J. Phys. Chem. **1992**, 96, 6738-6742

Hybrid Surfactants Containing Separate Hydrocarbon and Fluorocarbon Chains

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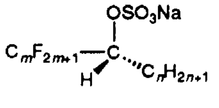
Two homologous series of double-tail hybrid surfactants containing a hydrocarbon chain and a fluorocarbon chain attached to the same hydrophilic head group have been synthesized. The micellar solutions of such hybrid surfactants have been studied by conductance, surface tension, ^{19}F NMR and ^1H NMR. The dependence of the cmc on the chain length follows Kleven's equation. The micellar aggregation numbers are 10–35 and become smaller as the chain length increases. When the hydrocarbon chain bears three carbons or more, both the fluorocarbon and the hydrocarbon chains are incorporated inside the micelle.

Introduction

There has been a continuous effort in industry to prepare new formulations of detergents by changing the compositions of the surfactants, builders, and additives. However, there is relatively little development in the synthesis and characterization of new surfactants that have unusual structures, properties, and applications. The hybrid surfactants described in this paper represent part of our effort in this direction. They are composed of a hydrocarbon (HC) chain and a fluorocarbon (FC) chain attached to the same hydrophilic head group and are a new category of compounds which have not been explored previously.

Double-tail surfactants with two HC chains attached to a sulfate head group have been studied by Winsor[1] and Evans[2] in the 1950s. These homologous compounds of sodium dialkyl sulfate have the structural formulae $RR'CHOSO_3Na$, in which R and R′ are unbranched HC chains with R having a longer chain length than R′. The hybrid surfactants reported here have similar structures, except that one of the chains is an unbranched FC chain.

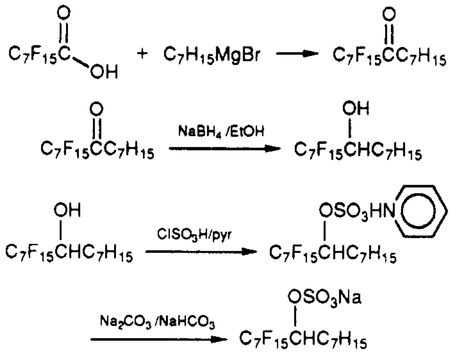
It has long been noticed that fluorinated surfactants are particularly efficient in lowering surface tension. Normally, in the mixture of a FC surfactant with a suitable HC surfactant, the FC surfactant reduces the surface tension while the HC surfactant aids in the reduction of the interfacial tension. The net result can be a system that easily wets and spreads on otherwise hard-to-wet surfaces.[3] However, for ionic surfactants with the same head-group charge, the application of this advantage of combined effect is limited because of the demixing of HC/FC mixed surfactants. To overcome this problem, some single-chain surfactants containing a FC segment and a HC segment were synthesized, and they show good wettability on solid substrates containing FC components.[4] Recently, Abenin and Cambon reported the synthesis of a series of double-tail HC/FC surfactants $R_FC_2H_4NHCH_2CHOHCH_2NR_{1H}R_{2H}$.[5] Such surfactants are very effective in lowering the surface tension or interfacial tension.[5] To our knowledge, hybrid surfactants containing separate FC and HC chains attached to the same head group have not been reported. In the present work, the synthesis, characterization, and the micellar properties of a homologous series of novel double-tail hybrid surfactant are described:



hybrid surfactants (abbreviation) F*m*H*n*, *m* = 6–9, *n* = 1–9)

Experimental Section

The hybrid surfactant F7H7 was synthesized through the following reactions:



$$C_7F_{15}COOH + C_7H_{15}MgBr \rightarrow C_7F_{15}COC_7H_{15} \quad (1)$$

$$C_7F_{15}COC_7H_{15} \xrightarrow{NaBH_4/EtOH} C_7F_{15}CH(OH)C_7H_{15} \quad (2)$$

$$C_7F_{15}CH(OH)C_7H_{15} \xrightarrow{ClSO_3H/pyr} C_7F_{15}CH(OSO_3HNC_5H_5)C_7H_{15} \quad (3)$$

$$\xrightarrow{Na_2CO_3/NaHCO_3} C_7F_{15}CH(OSO_3Na)C_7H_{15} \quad (4)$$

The syntheses of other compounds in the homologous series F*m*H*n* are similar. The detailed procedure is described in the following.

