Fluorocarbon-Hydrocarbon Interactions in Interfacial and Micellar Systems

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ABSTRACT

The interactions of fluorocarbons and hydrocarbons in liquid mixtures are known to be highly nonideal. Recent research has indicated that the unusual characteristics of such interactions have a significant influence on the behavior of many interfacial and micellar systems in which such interactions occur. Results from several different studies are presented. These involve (a) properties of partially fluorinated surfactants and lipids, including comments on the use of fluorine substituted groups as spectroscopic probes; (b) surface tensions of nonideal mixtures of liquid fluorocarbons and hydrocarbons and their interfacial tensions against water; (c) adsorptions of fluorocarbon and hydrocarbon surfactants to air/water, hexane/water, and perfluorohexane/water interfaces and a comparison of relative affinities; (d) formation of mixed micelles of fluorocarbon and hydrocarbon surfactants and evidence of partial miscibility of micelles; (e) comparison of adsorption of fluorocarbon and hydrocarbon surfactants to graphon; and (f) comparison of wetting of hydrocarbon-like solids by aqueous solutions of fluorocarbon and hydrocarbon surfactants.

INTRODUCTION

Fluorocarbon-hydrocarbon (FC-HC) interactions are encountered in a large number of interfacial, micellar and membrane-like systems. The systems may involve fluorocarbon or hydrocarbon liquids, completely or partially fluorinated surfactants, fluorocarbon polymers, fluorine-substituted groups in surfactants or lipids, or fluorocarbon anesthetic gases. FC-HC interactions thus may have a considerable bearing in many areas of technical interest such as wetting, foaming, spreading, formation of mixed micelles, and stabilization of emulsions and suspensions. Recent research has shown that the behavior of many such systems may be very significantly influenced by the unusual character of the mutual interactions of fluorocarbons and hydrocarbons as compared to their self-interactions. The purpose of this paper is to review some current research of interest for interfacial and micellar systems and to provide a unifying qualitative picture with some indications of possible applications of quantitative theories.

That fluorocarbon liquids and solids have low energy surfaces is well known. It is also well known that fluorocarbons are considerably more hydrophobic than hydrocarbons in aqueous solutions. Compared to hydrocarbons, fluorocarbons gases are less soluble in water (1). The superior hydrophobicity of fluorocarbons is reflected in lower critical micellization concentrations (cmc) of perfluorosurfactants when compared to hydrocarbon surfactants of the same chain lengths (2) and the increased ability of fluorocarbon surfactants to lower surface tensions of water (3). That the mutual interactions of fluorocarbons and hydrocarbons can be of importance in micellar systems was first pointed out in 1975 (1). Subsequently, many interesting examples of FC-HC interactions in interfacial and micellar systems have been demonstrated.

Fluorocarbon-Hydrocarbon Interactions in Liquids and Gases

Fluorocarbon and hydrocarbon liquids, although individually highly nonpolar, show very pronounced positive deviations from Raoult's Law in the vapor pressures of their mixtures (4). This nonideality effect is so intense that relatively large molecules such as heptane and perfluoroheptane are only partially miscible at room temperature. Even for miscible mixtures, the nonideality effects are very pronounced. For example, for the pair of liquids butane and perfluorobutane which are miscible at 25 C, the activity coefficient of the latter in butane at infinite dilution has a value of about 10 (4). These nonidealities are qualitatively in accord with solubility parameter theories, the parameters for heptane, 7.4 $(cal/cc)^{1/2}$, and perfluoroheptane, 6.0 $(cal/cc)^{1/2}$, differing significantly (4). However, quantitative theories based on the solubility parameter approach are not very successful (4). The origin of the unusual nature of FC-HC interactions can be traced back to the weak interactions between individual fluorocarbon and hydrocarbon molecules in the gas phase. From data on interaction virial coefficients of a number of binary mixtures of hydrocarbon and fluorocarbon gases, it has been found, for example, that the FC-HC interaction energies are about 10% weaker than the geometric means calculated from FC-FC and HC-HC interaction energies (5).

On the basis of such observations it was proposed that a mutual phobicity of hydrocarbons and fluorocarbons may be expected to play an important part in many interfacial systems where fluorocarbons and hydrocarbons interact, and that this effect may be juxtaposed on the well known hydrophobicity of both (1,6).

