

Colloid chemistry

Applications of microemulsions

from B.H. Robinson

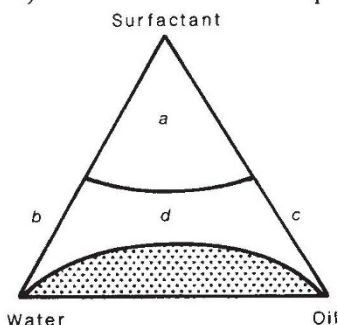
It is well known that oil and water do not mix. However, if a chemical dispersing agent, known variously as a surface-active agent, surfactant or detergent, is added then a 'microemulsion' liquid dispersion may well form. The surfactant, located at the interface between the two phases, dramatically lowers the oil-water interfacial tension. The dispersions are optically transparent and are generally thought to be thermodynamically stable. Until recently, physicists and physical chemists interested in the properties of the liquid state did not regard such systems worth serious study, believing that they were far too complex and irreproducible in their behaviour. But this situation is now changing rapidly and microemulsions are attracting wide interest in both industrial and academic research laboratories. On page 338 of this issue¹, and in a preceding paper², J. Tabony reports the results of a structural study of a surfactant-stabilized dispersion containing equal volumes of oil and water that indicates the presence of well-defined structural domains.

Most experimentalists have avoided the composition region in the middle of the triangular phase diagram (see figure), favouring the simpler 'precursor' systems along the water-oil and oil-surfactant sides of the triangle. In the absence of oil, surfactants spontaneously self-organize in water at low concentrations to form micelles, and as the surfactant concentration is increased, a variety of lyotropic liquid crystalline structures are formed. These soap-water systems are of great importance in detergency and are now quite well understood. In a similar way, certain surfactants, including phospholipids, form inverted micelles, which can readily take up water to form microstructural domains in which water is dispersed in oil in the form of essentially monodisperse aqueous droplets. Their size can be precisely controlled by varying the amounts of water and surfactant. In contrast, previous studies in the composition region (*d* of the figure) suggest the existence of open 'bicontinuous' sponge-like structures in which the surfactant forms an interface of rapidly fluctuating curvature but in which the net curvature (time- or space-averaged) is near zero³.

The results reported by Tabony in this issue were obtained using one of a range of neutron-scattering instruments which are available for structural and dynamic studies at the Institute Laue Langevin, Grenoble. Much new information on size, structure and motion of a whole range of colloidal dispersions is now becoming

available as a result of the successful exploitation of the Grenoble facility, and research will continue also at the pulsed-neutron source in the UK.

Neutrons are particularly useful for studies on liquid dispersions because the method of contrast variation (selective deuterium labelling of a component of the system) can reveal the internal structure of an individual droplet and motions of particular components. The accessible wavelength range is such that inter-droplet interactions are also readily studied using small-angle scattering methods⁴. Molecular motions on a very short (nanosecond) timescale can also be probed



Schematic triangular phase diagram of an oil-water-surfactant system. Shaded region, water-oil immiscibility region (2-phase); *a*, liquid-crystalline phases; *b*, micelles in aqueous solution; *c*, reversed-micelles in oil; *d*, concentrated single-phase microemulsion domain.

using inelastic scattering techniques.

Many detailed triangular phase diagrams for a range of surfactants are already available (for example, ref. 5) and furthermore, water can be substituted by several other polar solvents, for example, glycerol and formamide. Theoretical papers have stressed the importance of the shape of the surfactant molecule (and its natural curvature when adsorbed at the oil-water interface) in influencing the structures which form⁶, so we can now predict structures more effectively.

Why is industry interested in such microemulsions? There are a number of reasons. For example, the oil industry is keen in the longer term to exploit surfactant-enhanced tertiary oil recovery methods for which rheological properties of the microemulsion are important, and to explore the possibilities of gasoline substitutes based on liquid blends with alcohol. There are obvious applications in the food and cosmetics industries, particularly using phospholipid surfactants. Single component thermotropic (low molar mass) liquid crystals have already found wide application as electro-optic

display devices in watches and calculators. Applications of the lyotropic analogues, based on surfactant-water systems, have not been so forthcoming but the extra dimension introduced by the oil component produces a rich diversity of structures with potentially interesting rheological and electrical properties. Characterization of structure and interactions at the molecular level is the first step towards the exploitation of such new materials.

The possibility of precisely controlling the size and stability of the microstructure domains suggests interesting applications for liquid-membrane technology, and the compartmentalized liquid structures of high surface area provided by the oil-water dispersions suggest their use as a novel and versatile medium for chemical synthesis. The potential in this field is indicated in a recent review on enzyme processes in microemulsions⁷. Enzymes retain their activity in such dispersions and in an oil-rich medium the thermodynamic equilibrium of reactions is shifted in such a way that the possibility exists for catalysing reactions in the reverse direction to that favoured in aqueous solution, a process known as reverse enzyme synthesis. In this way, esters can be synthesized rapidly under mild conditions from carboxylic acids and alcohols, or oligopeptides can be prepared from amino acids.

Another potential use of the fluid but structured microdomains of the type reported by Tabony is in the preparation of microscopic particles of a desired size or shape reflecting the structure within the liquid dispersion. Small spherical metallic particles of, for example, platinum⁸ and cobalt boride have already been prepared successfully in water-oil microemulsion systems using this approach and the preparation of particles of other shapes should be possible in microemulsions which have a long-lived non-spherical microstructure. Such particles show catalytic activity in selective hydrogenation reactions⁹. J.H. Fendler has stressed the wide range of chemical processes, such as artificial photosynthesis, that may be facilitated by reaction at interfaces¹⁰. Microemulsions and the so-called 'liquid crystal microemulsions' as described by Tabony look to have considerable potential for exploitation in the near future. □

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