Interfacial properties and emulsion stability in fluorinated oil–non-fluorinated oil–surfactant(s) systems

Masamichi Morita[a], Mutsuo Matsumoto[b], Shinnosuke Usui[c], Takashi Abe[d], Nikolay Denkov[e], Orlin Velev[e] and Ivan B. Ivanov[e]

[a]Shiga Central Research Laboratory, Noevir Co. Ltd., Okada-choh, Yoh-ka-ichi, Shiga 527, Japan
[b]Institute for Chemical Research, Kyoto University, Kyoto 611, Japan
[c]Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai 980, Japan
[d]Government Industrial Research Institute, Nagoya, Hiratake-choh, Kita-ku, Nagoya 462, Japan
[e]Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry, Sofia University, Sofia 1126, Bulgaria

Abstract

The formation of interfaces and emulsions in systems comprising perfluoromethyldecalin (PFMD) and non-fluorinated oils with different polarities was investigated. The measured interfacial tension between the pure liquids was quantitatively interpreted in the framework of the Fowkes' model. The interfacial activity of several kinds of non-fluorinated, perfluorinated, ionic and non-ionic surfactants was explored. The perfluorinated non-ionic compound perfluoroalkyl-polyoxyethylene (PFPE) proved to be most effective as a surfactant in these systems. The critical micelle concentration and the areas per molecule at interfaces with several non-fluorinated oils were determined for this substance. In some cases where fluorinated alcohols were used as co-surfactants, ultra-low interfacial tension and microemulsion formation were observed. The stability of the emulsion using PFPE as a surfactant was also investigated. It was shown that the higher polarity of the non-fluorinated oils led to higher emulsion stability. The addition of fluorinated alcohols decreased the stability and reversed the macroemulsion type. The observed effects are discussed from the viewpoint of the chemical structure of the compounds.

Keywords: Fluorinated surfactants; interfacial tension; oil–oil interfaces; oil-in-oil emulsions.

Introduction

The interfacial properties of liquid–liquid systems play an important role in their practical application to food, paint, cosmetic and medical emulsions, as well as in polymerization, solvent extraction and other industrial processes. The use of perfluorinated surfactants has important advantages in some cases. In particular, they possess higher surface activity than that of the ordinary non-fluorinated surfactants at water–air, water–oil and oil–air interfaces. The versatility of the perfluorinated surfactants makes them an interesting subject for studying the interfacial properties in novel oil–oil disperse systems. The investigation of these systems is therefore very useful for the development of new industrial products consisting of oil-in-oil dispersions.

Shinoda et al. [1] carried out a systematic study of surface tension isotherms, critical micelle concentrations, Kraft points and some other surface and

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Correspondence to: M. Matsumoto, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.

colloidal properties of fluorinated surfactants in aqueous solutions. Ravey et al. [2] studied the surface-active behavior of fluorinated and ordinary non-fluorinated non-ionic surfactants in very dilute aqueous solutions. The results showed that the surface activity of these surfactants depended on the length of the hydrophobic chains. It turned out that the properties of a surfactant with given perfluorinated chains were close to those of a surfactant with the same polar head and proportionally longer hydrocarbon chain at a ratio of 1/1.7.

In oil–oil systems, LeGrand and Gaines, Jr. [3] measured the interfacial tensions between perfluoroalkanes (PFA) and *n*-alkanes on the one hand, and between PFA and poly(dimethylsiloxane)s or poly(isobutylene)s on the other hand (these liquids are partially miscible). The measured interfacial tensions were (depending on the molecular weight of the non-fluorinated oils) in the range 1–7 mN m^{-1}, 0.5–6 mN m^{-1} and 0.4–8 mN m^{-1} for the systems PFA–*n*-alkanes, PFA–poly(dimethylsiloxane)s and PFA–poly(isobutylene)s respectively. Johnson, Jr., and Dettre [4] measured interfacial tensions in the range 1.2–10.6 mN m^{-1} at the interfaces between *n*-alkane and *ω*-hydrotetrafluoropropanol or *ω*-hydrooctafluoropropanol or pentafluoropropanol. The interfacial tensions for *n*-alkane and poly(ethylene glycol) systems were also measured and their values were around 10 mN m^{-1}.

The formation and stability of oil-in-oil microemulsions and macroemulsions were also studied. Sharma [5] prepared the macroemulsion systems from aromatic solvents and ethylyne glycol, and showed that their stability is a function of the surfactant concentration. Fletcher et al. [6] prepared a microemulsion of glycerol in heptane stabilized with aerosol OT (di-2-ethylhexyl sodium sulphosuccinate). The drop sizes were determined with dynamic light scattering. It was shown that the droplet diameter depended on the molar ratio of glycerol to surfactant and was not dependent on the temperature. However, Friberg and Rong [7] pointed out that waterless dispersions formed

in formamide–sodium dodecylsulphate–hexanol–toluene systems were not microemulsions but molecular solutions with no colloidal structure. Rico and co-workers [8–14] published a series of papers dealing with the formation and preparation of waterless microemulsions. Water was replaced with formamide as a polar phase, and perfluorinated surfactants and perfluorodecalin were used in some sets of experiments [10,11]. The authors reported that large monophasic areas corresponding to several different types of microemulsion were found in system phase diagrams.

In the present study, the interfacial properties of perfluoromethyldecalin and ordinary non-fluorinated oil (or water) systems are explored. For this purpose measurements of the interfacial tension are carried out with a series of organic liquids of different polarity in the absence and in the presence of several types of surfactant. It is shown that perfluoroalkylpoly(oxyethylene) (PFPE) is a very effective non-ionic surfactant in these systems, while the non-fluorinated surfactants are rather inactive interfacially. Fluorinated alcohols, playing the role of co-surfactants, strongly affect the interfacial properties. The formation and stability of microemulsions and macroemulsions are investigated. It is proved that the addition of fluorinated alcohols decreases the stability and reverses the emulsion type.