Partially Fluorinated Surfactants and Lipids: Fluorine Substituted Groups as Spectroscopic Probes

One of the clearest examples of the importance of the nonideal FC-HC interactions in lipid assemblies is obtained from the cmc values of partially fluorinated hydrocarbon surfactants (1). Muller and coworkers prepared a number of ω-trifluoro (ω-CF_3) derivatives of surfactants for investigating micelle formation using ^{19}F nuclear magnetic resonance (NMR) (7-9). The ω-CF_3 group was introduced primarily to serve as a spectroscopic probe. Compared to the cmc values of the hydrocarbon analogs, the cmc of the ω-CF_3 derivatives were found to be higher by a factor of about 2. This was shown to be an anomalous result (1) since complete fluorination reduces the cmc values of surfactants very substantially (2). For example, the cmc of potassium perfluorooctanoate is about 13 times lower than that of potassium octanoate. The higher cmc of the partially fluorinated compounds compared to the nonfluorinated ones was ascribed to very significant FC-HC nonideality effects in the micelles which make micelle formation more difficult. Examples of other such systems have also been given (1).

The above nonideality effects, and some related effects expected from the surface activity of fluorocarbon moieties (10), have considerable bearing on the interpretation of data obtained by using fluorine substituted groups as spectroscopic probes for micelles or other lipid assemblies such as vesicles or membranes. ^{19}F NMR chemical shift data for micelles suggested a somewhat polar environment of the ω-CF_3 groups in the micelles of the partially fluorinated surfactants (7,8). This was originally ascribed to a considerable penetration of water into the interior of micelles (7). Many arguments and independent lines of evidence indicate that

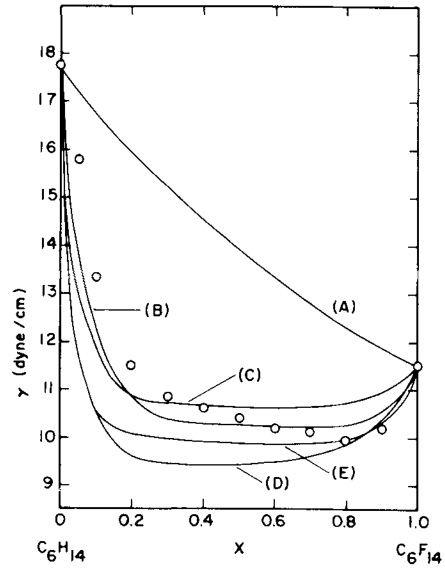

FIG. 1. Surface tensions, γ, of mixtures of hexane and perfluorohexane plotted against the mole fraction, X of C_6F_{14}. Temperature 25 C. Lines (A)-(E) represent theoretical calculations described in the text. Reprinted with permission from ref. 10. Copyright 1981 American Chemical Society.

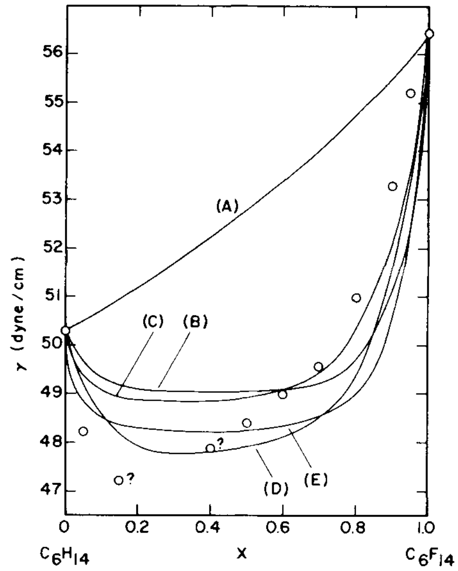

FIG. 2. Interfacial tensions, γ, against water, of mixtures of C_6H_{14} and C_6F_{14} at 25 C. Lines (A)-(E) represent theoretical calculations described in the text. Data points marked with a question mark were judged to be of somewhat lower reliability than others. Reprinted with permission from ref. 10. Copyright 1981 American Chemical Society.

this is unlikely (1). For example, the solubility of water in hydrocarbons is extremely low (11). Relatively low degrees of hydration of micelles were inferred from viscosity data (12). ^{19}F NMR relaxation data have also recently shown to be consistent with very little water in the interior of micelles (13). An alternative explanation for the polar character of the microenvironment of ω-CF_3 groups shown by the micellar chemical shift data can be offered based on the FC-HC nonideality effects in micelles and the expected interfacial activity of the ω-CF_3 groups (1,10). As a result of these interactions, ω-CF_3 groups in the micelles of ω-CF_3 substituted hydrocarbon surfactants are expected to be at the micelle/water interface region more than the omega groups in the case of hydrocarbon surfactants or perfluoro surfactants. Indeed, the ^{19}F NMR shift data for the terminal CF_3 group of sodium perfluorooctanoate and perfluorobutyric acid micelles indicate a less polar character than the CF_3 group of ω-CF_3 substituted hydrocarbon surfactant (1).

