-surfactant systems, $\Delta\delta = \delta_{obsd} - \delta_{mono}$, where δ_{obsd} is the chemical shift observed in the mixture of α-CD with the single SDeS or SPFO surfactant. The equilibrium constants were calculated with the methods described in our previous work.[12] The calculation of equilibrium

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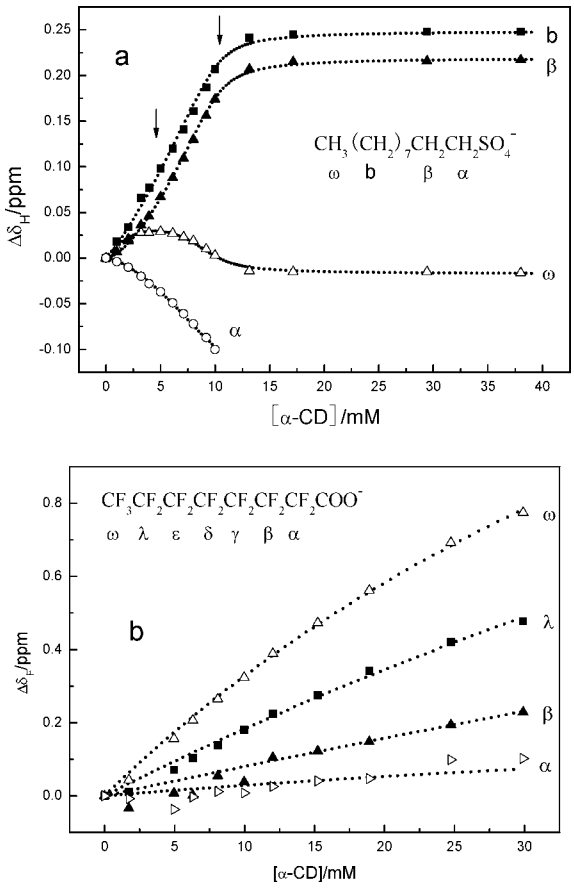

Figure 1. Chemical shift changes of (a) protons of SDeS and (b) fluorines of SPFO vs the concentration of α-CD in α-CD/single-surfactant mixtures. The concentration of the single surfactant was fixed at 5 mM. The dotted lines are simulated curves. In Figure 1a, the peak for α-CH_2 was overlapped by the α-CD peak as the CD concentration increased. In Figure 1b, only the curves for ω, λ, and β with small relative experimental errors were selected and fitted.

constants for the model of formation of 1:1 complex was performed using the nonlinear curve-fitting function in OriginPro 7.5, while that for the model of formation of both 1:1 and 2:1 complexes was performed using a CBASIC program written by us.

The binding constants for the 1:1 and 2:1 inclusion complexes (K_1 and K_2, respectively) are defined as

$$K_1 = \frac{CS}{C \cdot S} \tag{1}$$

and

$$K_2 = \frac{C_2S}{CS \cdot C} \tag{2}$$

where C, S, CS, and C_2S are the concentrations of free α-CD, the surfactant monomer, and the 1:1 and 2:1 complexes, respectively.

Results and Discussion

Systems of Single Surfactants with α-CD. The dependences of the chemical shift changes of the single surfactants SDeS and SPFO on the concentration of α-CD at a fixed surfactant concentration of 5 mM are shown in Figure 1a,b, respectively. In Figure 1a, peak α for SDeS was overlapped by the α-CD peak as the CD concentration increased, so the experimental data for α-CH_2 of SDeS could not be obtained at high concentrations of α-CD.

In Figure 1a, the shape of the $\Delta\delta_H$ curves shows the typical formation of 1:1 and 2:1 inclusion complexes, similar to that of α-CD and the single surfactant dodecyltrimethylammonium bromide (DTAB) reported in the literature.[5] Similar to the work in the literature,[5] two turning points were also observed. The two turning points (denoted by arrows in Figure 1a) were at α-CD concentrations of approximately 5 mM and 10 mM, respectively, consistent with the concentration of SDeS (5 mM). In the region before the first turning point, 1:1 complexes of α-CD with SDeS were mainly formed, and between the first and second turning points, 2:1 α-CD/SDeS complexes were significantly formed.

