

## Chapter 3. Small Angle X-Ray and Neutron Scattering – Its Application to Supramolecular Solutions

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### 3.1 A New Inversion Algorithm for Obtaining Density Profiles of Thin Films From X-Ray and Neutron Reflectivity Data

#### Sponsor

Argonne National Laboratory

#### Project Staff

Xiao-Lin Zhou, Gian P. Felcher, Professor Sow-Hsin Chen

Specular reflectivity spectroscopy has been developed in recent years to probe the one-dimensional scattering length density profile of molecular and magnetic thin films. To exploit this technique, a few x-ray and neutron reflectometers have been constructed and successfully operated. These spectrometers have the merit that data collection is simple and automatic. However, the data inversion process remains a practical challenge. On one hand, there is no closed-form expression for the reflection coefficient as a functional of the

sample profile. On the other hand, there exists no standard way to do inversion, namely, to compute the sample profile straight forwardly from the reflectivity data. Another complication of the situation is that the reflectometers in use at present only measure the squared amplitude of the reflection coefficient but not its phase. All this adds to the difficulty of developing a practical data inversion algorithm.

To develop an inversion scheme, successful attempts have been made to derive a mathematical relationship between the reflection coefficient and the sample profile. Then an iterative inversion procedure based on such a relationship has been devised. Preliminary computations using simulated reflection data have shown that this procedure can invert the data to reproduce the sample profile. More work is underway to investigate the extra measures necessary to make the algorithm effective on actual experimental data which contain error bars. To make this inversion scheme systematic and versatile, a variety of physical samples are to be used to test it. It is expected that this scheme can be applied to other wave propagation situations such as acoustic and elec-

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tromagnetic probing of layered structures of a wide range of scales.

## 3.2 Interlayer Diffusion in Langmuir-Blodgett Films

### Sponsor

U.S. Department of Energy  
DE-FG01-90ER45429

### Project Staff

Bruce L. Carvalho, Professor Sow-Hsin Chen

The Langmuir-Blodgett film deposition technique has been recently used to fabricate a variety of dense electronic and nonlinear optic devices on a single crystal silicon surface. Interdiffusion of polymer or surfactant molecules between multilayers in Langmuir-Blodgett films is therefore an important technological problem because it directly relates to the stability of such films as a function of temperature and age.

We have recently studied the interdiffusion of surfactant molecules using the neutron specular reflection technique. This is a new technique which allows one to obtain the refractive index profile, normal to the surface, with a spatial resolution of 15 Å. Because the refractive index can be easily related to molecular composition, this technique is seen as a powerful tool in understanding the structure of thin films. It should also be noted that since deuterated and protonated molecules have a different refractive index for neutrons, one can label an interface within a Langmuir-Blodgett film and it is precisely this kind of labeling that we have used to observe the self-diffusion of surfactant molecules.

An example of our neutron reflection measurement is shown in figure 1. For this measurement, we constructed a film that consisted of silicon then five layers of deuterated cadmium arachidate then four layers of protonated cadmium arachidate. This film was designed to emphasize the thickness of the deuterated layers and the sharpness of the deuterated-protonated interface. Figure 1 shows three neutron reflectivity measurements; the squares correspond to the as-made film; the crosses correspond to the same film after it was heated to 95°C for one hour; and the diamonds correspond to the same film after it was heated for another nine hours at 95°C. The as-made film shows interference fringes which are characteristic of the five deuterated layers and the initially sharp deuterated-protonated interface. The subsequent heatings show not only a decrease in reflectivity but also the introduction of another period for the interference fringes. Both observations indicate

that the deuterated-protonated interface has broadened substantially. We are presently formulating a model to account for this broadening. We have also begun to use the synchrotron x-ray reflectivity technique to study these same films. While the neutron reflection measurement is sensitive to the composition profile of hydrocarbons, the x-ray reflectivity technique is mainly sensitive to the cadmium ion concentration profile through the film's thickness.