Preparation of Ketone. A method for the synthesis of ketone containing a perfluoroalkyl group and a normal alkyl group was reported by Dishart and Levine.[6] We applied this method to synthesize the desired ketones through the reaction of a (perfluoroalkyl)carboxylic acid with a Grignard reagent. Pentadecafluorooctanoic acid (3.8 g, purchased from Aldrich, 98%) was dissolved in 20 mL of anhydrous diethyl ether, and the solution was added dropwise to a solution of heptylmagnesium bromide prepared from 5.3 g of 1-bromoheptane and 0.9 g of magnesium in 20 mL of ether. The reaction mixture was refluxed for 4 h after the addition of the acid was complete. The reaction mixture was acidified with cold 5% HCl solution. The mixture was extracted with ethyl ether (30 mL × 3). The ether extract was washed with saturated $NaHCO_3$ and saturated NaCl consecutively and then dried over $MgSO_4$. The solvent was evaporated to give a colorless oil. The pure compound was obtained by chromatography over silica gel, eluting with hexane (4.1 g, 88%).

^1H and ^{19}F NMR and MS data were consistent with the structure of the product.

Preparation of Alcohol. Reduction of the ketone with sodium borohydride was carried out to obtain the corresponding alcohol. A solution of 3.9 g of pentadecafluoroheptyl heptyl ketone and 30 mL of a 0.15% of $NaBH_4$ in ethanol was stirred at 0 °C for 2 h and then at room temperature for 0.5 h. Most of the ethanol was removed. The reaction mixture was acidified with 50% acetic acid at 0 °C and then extracted with ethyl ether (30 mL × 3). The extracted solution was washed with saturated $NaHCO_3$ and saturated NaCl and dried over Na_2SO_4. The solvent was removed in vacuum. The residue was separated by chromatography, eluting with hexane/ethyl acetate (5:1), to obtain the pure white solid product (3.4 g, 89%), which was a racemic mixture.

^1H and ^{19}F NMR and MS data were consistent with the structure of the product.

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TABLE I: Results of Elemental Analysis with High-Resolution FAB-MS Measurements for the Hybrid Surfactants F*m*H*n* with Different Values of *m* and *n*[a]

name	C cal	C found	H cal	H found	Na cal	Na found	F cal	F found	$(M + Na)^+$, cal	$(M + Na)^+$, found
F7H1	20.95	20.83	0.78	0.81	4.46	4.56	55.24	55.01	538.9386	538.9354
F7H2	22.66	22.20	1.14	1.13	4.34	4.35	53.78	53.23	552.9543	552.9553
F7H3	24.29	*b*	1.48	*b*	4.23	*b*	52.39	*b*	566.9699	566.9664
F7H4	25.83	25.64	1.79	1.76	4.10	4.03	51.09	51.47	580.9856	580.9858
F7H5	27.27	27.29	2.11	2.20	4.02	4.09	49.83	49.99	595.0012	595.0009
F7H6	28.69	28.11	2.41	2.28	3.92	4.01	48.63	47.98	609.0169	609.0113
F7H7	30.02	29.66	2.69	2.67	3.83	3.92	47.50	47.09	623.0325	623.0344
F7H8	31.29	30.73	2.93	2.99	3.75	3.56	46.41	45.97	637.0482	637.0464
F7H9	32.51	32.11	3.18	3.22	3.66	4.08	45.38	45.78	651.0638	651.0692
F6H6	29.11	28.87	2.63	2.81	4.29	4.12	46.06	45.27	559.0059	559.0071
F8H6	28.30	27.85	2.20	2.39	3.61	3.62	50.70	50.55	659.0280	659.0258
F9H6	28.00	27.38	2.06	1.93	3.35	3.80	52.60	51.93	709.0390	709.0381

[a] The elemental analysis was performed by Midwest Microlab, Indianapolis, IN 46250. [b] The sample for the elemental analysis of F7H3 decomposed.