Experimental

Materials

Perfluoromethyldecalin (PFMD) was always used as one of the oil phases. It was purchased from Rhône-Poulenc S.A. as a commercial product (Flutec PP-7).

The other oil phase for interfacial and emulsion studies consisted of non-fluorinated oils (NFOs) with different dielectric permittivities. These included formamide (FA), formic acid, glycerin, ethylene glycol (EG), propylene glycol (PG), 1,3-butylene glycol (1,3-BG), acetylacetone (AA), 1-hexanol, *n*-butyl chloride (BC), and methylisobutyl

ketone (MIBK) which were guaranteed reagent-grade chemicals purchased from Wako Pure Chemical Industries Ltd. Acetonitrile (AN), methanol (MeOH), acetone, benzene and carbon tetrachloride (CT) were products of Dojin Chemical Laboratories Ltd. under the Dotite Spectrosol trademark; 3-methyl-2-oxazolidone (MO) was supplied by Sanyoh Kasei Kohgyoh Ltd.; dipropylene glycol (DPG), extra pure reagent grade, was supplied by Nacalai Tesque Ltd. Doubly distilled water was used as a second phase in one of the experimental runs.

In the course of the experiments two kinds of surfactant were used: (a) hydrocarbon surfactants, such as aerosol OT (AOT), specially prepared by Nacalai Tesque Ltd., EPAN 740 (pluronic type of surfactant), from Daiichi Kougyoh Ltd., and di-stearyldimethylammonium bromide (DSDMAB), laboratory synthesized; (b) fluorocarbon surfactants such as PFPE, perfluoroalkylquaternary-ammonium iodide (PFQA) and sodium perfluorooctanoate (SPFO), all specially synthesized reagents [15,16].

In some of the experiments a number of fluorinated alcohols were used as co-surfactants. These include perfluorooctyl ethanol $C_8F_{17}(CH_2)_2OH$, perfluoroheptyl methanol $C_7F_{15}CH_2OH$, perfluoropropyl methanol $C_3F_7CH_2OH$, perfluoroethyl methanol $C_2F_5CH_2OH$, and 1-H-perfluorohexyl methanol $HC_6F_{12}CH_2OH$, purchased from PCR Inc. For clarity, the chemical formulae of the used surfactants are listed in Table 1. All the chemicals were used without further purification. For the sake of brevity some of the introduced abbreviations are used hereafter instead of their full names.

Methods

The interfacial tensions at PFMD–NFO interfaces were measured by using a laboratory-made spinning drop interfacial tensiometer. The cylindrical spinning cell had an inner diameter of 6 mm. Electronic control of the speed of rotation ensured a precision of ± 0.1 rev min^{-1}. The size of droplets inside the rotation capillary was determined micro-scopically with an accuracy to ± 0.01 mm after 5 min of rotation. The cell was mounted in an air-thermostatted cabinet at a temperature of 25°C sustained with a precision of ± 0.5°C. Prior to the measurements all pure PFMD–NFO systems and PFMD–NFO systems containing surfactants were allowed to equilibrate for 72 h at 25°C. The measurement procedures and the formulae for calculation of the interfacial tension were used as described in the literature [17–19]. The value of the interfacial tension was obtained by averaging about seven experimental values and its overall non-systematic error was typically estimated as being better than ± 0.3 mN m^{-1}.

Emulsions from PFMD–NFO–surfactant systems were obtained by an ultrasonic generator (Kaijoh Denki Co. Ltd, type 4335, 150 W, 29 kHz). Prior to emulsification, the probes consisting of 4 g of the two phases were allowed to equilibrate for more than 24 h at 25°C and were emulsified by shaking 50 times. Each probe was subjected to three subsequent cycles of 2 min of sonication and of 50 shakes. The stability of the emulsion was estimated by observing the volumes of the emulsion layers vs time at 25°C in test-tubes 90 mm in height and 13 mm in diameter.

Results and discussion

Interfacial tension at pure PFMD–non-fluorinated oil interfaces

Solubility experiments showed that PFMD is immiscible with polar non-fluorinated oils with dielectric permittivity ϵ_r greater than 20.7 (acetone), whereas apolar and non-polar liquids with lower permittivity are partially soluble in PFMD. The solubility of the investigated liquids at 25°C was as follows (weight per cent in saturated solution): 15.6, CT; 3.7, BC; 0.8, MIBK; 0.2, acetone.

The experimental results showed that PFMD forms interfaces with a large variety of liquids of different permittivities. In Fig. 1 the measured interfacial tensions, $\gamma_{1,2}$, at PFMD–NFO and PFMD–water interfaces are presented. The dielec-

TABLE 1

Chemical formulae and molecular weights of the surfactants used

Surfactant	Molecular weight	Formula
Hydrocarbon group Aerosol OT (AOT)	445	$C_8H_{17}OOCCH_2$ $\|$ $C_8H_{17}OOCCHSO_3Na$
EPAN 740 (Pluronic surfactant) (PO group) (EO group)	3333 2000 1333	CH_3 $\|$ $HO(CH_2CH_2O)_b(CHCH_2O)_bi(CH_2CH_2O)_bH$
Distearyldimethylammonium bromide (DSDMAB)	631	$(C_{18}H_{37})_2N(CH_3)_2Br$
Fluorocarbon group Sodium perfluorooctanoate (SPFO)	436	$C_7F_{15}COONa$
Perfluoroalkyl-poly(oxyethylene) (PFPE)	995	OH $\|$ $C_9F_{19}CH_2CHCH_2(OCH_2CH_2)_6OCH_3$
Perfluoroalkylquaternary-ammonium iodide (PFQA)	771	$OH \quad CH_2CH_2OH$ $\| \qquad \|$ $C_8F_{17}CH_2CHCH_2NCH_3 \qquad\quad I$ $\|$ CH_2CH_2OH

tric permittivity ϵ_r of the liquids varies between 2.2 for CT and 109 for FA. It is seen that $\gamma_{1,2}$ roughly increases with the increase in ϵ_r (respectively with the polarity) of the liquids. Furthermore, the interfacial tension can reach values as high as 32.0 mN m^{-1} for glycerin and FA and even 53.4 mN m^{-1} in the case of water.

