117. The Formulation of Four-Components Practically Perfluorinated Microemulsions

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(14.III.83)

Summary

Microheterogeneous systems consisting of sodium perfluorooctanoate (**1**), 2,2,3,3,4,4,4-heptafluoro-1-butanol (**2**), perfluorohexane (**3**) and water, representing the first practically perfluorinated microemulsions based on ionic surfactants have been formulated. A pseudoternary phase diagram shows a central region of turbid or transparent gels and two regions of monophasic systems (O/W- and W/O-microemulsions) which have been characterized by NMR. spectroscopy.

Microemulsions are fluid, transparent and thermodynamically stable microheterogeneous systems which are formed spontaneously by adding suitable surfactants to an otherwise non-miscible mixture of water and oil (hydrocarbon) (*e.g.* [1]). These systems are of great interest in both fundamental research and technical applications (*e.g.* biotechnology, polymerization, tertiary oil recovery). As surfactants, nonionic amphiphiles of the polyoxyethylene-type as well as ionic compounds with an aliphatic tail (*e.g.* potassium oleate, sodium lauryl sulfate (SLS)) are used, the latter combined with a cosurfactant (alcohol).

Fluorocarbon surfactants have also received some attention as emulsifiers in technical applications (polishes, wetting agents *etc.*) and as possible microemulsifying agents for artificial blood. However, to our knowledge, we report for the first time the formulation of four-components practically perfluorinated microemulsions.

The system studied is a quaternary mixture of sodium perfluorooctanoate (**1**; surfactant), 2,2,3,3,4,4,4-heptafluoro-1-butanol (**2**; cosurfactant), perfluorohexane (**3**; oil) and water[2]). We chose **1** as surfactant which is known to form normal micellar solutions when dissolved in water at room temperature (critical micellar concentration (CMC) = 3.1×10^{-2} mol/l [2]).

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[2]) **2** and **3** are perfectly miscible but are both insoluble in H_2O.

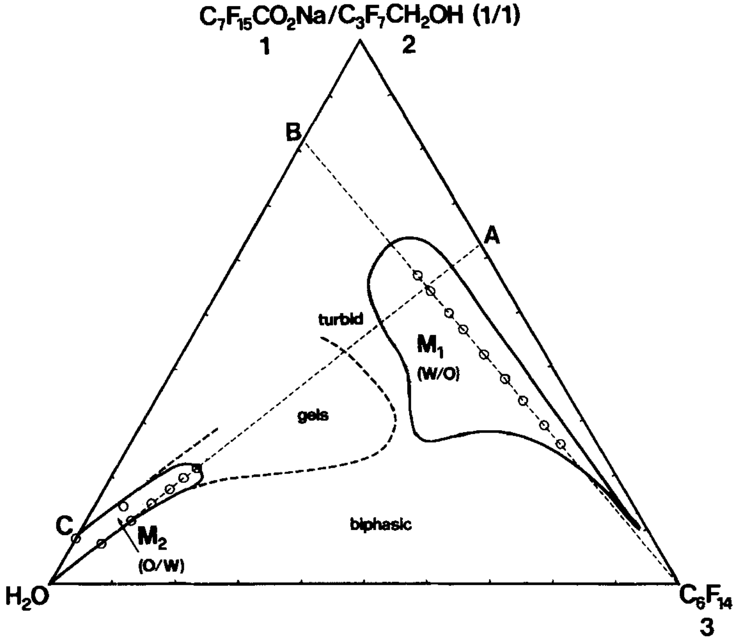

Fig. 1. *Pseudoternary phase diagram of the system* $C_7F_{15}CO_2Na$ (**1**)/$C_3F_7CH_2OH$ (**2**)/C_6F_{14} (**3**)/H_2O *in weight percent at 23°* (**1**/**2** weight (molar) ratio of 1:1 (1:2.2). M_1 and M_2 are the regions of the respective W/O- and O/W-microemulsions. Other areas of the diagram consist of heterogeneous non-miscible mixtures, of milky macroemulsions separating into two phases on standing or of transparent or more or less turbid gels)

Figure 1 shows the pseudoternary phase diagram[3]) for a constant surfactant/cosurfactant weight ratio of 1:1. The limits of the phase regions have been determined for the composition range of interest. Phase mapping has been done in following the general procedure of observing changes of the macroscopic properties (transparency and viscosity) of the system at room temperature. The corresponding experimental procedure implies the titration of different mixtures of **1**, **2** and **3** with water as well as of different mixtures of **1**, **2** and water with **3** [1b].