Synthesis of the Sulfonate Salt. Synthesis of the hybrid surfactant was accomplished by the known reaction of pure alcohol with chlorosulfonic acid in pyridine.[7] Chlorosulfonic acid (0.7 mL) was added slowly to pyridine (7 mL) in an ice-cooled flask. A solution of the alcohol (2.8 g) in 7 mL of pyridine was introduced gradually to the above mixture. The reaction mixture was warmed on a steam bath until it became clear, and the reaction was quenched by pouring the reaction mixture into an ice-cooled sodium carbonate solution (20 g in 40 mL of water, which had an excess $NaHCO_3$ to keep the solution saturated with the inorganic salt). The product was extracted with butanol (30 mL × 3). The solution was concentrated and filtered, and the solvent was removed to get a light yellow solid. A product was obtained by precipitation from diethyl ether–benzene (3.0 g, 88%).

Compounds obtained from the procedures described above were purified by two reprecipitations in anhydrous ether with benzene added in excess.[8] The products were then washed with benzene. The identification for each compound was performed by ^1H and ^{19}F NMR and confirmed by high resolution FAB-MS (fast atom bombardment mass spectrometry). Purity was examined by elemental analysis (Midwest Microlab laboratory). The results for all the homologue compounds we synthesized are shown in Table I.

The compounds F*m*H*n* thus obtained slowly hydrolyze in air through the adsorption of moisture. Therefore, they are stored in a desiccator at −25 °C. They also hydrolyze slowly in aqueous solution at room temperature, but all the physical measurements discussed were made within 20 h after the sample preparation, and the effect of the hydrolysis was not appreciable.

Physical Measurements. The values of conductance (σ) of the F*m*H*n* solutions were measured with a Synbron/Barnstead Model PM-70 CB conductivity bridge. The surface tension (γ) was measured on a Fisher tensiometer (Tensiomat 21) using the du Nouy ring method. A sample cell with constant temperature water passing through its jacket was used for both experiments. The FAB-MS work was done on a Kratos MS 25 RF mass spectrometer. The NMR experiments were all performed on a Varian VXR-500 spectrometer operating at 500 MHz for ^1H-1 and 470 MHz for ^{19}F. Solutions for the NMR measurements were prepared in 99.98% D_2O (purchased from MSD Isotopes). The probe temperature was controlled at 25 °C calibrated by ethylene glycol. The ^1H chemical shift was referred to HOD in the solvent as an internal reference (δ = 4.63 ppm), and the ^{19}F chemical shift was referred to trifluoroacetic acid as an external reference (δ = −78.45 ppm).

Critical Micelle Concentrations

The critical micelle concentrations (cmc) of F*m*H*n* with different *m* and *n* values were determined from conductance, surface tension, and NMR measurements at 25 °C. The results are listed in Table II, which shows that the cmc values determined from different methods agree with each other within experimental error. For the determination of the cmc by conductance measurement, the equivalent conductance is plotted against $\sqrt{c}$. Two linear segments intersecting at the cmc are obtained, because counterion binding to the micelles reduces the equivalent conductance above the cmc. The determination of the cmc by NMR will be discussed in more detail in the next section. Both the conductance and the NMR methods depend on the measurement of bulk solution properties, and the effect of small amounts of impurities on the cmc determination is unimportant. On the other hand, the surface tension of aqueous solutions is affected more by the presence of impurities. As in the case of branched hydrocarbon surfactants, these impurities are extremely difficult to remove.[9,10] Thus, the plot of surface tension against log *c* for F*m*H*n* compounds shows a shallow dip around the transition point due to small amount of impurities.[11] The concentration corresponding to the minimum surface tension is taken to be the cmc value in these measurements. Since the cmc's thus determined agree well with those measured from conductance and NMR, the results can be regarded as reasonable in spite of the small amounts of impurities present. Values of the surface tension at the cmc (γ_{cmc}) shown in Table II were obtained by extrapolating the linear segment at high concentration to the cmc. Although not extremely accurate, these values of γ_{cmc} give a general reference which indicates that the hybrid surfactants F*m*H*n* are a type of highly surface active agent.

TABLE II: Cmc's ($\times 10^{-3}$ M) at 25 °C for the Hybrid Surfactants F*m*H*n* with Different Values of *m* and *n*[a]

name	conductance	^1H NMR	^{19}F NMR	surface tension[b]
F7H2	4.6	4.6	4.5	4.5 (20)
F7H3	3.2	3.3	3.1	3.2 (20)
F7H4	2.2	2.2	2.2	2.0 (21)
F7H5	1.1	0.98	1.0	1.1 (21)
F7H6	0.79	0.77	0.78	0.78 (21)
F7H7	0.49	0.48	0.46	0.49 (21)
F7H8	0.26	0.26	0.27	0.28 (20)
F7H9	0.19	0.18	0.20	0.20 (20)
F6H6	3.3	3.2	3.3	3.2 (22)
F8H6	0.26	0.26	0.26	0.25 (20)
F9H6	0.049	*c*	*c*	0.045 (19)

[a] The uncertainties are about 5%. [b] Values in parentheses are surface tension (mN/m) at the cmc. [c] The cmc of F9H6 is very small; therefore, the signal intensities in the NMR spectra were too low to give accurate cmc valuesc.