## 3.3 Structure of a Protein/SDS Complex in Low Ionic Strength Solution Studied by Small Angle Neutron Scattering

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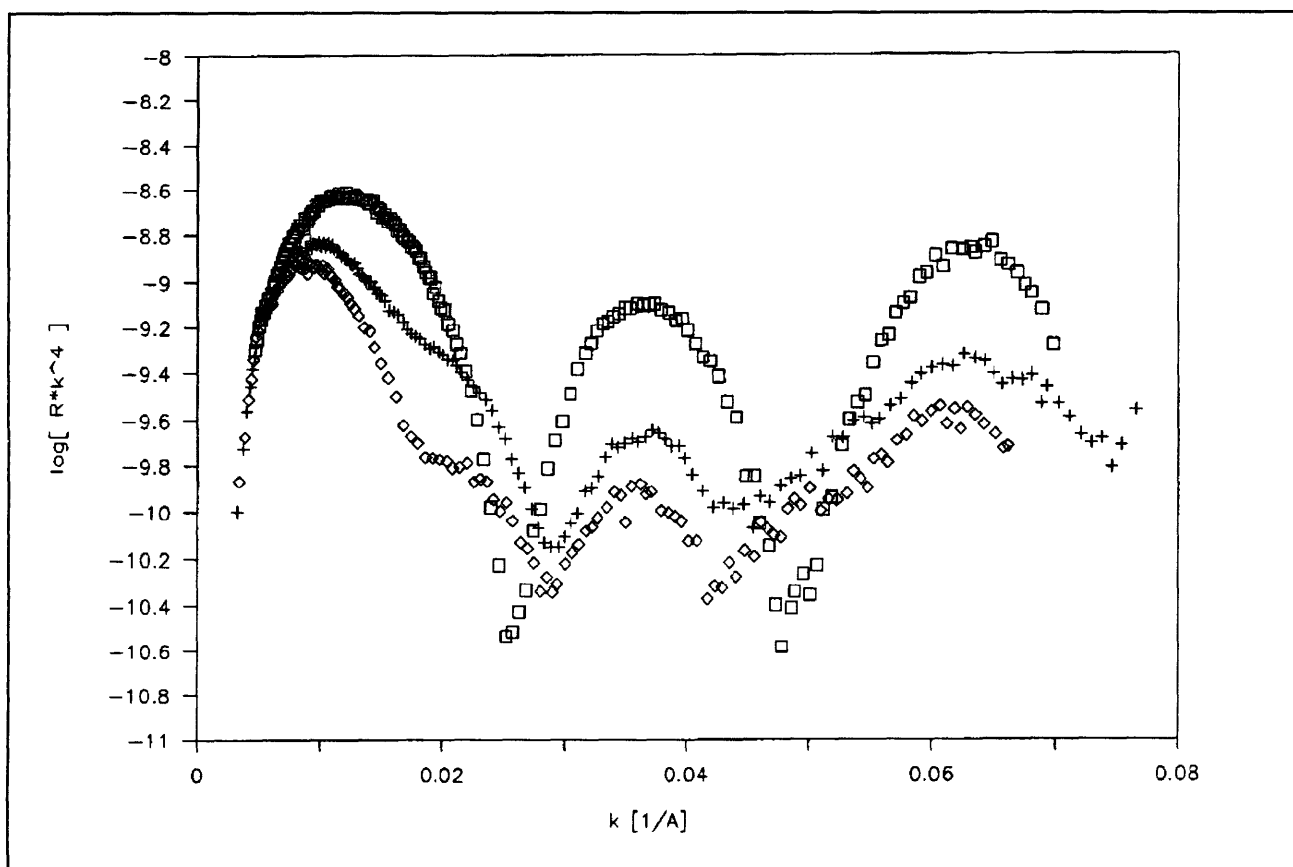
### Project Staff

Xuan-Hui Guo, Professor Sow-Hsin Chen

During the past few years we have studied the structure of bovine serum albumin (BSA)/sodium dodecylsulfate (SDS) complexes in solutions by small angle neutron scattering (SANS). We concluded that BSA/SDS complexes in high ionic strength solution were flexible polymer-like objects. This view has led us to discover the polymer-like phase separation phenomenon of BSA/SDS complexes in solution.

However, there are still some uncertainties on the structure of protein/SDS complexes in low ionic strength solutions. This case has practical interest because the conventional SDS polyacrylamide gel electrophoresis measurements are all carried out in low ionic strength solutions ( $I = 0.2$  M). The structure determination in this case would contribute significantly to the understanding of the gel electrophoresis.