The observed trend in the increase of $\gamma_{1,2}$ with ϵ_r is only qualitative and a more refined approach is necessary to reveal the relationship between the interfacial tension and the polarity of the liquids. According to Fowkes [20,21] the surface tension of a liquid can be separated into two parts:

$$\gamma_i = \gamma_i^d + \gamma_i^p \qquad (1)$$

where γ_i is the surface tension of liquid i, γ_i^d is its part due to London dispersion intermolecular forces, and γ_i^p is the remaining part of γ_i which is
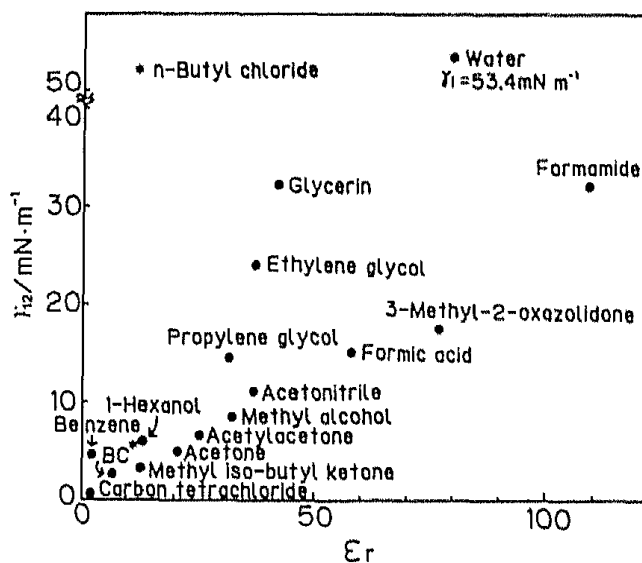

Fig. 1. Dependence of the interfacial tension $\gamma_{1,2}$ in PFMD–NFO systems on the dielectric permittivity ϵ_r of non-fluorinated oils.

due to short-range interactions like dipole–dipole interactions, hydrogen bonding etc. In the following consideration, 1 will represent PFMD and 2 the other liquids. Fowkes [20,21] showed theoretically that if one of the liquids has no polar components the interfacial tension $\gamma_{1,2}$ between two liquids 1 and 2 can be expressed as a sum of the energy of formation of the two liquid–air surfaces $(\gamma_1 + \gamma_2)$ and the energy of adhesion:

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{1/2} \qquad (2)$$

The experimental check of Eqn (2) for the water–hydrocarbon interfaces showed [20] that it holds very well with $\gamma_w^d = 21.8 \pm 0.7$ mN m^{-1} for the dispersion part of the surface tension of water. It is also known that for n-alkanes and perfluorinated alkanes $\gamma_1^p = 0$ [22]. The surface tension of PFMD was measured to be $\gamma_1 = 19.2$ mN m^{-1}, and hence we obtain

$$\gamma_1 = \gamma_1^d = 19.2 \text{ mN m}^{-1} \qquad (3)$$

By using Eqns (2) and (3) and values for the surface tension of the investigated liquids available from the literature, the dispersion part γ_2^d is estimated:

$$\gamma_2^d = [(\gamma_{1,2} - \gamma_1 - \gamma_2)/2]^2/\gamma_1 \qquad (4)$$

By using Eqns (1), (3) and (4) one can evaluate also the specific interaction part of the surface tension γ_2^p. In Fig. 2 the measured values of the interfacial tension $\gamma_{1,2}$ (circles) are compared with the calculated values of γ_2^p (crosses). The values of surface tension of the liquids, γ_2, were taken from Ref. [23]. One sees that values of the measured interfacial tension $\gamma_{1,2}$ were very close to the corresponding values of γ_2^p. For example, in the PFMD water system the measured interfacial tension was 53.4 mN m^{-1} and was equal to the calculated value for γ_w^p. The calculated value of γ_w^d, 19.4 mN m^{-1}, is close to that obtained by Fowkes [20] ($\gamma_w^d = 21.8$ mN m^{-1}). On the other hand, carbon tetrachloride molecules are non-polar with zero dipole moment and the interfacial tension of PFMD–CT is very low, $\gamma_{1,2} = 0.5$ mN m^{-1}. The dispersion part γ_2^d calculated by means of Eqn (4)
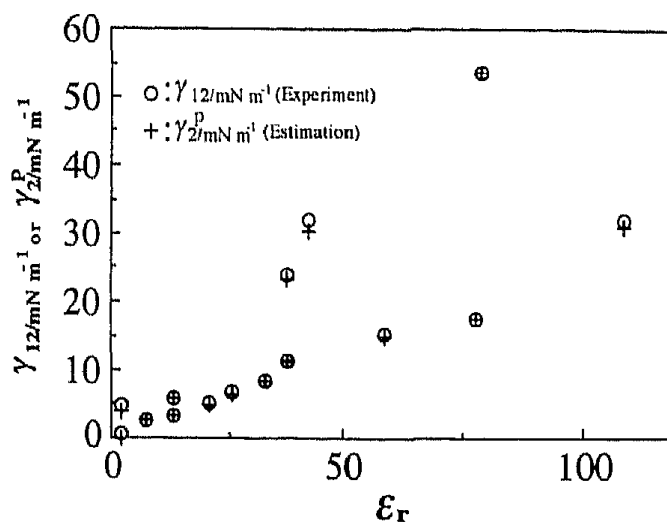