However, the corresponding relations of the chemical shift variations of protons ω and β were amazingly different from those of DTAB[5] or sodium alkyl carboxylate salts with α-CD[3] in previous works. The curve for proton ω of SDeS with the addition of α-CD (Figure 1a) resembled that for proton β of either $C_{11}H_{23}CO_2Na$[3] or DTAB,[5] whereas the curve for proton β of SDeS (Figure 1a) behaved similar to that of proton ω of either $C_{11}H_{23}CO_2Na$[3] or DTAB.[5] The difference was interesting and might be due to the effect of different headgroups on chemical shifts. The biphasic changes in Figure 1a could be divided in two groups: (1) protons b and β and (2) protons ω and α. Group 1 (the major hydrophobic chain) showed a continuous increase in $\Delta\delta_H$ with the addition of α-CD until the second turning point as a result of the effect of the all-trans conformation; in contrast, group 2 (end of the hydrophobic chain) showed a discrepancy before and after the first turning point. For example, the rate of decrease of the α curve became much faster after the first turning point because of the second stringed CD ring, while the ω curve showed positive and negative slopes before and after the first turning point, respectively. The decreasing trend of $\Delta\delta_H$ for α-CH_2 near the headgroup could be attributed to the dehydration effect, while that for ω-CH_3 might be due to the interactions with the hydroxyl groups on the annulus of α-CD. The initial increase in the $\Delta\delta_H$ curve of the terminal methyl ω was similar to ordinary situation of formation of 1:1 complexes.

It is known that the α-CD cavity has a volume[1] of 174 Å^3 and that the volume of a methylene group[18] is 27 Å^3; consequently, for geometrical reasons, all of the surfactant protons should be inside the cavity, in particular the protons of the surfactant methyl group. However, it is observed that the ω-CH_3 might be in a polar state and could even interact with the annulus hydroxyl groups of one of the stringed CDs as the chemical shift decreased. This might be attributed to the fact that the surfactant has a completely stretched configuration when two CD rings are stringed. The fully stretched hydrocarbon chain length[19] could be calculated as $l = 1.45 + 1.26n$, from which the chain length of SDeS was evaluated as approximately 14 Å. The structural height of α-CD[20] is about 6.4 Å, and its hydrated height[21] is about 3.1 Å. It is possible that the hydrocarbon chain of SDeS is fully stretched in the 2:1 α-CD/SDeS complexes.

As shown in Figure 1b, the $\Delta\delta_F$ curves increased with the addition of α-CD. It was found in Figure 1b that the changes in $\Delta\delta_F$ were relatively small in comparison with those of the SPFO/β-CD system[4,12] until α-CD was added to a high concentration. The change in $\Delta\delta_F$ was in the sequence $\omega > \lambda > \beta >$ α along the fluorocarbon chain from the terminal end, indicating that association of α-CD with the terminal unit of the SPFO tail occurred. It was also consistent with the literature[2]

Table 1. Equilibrium Constants for Formation of Compounds at 25 °C Compared with Similar Systems in the Literature

	K_1/M^{-1}	K_2/M^{-1}
α-CD/SDeS	$(6.1 \pm 1.8)\cdot10^3$	$(3.6 \pm 0.8)\cdot10^3$
	1890[a]	
α-CD/SPFO	11.5 ± 4.8	—
	28 ± 1[b]	
α-CD/$C_9H_{19}CO_2Na$	$(5.6 \pm 2.8)\cdot10^3$[c]	$(6.5 \pm 3.3)\cdot10^2$[c]
α-CD/$C_{11}H_{23}CO_2Na$	$(2.1 \pm 1.1)\cdot10^4$[c]	$(1.2 \pm 0.6)\cdot10^3$[c]
α-CD/DTAB	$1.82\cdot10^4$[d]	$3.5\cdot10^2$[d]

