Microstructure of Bicontinuous Phases in Surfactant Systems

Ian S. Barnes

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This thesis is the result of research carried out in the Department of Applied Mathematics at the Australian National University, the Département des Lasers et de Physico-Chimie of the French Commissariat à l’Energie Atomique at Saclay and at the Chemical Centre at the University of Lund in Sweden between March 1986 and March 1990.

Much of this work is the product of collaborations. The one-dimensional fluid analysis in Chapter 1 was done with John Mitchell. The models presented in Chapter 3 were developed jointly with Stephen Hyde, Barry Ninham and Thomas Zemb. The X-ray scattering work of Chapter 4 was done jointly with Thomas Zemb and with Paul-Joël Derian and Greg Warr. Thomas and Paul-Joël did the neutron scattering. The X-ray scattering experiments for Chapter 5 were done with Thomas Zemb, while Mario Corti and Vittorio Degiorgio did the neutron scattering. Barry Ninham told me about θ-functions for Chapter 6. The phase diagram work of Appendix A was done with Krister Fontell, and with the assistance of Tuck Wong and Ulf Olsson who ran NMR on my samples.

The work presented here is, however, my own. None of it has been submitted to any other institution for any degree.

Ian Barnes

Ian S. Barnes
Canberra
23 March 1990
Abstract

A geometric approach to microemulsions and other phases in surfactant systems is presented. The basic premise is that the behaviour of these systems is dominated by geometric constraints on microstructure. The utility of this approach is first demonstrated for the one-dimensional fluid, for which the statistical mechanics can be solved analytically, before being applied to more realistic but complex systems.

Small-angle X-ray and neutron scattering techniques are used to obtain structural information. A numerical method for calculating theoretical scattering curves from arbitrary models is presented. The importance of the real-space correlation function is emphasised, and it is used to obtain a plot of the scale dependence of the internal surface. A new technique is proposed for the division of two spectra from the same sample measured at different contrasts, which eliminates the underlying lattice and gives sensitive local information.

Two new geometric models for microemulsions are presented: a structure of interconnected cylinders and one of folded connected lamellae. It is shown that these models succeed where all others fail, in explaining the behaviour of the isotropic liquid phases found in ternary systems containing the double-chained cationic surfactant didodecyldimethylammonium bromide. This approach is also applied to two nonionic polyoxyethylene surfactant binary systems.

Similar methods are also applied to cubic liquid crystalline phases. It is shown by a simple calculation that the scattering from such structures is very sensitive to small changes. Certain of these structures are thought to follow periodic minimal surfaces. Approximations to these are investigated and in particular it is shown that periodic equipotential surfaces and periodic minimal surfaces with the same symmetry and topology are not necessarily identical.
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