We used perdeuterated SDS molecules to carry out SANS measurements. The solvent is a mixture 40% D<sub>2</sub>O and 60% H<sub>2</sub>O in which the contrast between proteins and solvent is matched, namely, only the perdeuterated SDS molecules can be seen in the SANS measurements. We systematically measured the SANS intensity distribution for the complexes in solution under different protein concentrations and ionic strength ( $I = .1$  M,  $.2$  M). It was found that the intensities for  $Q < 0.03\text{Å}^{-1}$  were considerably depressed due to the charge repulsion between complexes in solution. However, the intensities for  $Q > 0.03\text{Å}^{-1}$  are not affected by ionic strength and can be scaled into one curve after normalizing by the concentrations. We therefore concentrate mainly on the analyses



**Figure 1.** The logarithm of reflectivity  $\cdot k^4$  is plotted as a function of  $k$ , the incident neutron momentum for the as-made film (squares);  $T=95^\circ\text{C}$ , 1 hour (crosses) and  $T=95^\circ\text{C}$ , 10 hours (diamonds).

of the intensity distributions for  $Q > 0.03\text{\AA}^{-1}$ , to critically test all the proposed models.

We have compared SANS data with curves calculated based on all the proposed structural models. It was found that only one model is able to describe SANS data satisfactorily. That is the model in which the bound SDS molecules form micelle-like clusters, and the clusters are assumed to be correlated for portions of the flexible polypeptide chain, namely a Gaussian chain with an excluded volume effect. In figure 2 we show the comparison between SANS data and the calculated curves. The excluded volume exponent is found to be  $2/3$ , close to the Flory exponent  $3/5$ . From these careful measurements and analyses, we are confident that the structure of the complex in low ionic strength solution is also a polymer-like object. This conclusion, coming from SANS data analyses, further supports that the reptation mechanism, which we proposed earlier, is responsible for the protein separation in the process of protein-SDS polyacrylamide gel electrophoresis.

### 3.4 Isotope Effect in Phase Separation of a Lipid/Water Micellar System

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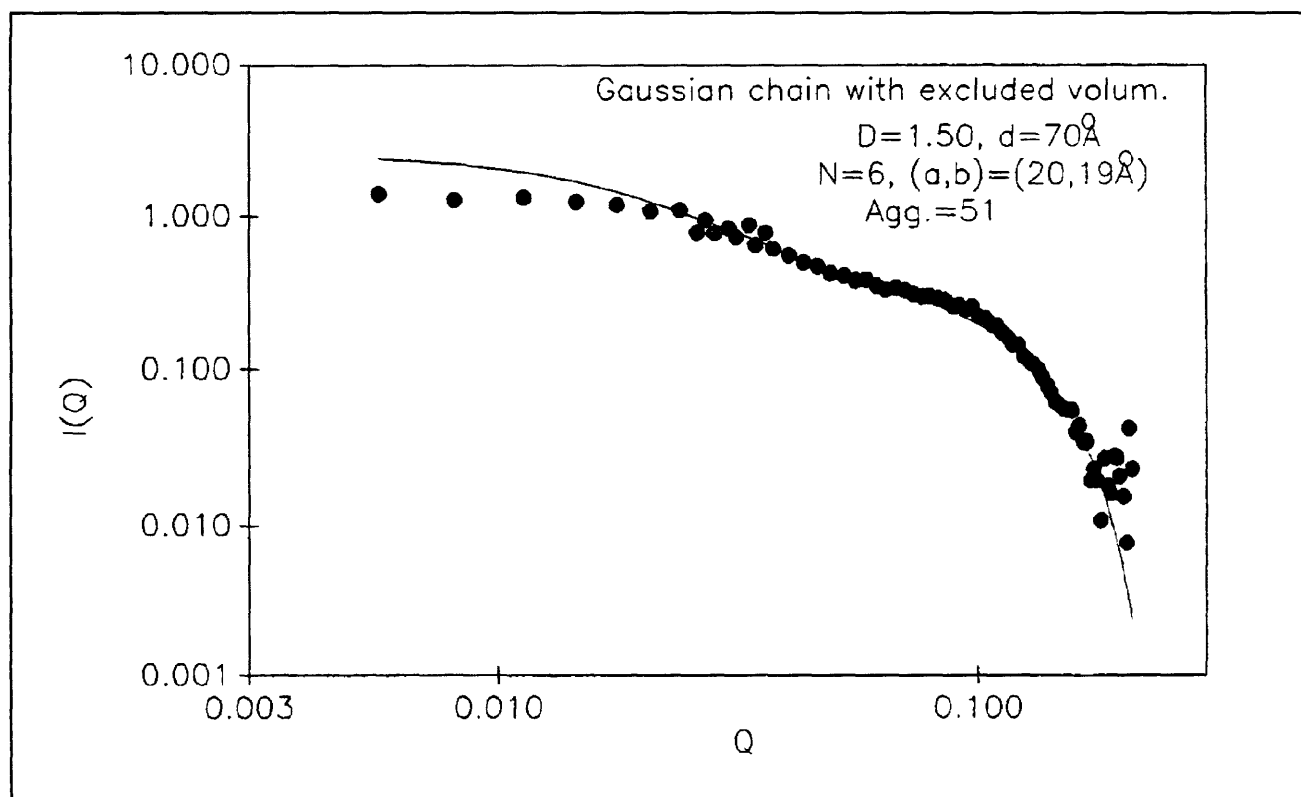
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Pierandrea Lo Nostro, Nadia Stubicar, Professor Sow-Hsin Chen