[a] From ref 24, where K_2 was not calculated. [b] From ref 2. [c] From ref 3, where the unit of K_2 is M^{-2}. [d] From ref 5.

showing that the cavity of α-CD is too small to accommodate the chain of SPFO, and weak association of the opening of the α-CD cone with the terminal tail of SPFO was found in the mixture of α-CD and single SPFO. This extracavity association is attributed to the interactions between the CF_3 groups and the hydroxyl groups at the α-CD annulus. It has been shown in the literature that α-CD favors the formation of a "conelike" structure rather than a "barrel-like" structure as in β- or γ-CD,[21] which might enable the weak association between SPFO and α-CD.

The binding constants of the complexes were determined by fitting the NMR data sets of $\Delta\delta$ versus [α-CD] in Figure 1 for the α-CD/single-surfactant systems. The calculated binding constants of 1:1 and 2:1 α-CD/SDeS complexes are shown in Table 1. It can be seen from Table 1 that the equilibrium constant for α-CD/SPFO association is quite small and consistent with that in the literature.[2] Table 1 also presents the values for similar α-CD/alkyl carboxylate systems in the literature.[3] We found it interesting that K_1 for α-CD/SDeS was close to that of α-CD/$C_9H_{19}CO_2Na$ while K_2 for α-CD/SDeS was close to that of α-CD/$C_{11}H_{23}CO_2Na$. It has rarely been seen that K_1 and K_2 were so close for inclusion complexes of linear aliphatic surfactants. This phenomenon of close K_1 and K_2 values has been found for surfactants with special structures, e.g., gemini surfactant.[22] However, in comparison with the curves with corresponding trend in the figures of similarly structured surfactants in the literature,[3,5] Figure 1a shows a more rapid increase extended to a 2:1 α-CD/SDeS concentration ratio (curves b and β) and a more clear-cut, sharper edge of the plateau (curves b, β, and ω), indicating that according to the experimental results we obtained, K_2 should be larger than those K_2 values in the references.[3,5] K_2 was found to be large enough that the edge of the plateau almost immediately appeared at a 2:1 α-CD/SDeS concentration ratio (Figure 1a), while it was greatly delayed to a lag after the 2:1 concentration ratio for the α-CD/DTAB system in the literature.[5] Thus, the K_2 value of around 10^3 for α-CD/SDeS could be reliable. Such close K_1 and K_2 values might be confusing, since they could give an illusion that the two products would significantly form together when the two equilibrium constants are close. To test this, the concentrations of the 1:1 and 2:1 complexes of SDeS with increasing [α-CD] corresponding to the determined K_1 and K_2 values were calculated and are listed in Table 2. However, they suggest that in this case, 1:1 α-CD/SDeS complexes prevailed over 2:1 ones in the initial region, but after the division by the α-CD/SDeS concentration ratio at approximately 1:1, 2:1 complexes would become dominant and then overwhelming. This is consistent with the successive shape of the curves with multiple turning points in Figure 1a.

Comparison of the α-CD/SDeS system with β-CD/SDeS [$K_1 = (7.0 \pm 2.9)\cdot10^3\ M^{-1}$; $K_2 = 41 \pm 31\ M^{-1}$] from our previous work[12] shows that the two K_1 values are close but the K_2 for

Table 2. Calculated Concentrations CS_H and C_2S_H for the 1:1 and 2:1 Complexes, Respectively, When α-CD at Concentration C_0 Was Added to a 5 mM SDeS Solution at 25 °C

C_0/mM	CS_H/mM	C_2S_H/mM
0.99	0.785	0.0882
2.04	1.34	0.318
3.22	1.73	0.687
3.95	1.88	0.965
5.01	1.97	1.42
6.11	1.93	1.95
7.11	1.78	2.47
8.00	1.56	2.96
9.18	1.19	3.58
9.98	0.932	3.94
13.14	0.363	4.62
17.15	0.182	4.81
29.42	0.0702	4.93
38.00	0.0489	4.95

