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Existence of a bicontinuous zone in microemulsion systems (*)

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Résumé. — L'interprétation conjointe d'expériences d'auto-diffusion et de conductivité montre qu'il existe, dans le domaine isotrope des microémulsions, une zone à caractère continu aussi bien pour la partie huileuse que la partie aqueuse. Sa délimitation est liée de manière importante, mais non unique, à la fraction volumique d'eau du système.

Abstract. — The interpretation of self-diffusion and conductivity studies shows the existence of a zone within the isotropic microemulsion domain, where the aqueous and oily phase are both continuous. The boundary of this zone is strongly but not uniquely related to the water volume fraction of the system.

1. Introduction. — The microstructure of the isotropic phase (usually called microemulsion) in complex surfactant systems (hydrocarbon-water-surfactant-alcohol) has been mainly studied in the regions rich in water or rich in oil [1, 2]. Light spectroscopy [3, 4] and small angle X-ray or neutron scattering [5, 6, 7] are usually interpreted in terms of droplets dispersed in a continuous medium. As the ratio oil/water is increased, some systems go from a direct (O/W) structure through a liquid crystalline phase to an inverted (W/O) structure [8, 9]. Some other systems present a continuous isotropic zone [10, 11]. The structure of the concentrated middle zone is still speculative. Self-diffusion and conductivity studies have been undertaken to gain insight into this region of the diagram.

2. Experimental methods and results. — The system chosen is decane/water/sodium p-octylbenzene sulfonate (OBS)/1-pentanol/sodium chloride. This last component was maintained at 0.3 wt. % with respect to water, so as to give a large homogeneous zone in the diagram. The studies reported here pertain to a constant ratio of the alcohol (CTA) to the surfactant (TA) of 2.1 by weight. The origin or methods of preparation of the products have been already detailed [12].

The open-ended capillary tube method using radioactive labelling was used for self-diffusion and has been described in reference [12]. The labelled atoms

were ^{22}Na , ^{36}Cl , ^{35}S , ^3H and ^{14}C . Data were taken at 25 ± 0.1 °C. Conductivity was measured at the same temperature at 4.0 kHz with a Leeds and Northrup admittance bridge.

Measurements of the diffusion coefficients of the surfactant D_s , the decane D_D , the water D_w , the sodium D_{Na} and the chlorine D_{Cl} as well as the conductivities were taken along the lines represented (Fig. 1) on a pseudo-ternary diagram. The results are plotted

Fig. 1. — The isotropic homogeneous zone of the pseudoternary diagram decane/water + 0.3 wt. % NaCl/1-pentanol/sodium p-octylbenzene sulfonate at CTA/TA = 2.1 by weight. Investigations were made along AA', BB', CC', DD', EE' and FF'.

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Fig. 2. — Self-diffusion coefficients along AA' as a function of the volume fraction of water. Decane- Δ -; water- $\blacktriangle$ -; sodium-O-; chlorine-+-; OBS $\bullet$.

Fig. 4. — Conductivity along AA' (O) and EE' ($\bullet$) as a function of the volume fraction of water. In the left upper corner, expended low water content part of AA'. The curves intersect at Φ slightly different that EE' and AA' on figure 1. This is probably due to uncertainty on the composition of the base solutions.

Fig. 3. — Self-diffusion coefficients along FF' as a function of the volume fraction of water. Same symbols as in figure 2.

on figures 2 to 7 as a function of the volume fraction of water Φ . This last quantity was computed taking as densities ($10^{-3} \text{ kg.m}^{-3}$) : 1.001 for water plus sodium chloride, 0.73 for decane, 0.8144 for pentanol [13], 1.11 for OBS [6] and assuming additivity of the volumes. Measurements of the density of the solution [11] and calculation of Φ assuming that only NaCl is dissolved in water yields a value differing only by 2 to 3 %.

Fig. 5. — Self-diffusion coefficients D_s ($\bullet$), D_{Na} (O) and D_D (Δ) along BB' as a function of the volume fraction of water Φ . The Φ scale is twice as large on figures 4, 5 and 6 as on figure 2.

Fig. 6. — Self-diffusion coefficients D_S (●), D_{Na} (○) and D_D (△) along CC' as a function of the volume fraction of water.

Fig. 7. — Self-diffusion coefficients D_S (●), D_{Na} (○) and D_D (△) along DD' as a function of the volume fraction of water.

