Perfluorinated Surfactants at the Perfluoropolyether - Water Interface

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ilarities between micelles and electrodes [29]. Other work in progress in our laboratory tries to compare the hydrophilicity of metals and polar species. It is expected that, given the similarities, the theoretical improvements in our knowledge of one system will help to improve our understanding of the others.

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Perfluorinated Surfactants at the Perfluoropolyether–Water Interface

A. CHITTOFRATI[1], D. LENTI[1], A. SANGUINETI[1], M. VISCA[1]*, C. GAMBI[2], D. SENATRA[2] and ZHOU ZHEN[2,]**

[1] *Montefluos S.p.A. Colloid Laboratory, 15047 Spinetta Marengo (Italy)*
[2] *Physics Department, University of Florence, Largo E. Fermi 2, 15028, Arcetri, Florence (Italy)*

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ABSTRACT

Perfluoropolyether (PFPE) surfactants have been shown to be very effective in the solubilization of PFPE oils, allowing the preparation of a novel class of monophasic, clear, isotropic liquid systems that behave as true microemulsions. Short chain alcohols and fluorinated alcohols could be used as cosurfactants. When short chain hydrocarbon alcohols were used, O/W systems could be obtained. The effect of the alcohol was found to be a cosolvent for the fluorinated surfactant. Fluorinated alcohols, on the contrary, favoured a negative interfacial curvature, with preferred formation of W/O systems.

INTRODUCTION

Fluorocarbons (FC) are a class of compounds showing peculiar characteristics, including thermal, chemical and biological inertness, high permeability to gases, and low compatability with both aqueous and hydrocarbon based systems.

The high stiffness of the fluorocarbon chain, due to the presence of the bulky fluorine atoms, allows FC to be liquid only at very low molecular weights. At higher chain lengths, the FC prototype, polytetrafluoroethylene, is indeed a crystalline solid.

Studies on liquid perfluorocarbons, and on the interactions of FC with aqueous systems could be carried out, only in a limited range of molecular weights. Fluorocarbon microemulsions, for example, have been prepared in the presence of fluorinated surfactants, for applications such as blood substitutes, using low boiling point products like perfluoroheptane or perfluorodecaline [1–4].

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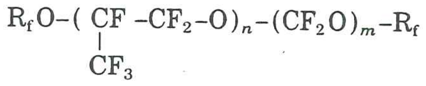
*To whom all correspondence should be addressed.
**On leave from Hubei University, People's Republic of China.

A higher degree of freedom in terms of molecular weight and temperature range of existence in the liquid state, without loss of the main properties of fluorocarbons, could be obtained using perfluoropolyethers.

Perfluoropolyethers (PFPE) are a class of fluorinated polymers having the general structure:



$$R_fO{-}(\underset{\substack{|\\ CF_3}}{CF}{-}CF_2{-}O)_n{-}(CF_2O)_m{-}R_f$$

where $n/m = 20–40$, in general, and R_f is a C1–C3 perfluorinated end group.

The presence of the ether bridges in the polymer chain allows the polymer molecules a high degree of conformational freedom, without significant loss in the fluorocarbon-like behaviour. Indeed, in the presence of the neighbouring fluorinated carbons the oxygen atoms do not retain any hydrophilic character. These polymers are characterized essentially by the same properties of conventional FC, and show furthermore a very wide range of existence in the liquid state, even at molecular weights as high as 10,000 or more, PFPE could be prepared industrially by UV photoinitiated oxidation of perfluoropropene at temperatures ranging between −40 and −80 °C [5].

As intermediates of the production process, functional products could be obtained, characterized by a single carboxylic end group.

The completely fluorinated and functional products, obtained from the industrial process, are in general polydispersed. However, monodispersed fractions could be obtained by distillation.

Functional PFPE, in the MW range 360 to 900 were found to be very effective surfactants.