α-CD/SDeS is much larger than that for β-CD/SDeS. This could be ascribed to the smaller size of α-CD. When the two systems α-CD/SDeS and β-CD/sodium dodecyl sulfate (SDS)[12] are compared, it is found that although both systems can significantly form 2:1 complexes, K_2 for α-CD/SDeS is much larger than that for β-CD/SDS [$(1.0 \pm 1.0)\cdot10^2\ M^{-1}$]. The case is similar for a comparison of the α-CD/SDeS and α-CD/DTAB systems.[5] This is reasonable on the basis of the positions of the plateau edges in these figures (Figure 1a, ref 5, and ref 12; the final plateau does not occur in the figure from ref 12). This could be attributed to the larger values of K_1 for β-CD/SDS [$(4.9 \pm 2.6)\cdot10^4\ M^{-1}$][12] and α-CD/DTAB (Table 1);[5] in other words, for the system investigated here, the relatively smaller tendency to form 1:1 complexes could induce the formation of 2:1 complexes when these two inclusion complexes coexist. In comparison to several ordinary analogue systems above, only the α-CD/SDeS system studied here showed such a specialty of a relatively large K_2. The reason is unclear, and we infer that both the appropriate chain length of C_{10} and the headgroup of $-SO_4^-$ might work to accommodate a critical state with restrained K_1 and enlarged K_2, respectively.

System of Mixed Surfactants with α-CD. In order to avoid the formation of micelles, the total concentration of surfactants (C_t) was kept constant at 5 mM, which is below the cmc determined by fluorescence (Figure 2). Pyrene is commonly used as a fluorescence probe to study micellar systems. The value of

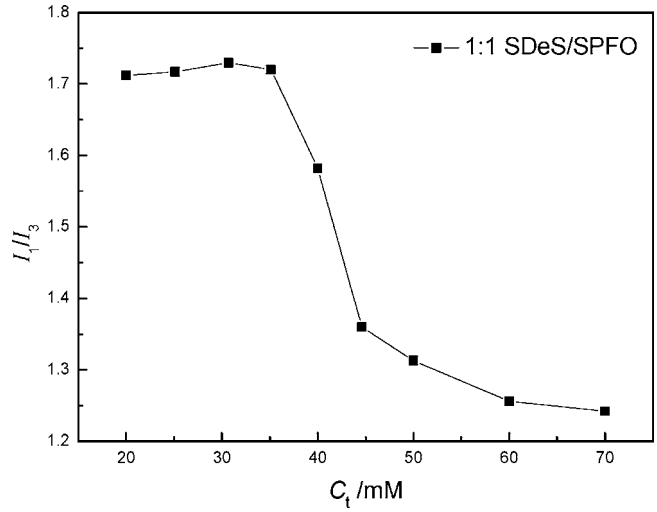

Figure 2. Plot of pyrene fluorescence intensity (I_1/I_3) as a function of the total concentration of surfactants (C_t) in an equimolar mixture of SDeS and SPFO at 25 °C. It shows that the cmc of the SDeS/SPFO mixture is approximately 40 mM.