Two separated areas of transparent, fluid, monophasic systems, M_1 and M_2, have been found: they correspond qualitatively to the two classical types of microemulsions, usually described as stable dispersions of microdroplets of water in oil (W/O) at low water content and of microdroplets of oil in water (O/W) at low oil content, stabilized by an interfacial mixed film of surfactant and cosurfactant. Their transparency indicates a droplet size of about or smaller than 10 nm. Upon ultracentrifugation of several samples of M_1 and M_2, no separation or stratification occurs, and their long term stability has been tested over several months. The conductivity of M_1- and M_2-systems located along the axis A-H_2O *(Fig. 1)* varies similarly to that of the perhydrogenated microemulsions consisting of water/SLS/1-butanol/cyclohexane [4a].

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[3]) Pseudoternary phase diagrams are very convenient and widely used to picture microemulsions and related structures [1b] [3].

The results of transparency, viscosity and conductivity measurements, the observed stability on standing and upon ultracentrifugation, the spontaneous formation, as well as the location of the M_1- and M_2-systems in the phase diagram with respect to the location of known perhydrogenated microemulsions are strong evidence that M_1- and M_2-systems might be microemulsions. This interpretation is supported by the NMR. data given below and we will therefore refer to the two systems as M_1 (W/O) and M_2 (O/W) microemulsions.

The M_1-region (W/O) extends along the surfactant/cosurfactant-oil axis, shrinking towards the oil apex; all the M_1-microemulsions are fluid, non foaming liquids. By progressive addition of water, some W/O-microemulsions can invert into fluid O/W-microemulsions, passing through a turbid stage, then through more viscous, transparent or opalescent gels (*e.g.* axis A-H_2O, *Fig. 1*).

The M_2-region (O/W) is small, and corresponding microemulsions contain at least 70% (weight) of water. Close to the water apex (≥90% water), ternary monophasic systems without oil, alcohol 'swollen' micelles, are formed.

The results of ^{1}H-NMR. spectroscopic investigations comply with the presence of molecular organizates in the systems M_1 and M_2. Microemulsions along the axis B-3 of the M_1-region, along the axis A-H_2O of the M_2-region and the ternary mixture C *(Fig. 1)* have been prepared with D_2O and consequently leave but two signals for the remaining protons of the α-methylene group (triplet, $J_{(CH_2-CF_2)} = 15$ Hz) and the OH-function (singlet) of alcohol **2**.