We have found that the upper consolute temperature of the dioctanoyl-phosphatidylcholine ( $\text{diC}_8\text{-PC}$ )/water system has a substantial isotope effect. The consolute temperature of  $\text{diC}_8\text{-PC}/\text{H}_2\text{O}$  system is 318 K, while that of  $\text{diC}_8\text{-PC}/\text{D}_2\text{O}$  is 332 K, with a difference of 14 K. The complete binodal curves for  $R (= \text{D}_2\text{O}/\text{H}_2\text{O } v/v)$  ranging from 1.00, 0.66, 0.50, 0.33, to 0.00 have been determined. The consolute temperature scales linearly with  $R$ .

It is known that a fraction of hydrogen bonding in  $\text{D}_2\text{O}$  is higher than in  $\text{H}_2\text{O}$  at the same temperature in the vicinity of the room temperature. Therefore, the hydrophobic effect of  $\text{diC}_8\text{-PC}$  in  $\text{D}_2\text{O}$  is



**Figure 2.** Comparison of the SANS intensity distribution with the calculated curve using a model in which the bound SDS molecules form micelle-like clusters and the clusters are correlated by portions of the flexible polypeptide chain, namely assumed to be a Gaussian chain with an excluded volume effect.

expected to be higher than in H<sub>2</sub>O; this explains the observed temperature effect on phase separation.

We have measured the light-scattering intensities as a function of the molar fraction of lecithin in the solution and found that it is peaked at the critical molar fraction which is 0.0008 for diC<sub>8</sub>-PC/D<sub>2</sub>O/H<sub>2</sub>O (R = 0.50) and 0.0010 for R = 1.

### 3.5 Measurement and Interpretation of Counterion Distribution Around Cylindrical Polyelectrolytes

#### Sponsor

Exxon Fellowship

#### Project Staff

Szu-Li Chang, Professor Sow-Hsin Chen

Counterion distributions around rod-like polyelectrolytes in solution are measured directly using small angle x-ray scattering (SAXS). Two systems are studied: cylindrical micelles formed by