The aim of the present work is the study of the PFPE–water interface, and if there are conditions of formation of PFPE microemulsions, in the presence of PFPE surfactants and fluorinated or hydrocarbon alcohols. Due to the many parameters involved and to the complexity of the system, only preliminary data will be presented, indicative of the fascinating research possibilities provided by a truly industrial system. More quantitative data will be the subject of a second publication [6].

EXPERIMENTAL

Materials

Galden PFPE fluids and Galden carboxylates were industrial, polydispersed products by Montefluos S.p.A., Milan, Italy.

Samples with narrow molecular weight distribution were prepared by distillation under reduced pressure.

The surfactants used in the present work were the ammonium salts of the PFPE carboxylates, and were prepared by neutralization of PFPE carboxylates with aqueous ammonia, and subsequent drying at 60 °C under vacuum for several days.

As the oil phase, a distilled industrial fraction of PFPE oil with an average molecular weight of 800 was used.

Fluorinated and hydrocarbon alcohols were of reagent purity, and water was deionized and doubly distilled in an all Pyrex apparatus.

The fluorinated alcohol, having a perfluoropolyether structure, was obtained by reduction of the carboxylic group to $-CH_2-OH$ with $NaBH_4$.

Procedures

Surface and interfacial tensions were determined at 25 °C by the Du Nouy ring method on a Kruss 110 tensiometer as a function of the surfactant concentration, allowing 30 min of equilibration time.

The solubilization limit of isotropic, monophasic region was determined by preparing samples of known composition in a series of test tubes.

After being left to equilibrate for 30 min at constant temperature the number and type of phases was noted and the samples were remixed and observed at another temperature.

This equilibration period was found to be sufficient for the determination of the type of phase equilibria, although true thermodynamic equilibrium may require a longer time.

The onset of phase separation was determined from the turbid, milky appearance of the system, while a bluish or translucent appearance was not considered as the onset of phase separation.

Birefringence was determined by viewing the sample through two cross polarized plates.

When clear, isotropic phases were found, reversibility towards phase separation induced by temperature changes, dependence upon the order of addition of components and centrifugation stability were checked.

RESULTS AND DISCUSSION

Surfactant–water system

A typical product of the industrial synthesis process is a mixture of PFPE acids having equivalent weights between 350 and 800, and an average equivalent weight (EW) of about 690. By distillation under reduced pressure, different fractions having narrower equivalent weight distribution (EWD), and even monodispersed products could be obtained.

The c.m.c. values of the surfactants depends upon the average EW and the polydispersity, as shown in Table 1. Samples S4 and S5 were two different

TABLE 1

Critical micellization concentrations at 25 °C of perfluoropolyether surfactants of different equivalent weights

	EW	c.m.c. (*M*)
S6	381	$3.0 \cdot 10^{-2}$
S1	528	$3.0 \cdot 10^{-3}$
S2	652	$6.0 \cdot 10^{-4}$
S5	685	$2.5 \cdot 10^{-4}$
S3	707	$4.0 \cdot 10^{-5}$
S4	711	$2.0 \cdot 10^{-4}$

TABLE 2

Interfacial tensions of PFPE surfactant solutions at 25 °C; PFPE, MW = 800

c/c.m.c.	Interfacial tension (mN m^{-1})	
	APFO	S6
0.1	11	7
0.5	5	1
1.0	1	near zero

polydispersed industrial batches, with standard deviations of the EW ≥50%. Samples S1, S2, S3 and S6 were obtained from sample S5, and were of narrow molecular weight distribution.

It is noticeable that there is very little difference between the c.m.c. values of samples S5 and S4, indicative of a levelling effect of the polydispersity of the surfactants. Indeed, substantially the same results have been obtained on different batches of polydispersed surfactants, with EW ranging between 670 and 700.

The effect of the polydispersivity and the possible presence of isomeric structures, and particularly the small amounts of bifunctional molecules could account for the differences between the c.m.c. values reported in the present work and the values published by Caporiccio et al. [7] on strictly monodispersed surfactants.

When the concentration of PFPE surfactants was increased well above c.m.c., highly viscous and birefringent solutions could be obtained, mainly with the samples with higher EW.