Although later work by Muller (14) indicates that the ^{19}F chemical shift parameter has a very complex relation to the nature of the molecular environment, and thus quantitative estimates of hydration or water penetration in the case of micelles are not reliable, the qualitative results and their reinterpretations (1) point out that much care is needed in interpreting results from spectroscopic probes. Some of the uncertainties involved have been discussed in detail in connection with other systems (15,16). With regard to the possible magnitude of FC-HC interactions in lipids, the work of Sturtevant et al. (17) is of considerable additional interest. These authors have studied the thermotropic behavior of three partially fluorinated phospholipids, 1,2-di(X,X-difluoromyristoyl)phosphatidyl-choline with X=4, 8 or 12. All three were shown to have transition enthalpies approximately twice that of the unsubstituted lipid. It was also found that the substituted lipids from strikingly nonideal mixtures with the unsubstituted ones. Sturtevant et al. (17) also suggest the need for due caution in using fluorine-substituted lipids as probes of bilayers or membranes.

An interesting example of how FC-HC interactions can affect solubilization capacity has been given by Gerry et al. (18). These authors showed that the solubility of the nonionic dye Orange OT in the micelles of ω-trifluorododecyltrimethylammonium bromide is about one-half of that in the micelles of the nonfluorinated parent compound.

Surface Tensions of Liquid Mixtures and Their Interfacial Tensions Against Water

Surface and interfacial tension data for a number of binary mixtures of fluorocarbon and hydrocarbon liquids have been reported recently (10). These investigations were carried out to examine the simplest fluid interfacial systems in which FC-HC interactions are likely to play an important role. Data for miscible systems close to but below phase separation temperature and those for immiscible pairs above the phase separation temperature show very pronounced deviations from ideal behavior (10). Figure 1 shows some surface tension data for mixtures of the miscible pair hexane and perfluorohexane. Figure 2 shows the interfacial tension data for these mixtures against water. Both curves show the unusual characteristic of a minimum. Thus both at the air/liquid and the water/liquid interface, fluorocarbons are surface active as dilute solutions in hydrocarbons and hydrocarbons are surface active as dilute solutions in fluorocarbons. The data have been analyzed using a monolayer model for the surface and several models of nonideality of the FC-HC liquid mixtures, assuming that the surfaces and interfaces are ideal. Curves marked (A) in Figures 1 and 2 indicate expected behavior for ideal liquid mixtures. The data indicate clearly the magnitude of the deviations from this model. Curves marked (B), (C) and (D) in Figures 1 and 3 were obtained by using variations of a regular solution approach to describe the nonideality of the liquid mixtures, the interaction parameter for nonideality being estimated from critical solution temperature data (19). Curves marked (E) were calculated by using activity coefficients of hexane and perfluorohexane estimated from vapor pressure data (20). It is interesting to note that although none of the theoretical models is entirely satisfactory, the models B-E do reproduce the broad features of the experimental curves. Thus, both the mutual reciprocal surface activities of fluorocarbons in hydrocarbons in dilute solutions and vice versa, and the existence of the minima in these curves can be ascribed to the intense nonideality of mixing in

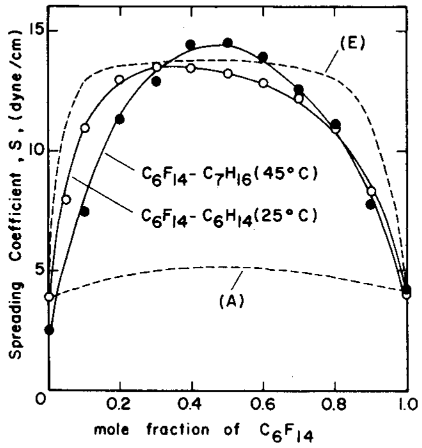

FIG. 3. Initial spreading coefficients on water, S, for mixtures of C_6F_{14} and C_6H_{14} at 25 C and C_6F_{14} and C_7H_{14} at 45 C. Lines (A) and (E) represent calculated values mixtures of C_6H_{14} and C_6F_{14}. Both models assume ideality for the surface and interface. Model (A) assumes C_6H_{14} and C_6F_{14} mixtures are ideal. Model (E) incorporates activity coefficients from vapor pressure data (see text). Reprinted with permission from ref. 10. Copyright 1981 American Chemical Society.