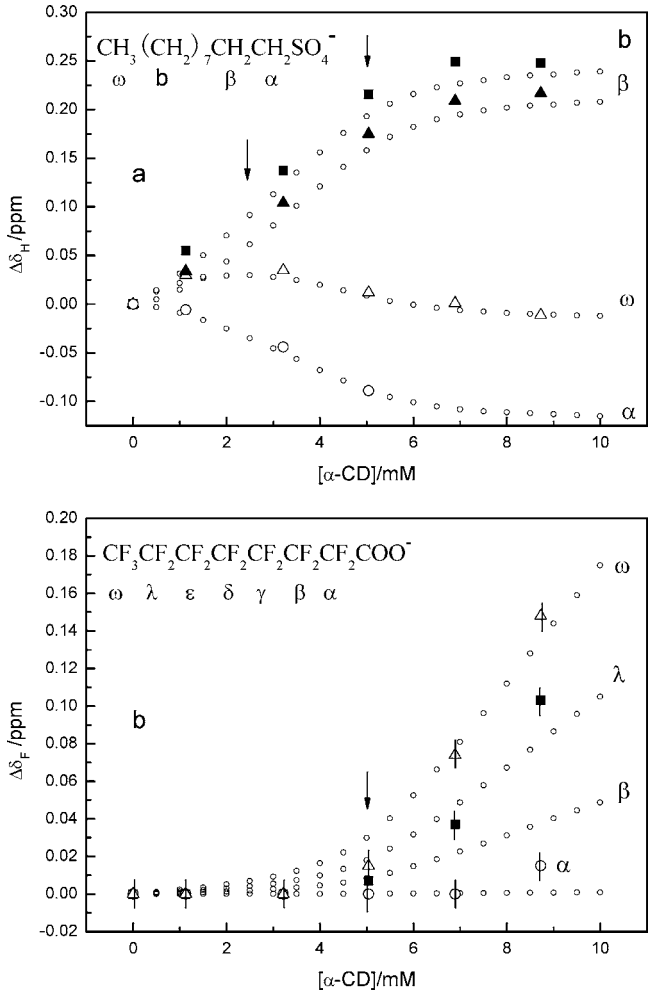

Figure 3. Chemical shift changes of (a) protons of SDeS and (b) fluorines of SPFO vs the concentration of α-CD in the equimolar mixture of SDeS/SPFO. The total concentration of surfactants (C_t) was fixed at 5 mM. The error bars in Figure 3b denote the data range of the chemical shifts in repetitive tests. The dotted lines are the simulated chemical shift changes for the SDeS/SPFO mixture predicted from the single surfactants with the addition of α-CD.

I_1/I_3 is very sensitive to the polarity of the microenvironment. The cmc value was approximately 40 mM, as shown in Figure 2.

Figure 3 shows the chemical shift changes of ^{1}H ($\Delta\delta_H$) and ^{19}F ($\Delta\delta_F$) in an equimolar SDeS/SPFO mixture upon the addition of α-CD. The total concentration of the mixed surfactants (C_t) was fixed at 5 mM (i.e., the concentrations of SDeS and SPFO were 2.5 mM). Since C_t is below the cmc of the equimolar mixture of SDeS/SPFO (40 mM), there were no micelles in the system investigated. In Figure 3a, the α peak of SDeS was overlapped by the peaks of α-CD when the concentration of α-CD was increased. Thus, the $\Delta\delta_H$ data for proton α at high concentrations of α-CD were hard to obtain. On the basis of the same considerations as in our previous work,[12] the synergism between SDeS and SPFO could be ignored, so the chemical shift changes in the ^{1}H and ^{19}F NMR spectra could be ascribed to their respective interactions with α-CD, i.e., their inclusion information in the equimolar SDeS/SPFO mixture could be obtained individually from the ^{1}H and ^{19}F NMR spectra.

In Figure 3a, the shape of the $\Delta\delta_H$ curves is quite similar to that for SDeS alone with α-CD (Figure 1a). Two turning points (denoted by arrows) were found at α-CD concentrations of approximately 2.5 mM and 5 mM. Consistent with Figure 1a, the positions of the turning points showed that 1:1 and 2:1 complexes of α-CD/SDeS were preferentially formed.

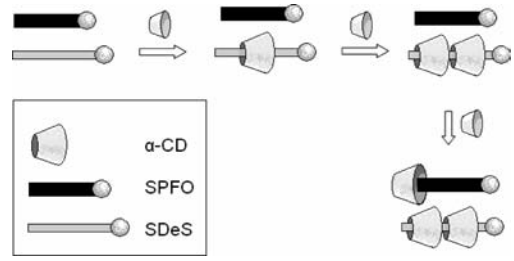

Figure 4. Inclusion process in the equimolar SDeS/SPFO mixture with the addition of α-CD. The conformations of the complexes are only for illustration.