The cmc's for these hybrid surfactants can be fitted to the Klevens equation:[12]

$$\log (\mathrm{cmc}) = A - Bl \qquad (5)$$

where *l* is the number of carbon atoms in the varying chain length. Plots for the F7H*n* and F*m*H6 series (Figure 1) show that their cmc values obey the Kleven's equation well. From a least-squares fitting of the data to eq 5, the constants *A* and *B* obtained are −1.9 and 0.21 for the series of F7H*n* (*l* = 2, 3, ..., *n*), and 1.1 and 0.60 for the series of F*m*H6 (*l* = 6, 7, 8, 9), respectively. These values indicate that the cmc of F*m*H*n* is reduced by about 35%

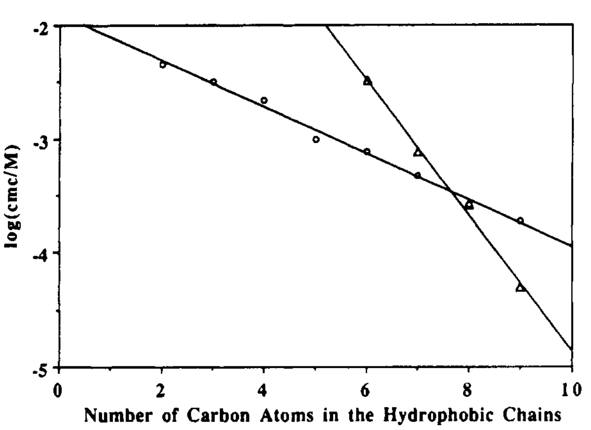

Figure 1. Plots of log (cmc/M) for the hybrid surfactants F7H*n* (○) and F*m*H6 (△) against *n* or *m*.

for each additional CH_2 group in the HC chain and 75% for each additional CF_2 group in the FC chain. According to the literature, for normal single-chain anionic surfactants, the cmc is usually reduced by 50% for each CH_2 group added to the HC chain, and 75% for each CF_2 group added to the FC chain.[12] Thus, for the hybrid surfactants, the effect of the addition of one CH_2 group to the HC chain of F7H*n* is smaller than that for the normal single-chain HC surfactant, whereas the effect of the addition of one CF_2 group to the FC chain of F*m*H6 is the same as that for the single chain FC surfactant. A possible reason for this is that the fluorocarbon chain in the hybrid surfactants affects the micellization process more than the hydrocarbon chain, so that the overall effect of the increase of one CH_2 group is not as large as it is for pure hydrocarbon surfactants. These findings are consistent with the observations for structure–property relationships for the cmc in the literature which compare results to the corresponding hydrocarbon surfactants. Specifically, it has been suggested that each fluoromethylene unit in a hydrophobe is approximately equivalent to 1.5 methylene units[13] and that each methylene group in a branched chain corresponds to an extension of the main chain by 0.5 methylene unit.[12] For this hybrid surfactant series, multiple linear regression analysis of cmc data yielded a straight chain hydrocarbon equivalent of $N_{eq} = 1.65m + 0.65n$ with *m* being the number of carbon atoms in the fluorocarbon chain, and *n* in the hydrocarbon chain.

For F7H*n*, the solubility of compounds with chain length $n \geq 3$ is higher than 10 times of the corresponding cmc values. As the chain length decreases from $n = 3$ (cmc = 3.3×10^{-3} M) to $n = 2$ (cmc = 4.6×10^{-3} M), the solubility decreases from more than 18×10^{-3} to 5×10^{-3} M. For F7H1, the solubility is more limited and solutions with higher concentrations could not be prepared because the Krafft point is above room temperature. The F7H1 tail group is not sufficiently hydrophobic to create the entropic driving force needed for micellization. The solubility of F7H2 is also rather limited, only slightly higher than the cmc. It is possible that the aggregation number of F7H2 micelle is very small, so that monomer concentration must increase significantly above the cmc and the total solubility is again limited by the solubility of monomer. The aggregation numbers of other F*m*H*n* compounds will be discussed in the following section.