A most important property of the aqueous solutions of PFPE surfactants is the lowering of the interfacial tension with PFPE oils. Table 2 shows the interfacial tensions between aqueous surfactant S6 and ammonium perfluorooctanoate (APFO) solutions of varying concentrations and PFPE oil having an average molecular weight of 800. S6 shows a behaviour in water similar to APFO, both with respect to c.m.c. and ultimate surface tension. The comparison between the two surfactants indicates a higher efficiency of PFPE surfactant S6, having the same molecular structure as the PFPE oil.

The dramatic lowering of the interfacial tension with PFPE oils was assumed as an indication of the possibility of solubilizing perfluoropolyethers in aqueous PFPE surfactant solutions.

Surfactant–oil–water system

In order to understand the behaviour of W/S/O ternary system, the surfactant chain length was considered.

With increasing hydrophobic chain length from EW 380 to 700 the solubility of PFPE surfactants in water dramatically decreases, while the solubility in the oil phase increases. In a ternary system the solubilizing capacity of the surfactant solutions were found to be strictly related to the solubility of the amphiphilic molecules.

As an example, as shown in Table 3, a short chain surfactant solubilized the oil in the water-rich side of the phase diagram, while the surfactant with highest EW (S3) allowed the solubilization, at room temperature, of water in the oil-rich region. By using a surfactant with an intermediate molecular weight (S2), however, the situation depicted in Fig. 1 in the water-rich region was observed. At lower temperatures, only cloudy or turbid phases were recorded, while at higher temperatures (> 50 °C) the formation of a clear, isotropic fluid phase takes place, characterized by spontaneous formation, reversibility with respect to phase separation induced by cooling, and indefinite stability within the temperature range of existence.

In order to determine the rate of equilibration of the system, the temperature range of existence at a fixed composition was studied. As reported in Table 4, only slight changes were recorded over a period of 14 days. This fact allowed

TABLE 3

Examples of PFPE microemulsions obtained with surfactants of different equivalent weights. Oil phase: PFPE, MW = 800. Compositions are expressed as %

Surfactant MW	Temperature range (°C)	% W	% S	% O
596	$27 < T < 60$	51.0	30.6	18.4
	$45 < T$	73.6	16.5	9.9
	$67 < T$	81.9	11.3	6.8
707 (S3)	20	5.4	33.1	61.6
	20	11.9	30.8	57.3