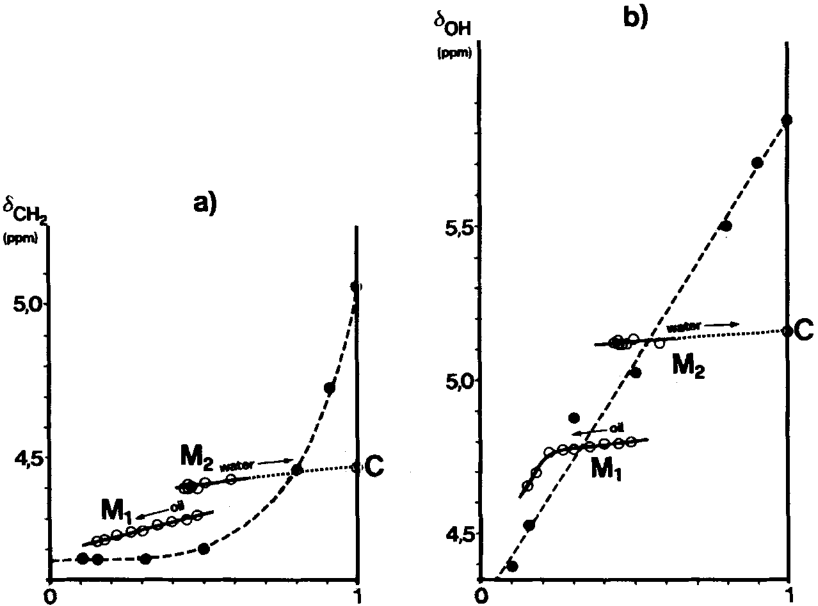

Fig. 2. *Chemical shifts (δ) of the α-CH_2* (Fig. 2a) *and of the OH-groups (Fig. 2b) of* **2** *as a function of the weight* **2**/(**2**+**3**) *in different M_1- and M_2-microemulsions* (——), *linked arbitrarily to the corresponding chemical shifts of the ternary mixture C* (·····) (M_1 microemulsions are located along the axis B-3, and M_2-microemulsions are mainly located along the axis A-H_2O (see *Fig. 1*). Chemical shifts of simple mixtures of **2** and **3** (- - -) are shown for comparison)

A series of measurements carried out on simple mixtures of **2** and **3** show that the chemical shifts of the CH_2-group (δ_{CH_2}) and the OH-group (δ_{OH}) depend strongly on the weight ratio **2**/**2**+**3** *(Fig. 2)*, indicating important aggregation effects for high concentrations of the alcohol **2**. In contrast, δ_{CH_2} measured for the M_1-, M_2- and C-systems mentioned above depend only slightly on the same weight ratio and consequently on their composition *(Fig. 2a)*; this result signals a predominant and practically invariable environment of the alcohol molecules, as expected in the presence of interfaces where the alcohol is mainly located. The same conclusion is drawn from measurements of the variation of δ_{OH} *(Fig. 2b)*. For M_2-microemulsions as well as for the ternary system C, a virtually constant δ_{OH} is found which must characterize the similar organization of their O/W-interfaces. The corresponding δ_{OH} of the M_1-microemulsions is different from that found for the M_2-systems but remains equally unchanged (until the ratio **2**/**2**+**3** drops below 0.2). The different δ_{OH}-values (and to a lesser extent the different δ_{CH_2}-values) picture the different organization of the W/O-interfaces, with respect to those of O/W-microemulsions. A key factor of the differences observed might be the interaction between the OH-groups at the interface and the bulk or dispersed aqueous phase.

The sudden drop of δ_{OH} for ratios **2**/**2**+**3** < 0.2 occurs for microemulsions located on the B-**3** axis close to the border region towards the oil apex *(Fig. 1)*. The concentration dependence observed is similar to that found in alcohol/oil mixtures and implies the dissolution of **2** in **3** to a large extent, **3** being the bulk phase; monodisperse-spheric-reversed micelles might not be found in this region, as already demonstrated for microemulsions of very low H_2O-content [4d] [5].

The microscopic polarity at micellar interfaces may be probed spectrophotometrically by pyridine *N*-oxide being located in all cases previously investigated at the interface [4b]. The corresponding Z-values [6] are in between those of the alcohol used as cosurfactant and of water. This classical analytic method is not very informative in this particular case of perfluorinated microheterogeneous systems, since the Z-values of **2** and H_2O have been found to be almost identical (93 and 93.5 kcal · mol^{-1}, respectively)[4].

Changes in temperature affect the thermodynamic stability of fluorinated W/O-microemulsions (M_2-systems) and phase separation may occur above *ca.* 40°[5].

The phase behaviour of the fluorinated systems investigated, exhibiting two discrete monophasic areas, is qualitatively similar to that of microemulsions made from potassium oleate and 1-hexanol [1b] [4c]. Since sodium perfluorooctanoate has a CMC [2] and a chain length closer to that of SLS, we would rather have expected but one monophasic area extending continuously from the oil side to the H_2O-side of the diagram [3] [8] as observed for systems such as H_2O/SLS/butanol/cyclohexane or benzene [4]. However, unlike 1-butanol, **2** is not soluble in H_2O; as a cosurfactant, **2** is strongly adsorbing at the interface and can only exchange with the oil phase, thus, producing more ordered interfaces than 1-butanol

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[4] Z-values are 93–94 kcal · mol^{-1} for both M_1- and M_2-microemulsions and 63.5 kcal · mol^{-1} for the perfluorinated oil **3**.