Fig. 2. Dependence of the interfacial tension $\gamma_{1,2}$ (O) in PFMD–NFO systems and of the polar component of the surface tension γ_2^p (×) on the dielectric permittivity (ε_r) of non-fluorinated oils.

practically coincides with the total surface tension ($\gamma_2^p \approx 0$) which is quite reasonable for such molecules.

The relationship between $\gamma_{1,2}$ and γ_2^p can be revealed by combining Eqn (2) with Eqns (1) and (3), resulting in

$$\gamma_{1,2} = (\sqrt{\gamma_1} - \sqrt{\gamma_2^d})^2 + \gamma_2^p \qquad (5)$$

The calculated values of γ_2^d are between 16 and 33 mN m^{-1}. Hence the first term in the right hand side of Eqn (5) is smaller than 2.2 mN m^{-1} (in most of the cases it is even smaller than 1 mN m^{-1}). This means that $\gamma_{1,2}$ is almost entirely determined by γ_2^p:

$$\gamma_{1,2} \approx \gamma_2^p \qquad (6)$$

or, in other words, that the major contribution to the energy of interfacial tension is due to the work done in transferring molecules from the bulk of the polar liquids to the interface.

Equation (5) demonstrates also why in some cases the measured interfacial tensions are slightly larger than γ_2^p (see Fig. 2). If the calculated value of γ_2^d is much larger (or smaller) than γ_1, the first term in Eqn (5) cannot be entirely neglected and contributes to $\gamma_{1,2}$. For example, for benzene, $\gamma_2 = 31.6$ mN m^{-1}, while γ_2^d is calculated to be 27.9 mN m^{-1} and the remaining part of the surface tension

γ_2^p is 3.7 mN m^{-1}. Incorporating these values in Eqn (5) one sees that the first term is equal to 0.8 mN m^{-1} and cannot be neglected in comparison with the small second term.

Similar calculations show that the low interfacial tension at fluorinated alkane–non-fluorinated alkane interfaces can be explained by the fact that only dispersion interactions are effective in these cases, i.e. $\gamma_2^p = 0$. Then Eqn (5) transforms to

$$\gamma_{1,2} = (\sqrt{\gamma_1} - \sqrt{\gamma_2^d})^2 \qquad (7)$$

Usually the surface tension of alkanes is between 20 and 30 mN m^{-1} and that of fluorinated alkanes is between 12 and 20 mN m^{-1} [23]. Thus the interfacial tensions have to be of the order of several millinewtons per metre. For example, the surface tension of perfluorohexane and decane are $\gamma_1 = 13.8$ mN m^{-1} and $\gamma_2 = 25.7$ mN m^{-1} at 25°C, respectively, and the corresponding calculated value of the interfacial tension is $\gamma_{1,2} = 1.8$ mN m^{-1}. Experimentally, the value $\gamma_{1,2} = 3.1$ mN m^{-1} was determined [23].

Interfacial activity of surfactants in systems with PFMD–non-fluorinated oil interfaces

The interfacial activity of surfactants depends strongly on the chemical nature of the "heads" and "tails" of their molecules. The chemical compatibility of these two parts of the molecules with the two adjacent liquids is an important condition for the manifestation of pronounced amphiphility of the surfactants. In this section we explore the influence of different types of surfactant on the interfacial tension between PFMD and a number of ordinary NFOs. As a quantitative measure of the surfactant interfacial activity we use the initial slope G of interfacial tension isotherms, as defined in Ref. [24]:

$$G = -(\mathrm{d}\gamma_{1,2}/\mathrm{d}C)_{C\to 0} \qquad (8)$$

where C is the bulk surfactant concentration.

The combination of Eqn (8) with the Gibbs adsorption isotherm leads to a linear dependence

of the adsorbed amount of surfactant on its concentration (Henry's law):

$$\Gamma_s = (G/RT)C = HC \qquad (9)$$

Here, Γ_s is the surface concentration, R the gas constant, T the temperature and H Henry's constant. Equation (9) demonstrates the close relationship between the interfacial activity and the adsorption activity of the surfactants. All the factors enhancing the surfactant adsorption lead to a decrease in the interfacial tension.

