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MICROEMULSIONS AND COLLOIDS

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I - The Colloidal state of matter

Colloidal systems can be defined by the fact that a large fraction of matter is located in the surface region. An equivalent definition is to focus on the ratio of volume to surface of the sample which determines a length which is characteristic of the degree of dispersion in the system.

The first point of view is useful when considering the anomalous properties of matter at the surface boundary which could be predominant in colloidal systems in contrast to the usual case of bulk material where their relative effects on the properties of the whole system are negligible. The second approach is mainly centered on the existence of small particles of one phase dispersed in another phase. Many examples exist in nature : sols, smokes which are solid particles suspended respectively in a liquid or gazeous phase, emulsions which are dispersions of liquids. Since the particles are caracterized by a surface Gibbs energy, these systems are thermodynamically unstable, and they undergo a spontaneous reduction of the surface by recrystallization (aging) or coalescence in the case of liquid droplets. Also particle aggregation (flocculation) may occur in the course of time. In fact these systems are very often in a metastable state since some special state of the surface (presence of electrical charges or adsorbed macromolecules) prevent the attractive Van der Waals forces between the particles to induce irreversible aggregation of the particles.

The definition of the colloidal scale is not very precise ; one usually says that the colloidal particle should be large enough to have some global average characteristics and at the same time small enough to be subjected to Brownian motion which prevents spontaneous sedimentation. This leads the colloidal sizes to extend from several tens of Ångström to one micron.

This large size leads to some characteristic quantitative differences in solution properties and corresponding shifts in experimental techniques for studying them as compared to more conventional solutions of small molecules.

Independently from their technological importance, colloidal systems are presently the object of an intense scientific activity since they are unique systems for the study of interactions which are of the order of kT in the intermediate range of distances about several hundreds of Ångström. In that respect, the scale of size is more important than the chemical nature of the particles (this is the case for the mechanical properties of colloidal crystals).

II - Microemulsions

Microemulsions are very minute dispersions of one liquid in another (i.e. water and oil) ; their main difference with the ordinary emulsions resides in the typical size of 100 Å instead of ten microns, which explains their almost complete transparency to visible light. Moreover, they are of low viscosity which is of technical interest. Without entering the details of their chemical composition which could be very complex, one can consider three different phases : oil and water (each of them being either continuous or dispersed) and an interfacial film made up of special molecules. These molecules (named "surfactants") adsorb spontaneously at interfaces and separate the oily and aqueous phases, thus decreasing the surface Gibbs energy.

Microemulsions raised a great interest in the recent past years due to their possible use in oil recovery and the results of numerous structural studies emphasized their aspect of model colloids : the liquid particles are well-defined spheres, the radius of which being determined by the amount of surfactant molecules. A precise description of the interfacial film was obtained[1].

Microemulsions behave as liquid dispersions[2,3] : the osmotic compressibility is in some cases identical to that of a hard-sphere liquid ; in other cases, Van der Waals attraction occurs as a perturbing term of the equation of state.

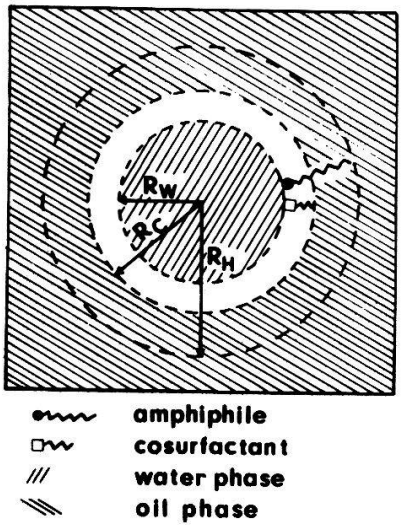

Figure 1 : structure of the interfacial film : R_w, radius of the water core ; R_H, hydrodynamic radius (radius of a moving droplet as seen in viscosity and centrifugation experiments) ; R_c corresponds to the discontinuity in chemical composition due to the limit of penetration of the oil in the film. R_c also determines the hard-sphere radius.

Most of these conclusions were drawn from measurements such as static scattering of light or neutrons. Some problems appeared in the consistency of the results when comparing with dynamical measurements such as quasi-elastic light scattering. The Einstein relationship which relates the intensity of scattered light, the sedimentation coefficient and the diffusion coefficient, is not verified for microemulsions[4]. Moreover measurements of diffusion coefficients by spin-echo NMR technique give values which are too high for large droplets[5,6].

Another experiment shows both the validity and the limits of the "droplet model" of microemulsions. Measurements of low-frequency (600 Hz) electrical conductivity performed in a microemulsion exhibit an increase of almost four decades within a few per cent near a thereshold concentration[7]. Quantitative analysis indicates a percolation mechanism due to an infinite aggregate of droplets at a certain concentration (ϕ_c) which is clearly distinct from the structural inversion (ϕ_p) corresponding to water in oil → oil in water droplets.