[5] For detailed investigations of the thermodynamic stability of perhydrogenated microemulsions in function of the temperature, see *e.g.* [7].

[9]. Consequently, more organized crystal-like structures at the central part of the diagram, where intermediate concentrations of H_2O and oil **3** are involved, are generated. The dimension of this intermediate region depends on the variation of the ratio surfactant/cosurfactant (**1/2**). Increasing the content of alcohol **2** to a weight (molar) ratios of 1:2 (1:4.4) and subsequently to 1:3.5 (1:7.8), the M_1-region is found to undergo small changes (*ca.* 10%) of its size at the limit towards the H_2O-apex. At the same time, the M_2-region is completely eliminated. For smaller concentrations of alcohol **2** (weight (molar) ratios of 1:0.5 (1:1.1) and 1:0.1 (1:0.22)), both regions of microemulsions are disappearing and only transparent ternary monophasic systems remain on the **1/2**-H_2O axis for $\geqq 70\%$ (weight) of H_2O. We assume therefore that we attain for both monophasic regions (M_1 and M_2) approximate maximum surfaces at weight (molar) ratio **1/2** of 1:1 (1:2.2).

Those results comply with earlier published rules, where a molar ratio surfactant/cosurfactant $\leqq 1$ is necessary in order to formulate a four components perhydrogenated W/O-microemulsions [1b] and where a corresponding molar ratio of 0.5 (2 alcohol molecules per surfactant molecule) is typically found at the interface of four-component microemulsions [9].

Similar phase diagrams are obtained when perfluorooctane is taken instead of **3**. But no microemulsions are formed when perhydrogenated oils or 1-butanol are used as substitutes of their fluorinated analogs.

This work is supported by the *Swiss National Science Foundation*. The authors would also like to thank Dr. *H. Barthelt* and *Hoechst Aktiengesellschaft* for providing them with some precious research samples.

Experimental. – *Material.* Sodium perfluorooctanoate (**1**) has been prepared from the corresponding carboxylic acid (perfluorooctanoic acid, *Fluka*) [2b]. 2,2,3,3,4,4,4-heptafluoro-1-butanol (**2**) (*Ventron GmbH*) and perfluorohexane (**3**) (*Riedel-De Haën AG*) were used as supplied. Pyridin *N*-oxide (*Fluka*) was recrystallized from petroleum ether. The quaternary mixtures (**1/2/3**/water) have been prepared with triply distilled H_2O at r.t. (22–23°).

Pseudoternary phase diagrams. The limits of the phase regions have been determined for constant **1/2** weight ratios (*e.g.* 1:1, *Fig. 1*), by either titrating different heterogeneous mixtures containing **1**, **2** and **3** with up to 90% of H_2O, or titrating different monophasic as well as heterogeneous mixtures containing **1**, **2** and H_2O with **3**. The diagrams have been drawn in weight percent.

^1H-NMR spectra have been recorded on a *Varian T-60* and a *Brucker FT W-80* spectrometer with TMS as external reference. A series of spectra has been obtained in the M_1-region by adding growing amounts of oil **3** (axis B-3, *Fig. 1*), and in the M_2-region by adding growing amounts of H_2O (axis A-water, *Fig. 1*). For this purpose, D_2O (99.9%) has been used for the preparation of the microemulsions and of the ternary mixture C. (The same phase diagram was obtained when D_2O was used instead of H_2O).

UV. spectra have been recorded on a *CARY 219* spectrophotometer. λ_{max} of pyridine *N*-oxide dissolved in the different solvents (**2**, **3**, H_2O) and in the microheterogeneous systems have been determined and used for the calculation of the corresponding Z-values [4b] [6].

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