NMR Study of Micellization

In the ^{19}F NMR spectra of F*m*H*n*, all the ^{19}F resonance peaks are resolved. In the ^1H NMR spectra, only the peaks for the two CH_2 groups close to the sulfate head group and the CH_3 group are well resolved; the peaks for other CH_2 groups are superimposed on each other.

The dependence of the ^{19}F chemical shift (δ_F) for the CF_3 group on the reciprocal concentration ($1/c$) for F7H4 is shown in Figure 2a, and the dependence of the ^1H chemical shift (δ_H) of the CH_3 group on the $1/c$ for the same surfactant is shown in Figure 2b. The chemical shifts for other nuclei in the same compound show similar characteristics except that their changes are smaller than those of terminal groups because the latter experience a more pronounced change in their environment during the micellization process. Therefore, only the chemical shifts of the terminal groups will be discussed here.

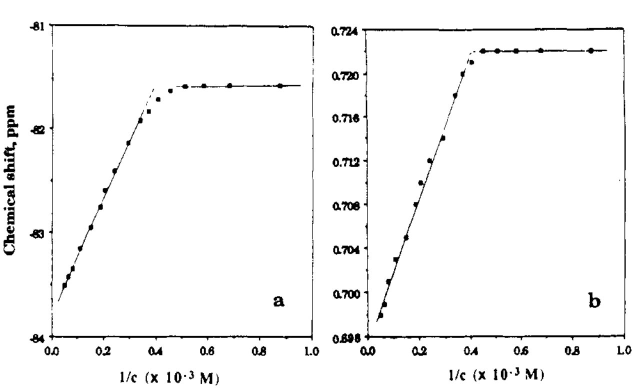

Figure 2. Chemical shifts of (a) the CF_3 group and (b) the CH_3 group in F7H4 plotted against the reciprocal of surfactant concentration.

Below the cmc, the observed chemical shifts represent the chemical shifts of the monomers and are usually constant. Above the cmc, if the exchange rate of the surfactant molecules between the monomer and the micellar states is fast compared with the chemical shift difference between the two species (on a hertz scale), the observed chemical shift is a weighted average value of the monomer and micelle:[14]

$$\delta_{obs} = (c_{mo}/c)\delta_{mo} + (1 - c_{mo}/c)\delta_{mi} \qquad (6)$$

where δ_{obs} is the observed chemical shift at concentration c (≥cmc), c_{mo} is the monomer concentration, δ_{mo} is the monomer chemical shift which is directly obtained from the experimental chemical shift below cmc, and δ_{mi} is the micelle chemical shift. If the change of monomer concentration above the cmc is negligible and $c_{mo} \approx$ cmc, then δ_{obs} is a linear function of $1/c$ above the cmc:

$$\delta_{obs} = \delta_{mi} + (\delta_{mo} - \delta_{mi})\mathrm{cmc}/c \qquad (7)$$

As it is shown in Figure 1, both $\delta_F - 1/c$ and $\delta_H = 1/c$ curves are composed of two linear segments connected by a small curved region. The concentration at the intersection point of the two segments is usually taken as the cmc, and δ_{mi} can be obtained by extrapolating the $\delta_F - 1/c$ plot to $c = \infty$ ($1/c = 0$).[14] For the hybrid surfactants, the cmc's obtained from ^1H-1 and ^{19}F data are about the same, and are consistent with the values obtained from the other measurements (Table II). This is in contrast with mixtures of some anionic fluorocarbon and anionic hydrocarbon surfactants, for which the cmc values obtained from ^{19}F and ^1H NMR are different from each other.[15] In these mixed surfactant systems, the coexistence of two kinds of micelles corresponding to two cmc's has been proposed by many investigators.[15-18] The F*m*H*n* hybrid surfactants studied here are not likely to form two types of micelles because the hydrocarbon and fluorocarbon moieties are covalently linked.