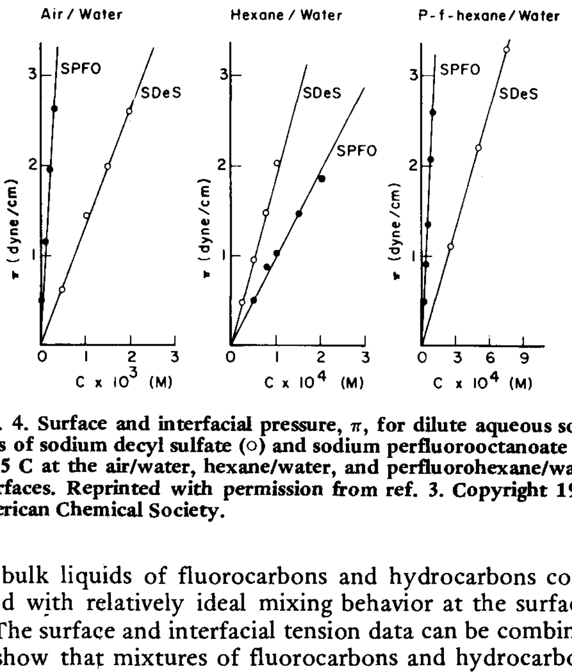

FIG. 4. Surface and interfacial pressure, π, for dilute aqueous solutions of sodium decyl sulfate (○) and sodium perfluorooctanoate (●) at 25 C at the air/water, hexane/water, and perfluorohexane/water interfaces. Reprinted with permission from ref. 3. Copyright 1981 American Chemical Society.

the bulk liquids of fluorocarbons and hydrocarbons combined with relatively ideal mixing behavior at the surface.

The surface and interfacial tension data can be combined to show that mixtures of fluorocarbons and hydrocarbons have much higher initial spreading coefficients than the pure liquids. Figure 3 shows some data for the binary mixtures of two pairs of fluorocarbons and hydrocarbons (10). The initial spreading coefficient, S, was calculated from the equation:

$$S = \gamma_W - (\gamma_S + \gamma_i) \qquad [1]$$

where γ_W and γ_S are the surface tensions of water and the organic liquid, and γ_i is the interfacial tension. The spreading coefficients of some of the mixtures are markedly higher than those of the pure liquids. In the case of the data for mixtures of hexane and perfluorohexane, the comparison of the experimental data with the theoretical curve marked (A), which is based on ideal solution calculations, indicate clearly that the FC-HC nonideality effects are primarily responsible for the unusually high spreading coefficients of their mixtures. The theoretical curve marked (E), based on activity coefficients in the FC-HC mixtures determined from vapor pressure data (20), provides a reasonable description of the experimental data. The unusually high spreading coefficients of some of the fluorocarbon-hydrocarbon mixtures is likely to be of considerable practical interest.

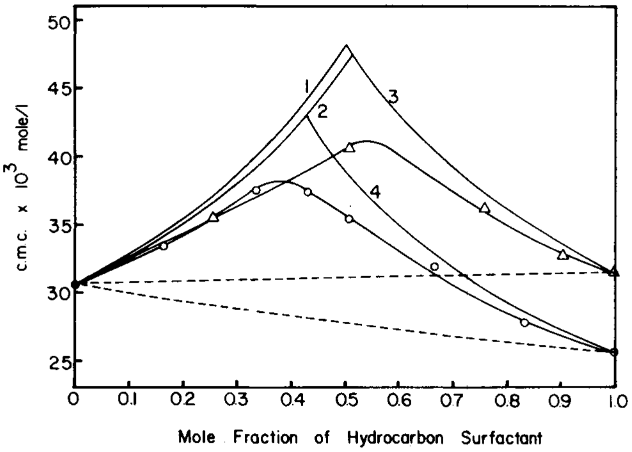

FIG. 5. Critical micellization concentrations of mixtures of sodium perfluorooctanoate with sodium decyl sulfate (△) and with sodium laurate (○) at 25 C. All measurements in 0.001 N NaOH. Dashed lines show expected values for ideal mixing of micelles. Curves 1-4 represent expected values for complete demixing of micelles using parameters described in reference 6. Reprinted with permission from ref. 6. Copyright 1976 American Chemical Society.