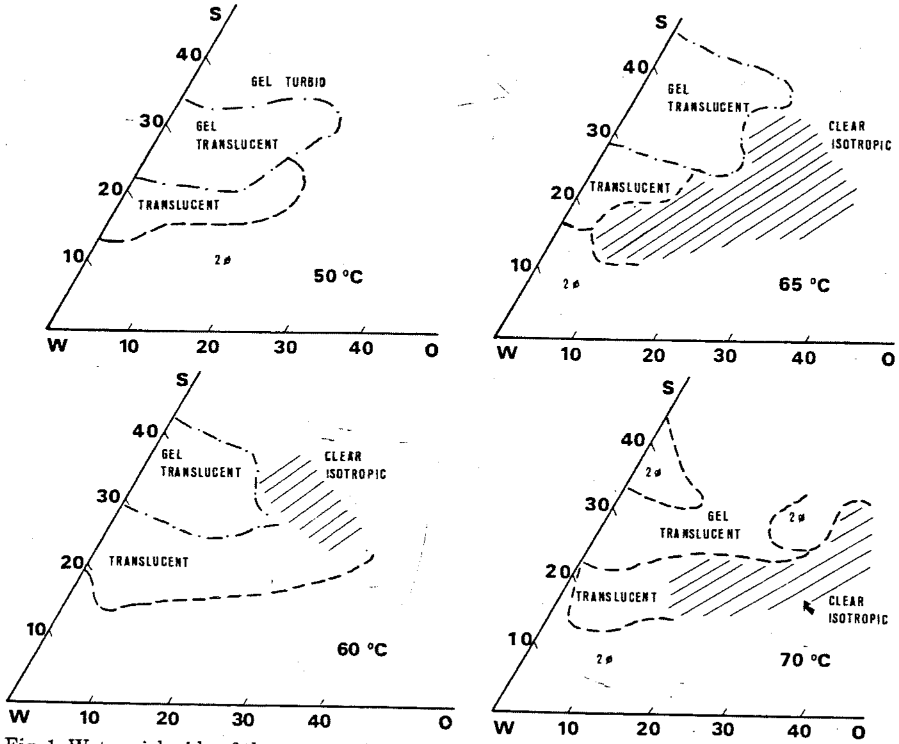


Fig. 1. Water-rich side of the ternary phase diagram water S2 surfactant/PFPE oil (MW=800) at different temperatures.

TABLE 4

Temperature range of existence of a PFPE microemulsion as a function of aging time. Microemulsion composition; surfactant S2: 31%, water: 51%, oil: 18%

Time (days)	Temperature range of existence (°C)
0	57–80
7	55–81
14	54–82

us to assume that qualitatively valid information on the existence of monophasic areas in the ternary phase diagram could be obtained even after an aging time as short as 1/2 h.

In the diagrams shown in Fig. 1, it is noticeable that there are wide translucent birefringent areas, located in the water-rich region. These areas should be characterized by a liquid crystalline ordering of surfactant chains, due to their bulky molecular structure.

Surfactant–alcohol–oil–water pseudoternary system

The behaviour of fluorinated and hydrocarbon surfactants in aqueous solutions is known to be modified by the addition of hydrocarbon alcohol. Particularly short chain alcohols which tend to enhance solubility and c.m.c. values of the surfactants, due to the modifications induced by the alcohols in the dielectric constant and structure of the solvent [8–11]. Longer chain alcohols on the contrary, promoted the micellization of the surfactant.

The case of PFPE surfactants has been studied using the sparingly water soluble and polydispersed sample S5. The observed trends are reported in Fig. 2 and Table 5.

The concentration of ethanol in aqueous solutions greatly enhances the PFPE

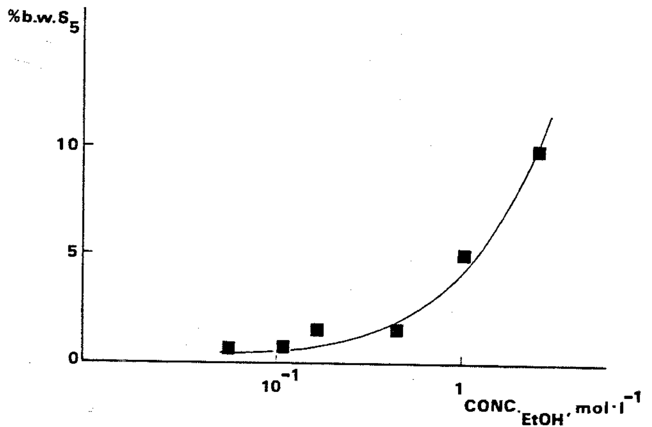


Fig. 2. Solubility of S5 surfactant as a function of ethanol concentration in aqueous solutions.

TABLE 5

Critical micellization concentrations of PFPE surfactant S5 in the presence of ethanol at different concentrations

Ethanol conc (*M*)	c.m.c. ($1 \cdot 10^{-4}$ *M*)
–	2.5
0.18	3.5
0.40	3.5
0.90	5.0

surfactant solubility (Fig. 2), along with increases in the c.m.c. values (Table 5), which eventually could no longer be determined.

However, as shown in Fig. 3, no modification in the interfacial tension between the surfactant solution and PFPE oil occurs in a wide range of ethanol concentrations. When the alcohol effect prevails, the interfacial tension sharply increases ($C > 0.1\ M$).