3. Discussion. — The discussion is centred on the structural implications of the data presented. Let us note first that the various measured quantities are all apparent quantities. They depend on the geometrical arrangement in space of the aqueous and the oily part of the microemulsion, as well as on the properties specific to each of these media. The diffusion coefficient of decane for instance depends on the geometry of the oil rich *phase* as well as on its composition.

At high water volume fraction, the water is expected

to be continuous, and the decane in the form of droplets surrounded by the surfactant, the pentanol being partitioned mainly between this interface and the decane. With such structure, the self-diffusion coefficients D_S and D_D should be about equal. This is found toward point F (Fig. 3) and small-angle neutron scattering has shown that, at this point, we are indeed in the presence of a O/W microemulsion [15]. The contribution of OBS dissolved in water to D_S is certainly small and would tend to increase this coefficient (at the c.m.c. D_S has the value

$$6.15 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1} [14]).$$

The fact that D_S shows very little variation throughout the composition field investigated is an indication that the previous effect is insignificant.

At low water volume fraction, one expects W/O microemulsions which are identical to inverse micellar solutions [16]. With such a structure, D_{Na} and D_{Cl} would be equal to D_S . This is observed near A'.

At intermediate volume fraction of water, all diffusion coefficients are above D_S . This is not compatible with structures where one of the *phases* is totally enclosed in the other. The increase in conductivity between $\Phi \sim 12$ and 20 % water seems to indicate for instance that the water structure opens up. Whether the two *phases* are completely interconnected cannot be proved. However the linearity of λ with Φ along AA' between 20 and 40 % suggest that this might be true for water. As far as the instantaneous structure is concerned, these microemulsions could be compared to porous media or phase separated glasses [17-19]. Since the diffusion coefficient of decane in decane pentanol mixtures is not known, nor the partition coefficient of pentanol between the decane and the interface, such a model cannot be used to evaluate the apparent diffusion coefficient of the decane and compare these values with the experimental ones. But it is clear that there is no sudden inversion from a W/O to a O/W microemulsion along lines like AA'.

This transition region, characterized by continuous paths for oil and water, has been called bicontinuous [20]. Its extension can be very approximatively sketched on the basis of diffusion data, in particular D_{Na} . For instance BB' does not enter this region, DD' lies probably in it, CC' is a border case, AA' and EE' cross it.

All the data presented suggest that the limit of the full bicontinuous region does not follow a constant Φ line. This would be in agreement with calorimetric data on other microemulsions systems [21]. Note also that D_D has different values at the same Φ . This probably indicates a strong influence of the alcohol content in the oily phase.

Let us note also that the value of D_w at the lowest Φ along AA' may not be quite representative of the water diffusion, since it is known that there is proton exchange between pentanol and water [22]. The water dissolved in the decane could also contribute to D_w .

An evaluation made by the method of Graciaa *et al.* [23] along the two phases equilibrium line indicates that the water content is about 2.5 wt. % of the pentanol content. This water being associated with the alcohol has probably a self-diffusion coefficient much lower than it has in pure water (table I). Therefore, it cannot participate significantly in the increase found along AA'.

Table I. — *Reference self-diffusion coefficients* ($10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$).

D_D in pure decane	D_W in pure water	D_{Na} in water containing 0.3 wt. % NaCl [14]	D_S at the c.m.c. ($1.28 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$) [14]
13.1	22.5	12.8	6.15

4. **Conclusions.** — Self-diffusion and conductivity measurements along various lines of a pseudo-ternary

diagram oil-water-surfactant-alcohol show that the solutions in the homogeneous region (microemulsion) can exist under very different structures. For the particular system studied a bicontinuous structure seems to exist at water volume fraction between ~ 16 and 40 %. This type of two phases structure separated by an extended interfacial structure has been suggested by Adamson [24] and Scriven [20]. In the whole domain of investigation, there is no inversion of the structure contrary to what has been proposed for others systems [7]. The path from W/O to O/W microemulsions seems to cross necessarily an extended bicontinuous zone. Its boundaries are strongly related to the water volume fraction of the solutions but depend however on other factors. Their determination is certainly a prerequisite for further physico-chemical studies of these systems.

There are also suggestions that structures different from direct, inverted or bicontinuous exist in this *homogeneous* zone. Investigation along this lines are in progress.

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