Adsorption of Fluorocarbon and Hydrocarbon Surfactants to Fluid Interfaces

In order to examine to what extent fluorocarbon and hydrocarbon surfactants differ with respect to their adsorbability to fluid interfaces, surface and interfacial tensions of aqueous solutions of sodium perfluorobutyrate, sodium perfluorooctanoate (SPFO), sodium perfluorodecanote, sodium octyl sulfate, and sodium decyl sulfate (SDeS) at the air/water (A/W), hexane/water (H/W) and perfluorohexane/water (p-f-H/W) interfaces have been measured (3). The dilute solution data give a measure of the affinity of a surfactant for the interface (3). Figure 4 shows a comparison of the dilute solution surface pressures, π (dynes/cm), for SPFO and SDeS at these interfaces. π is the difference between the measured surface (interfacial) tension γ, from the surface (interfacial) tension for pure solvents, γ_0. In the region where π values are less than 2 dynes/cm, π was found to be proportional to the surfactant concentration c. This is consistent with a themodynamic model of adsorption. For very low values of π, the mutual interactions of adsorbed molecules in the adsorbed layer are minimal. The initial dπ/dc values, therefore, provide a direct relative estimate of the affinity of the surfactants for the interfaces (3). At high concentrations approaching the cmc region, the adsorption of all the surfactants investigated had limiting values which varied over a small range at the various interfaces, 3.1-3.4 × 10^{10} mol/cm^2 (3).

A comparison of the SPFO and SDeS π values at various interfaces in dilute solutions (Fig. 4) underscores several interesting aspects of the relative hydrophobicities of fluorocarbon and hydrocarbon surfactants as also the significant role of the nonideal nature of FC-HC interactions at fluid interfaces. SPFO and SDeS were chosen for comparison because they have nearly identical cmc values (Fig. 5). The calculated free energies of micelle formation differ only slightly, that for SDeS being somewhat more favorable for micelle formation (3). At the A/W interface, however, SPFO is much more surface active than SDeS, the dπ/dc value being higher by a factor of 6.5. Thus, there is a substantial difference in the expression of the hydrophobicity of the two surfactants in micelle formation on the one hand and adsorption at the A/W surface on the other. This result is in marked contrast to the well known fact that the tendency to form micelles and the tendency to adsorb to fluid interfaces parallel each other for homologous surfactants (1,21, 22). It has been pointed out that hydrophobic interactions are not entirely the result of hydrophobic groups being "squeezed out of water" (20,21): a major contribution to free energies of adsorption and free energies of micelle formation derives from the interactions of the chains with interfaces in the case of adsorption and with each other in the case of micelles. The chain-chain interactions are expected to be weaker for fluorocarbons than for hydrocarbons (3). From this point of view, the superior surface activity of SPFO at the A/W surface with respect to SDeS can be ascribed to a more pronounced role of chain-water interactions in the net expression of hydrophobicity. This conclusion is in qualitative agreement with the finding from a high pressure study on micelle formation that the volume change in micelle formation is more than twice as high for SPFO than for SDeS (23).

The most striking feature of the data in Figure 4 is the *reversal* of relative affinity of SPFO and SDeS for the H/W interface in comparison to the A/W interface. At this interface, the dπ/dc value of SDeS is higher than that for SPFO by a factor of 2.0. At the p-f-H/W interface, however, the dπ/dc value of SPFO is higher than that for SDeS by a factor of 6.3, similar to the factor for the A/W interface. These data indicate very clearly the significance of FC-HC nonideality effects at fluid interfaces. The dπ/dc value of SDeS increases by a factor of 14.5 as the interface changes from A/W to H/W. This well known greater affinity of hydrocarbon surfactants for hydrocarbon/water interfaces as compared to air/water interfaces can be ascribed to more favorable interactions of hydrocarbon chains at the hydrocarbon/water interfaces. The dπ/dc value of SPFO, however, increases by a factor of only 1.1 as the interface changes from A/W to H/W corresponding to very little added contribution to adsorbability. A combination of these two effects results in a reversal of affinity of SPFO and SDeS at the H/W interface as compared to the A/W interface.