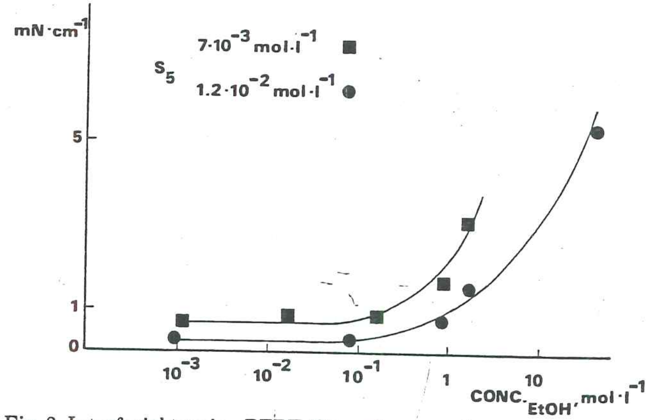


Fig. 3. Interfacial tension PFPE/S5 surfactant solutions as a function of ethanol concentration.

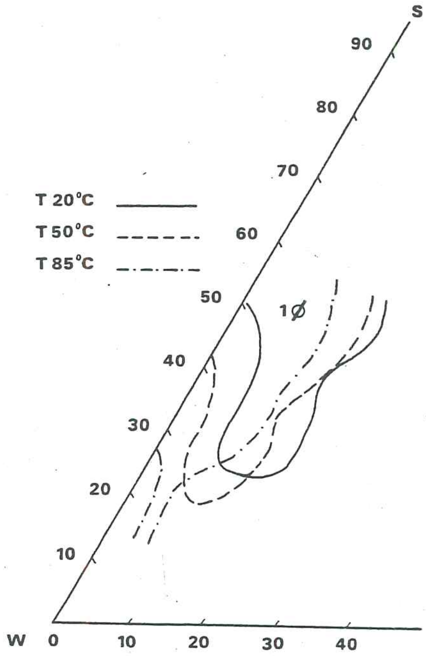


Fig. 4. Monophasic, isotropic areas in the water-rich region of the phase diagram S4+EtOH (molar ratio=0.3)/water/PFPE oil (MW=800) as a function of temperature.

Furthermore, the addition of ethanol to the surfactant solution causes the birefringent phase to disappear, with the formation of low-viscosity isotropic solutions.

The examination of a pseudoternary system with an S4/EtOH molar ratio of 0.3 showed, in a quite wide area near the W/(S+EtOH) edge, the formation of an isotropic clear phase (Fig. 4) for temperatures ranging between 20 °C and 85 °C.

In order to evaluate the effect of ethanol, three points of ternary phase diagram have been chosen (*a,b,c* in Table 6), and the evolution of the system has been studied as a function of temperature and ethanol concentration. The resulting diagrams are reported in Fig. 5.

At low alcohol concentration, the system showed only a turbid, gel-like phase, which at higher temperatures separated into two phases.

After the addition of ethanol up to an S/EtOH ratio of about 4.5 by weight (0.3 by mole) for the three investigated points, a single clear birefringent phase was obtained, which upon further addition of ethanol evolved into transparent, isotropic single phase. The monophasic area is quite large. Phase separation occurred at a surfactant to alcohol ratio of about 1.5 by weight (0.1 by mole). The phase separation of the system is more evident at temperatures higher than 40 °C, while the pseudoternary system is more stable at lower temperatures.

The behaviour of the binary, ternary and pseudoternary systems indicates that the main effect of ethanol, as an example of a short chain alcohol, on the system should initially be a sharp increase in the solubility of the surfactant, without appreciable modification in the PFPE–water interfacial tension. Such a cosolvent effect is also suggested by the increase in the surfactant c.m.c. and has already been described for hydrocarbon surfactant solutions [8] and differs from the effect of a true cosurfactant, for example, pentanol in the SDS–water–hydrocarbon oil system [12].

The increase in the available interfacial area due to the higher water solubility of the surfactant could explain the formation of microemulsions in the water-rich region of the phase diagram. The rise in the interfacial tension at very high ethanol concentrations should in turn explain the phase separation of the system, due to a decreased affinity of the surfactant for the oil phase.