Figure 3 presents the isotherms of interfacial tension for six surfactants (AOT, EPAN 740, DSDMAB, SPFO, PFPE and PFQA) at PFMD formamide interfaces. The concentration is given in moles per cubic decimetre of the total amounts of surfactants per volume of the formamide; the partition coefficients of the surfactants were not determined. It is seen that such an effective surfactant as AOT at water hydrocarbon oil interfaces does not show marked interfacial activity at the PFMD–FA interface (curve 1), and high concentrations (0.1 M) of this substance are necessary to lower the interfacial tension appreciably. Along with Eqns (8) and (9) this experimental fact suggests that the adsorption of AOT molecules at the interface is rather low. A similar interfacial tension isotherm (curve 2) was obtained for sodium perfluorooctanoate (SPFO). These results were probably due to the fact that $-SO_3Na$ and $-COONa$ groups
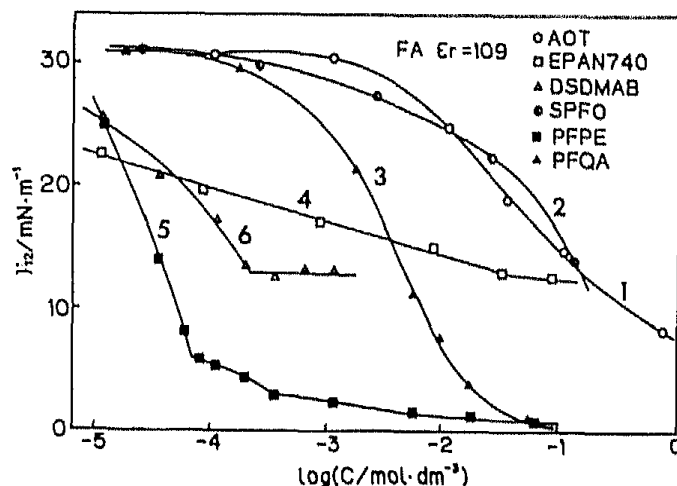

Fig. 3. Effect of the surfactant concentration C on the interfacial tension $\gamma_{1,2}$ of PFMD–FA systems.

possess poor solvation interactions with FA molecules and do not fully dissociate. The FA phase appears to be a better solvent for large non-ionic head groups and a good medium for the ionization of large head ions [10]. For example, trimethylammonium halides are typical supporting electrolytes in polar non-fluorinated oils [25–29]. Thus perfluoroalkylquaternaryammonium iodide (PFQA) (curve 3), EPAN 740 (curve 4), perfluoroalkylpolyoxyethylene (PFPE) (curve 5) and distearyldimethylammonium bromide (DSDMAB) (curve 6) have large head groups and show higher interfacial activity. In particular, PFPE and DSDMAB reduced the interfacial tension from 32 to 6 mN m^{-1} and from 32 to 13 mN m^{-1} at concentrations of $6.5 \cdot 10^{-5}$ M and $2.0 \cdot 10^{-4}$ M respectively. These concentrations corresponded to a distinct discontinuity in the interfacial tension isotherms, and are probably the concentrations at which micelle formation occurs. The fact that large head groups correspond to higher surface activity at PFMD–FA interfaces leads to the conclusion that these groups interact well with FA molecules; solvation, as well as significant ionization of the head groups at the interfaces, is considered to decrease γ_{FA}^0 at the interfaces (see Eqn (6)).

In Fig. 4 the isotherms of interfacial tension for the interface PFMD–MO are plotted. MO is an organic liquid with dielectric permittivity close to
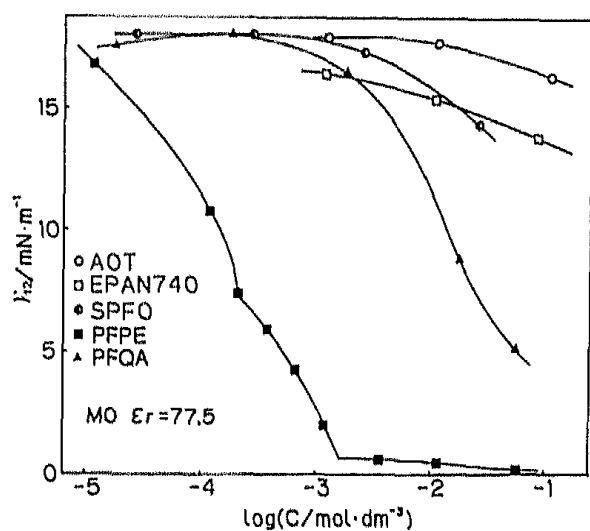
that of water ($\varepsilon_1 = 77.5$ for MO). The curves exhibit similar shapes (see Fig. 3), but are shifted to higher surfactant concentrations in comparison with the previous system (PFMD–FA). The perfluorinated surfactant PFPE shows the highest interfacial activity. At a surfactant concentration corresponding to critical micelle concentration (CMC) ($C = 1.5 \cdot 10^{-3}$ M) the interfacial tension was $\gamma_{1,2} = 0.6$ mN m^{-1} and afterwards it only slightly decreased with increasing concentration.

Figure 5 presents the isotherms for PFMD–MeOH and PFMD–MIBK interfaces. Since MeOH and MIBK are liquids with lower dielectric permittivities ($\varepsilon_r = 32.6$ and $\varepsilon_r = 13.1$ respectively), it is not surprising that only PFPE preserved its interfacial activity and lowered the interfacial tension.

We carried out further experiments with the non-polar liquid CT ($\varepsilon_r = 2.02$). It turned out that for all the surfactants except PFPE, the interfacial tension did not change even at surfactant concentrations as high as 0.1 M.

Figure 6 summarizes the interfacial tension isotherms of PFPE, which indicated the highest interfacial activity for different pairs of liquids. For low surfactant concentrations ($C < 10^{-5}$ M), the measured interfacial tensions decreased with the decrease in ε_r. At higher concentrations the isotherms crossed one another. From these curves one can determine the interfacial activity G, the CMC and the area A_0 per molecule in the interfacial layer at the CMC. The latter value was calculated by means of the Gibbs equation:

$$1/A_0 = -1/KT(\mathrm{d}\gamma_{1,2}/\mathrm{d}\ln C) \tag{10}$$

Fig. 4. Effect of the surfactant concentration C on the interfacial tension $\gamma_{1,2}$ in PFMD–MO systems.
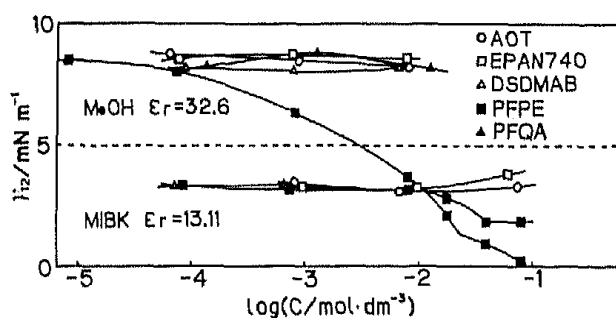