a comb-shaped copolymer poly-(1-octadecene-co-maleic anhydride) (PODMA), neutralized by CsOH, in aqueous solution; and 500Å persistence length DNA fragments in aqueous solution having Na<sup>+</sup> or Cs<sup>+</sup> as counterions respectively. A new method of SAXS data analysis is developed. Poisson-Boltzmann (P-B) equation in the cell model is used to compute the counterion distributions. Comparison of SAXS data for the PODMA case with the theory shows that the P-B solution overestimates the charge accumulation on the micellar surface due to the very high linear charge density parameter  $\xi$  ( $\approx 33$ ) of the micelle, while for the case of CsDNA, one needs to assume considerable amount of counterions present in the major and minor grooves of the double helices. Figure 3a shows the scattering length density profile for a single PODMA micelle enclosed in a cell of radius  $R=201\text{\AA}$ . This is a sample containing 1wt% PODMA in aqueous solution fully neutralized by CsOH. Figure 3b shows a comparison of SAXS data with the theoretical calculation of the scattering intensity distribution in absolute scale. The dotted line gives the micelle's only contribution, which is seen to be negligibly small. The counterion's only contribution is shown by the dashed line, which is a much larger contribution. The solid line is due to a coherent sum of the

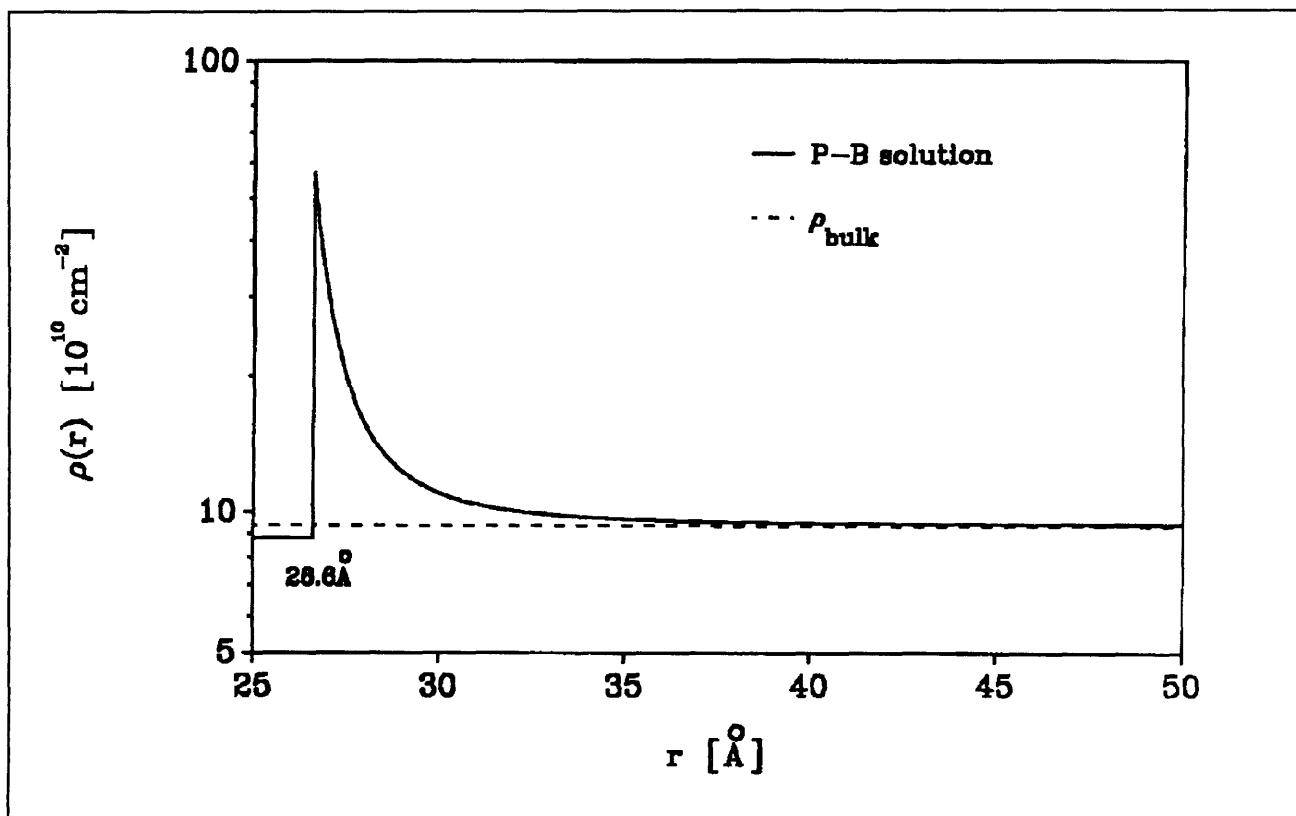


Figure 3a. Scattering length density distribution for a single PODMA micelle enclosed in a cell of radius  $R=201\text{ \AA}$ .

above two contributions which is the quantity to be compared with experimental data. In the small  $Q$  region, the agreement of the theory with the experiment is quantitative, including the correct prediction of the dip in the curve due to the discontinuity of the scattering length density at the micellar surface.