The disappearance of the birefringent phases and the onset of the monophasic region at a constant surfactant/alcohol ratio (Fig. 5) indicate, however, that ethanol could modify the structure and rigidity of the interface favouring a positive curvature. Indeed, a possible mechanism of adsorption of the short chain alcohol at the PFPE–water interface could be the interaction of the –OH group with the surfactant carboxyl groups. Similar behaviour was reported in perfluorosurfactant solutions in the presence of short chain alcohols [13].

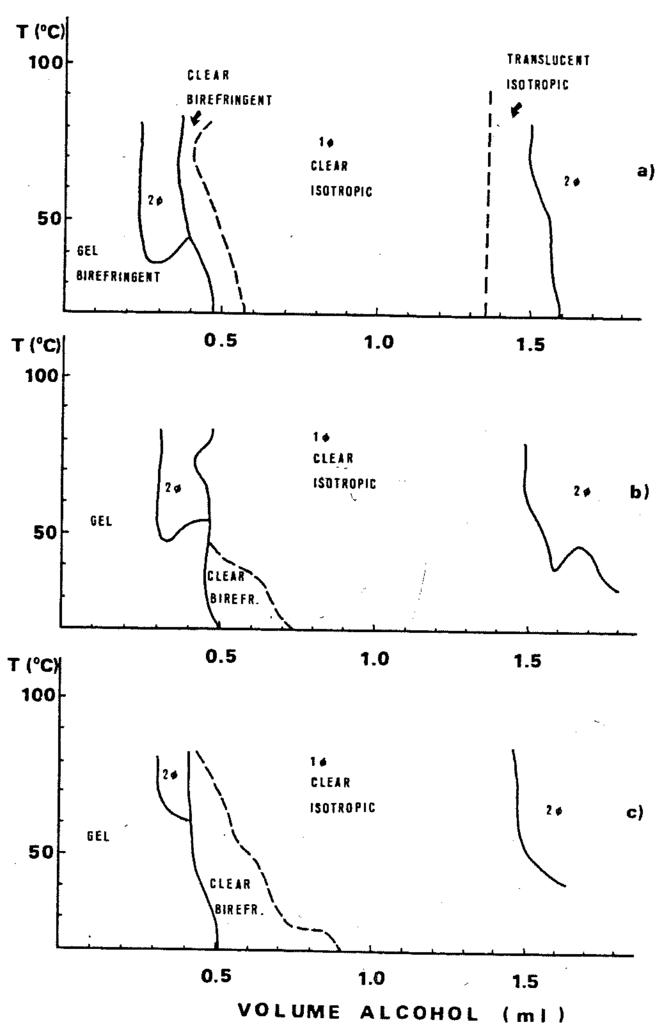


Fig. 5. Evolution of the systems having the starting compositions shown in Table 6 as a function of temperature and ethanol volume.

TABLE 6

Starting compositions (by weight) in the ternary phase diagram S5 surfactant–water–PFPE oil studied as a function of the temperature and ethanol concentration

	S	W	O
a	48.0	40.0	12.0
b	37.9	52.6	9.5
c	31.3	60.9	7.8

Long chain alcohols, with low solubility in water, have been reported to penetrate hydrocarbon surfactant micelles, due to hydrophobic interaction, and consequently reduce the free surfactant monomer concentration and c.m.c. [8–11].

Similar behavior was found in PFPE surfactant solutions, as shown in Table 7, where the c.m.c. values of S5 are reported at different surfactant to alcohol ratios for 1-hexanol and 1-nonanol.