A comparison that gives a more direct evidence of the role of nonideal FC-HC interactions is the change in dπ/dc of SPFO and SDeS on changing the interface from H/W to p-f-H/W. In the case of SPFO, the value of dπ/dc increases by a factor of 2.8 whereas in the case of SDeS it decreases by a factor of 4.6.

A detailed examination of the free energies of adsorption to the A/W, H/W, and p-f-H/W interfaces of the surfactants mentioned reveals some interesting trends (3). The difference in this free energy of adsorption between the H/W and the p-f-H/W interfaces can be ascribed to the excess free energy of mixing of fluorocarbons in hydrocarbons and hydrocarbons in fluorocarbons arising from the nonideality of mixing. Using a regular solution theory approach and interaction parameters derived from critical solution temperature data (19), moderately good agreements with these changes in free energy have been found (3). For purposes of predicting chain length effects, an additional quantity of interest has been derived from the dπ/dc data, namely the incremental free energy changes, $\Delta\Delta G^\circ$, of adsorption on adding a -CH_2- or a -CF_2- group to a hydrocarbon or a fluorocarbon chain. These $\Delta\Delta G^\circ$ values are likely to be a measure of the intrinsic hydrophobic effect of increasing the chain length, independent of the effects of polar head groups (21,22). Figure 6 shows schematically these estimated values. The $\Delta\Delta G^\circ$ values for a -CF_2- group at the A/W interface is nearly twice the value of the -CH_2- group, thus reflecting the greater surface activity of fluorocarbons. The interactions at the other interfaces relative to the A/W interface shows the relative strength of hydrocarbon-hydrocarbon interactions (-CH_2- group at the H/W interface) as compared to fluorocarbon-fluorocarbon interactions (-CF_2- group at the p-f-H/W interface). The FC-HC mutual interaction effects are clearly exhibited by the $\Delta\Delta G^\circ$ values of a -CH_2- group becoming more positive by 130 cal/mole when a H/W interface is replaced by a p-f-H/W interface, the corresponding $\Delta\Delta G^\circ$ value of a -CF_2- group becoming more negative by 70 cal/mole. These changes in $\Delta\Delta G^\circ$ have also been found to be consistent with some theoretical calculations (3).

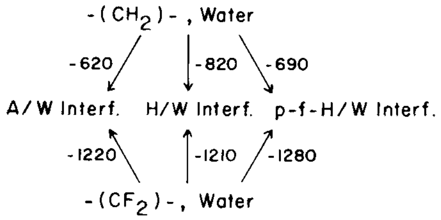

FIG. 6. Incremental free energies of adsorption per -CH_2- and -CF_2- group, $\Delta\Delta G^\circ$, in cal/mole, at 25 C, to air/water, hexane/water and perfluorohexane/water interfaces.

Formation of Mixed Micelles

The mutual antipathy of fluorocarbons and hydrocarbons has been demonstrated in many studies on the formation of mixed micelles of fluorocarbon and hydrocarbon surfactants. Figure 5 shows some illustrative cmc data for mixtures of SPFO and SDeS and sodium laurate (6). The cmc values of the individual surfactants are very similar. The dashed lines indicate the expected cmc values of ideal mixing. The experimental values are considerably higher, particularly in the middle of the mixing range. This can be ascribed to the nonideality of mixing of the fluorocarbon and hydrocarbon chains. Some curves calculated for the extreme case of complete demixing of the micelles, i.e., no incorporation of the fluorocarbon surfactant in micelles of the hydrocarbon surfactant and vice versa, are also shown in Figure 5. When compared to these curves, the experimental data indicate that some mixing takes place but the nonideality of mixing is indeed severe. In mixtures of SPFO and sodium dodecyl sulfate (SDS), these nonideality effects are even more severe than in the case of SPFO and SDeS because of the longer chain in SDS (6). Differential conductance data in mixtures of SPFO and SDS show evidence of partial miscibility of micelles and the coexistence of fluorocarbon-rich and hydrocarbon-rich micelles (6). This microscopic phase separation had been previously proposed (1) for explaining some complex surface tension data in mixtures of perfluorooctanoic acid and SDS reported by Klevens and Raison some years ago (24).

The differential conductance data for mixtures of SPFO and SDS (6) as also the interpretation of surface tension data of mixtures of perfluorooctanoic acid and SDS (1) indicate that such systems have a second transition at concentrations well above the ordinary cmc. A new kind of micelles appears in the second transition region (1,6). This second transition resembles a cmc transition and, may be described in approximate terms as a second cmc. Mysels (25) has shown that under some circumstances there may also exist a critical demicellization concentration.