The effect of intermolecular interaction on chemical shielding is generally such that a more polarizable environment would reduce the shielding and lead to a larger chemical shift.[19] The refractive indices and therefore the polarizability follows the trend of HC > water > FC.[20] Therefore, when a HC surfactant molecule is transferred from an aqueous environment to a HC-rich environment upon the aggregation of monomers into micelles, the shielding of the CH_3 group decreases and its chemical shift increases (Table III, second row). When FC surfactant monomers aggregate to form micelles, the CF_3 group in the surfactant molecule would be transferred from an aqueous environment to a FC-rich environment, causing its shielding to increase and chemical shift to decrease (Table III, third row). For the hybrid surfactant, the micellar chemical shifts for the CH_3 and CF_3 groups in F*m*H*n* are smaller than the corresponding monomer chemical shifts (Table III). This is an indication that the interior of the micelles formed by the hybrid surfactants is less polarizable[19] than the aqueous environment. In other words, in the micelle interior, the effect of the FC chain dominates the chemical shift.

TABLE III: Chemical Shift Difference ($\Delta\delta = \delta_{mi} - \delta_{mo}$, ppm) for the CF_3 and CH_3 Groups at 25 °C and the Micelle Aggregation Numbers (N) for F*m*H*n* with Different Values of *m* and *n*[a]

compound	$\Delta\delta$(F)	$\Delta\delta$(H)	N
SDS		+0.05[b]	71[c]
SPFO	−2.60		27 ± 7
F7H3	−2.31	−0.04	16 ± 8
F7H4	−2.24	−0.02	25 ± 9
F7H5	−2.17	−0.02	31 ± 19
F7H6	−2.09	−0.02	18 ± 2
F7H7	−2.00	−0.03	16 ± 1
F7H8	−1.86	−0.03	10 ± 5
F7H9	−1.60	−0.03	12 ± 6
F6H6	−1.92	−0.03	20 ± 5
F8H6	−2.20	−0.03	11 ± 6

[a] The chemical shifts for F7H2 are not available at higher concentrations due to the limitation of solubility. [b] Data from ref 11. [c] Data from ref 24.

Since the absolute values of ($\delta_{mi} - \delta_{mo}$) for CH_3 are small, their quantitative dependence on the change of the chain length is not obvious. On the other hand, the values of ($\delta_{mi} - \delta_{mo}$) for the CF_3 group in F7H*n* become less negative with the increase of *n*, indicating that the interior of the micelle become less FC-rich as the HC chain length becomes longer. In contrast, the corresponding values in the F*m*H6 series become more negative with the increase of *m*, indicating that the interior of the micelle becomes more FC-rich as the FC chain length becomes longer. However, because the interior of a micelle formed by F*m*H*n* is composed of both FC chains and HC chains, even the smallest ($\delta_{mi} - \delta_{mo}$) value for the CF_3 group (−2.3 ppm for F7H3 and −2.2 for F8H6) is still less negative than that for the pure FC surfactant sodium perfluorooctanoate (SPFO), for which $\delta_{mi} - \delta_{mo} = -2.6$ ppm.

When $c \gg$ cmc, the second term in eq 6 dominates, and the small change in c_{mo} does not affect the δ_{obs} appreciably. Therefore, δ_{obs} can be approximately considered to be a linear function of $1/c$. However, in the region where $c \approx$ cmc, δ_{obs} is very sensitive to the change of c_{mo}. If c_{mo} is not a constant, eq 6 cannot be simplified to eq 7. Then, a curved region near the cmc instead of a sharp break is observed in the plot of δ versus $1/c$. The curvature should be more obvious if there is a larger variation of c_{mo} with the total concentration; this is the case for the F*m*H*n* hybrid surfactants (Figure 2). For simplification, we neglect the effects of counterion binding and activity coefficients and consider the equilibrium

$$NS^- \rightleftharpoons S_N^{N-} \tag{8}$$

for which

$$K \approx [(S_N)^{N-}]/[S^-]^N \tag{9}$$

where S^- represents the F*m*H*n* anion and N is the aggregation number. Now, c_{mo} depends on N and is a function of the total concentration. To obtain an approximate value of the aggregation number for the micelles formed by the hybrid surfactants, the total surfactant concentration is expressed by