Fig. 5. Effect of the surfactant concentration C on the interfacial tension $\gamma_{1,2}$ in the PFMD–MeOH and PFMD–MIBK systems.
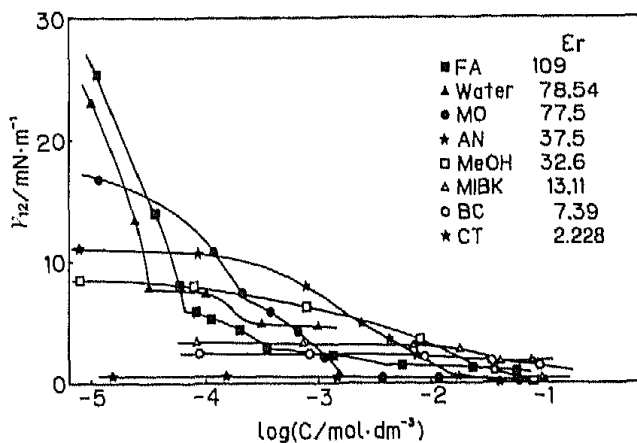
Fig. 6. Effect of the PFPE concentration on the interfacial tension $\gamma_{1,2}$ of PFMD–NFO systems: ■, FA; ▲, water; ●, MO; ★, AN; □, MeOH; △, MIBK; ○, BC; ☆, CT.

where K is the Boltzmann constant and the derivative $(\mathrm{d}\gamma_{1,2}/\mathrm{d}\ln C)$ is taken at the CMC. The PFPE is in fact a mixture of species with different degrees of ethoxylation; since C in Eqn (10) is the total surfactant concentration, the calculated values of A_0 are thereby averaged over different fractions [30]. The results in Table 2 demonstrate that the higher the value of ϵ_r the greater is the interfacial activity. The CMC and A_0 values decrease considerably with increase in ϵ_r. The only exception is water which, in spite of its lower dielectric permittivity compared with FA, exhibits smaller values of the CMC and A_0.

The role of the polarity of non-fluorinated oils on the interfacial tension at a high concentration of PFPE (5 wt.%) is shown in Fig. 7. The relative interfacial tension γ_{rel} is defined as

$$\gamma_{rel} = \gamma_{1,2}^{C=5\,\text{wt.\%}}/\gamma_{1,2}^{C=0\,\text{wt.\%}} \tag{11}$$

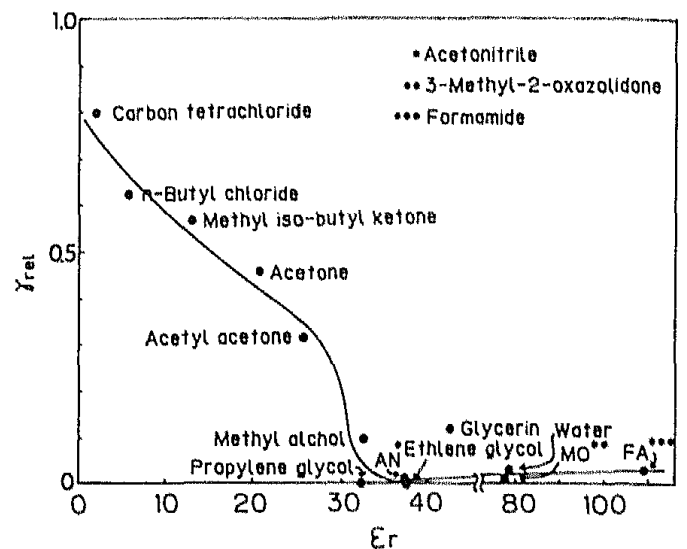Hence γ_{rel} is a measure of the interfacial activity

Fig. 7. Dependence of the relative interfacial tension γ_{rel} at a constant concentration of PFPE (5 wt.%) on the dielectric permittivity ϵ_r of non-fluorinated oils.

of PFPE at the high concentration. $\gamma_{rel} = 1$ corresponds to an absence of interfacial activity and γ_{rel} close to zero corresponds to high interfacial activity. One sees from Fig. 7 that γ_{rel} decreases with the increase in ϵ_r. For $\epsilon_r < 25$, γ_{rel} was greater than 0.3, which means that in this case PFPE was rather interfacially inactive as a surfactant. For $\epsilon_r > 30$, γ_{rel} was smaller than 0.1 and extremely low values of γ_{rel} were obtained with PG and EG. Figure 8 shows the interfacial tensions between PFMD and PG or between PFMD and DPG as a function of the concentration of PFPE. In both cases apparently very low interfacial tensions were obtained. For the concentrations above 3 wt.% near to the minimum in the interfacial tension isotherm of PG, we found so-called surfactant intermediate layers, which increased their volumes with increasing tem-