An approximate theoretical treatment of the nonideality of mixing in micellar systems based on the regular solution approach was suggested some years ago to examine some unusual solubilization data (26). This approach has been ex-

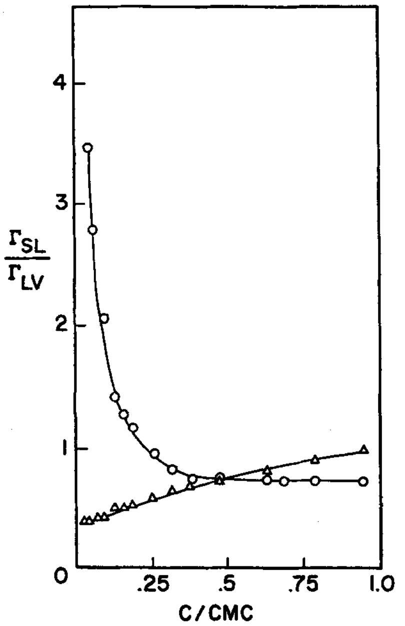

FIG. 7. Ratios of adsorptions to the graphon/water interface, Γ_{SL}, and to the air/water interface, Γ_{LV}, at 25 C for sodium decyl sulfate (○) and sodium perfluorooctanoate (△). Concentration scale c/cmc is a reduced scale. The cmc values are very similar (see Fig. 5).

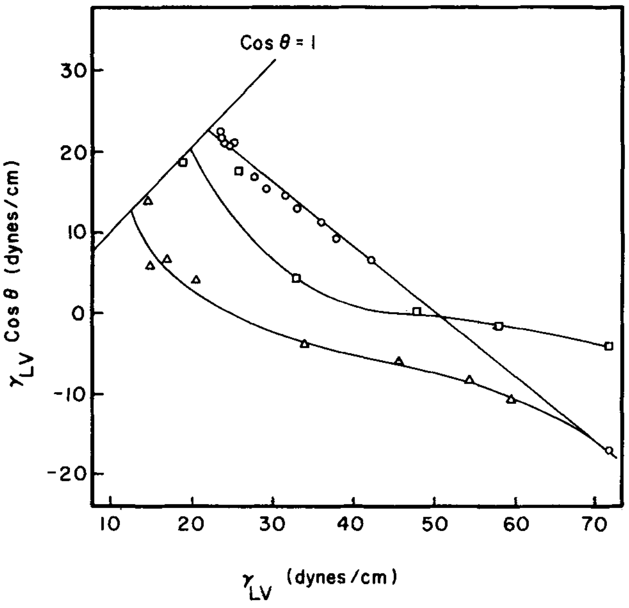

FIG. 8. Contact angle data, θ, for Aerosol OT in 0.1M NaCl on paraffin (○), perfluorooctanoic acid on paraffin (△) and perfluorooctanoic acid on polyethylene (□), represented as plots of γ_{LV} cos θ against surface tension of solution (γ_{LV}).

tended to the case of mixtures of fluorocarbon and hydrocarbon surfactants. The approach gives reasonable descriptions of cmc data (27,28). It can also be extended to concentrations above the cmc to give reasonable accounts of compositions of micelles, the apparent second cmc and, under certain circumstances, the existence of a critical demicellization concentration (27,29). Many of these phenomena have been studied by using ^{19}F nuclear magnetic resonance (27,29). Funasaki et al. (30-32) have also examined many other systems in which pronounced nonideal FC-HC interactions are involved in mixed micelles.

Adsorption to Low Energy Solids and Wetting Powers of Fluorocarbon and Hydrocarbon Surfactants