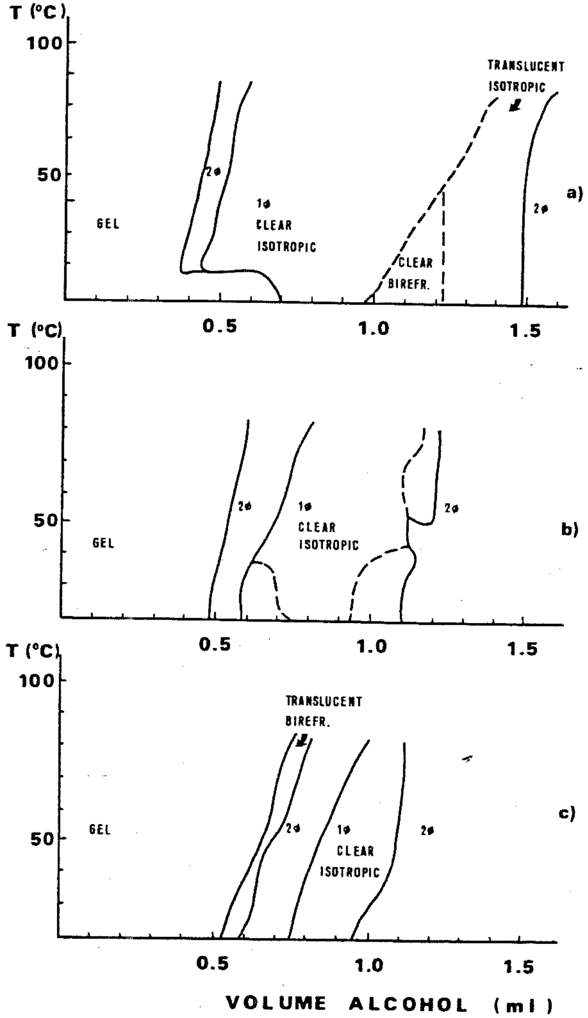


Fig. 6. Evolution of the systems having the starting compositions shown in Table 6 as a function of temperature and 1-hexanol volume.

TABLE 7

Critical micellization concentrations of PFPE surfactant S5 in the presence of hydrocarbon long chain alcohols at different surfactant/alcohol ratios

Alcohol	Ratio	c.m.c. ($1\cdot 10^{-4}\,M$)
none	-	2.5
C6OH	0.91	1.2
C6OH	0.15	1.0
C9OH	1.8	1.5

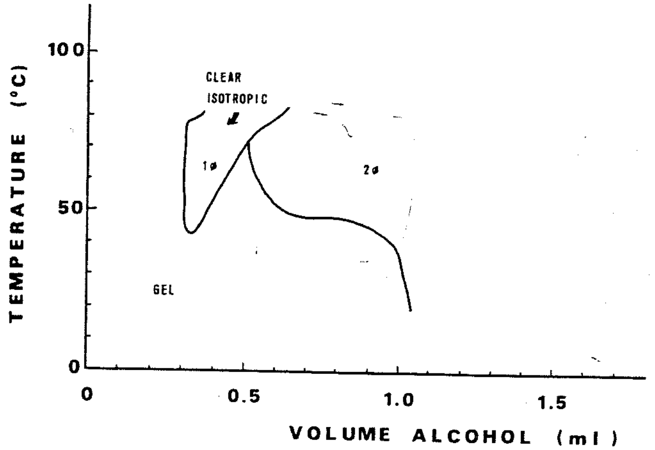


Fig. 7. Phase diagram showing the evolution of point *a* (Table 6) as a function of temperature and PFPE alcohol volume.

The evolution of the ternary systems of Table 6 as a function of the 1-hexanol concentration is reported in Fig. 6.

The effect of the long chain alcohol is somewhat similar to that of ethanol at the higher PFPE surfactant concentration (point *a*, Table 6), but a much narrower monophasic area is recorded at higher dilutions of the system (point *b*, *c*, Table 6).

In the case of hexanol, however, the formation of the microemulsion should be attributed to the coadsorption of the hydrocarbon alcohol in the interfacial layer, since the long chain alcohol is only slightly soluble in water and insoluble in the oil phase.

The boundary of the monophasic area at the lower alcohol content corresponds to a molar concentration of about one third of that required for ethanol. This fact is related to the alcohol chain length and to the probably higher penetration in the interfacial layer driven by the (weak) hydrophobic interaction between the hydrocarbon and fluorocarbon chains.

