THE PHYSICS OF MICROEMULSIONS AND AMPHIPHILIC MONOLAYERS

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ABSTRACT

Surfactants are amphiphiles that combine hydrophobicity with hydrophilicity behavior; namely, they prefer to reside or to create spontaneously liquid/liquid or liquid/gas interfaces. We give here three examples of amphiphilic systems: (i) insoluble monolayers of lipids or fatty acids at the water/air interface – called Langmuir monolayers. (ii) Micellar solutions where the solvent can be either an aqueous solution or a non-polar organic solvent like oil. (iii) Microemulsions which are thermodynamically stable, fluid, oil-water-surfactant mixtures; most microemulsions contain also cosurfactant (alcohol) and/or salt. In this extended abstract we will briefly review some of the main results obtained for Langmuir monolayers and microemulsions.

Insoluble amphiphilic monolayers spreaded on the water/air interface are of basic interest because of their variety of two-dimensional phase transitions. In addition, they serve as simple models for biological cell membranes. The main experimental technique used to study Langmuir monolayers is a film balance technique which has been invented by Langmuir (1917), (1933) (for a review see, e.g., Adamson (1982), Gaines (1966)). Using this method, surface isotherms measuring surface pressure as function of area per molecule yield a rich variety of surface phases (Gaines (1966)). At very low surface pressures (less than 1 dyn/cm) the monolayer undergoes a two-dimensional liquid-gas transition (Hawkins and Benedek (1974), Kim and Cannell (1975), (1976a)). At higher surface pressure a peculiar "kink" in the isotherms is seen in many experiments. The origin of this singularity is not clear and is a matter of dispute (Pallas and Pethica (1985), Middleton et al (1984), Bell et al (1981), Legre et al (1984) and reference therein). It has been interpreted either as a second-order transition between two liquid phases (termed "liquid-expanded" and "liquid-condensed") or as a first-order transition between liquid and solid phases under poorly controlled conditions: presence of impurities, undersaturated water vapor pressure, retention of the spreading solvent, or non-equilibrium determination of the isotherms (Middleton et al (1984)). At the very compressed state, the monolayer behaves as a solid. It is rather incompressible and will collapse as the surface pressure becomes too high (roughly of the order of 30 dynes/cm).

Recently, other experimental techniques have been developed and applied to the study of structural properties of monolayers. Among others they include electric surface potential (Helm et al (1986), Middleton and Pethica (1981), Kim and Cannell (1976b)), viscoelastic measurements (Abraham et al (1985)), non-linear optics (Rasing et al (1985)), epifluorescence microscopy (McConnell et al (1984), Löesche et al (1983), Löesche and Möhwald (1984), Löesche and Möhwald (1985), Moore et al (1986)), and grazing incident X-ray diffraction from a synchrotron source (Kjaer et al (1987), Dutta et al (1987), Barton et al (1988)). The epifluorescence microscopy, for example, allows direct visualization of monolayers on a length scale of micrometers. In lipid monolayers, an organization of liquid-like and solid-like regions repeating themselves periodically is observed. Those domains can be stripe-like, rounded, or spiral with a definite handness for monolayers of chiral lipids. The grazing incident X-ray diffraction allowed, for the first time, to obtain microscopic structural information on monolayers directly on the air/water interface. Crystalline order has been examined and positional as well as orientational correlation lengths have been calculated. We expect that these two advanced methods – X ray scattering and epifluorescence microscopy – will hopefully clarify in the future the nature of the liquid-expanded liquid-condensed transition.

On the theoretical level, a simple Van der Waals equation of state have been proposed to describe the dilute regime of monolayers (Langmuir (1933), Kirkwood (1943), Adamson (1982)). For the more condensed phases the situation is less clear. Several works proposed an explanation of the liquid-expanded liquid-condensed transition by a coupling between the monolayer surface concentration and an additional orientational order parameter of the chains (Legre et al (1984)). Recently, a possible explanation of the modulated structure seen in the epifluorescence experiments has been proposed (Andelman et al (1985), Keller et al (1986), Andelman et al (1987a)). Phase diagrams involving transition between stripe, hexagonal and isotropic phases have been calculated close to a critical point using a Landau-Ginzburg expansion and at low temperatures. The main idea is to consider the effect of dipolar interactions on the creation of modulated phases. The dipoles can be either permanent or induced in a charged monolayer. The competition between the long-range dipolar interaction and the two-dimensional line tension determines the periodicity of the undulations. Other interesting questions which have been recently addressed include the dynamics of growth and spinodal decomposition of dipolar monolayers in the absence of gravity (Brochard et al (1987)), and chirality discrimination in racemic monolayers of lipids which show spiral growth (McConnell et al (1984), Löesche and Möhwald (1984) and (1985), Andelman and deGennes (1988), Andelman (to be published)).