### 3.6 Aggregation Behavior and Phase Transition of Semifluorinated $n$ -Alkanes in Hydrocarbons and Fluorocarbons

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University of Florence, Italy

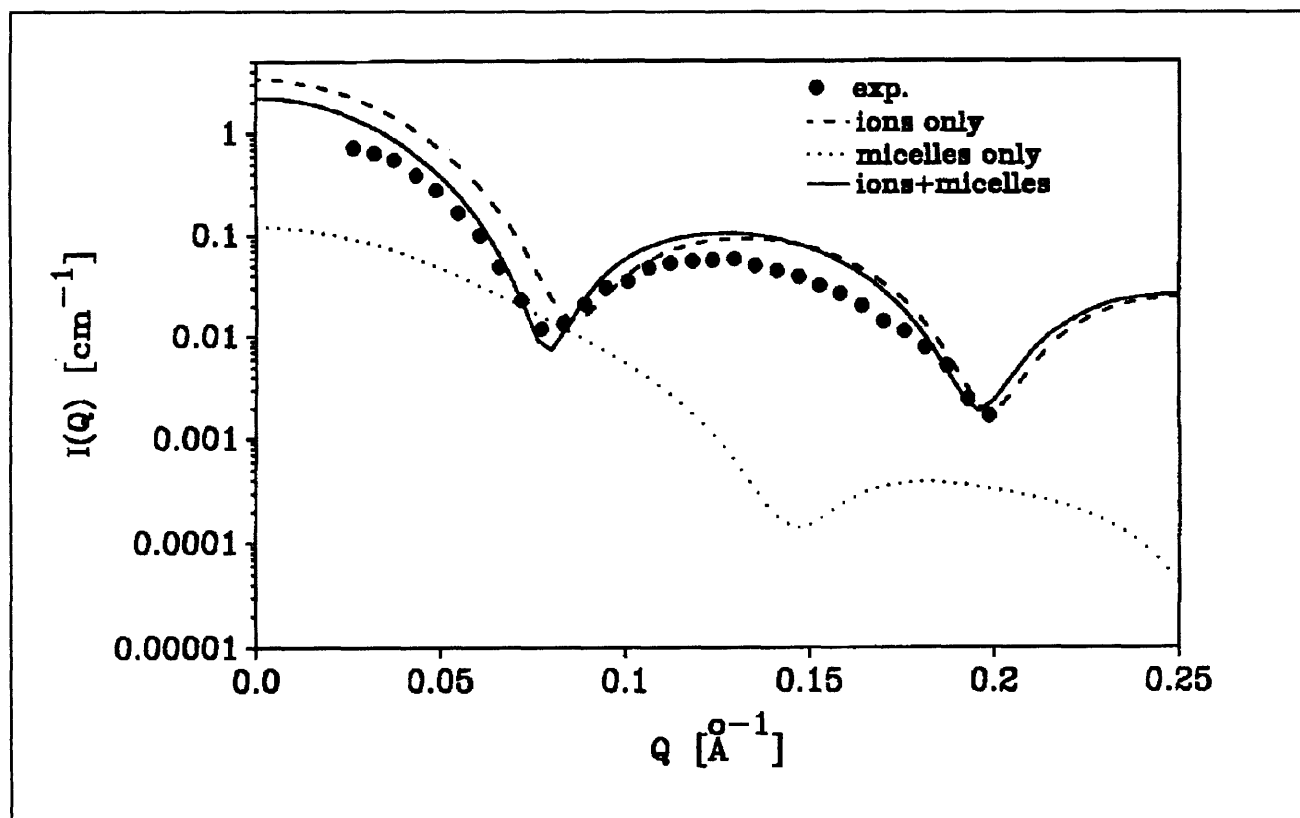
#### Project Staff

Pierandrea Lo Nostro, Professor Sow-Hsin Chen

Amphiphilic molecules contain a polar head group (hydrophilic part) and one or more aliphatic chains which constitute the hydrophobic part, so that, when they are dissolved in an aqueous medium, they can produce several kinds of aggregates, such as micelles, vesicles, discs and cylinders.