As shown in Figure 3b, the $\Delta\delta_F$ did not change until the turning point (denoted by the arrow) at approximately 5 mM α-CD. The turning point in Figure 3b was quite identical with the second turning point in Figure 3a. When the concentration of α-CD was further increased, the $\Delta\delta_F$ curves for the ω, λ, and α fluorines were all increased, indicating that the association of α-CD with the terminal of the SPFO tail was formed. The trend of the $\Delta\delta_F$ curves is also similar to that for the system with α-CD and SPFO only (Figure 1b).

The similarity in the shapes of the chemical shift changes for the surfactant mixture and the single surfactants with α-CD encouraged us to simulate the surfactant mixture using the single surfactants. In our previous work on mixtures of CD with mixed surfactants, there was no prediction of the NMR results for the mixed surfactants using the results for the addition of CD to the single surfactants. The method of prediction and the predicted equilibrium concentrations of the species in the SDeS/SPFO/α-CD mixture for a series of added α-CD concentrations are shown in the Supporting Information. The simulated NMR chemical shift changes in the mixture (shown in Figure 3 as dotted lines) were also compared with the experimental results and found to be consistent with the experimental data. Because the chemical shifts of fluorine α for SPFO only with α-CD (Figure 1b) have a relatively large experimental error, the simulation in Figure 3b for fluorine α has a relatively large deviation from the experimental data; however, the trend is consistent with the experimental data. This shows that prediction of the results for the SDeS/SPFO mixture from the results for the single surfactants with α-CD is applicable, as the interactions between SDeS and SPFO and their complexes can be neglected.

The cmc values of SDeS and SPFO were quite close,[12] which means that they show similar hydrophobicities in aqueous solution. In our previous work, β-CD exhibited significant selectivity for inclusion of SPFO in the SDeS/SPFO mixture. However, the combined results of the ^{1}H and ^{19}F NMR analyses (Figure 3a,b) show that α-CD preferentially formed complexes with SDeS in the equimolar mixture of SDeS/SPFO, and only weak extracavity association between the hydroxyl groups at the opening of α-CD with the terminal of SPFO tail was observed. The positions of the turning points show that the association between α-CD and SPFO occurred after the near saturation of the formation of 2:1 α-CD/SDeS complexes (Figure 4), which is consistent with the magnitude of the binding constants of the complexes (Table 1). It is also consistent with the structural character of the two surfactants and α-CD. It is known that the cavity diameter of α-CD is about 5.7 Å,[1] and the diameters of CH_3 and CF_3 are estimated to be 4 Å and 7 Å, respectively.[2,23] In conclusion, the size fit between the host and guest molecules dominates the formation of the inclusion complexes, as the two surfactants showed almost the same hydrophobicity.

Summary

When α-CD was added to an equimolar mixture of SDeS and SPFO, α-CD exhibited significant selectivity for the hydrogenated surfactant because of the better fit between the host and guest molecules. This finding might have prospects in the field of separation by chromatographic techniques, e.g., separation in mixed hydrogenated/fluorinated species could be achieved if α-CD were attached by a covalent bond to some solid substrate. The specialty of the system containing α-CD and SDeS only, involving the strange chemical shift variation and the relatively large K_2 as observed with the NMR method, still needs further discussion for a better explanation.

Supporting Information Available:

^{1}H and ^{19}F NMR spectra as an example of the effect of adding α-CD to SDeS and SPFO, respectively; equilibrium concentrations of α-CD/SPFO additives in the system of α-CD with the single surfactant SPFO; parameters and binding constants obtained from fitting and simulation; process of simulation of chemical shift changes for the mixed surfactants from the single surfactant with α-CD; predicted equilibrium concentrations of the species in SPFO/SDeS/α-CD mixtures for a series of added concentrations of α-CD; and all of the experimental NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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