TABLE 2

Interfacial and bulk properties for PFPE in PFMD–non-fluorinated liquid systems

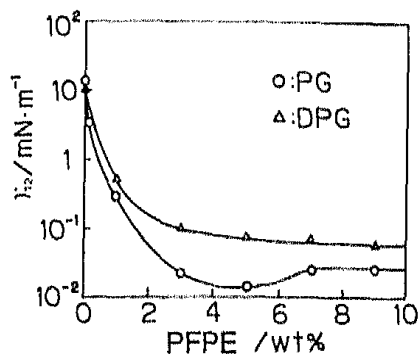| Non-fluorinated liquids	ϵ_r	A_0 (Å^2 molecule^{-1})	$10^{10}\,\Gamma_s$ (mol cm^{-2})	CMC (mol dm^{-3})	$10^{-9}G$ (erg cm mol^{-1})
MeOH	32.6	176	0.9	$2.5\cdot10^{-2}$	<0.02
AN	37.5	154	1.1	$1.5\cdot10^{-2}$	~0.02
MO	77.5	53	3.0	$2.1\cdot10^{-4}$	~0.07
Water	78.5	22	7.5	$3.2\cdot10^{-5}$	~3.0
FA	109	33	5.1	$7.1\cdot10^{-5}$	~0.6

Fig. 8. Interfacial tension isotherms between PFMD and PG or DPG as a function of PFPE concentration.

perature, but there was no spontaneous emulsification and no formation of microemulsions.

Influence of co-surfactant species on the interfacial properties of PFMD–non-fluorinated oil–PFPE or SPFO systems

When surfactants are present at oil–water interfaces, the addition of properly chosen co-surfactants such as alcohols can lower appreciably the interfacial tension at oil–water interfaces. Often, this process is accompanied with spontaneous emulsification and formation of micro-emulsions. In the case of perfluorinated oil and surfactant systems, one can expect that fluorinated alcohols can be used as co-surfactants. In this section the effects of fluorinated aliphatic alcohols on the interfacial tension at the boundary between PFMD and non-fluorinated oils with PFPE or SPFO as a surfactant are described.

The dependence of the interfacial tension $\gamma_{1,2}$ for the system (PFMD–FA–0.5 wt.%PFPE) on the concentration of added fluorinated alcohols is shown in Fig. 9. Curve 1 corresponds to $C_7F_{15}CH_2OH$ and curve 2 to $C_8F_{17}(CH_2)_2OH$. The addition of a small amount of the alcohol (up to about 0.4 wt.%) lowered the interfacial tension below 0.1 mN m^{-1}. At concentrations higher than about 0.4 wt.% the interfacial tension increased. The observed minima in these curves can be explained in the following way: when a small amount of alcohol (soluble in PFMD and insoluble in FA) is added to the system, the alcohol adsorbs
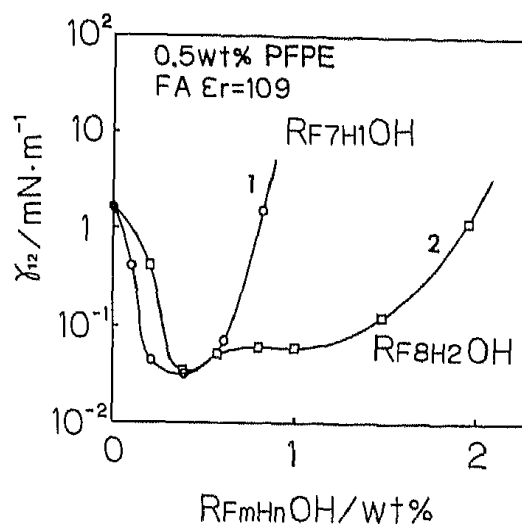

Fig. 9. Effect of the co-surfactant concentration on the interfacial tension ($\gamma_{1,2}$) of PFMD–FA systems in the presence of 0.5 wt.% PFPE: curve 1, $C_7F_{15}CH_2OH$; curve 2, $C_8F_{17}(CH_2)_2OH$.

at the interface together with PFPE molecules. This additional co-adsorption of alcohol leads to a decrease in the interfacial tension (synergism). The increase in the interfacial tension (antagonism) at alcohol concentrations higher than 0.4 wt.% is attributed to the desorption of PFPE from the interface, and its replacement by the alcohol. These effects turned out to be dependent on the type of the oil phase. For example, the interfacial tension of the PFMD–EG system containing 5 wt.% PFPE indicated only antagonism with the addition of $C_8F_{17}(CH_2)_2OH$ (see Fig. 10). This was also true
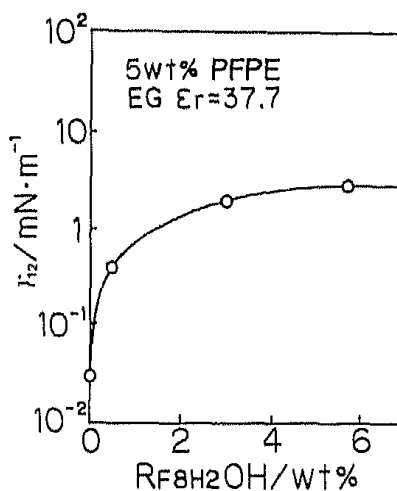

Fig. 10. Effect of the co-surfactant ($C_8F_{17}(CH_2)_2OH$) concentration on the interfacial tension ($\gamma_{1,2}$) between PFMD and EG containing 5 wt.% PFPE.

for the PFPE–AN system. No effect of the same alcohol on the interfacial activity was found for PFMD–MO and PFMD–acetone systems, and only a synergism was observed in the systems PFMD–water and PFMD–CT.