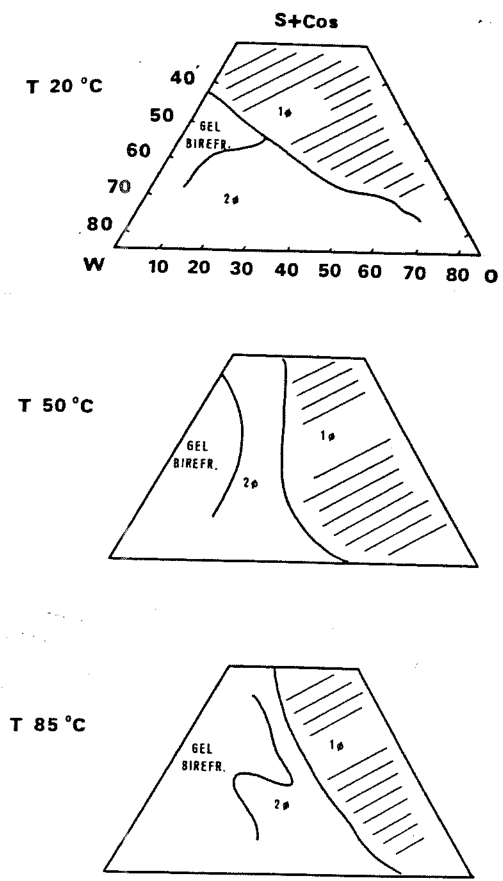


Fig. 8. Monophasic region (shaded area) in the pseudoternary phase diagram S4+dodecafluoroheptanol/water/PFPE oil (MW=800) at different temperatures.

The behaviour of the water–surfactant–oil system has also been studied in the presence of the fluorinated alcohol dodecafluoroheptanol $H(CF_2)_6CH_2OH$ and of a PFPE alcohol prepared by chemical reduction of the PFPE carboxylic acid of EW 668. Both alcohols are insoluble in water and soluble in oil. Using the PFPE alcohol, the points having the composition reported in Table 6 have been examined.

As shown in Fig. 7, a monophasic area was only found at temperatures greater than 40 °C, with the highest surfactant concentration.

Using dodecafluoroheptanol, the pseudoternary phase diagram reported in Fig. 8 was constructed. The shift of the monophasic region towards the surfactant and oil-rich regions of the diagram is noteworthy.

The coadsorption of the fluorinated alcohols at the interface is apparent

TABLE 8

Interfacial tensions between PFPE and aqueous solutions of surfactant S5 ($3\cdot10^{-4}$ *M*) as a function of PFPE alcohol concentration in the oil phase

PFPE alcohol concentration (*M*)	Interfacial tension (mN m^{-1})
0	6
$8.7\cdot10^{-4}$	3
$1.7\cdot10^{-3}$	3
$5.2\cdot10^{-3}$	2.5
$1.0\cdot10^{-2}$	2.5

from the lowering of the PFPE oil–water interfacial tensions reported in Table 8. The penetration of the alcohol in the surfactant layer, and the large cross-sectional area of the PFPE chain compared with that of the alcohol head group should in turn be responsible for the negative curvature of the interface [14,15].

CONCLUSIONS

Perfluoropolyether surfactants have been shown to be very effective in the solubilization of perfluoropolyether oil allowing the preparation of a novel class of fluorinated, monophasic, clear, isotropic liquid systems that behave as true microemulsions.

The polydispersity of the products allows a number of degrees of freedom in selecting the molecular weight of the surfactant and of the oil phase.

Short chain surfactants are very soluble in water and are expected to form O/W ternary microemulsions.

W/O ternary microemulsions could be obtained using oil soluble long chain surfactants. Lyotropic mesophases, characterized by high viscosity and strong birefringence could be obtained in the water-rich region of the diagram.

The presence of hydrocarbon alcohols had a tremendous effect on the W/long chain surfactant/O system. Short chain alcohols behaved essentially as cosolvents for the surfactant, while long chain alcohols showed evidence of coadsorption at the interface. In all cases, O/W microemulsions were formed, with disappearance of the birefringent phases.

Fluorinated alcohols, on the contrary, favoured a negative interfacial curvature, with preferred formation of W/O systems.

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