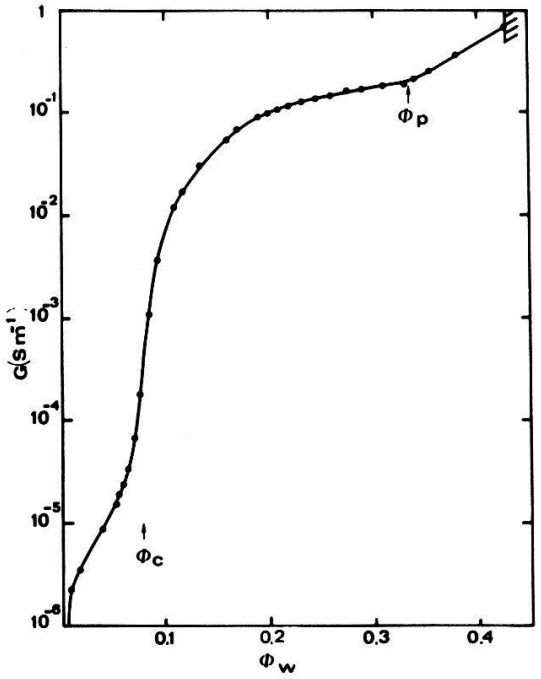

Figure 2 : variation of the conductivity of a microemulsion (logarithmic plot) versus water concentration.

Nevertheless the mechanism of electrical conduction between aqueous droplets surrounded by the insulating interfacial film is not clear. In fact, different experiments indicate a fast exchange of internal constituents of droplets which could be represented by Figure 3.

This model of the structure of microemulsion is clearly not the only one, and the existence of well-defined objects has be denied and intermediate structures were proposed (Figure 4).

At that point, leaving the particle point of view, we switch back to the first definition of colloidal systems which emphasizes the role of the interface. The interfacial film of microemulsions has two main characteristics as compared to the well-known lyotropic liquid-crystal systems : it promotes almost zero interfacial tension between the two immiscible liquids (oil and water) and is highly flexible[9]. A variety of structures could thus be explained.

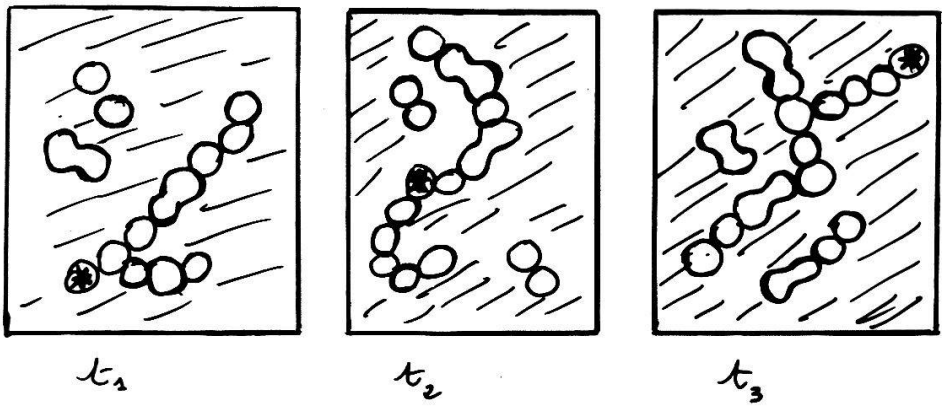

Figure 3 : schematic representation of the evolution with time ($t_3 > t_2 > t_1$) of the droplets of a microemulsion. The star represents the labelled molecule under study.

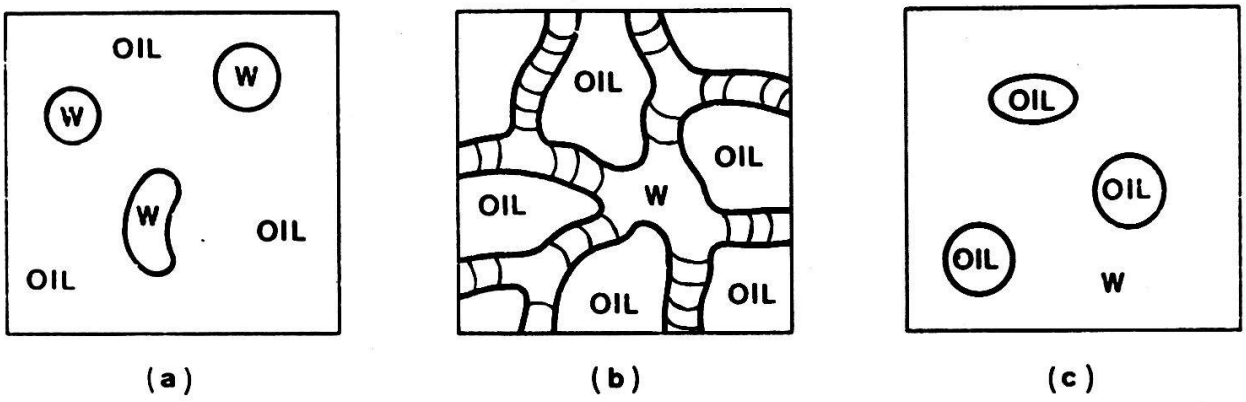

Figure 4 : schematic representation of bicontinuous structures, first proposed by Scriven.

The existence of the ultra-low interfacial tensions which are measured in particular microemulsions led to a new point of view which distinguishes them from other colloids. It has been shown than interfacial tensions and phase-volume diagrams can be interpreted in terms of the modern theory of critical phenomena[10].

As a conclusion, microemulsions are fascinating systems. They have in common many macroscopic physical properties such as transparency, fluidity but, depending on the particular chemical composition, various structural facets appear. They go from true particulated colloids, to systems in dynamical exchange, and for some cases, to critical mixtures which put them in continuity to true solutions.

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