A different type of an amphiphilic system forming a complex fluid are microemulsions. Like regular emulsions, these are fluid mixtures of oil, water and surfactant but where the oil and water remain separated in coherent domains that are quite small; typically of the order of tens or hundreds of Angstroms in size. Because the surfactant molecules prefer the water-oil interface over bulk oil or water environments, they create an extensive oil-water interface inside the bulk phase. Moreover, due to their small droplet size, microemulsions are believed to be thermodynamically stable.

For many years, microemulsions were studied especially with regards to their phase diagrams (Shinoda and Saito (1968), Robbins (1977)). For a review see Mittal (1977), Mittal and Lindman (1984) and (1987). More recently, experiments probing structural and physical behavior have been performed. For a review on these newer experimental techniques see, e.g., Safran and Clark (1987), Meunier et al (1987). More microscopic investigations involve light, X-ray and neutron scattering (Huang et al (1983), Auvray et al (1984)) and quenched freezing electron microscopy (Jahn and Strey (1987)). Experimentally, it has been observed that the configuration of the oil and water domains varies with the relative composition of water, oil and surfactant. For small fractions of oil in water or water in oil, the structure is that of compact globules (Calje et al (1977), Robbins (1977), Ober and Taupin (1980), Roux et al (1984), Huang et al (1983), Kotlarchyk et al (1984)). However, when the volume fractions of oil and water become comparable, one expect random bicontinuous structure to form (Scriven (1977), Auvray et al (1984), Kaler et al (1983), Talmon and Prager (1978) and (1982), Cazabat et al (1982)). Under other conditions, for example, when the volume fraction of the surfactant is higher than a few percent, various ordered structures reminiscence of liquid-crystalline phases may also arise (Ekwald (1975), Bellocq and Roux (1986), Smith (1984)). Those are phases such as cubic, lamellar or cylindrical and show Bragg peaks in scattering experiments.

Microemulsion phases exist as single phases or coexist with excess water, excess oil or both. We will not discuss here more complicated multiphase coexistences. Of particular interest is the so-called middle-phase microemulsion where the microemulsion phase coexists simultaneously with both excess water and oil. In such situations the liquid/liquid interfacial tension is ultralow: $10^{-3} - 10^{-5}$

dynes/cm (Saito and Shinoda (1970), Ruckenstein and Chi (1975), Guest and Langevin (1986)). The middle-phase microemulsion can be used in applications like chemically enhanced oil recovery (Shah (1981)). Temperature, salinity and the cosurfactant (alcohol) also play an important role in the relative stability of one phase with respect to the others and the global extent of the coexistence regions (Cazabat and Langevin (1981), Mittal and Lindman (1984), (1987), Safran and Clark (1987)).

Theoretically, the most challenging problems are the ones related to the interplay between structural properties and macroscopical phase behavior. In addition, it is highly desired both from basic and applied point of views to understand the influence of external controlled parameters such as temperature, salinity, and cosurfactant concentration on micro- and macroscopical properties. Two different theoretical approaches have been proposed to predict phase diagrams and structure. The first one is the so-called "phenomenological" approach where the surfactant interfaces are considered as independent entities. Those interfaces separating regions of oil and water are characterized by model dependent energetics. In most of the proposed models, each fluctuating interface is characterized by interfacial and curvature energies. Since the characteristic length scales are much bigger than molecular sizes, a continuum approximation that depends on several parameters can be made. For microemulsion phases of compact globules (spheres or cylinders), in the very dilute limit (e.g., a small volume fraction of water in oil), the stability, phase diagram and fluctuations of such objects have been calculated (Huh (1979), (1984), Safran and Turkevich (1983), Safran et al (1984), Roux and Coulon (1986)). In some cases globule-globule interactions have been considered as well. For cylindrical phases, fluctuations can be treated similarly to the case of semi-flexible polymers in solution (Safran and Turkevich (1983), Safran et al (1984)).