A comparative study of the adsorption of SPFO, SDeS and SDS from aqueous solutions to graphon has revealed that at the graphon-water interface also SPFO behaves in a qualitatively different manner than SDeS or SDS (33). These data and a detailed interpretation will be presented later (33). Some implications of this difference in adsorption behavior for wetting of low energy solids have been examined recently (34). Figure 7 illustrates the differences between SDeS and SPFO in their relative adsorbabilities to graphon-water interface and to the A/W interface. The adsorption to graphon, Γ_{SL}, was determined directly from adsorption experiments (33). The adsorption to the A/W interface, Γ_{LV}, was estimated from surface tension data. The ratio of the two adsorptions, Γ_{SL}/Γ_{LV}, is plotted in Figure 7 against a reduced concentration scale, c/cmc. In the case of SDeS Γ_{SL} is considerably higher than Γ_{LV} in dilute solutions indicating a greater affinity of these surfactants for the solid/liquid interface. With increasing concentration the ratio decreases rapidly and then remains at a value slightly lower than unity over a considerable range of concentrations. For SPFO, in contrast, Γ_{SL} in dilute solutions is considerably less than Γ_{LV}. At higher concentrations, however, the Γ_{SL}/Γ_{LV} ratio increases and eventually exceeds the value of Γ_{SL}/Γ_{LV} for SDeS in the cmc region. The relatively low ratios of Γ_{SL}/Γ_{LV} in dilute solutions of SPFO can be ascribed in part to high values of Γ_{LV}. But a direct comparison of the Γ_{SL} data indicate that SPFO has a lower affinity for the graphon/water interface at low coverages than SDeS (33). Thus, the interactions of the fluorocarbon chain with graphon at low coverage are less favorable than in the case for SDeS. At higher coverages, significant chain-chain attractive interaction effects in the case of SPFO increase Γ_{SL} levels to values higher than that for SDeS (33).

The relative adsorbability data of Figure 7 provide a good explanation for the unusual wetting characteristics of fluorocarbon surfactants compared to hydrocarbon surfactants for relatively low energy solids (34,35). Figure 8 presents some contact angle data to illustrate some points. The contact angle of a liquid on a solid, θ, can be represented by the Young equation.

$$\text{Cos}\,\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad [2]$$

where γ_{SV}, γ_{SL} and γ_{LV} represent the solid-vapor, solid-liquid, and liquid-vapor surface tensions. Figure 8 shows plots of γ_{LV} cos θ against γ_{LV} for aqueous solutions of a hydrocarbon surfactant, Aerosol OT (AOT), and perfluorooctanoic acid (PFO) on a low energy paraffin surface (34). Some contact angle data of PFO solutions on polyethylene obtained by Bernett and Zisman (35) are also shown. The cos θ = 1 line represents wetting. When PFO and AOT solutions of the same surface tension, γ_{LV}, are compared in the case of paraffin, the PFO solutions show much poorer wetting power, and a lower value of the critical surface tension required to obtain a contact angle of 0°. Bernett and Zisman (35) noted similar differences between hydrocarbon surfactants and PFO on polyethylene. They ascribed the poorer wetting power of PFO to a reduction of γ_{SV} in Equation 2 caused by the adsorption of PFO at the solid/vapor interface. An alternative explanation of many such phenomena has been proposed and attention has been drawn to the role of unequal adsorption of surfactants and wetting agents to the solid/liquid and the liquid/vapor interfaces in determining wetting behavior (34). This approach is shown below to be particularly pertinent in the comparison of fluorocarbon hydrocarbon surfactants as wetting agents.

By combining the Young equation with the Gibbs equation, Lucassen-Reynders (36) showed that

$$\frac{d\,(\gamma_{LV}\cos\theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \qquad [3]$$

where Γ_{SV} represents the adsorption of the surfactant or wetting agent to the solid/vapor interface. The equation shows the importance of relative values of Γ_{SL} and Γ_{LV} in determining θ even if Γ_{SV} is zero. Such data for SDeS and SPFO can be used to simulate wetting curves on graphon (34). It is found that as a result of the low values of the Γ_{SL}/Γ_{LV} ratios for SPFO as compared to SDeS over a wide range of concentrations (Fig. 7) poorer wetting, i.e., higher contact angles, are to be expected for SPFO than for SDeS. The simulated wetting curves are similar to the curves of AOT and PFO on paraffin (Fig. 8). The γ_{LV} cos θ vs γ_{LV} curve for AOT indicates a slope of about -1 over essentially the whole range of γ_{LV} values indicating that Γ_{SL}/Γ_{LV} is about unity. This appears to be reasonable for a hydrocarbon surfactant and paraffin. In the case of PFO, however, the slope of the γ_{LV} cos θ vs γ_{LV} curves shows a complex variation suggesting that Γ_{SL}/Γ_{LV} is low in dilute solutions of PFO, i.e., for high values of γ_{LV}, but increases at high concentrations of PFO, in a manner similar to the Γ_{SL}/Γ_{LV} data of SPFO on graphon (Fig. 7). Thus, the unusual characteristics of FC-HC interactions appear to play an important role in determining wetting of hydrocarbon-type surfaces by fluorocarbon surfactants.

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