$$c = [S^-] + N[(S_N)^{N-}] = c_{mo} + NKc_{mo}^{\ N} \tag{10}$$

Substituting eq 10 into eq 6, the chemical shift can be calculated by treating K and N as adjustable parameters and minimizing $\sum(\delta_{mo} - \delta_{mi})^2$ for different surfactant concentrations.[21] The aggregation numbers for the micellar solutions of F*m*H*n* obtained from the nonlinear least-squares calculations are listed in Table III. As an example, the calculated chemical shift dependence on concentration (dashed line) for F7H4 is shown together with the experimental data in Figure 3. The agreement between the experimental data and the calculated curve is reasonably good. The calculated monomer and micelle concentrations for F7H4 are plotted in Figure 4, which shows that the monomer concentration c_{mo} does increase slightly with increasing c around the cmc. The change in c_{mo} becomes insignificant at higher total concentrations. The micelle concentration increases almost linearly with the increase of total surfactant concentration. For comparison, a similar calculation has been applied to the micellar system of SPFO and the best fit of N is 27 ± 7 (0.035 M < c < 0.10 M). A values of N = 7 for SPFO was reported by Turro and Lee by the use of a solubilization/luminescence method.[22] A more recent small angle neutron scattering (SANS) study by Berr and Jones indicated that N is strongly dependent on concentration and ranges from 26.5 to 40.9 as the concentration increases from 0.10 to 0.51 M.[23] The N value we obtained for SPFO from the NMR data agrees well with the results of Berr and Jones in the same concentration range. We must caution that eq 10 is an over-simplified representation because the effects of counterion binding and activity coefficients are neglected. Although the calculated N values are not exact, they are nevertheless good approximations to describe the micelle sizes for the hybrid surfactants. The data in Table III show that the aggregation numbers for the hybrid surfactants are quite small, namely, $N \approx 20$. Because of the uncertainty in the values of N thus determined, we are reluctant to put any significance in their possible dependence on the chain lengths. If there is a variation in the aggregation number, it may cause a change in the exposure of the HC and FC chains to water and affect their chemical shifts. However, this effect is not very important for the terminal CH_3 and CF_3 groups, and the previous discussion relating to the chemical shift data in Table III should be valid regardless of possible variations of the aggregation numbers with the chain length.

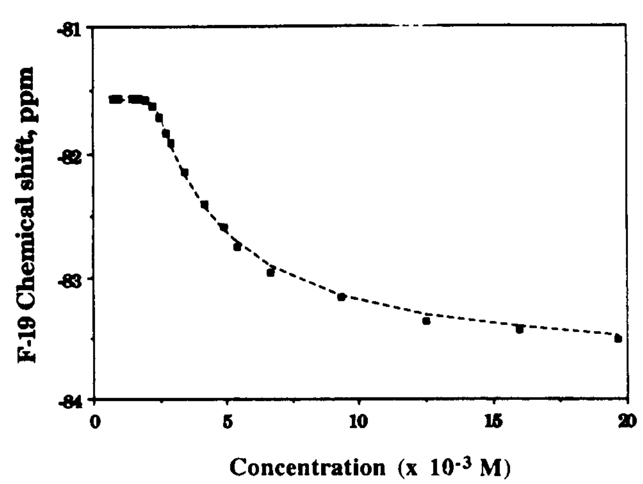

Figure 3. Chemical shift of the CF_3 group in F7H4 plotted against surfactant concentration; the dashed line is the calculated data.

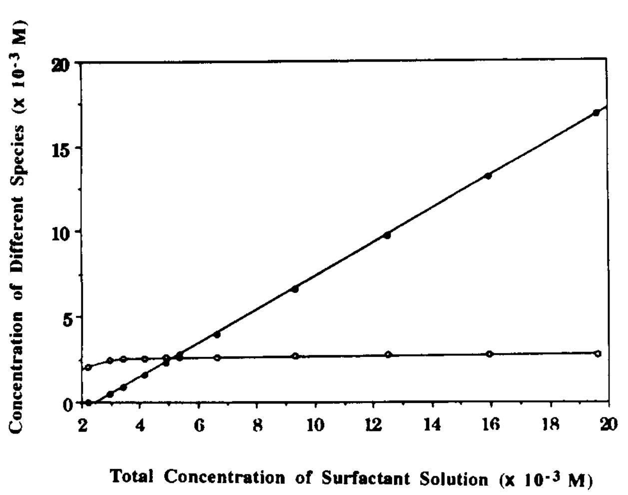

Figure 4. Calculated concentrations of monomer (○) and micelle (●) for F7H4 plotted against the total concentration.