However, no doubt that the phase which is the most difficult to understand from first principles is the bicontinuous phase, since it is composed of an ensemble of random fluctuating surfactant interfaces separating coherent regions of oil and water on length scales of many individual molecules. The first attempt to deal with the bicontinuous phase from a thermodynamical point of view has been proposed by Talmon and Prager (1978) and (1982). Later works developed more refined models predicting phase diagrams of bicontinuous phases (Jouffroy et al (1982), Widom (1984), Safran et al (1986) and (1987), Andelman et al (1987b)). Most of these works have considered the surfactant film as a two-dimensional fluid whose energy is mainly determined by its curvature coefficient and spontaneous radius of curvature. In one case (Widom (1984)), the film has been treated as a compressible two-dimensional fluid of surfactant molecules. The stability of the macroscopic phase depends on the delicate balance between the configurational energy (interfacial and curvature) and the entropy of such fluctuating interfaces. The free-energy that determines the phase behavior is calculated within mean-field approximation and in some works (Andelman et al (1987b), Safran et al (1986), (1987)) the size-dependent bending (curvature) coefficient (Helfrich (1973), (1978), (1985) and (1987)) is taken explicitly into account. Some results exist already on the influence of temperature, salinity and cosurfactant on the phase behavior but only in an indirect way. It is thought that salinity and cosurfactant influence the bending constant and the spontaneous radius of curvature (deGennes and Taupin (1984)). Calculations of phase behavior as function of the latter two parameters exist (Cates et al (1988)), but the actual dependence of those parameters on the experimentally controlled variables: salinity, cosurfactant and temperature is not presently known in a more quantitative way.

Scattering and quenched freezing microscopy of the random bicontinuous microemulsion support the generally believed picture of the structure of this phase (Auvray et al (1984), Jahn and Strey (1987)). Theoretical calculations of the structure factor of the bicontinuous phase have been done either starting from a purely geometrical construction of the bicontinuous phase (Zemb et al (1987), Teubner and Strey (1987), Berk (1987), Vonk et al (1988)) or by calculating the fluctuations around the mean-field free energy used for the phase diagram (Milner et al (1988), Widom (to be published)).

We briefly mention the other theoretical approach of calculating phase diagrams of microemulsion. The starting point here is to introduce a lattice model for the three component liquid mixture: water, oil, and surfactant (Wheeler and Widom (1968), Widom (1986), Schick and Shih (1986), Chen et al (1987)). Interactions between single molecules are introduced and the amphiphilicity of the surfactant is simulated by introducing a preferred interaction of one surfactant molecules to have as its nearest neighbor an oil molecule from one side and a water molecule from the other side. In this way, the tendency of the surfactant molecule to form an interface between the oil and water is achieved. Further refinements of this microscopic spin model were introduced by considering longer-range interactions. Such an approach is suitable to the study of concentrated surfactant solutions where ordered phases are formed. For surfactant that are partially miscible in the two solvents, thus having a poor amphiphilicity, such an approach is based on a generalized three-component liquid mixture model. However, for bicontinuous phases of surfactants that are quite immiscible in both solvents, it is very difficult to obtain structural information on mesoscopic length scales starting from such a microscopical model although these models give a possible explanation for the ultralow surface tension and predict phase diagrams that capture some of the features of the middle-phase microemulsion.

In this short contribution we summarized current research interests in microemulsions and Langmuir monolayers. Emphasis have been put on the more microscopical and physical approach exploring the connection between phase transitions and structure. We hope that recent advances in experimental techniques will induce more theoretical investigations of these systems. As is discussed in more details by the other contributors to these proceedings, the physics of fluctuating membranes and interfaces is quite interesting and novel from a theoretical point of view. Hopefully, those novel ideas will be applied in the future to more specific, and in some sense more complicated, amphiphilic systems as the ones mentioned here.

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