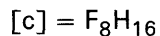
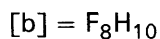
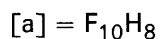
Usually the polarities of the hydrophilic and the hydrophobic parts are very different. In fact the head group can be either ionic or non-ionic but it is always highly polar, whereas the hydrophobic part is commonly consisting of  $-\text{CH}_2-$  groups which are apolar. Therefore, an amphiphile can produce aggregates in water solutions only if the difference in polarity of the two parts of the molecule is considerably large.

The syntheses of molecules like  $\text{F}(\text{CF}_2)_m(\text{CH}_2)_n\text{H}$  and  $\text{F}(\text{CF}_2)_m(\text{CH}_2)_n(\text{CF}_2)_p\text{F}$  (or shortly  $\text{F}_m\text{H}_n$  and  $\text{F}_m\text{H}_n\text{F}_p$  respectively) are relatively recent; "m" and "n" can vary between 2 and 20. In this case the polarity of the two chains, the fluorocarbon chain and the hydrocarbon one, are very close, therefore we cannot use water to distinguish them. On the other hand, a fluorinated solvent or a hydrocarbon can interact differently with them. A few years ago, the formation of *star micelles* in fluorocarbons was reported for the first time for these kind of compounds. In fact the molecules aggregate in such a way that the fluorinated chains face the solvent, whereas the hydrogenated parts collapse together and form the core of the micelle. Conversely, in a hydrogenated solvent, the hydrocarbon chain will face the solvent and the fluorinated chain will constitute the inner part.

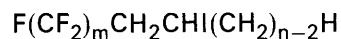
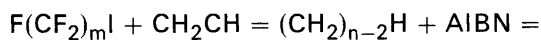


**Figure 3b.** The comparison of the experimental and calculated SAXS intensities for 1wt% PODMA in aqueous solution fully neutralized by CsOH.

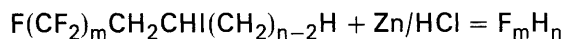
We synthesized three different chemicals:



in two steps:



This is a radical reaction initiated by AIBN (azo-bis(isobutyro-nitrile)). The intermediate then reacts with zinc and gaseous hydrogen chloride to give the semifluorinated n-alkane:



Through light-scattering measurements we investigated the formation of aggregates: compounds [a] and [b] did not produce any aggregate in

perfluorohexane, perfluorooctane and n-octane; [c] gave large micelles in perfluorooctane above 40°C, with CMC = 5.4% at 51°C.

Compound [c] also showed an interesting phase transition in perfluorooctane and n-octane. In fact, at low temperatures it forms a white gel that melts at higher temperatures to give a transparent liquid. This phase transition occurs between 25° and 40°C for concentration of  $F_8H_{16}$  between 2.5% and 20% in perfluorooctane. In n-octane the phase transition occurs at much lower temperatures, below 0°C.

### 3.7 Light Scattering From Dense Percolating Microemulsions

#### Sponsor

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#### Project Staff

Dr. Piero Tartaglia, Dr. Jacques Rouch, Professor  
Sow-Hsin Chen

The theory of static and dynamic light scattering from a system of dense, surfactant coated water droplets dispersed in oil, forming polydisperse fractal percolation clusters, is formulated. The scattering intensity shows the characteristic  $q^{-D(3-\tau)}$  behavior at large  $q$ , and the density-density time correlation function, while initially decaying exponentially, evolves continuously into a stretched exponential asymptotically with a characteristic exponent  $\beta = D/(D + 1)$ . A set of static and dynamic light scattering measurements of the AOT-water-decane microemulsions are analyzed to substantiate the predicted behavior. The theory, applicable for microemulsions near the percolation threshold, bears striking resemblance to the well-known static and dynamic fluctuation theory near the consolute point of binary mixture of liquids. Both theories share a common feature: the scaled intensity and linewidth can be expressed in terms of universal functions of the single scaling variable  $x = q\xi$ .

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