Conclusion

Two homologous series of novel double-tail hybrid surfactants (F*m*H*n*) have been synthesized. These surfactants contain a FC chain and a HC chain attached to the same hydrophilic head group. The dependence of the cmc on the chain length of both hydrocarbon and fluorocarbon chain has been studied. The results indicate the following: (1) For F7H1, the compound does not form micelles up to its solubility limit. For F7H2, the solution becomes saturated at a concentration slightly higher than the cmc. (2) For $n \geq 2$, the introduction of each CH_2 group to the hydrocarbon chain reduces the cmc by about 35%, and the introduction of each CF_2 group to the fluorocarbon chain reduces the cmc by about 75%. (3) For $n \geq 3$, changes in both the ^{19}F and ^1H chemical shift upon micelle formation indicate that both the FC and HC chains of the F*m*H*n* are incorporated inside the micelle and that the interior of the micelle becomes more FC-rich as *n* decreases or *m* increases. (4) The aggregation number of the micelles as estimated from the NMR data is about 10-35. Except for compounds with a short HC chain, the aggregation number decreases with the increase of the length of either chain.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CTS-9812806 and the Oklahoma Center for the Advancement of Science & Technology (OCAST) Award No. ARO-075. We gratefully acknowledge the assistance of industrial sponsors of the Institute for Applied Surfactant Research, including Kerr-McGee Corporation, Sandoz Chemicals Corp., E. I. Du Pont de Nemours & Co, and Union Carbide Corp. We are indebted to Dr. Richard G. Weiss for suggesting the procedure in ref 6 regarding the synthesis of the ketones.

Registry No. F_7H_1, 142066-23-7; F_7H_2, 142066-24-8; F_7H_3, 142066-25-9; F_7H_4, 142066-26-0; F_7H_5, 142066-27-1; F_7H_6, 142066-28-2; F_7H_7, 142066-22-6; F_7H_8, 142066-29-3; F_7H_9, 142066-30-6; F_6H_6, 142066-31-7; F_8H_6, 142066-32-8; F_9H_6, 142066-33-9; $C_7F_{15}COC_7H_{15}$, 142066-20-4; $C_7F_{15}CH(OH)C_7H_{15}$, 142066-21-5; $ClSO_3H$, 7790-94-5; pyridine, 110-86-1; pentadecafluorooctanoic acid, 335-67-1; heptylmagnesium bromide, 13125-66-1.

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Electrochemical Oxidation of Ni(111)c(4×2)-CO in Alkaline Electrolytes

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(Received: March 16, 1992; In Final Form: April 27, 1992)

The electrochemical properties of Ni(111)c(4×2)-CO surfaces prepared in ultrahigh vacuum (UHV) have been examined in 0.1 M KOH using a UHV electrochemistry transfer system. The results obtained indicate that the CO layer remains intact up to the moment of contact with the electrolyte and can be subsequently electrooxidized quantitatively to yield CO_2 (e.g., mostly carbonate) as the product.

Introduction

A detailed characterization of the electrochemical properties of well-defined electrode surfaces is of crucial importance to the further understanding of structural effects in electrocatalysis.[1] Much of the interest in this area has centered around the electrooxidation of a variety of small organic compounds, including methanol and formic acid on platinum and on other metal electrodes, because of their potential application in fuel cells.[2] These reactions are accompanied by the formation of adsorbed carbon monoxide, a species that blocks surface sites leading to losses in electrocatalytic activity.[3] The extraordinary progress made over the past few years toward elucidating important aspects of this poisoning phenomena is owed primarily to the development of procedures for the preparation of high-quality single-crystal surfaces which do not rely on the use of ultrahigh-vacuum (UHV) surface science techniques.[4] Particularly noteworthy is the work of Weaver and co-workers,[5] who have made extensive use of these methodologies for studying the effects of coverage and applied potential on the binding properties of CO on a number of low-index single-crystal surfaces including Pt, Rh, and Au, using in situ Fourier transform infrared reflection absorption spectroscopy. Although such non-UHV strategies for the preparation of single-crystal surfaces appear to be suitable for fairly noble metals, no simple method has yet been described for more active materials such as Ni and other first-row transition metals.

This paper will present voltammetric curves for the electrooxidation of irreversibly adsorbed CO on UHV-prepared Ni(111)

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0022-3654/92/2096-6742$03.00/0