In Fig. 11 the effect of the fluorinated alcohol series on the interfacial tension in the system of PFMD–FA–5 wt.%SPFO is shown. Five substances with different chain lengths of the fluorinated and non-fluorinated parts of their molecules have been investigated. In spite of the similar chemical structures of the alcohols, their effect on the interfacial tension was different: $HC_6F_{12}CH_2OH$ (curve 1) and $C_3F_7CH_2OH$ (curve 2) hardly affected $\gamma_{1,2}$; the addition of $C_2F_5CH_2OH$ (curve 3) initially decreased $\gamma_{1,2}$ by about a factor of 10 but at higher concentrations its impact was to increase $\gamma_{1,2}$. $C_8F_{17}(CH_2)_2OH$ (curve 4) decreased $\gamma_{1,2}$ by about two orders of magnitude and a value of 0.1 mN m^{-1} was reached at a concentration of 5 wt.%. The most interesting result was obtained when $C_7F_{15}CH_2OH$ was used as a co-surfactant (curve 5). A concentration of 6 wt.% caused a great reduction in $\gamma_{1,2}$ and an ultra-low interfacial tension was obtained. Above a concentration of 6 wt.% the interfacial tension markedly increased. In principle, these phenomena could be explained in a similar way to the effects shown in Figs 9 and 10, which were discussed above in terms of synergism and antagonism.
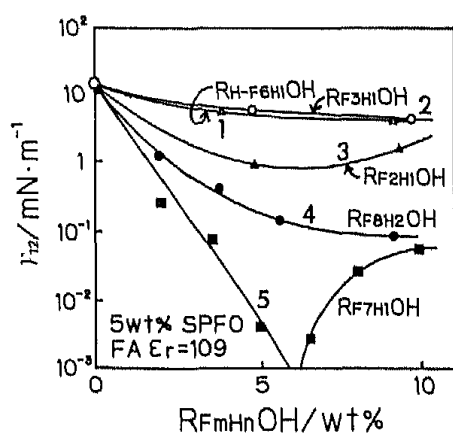
Preparation and stability of oil-in-oil emulsions

The stability of waterless (oil-in-oil) emulsions is an area which has not been widely exploited [5–14]. In this section we describe the preparation and stability of emulsions of PFMD in non-fluorinated oils or non-fluorinated oils in PFMD.

The ultra-low interfacial tension is usually caused either by the addition of electrolyte when ionic surfactant is used or by increasing the temperature in the case of non-ionic surfactants at oil–water [31–33] or oil–oil interfaces [14]. In the system under investigation (PFMD–FA–SPFO), similar ultra-low interfacial tensions were attained by adjusting the concentration of an alcohol in the PFMD phase (see Fig. 11). This phenomenon allows us to suppose that stable microemulsions can be formed in the PFMD and/or FA phase. Figure 12 presents the type and the volume fraction of the microemulsions formed as a function of the concentration of $C_7F_{15}CH_2OH$. The starting volume ratio of the PFMD phase (containing the alcohol) to the FA phase (with dissolved 5 wt.% SPFO) was 40%. In the hatched region we obtained transparent PFMD-in-FA (Winsor I) and FA-in-PFMD (Winsor II) microemulsions with clear phase inversion at a critical concentration of the alcohol. The microemulsified volume markedly depended on the alcohol concentration. The FA-in-PFMD microemulsions with 6.52 wt.% FA were prepared with a drop diameter of about 39 nm,

Fig. 11. Effect of co-surfactant species on the interfacial tension $\gamma_{1,2}$ between PFMD and FA containing 5 wt.% SPFO: curve 1, $HC_6F_{12}CH_2OH$; curve 2, $C_3F_7CH_2OH$; curve 3, $C_2F_5CH_2OH$; curve 4, $C_8F_{17}(CH_2)_2OH$; curve 5, $C_7F_{15}CH_2OH$.
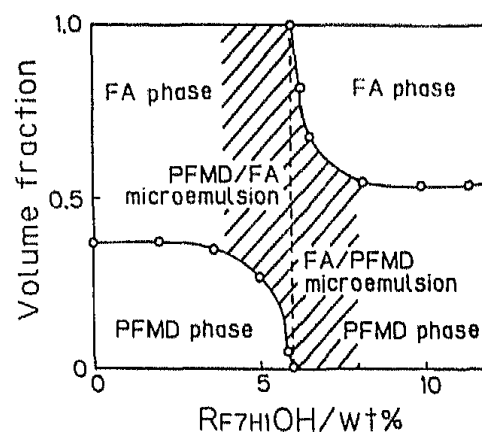

Fig. 12. Influence of the co-surfactant ($C_7F_{15}CH_2OH$) concentration on microemulsion formation in PFMD–FA systems containing 5 wt.% SPFO.

measured by dynamic light scattering. These micro-emulsions were very stable (for more than 3 months) as long as the temperature was kept constant.

Another set of emulsions was performed with PFMD non-fluorinated oil-PFPE systems without alcohol. The stabilities of macroemulsions from non-fluorinated oils with different dielectric permittivities, ϵ_r, stabilized with PFPE, are compared in Fig. 13. The height of a column represents the volume fraction of the emulsion after a period of 1 h (open) and after 7 days (hatched), where the volume fraction is the ratio of a cream phase volume to the total volume. The left-hand column corresponds to a surfactant concentration of 1 wt.%, and the right-hand column corresponds to 5 wt.%. It is clearly seen that both short term and long term stabilities of the emulsions markedly increase with increasing ϵ_r. This observation coincides well with the dependence of the dielectric permittivities of non-fluorinated oils on the interfacial activity of PFPE reported above (Figs 6 and 7 and Table 2), although there is no theoretical justification for such a coincidence. It is worth noting that a higher concentration of surfactant is not necessarily related to a higher stability of the macroemulsions.

Figure 14 shows the influence of co-surfactant species on the formation and stability of macroemulsions in PFMD-FA-PFPE systems. In these cases, the addition of alcohols decreases the stability of the macroemulsions (Figs 14(a) and 14(b)), although the addition of a small amount of alcohol makes the interfacial tension lower (see Fig. 9). This fact suggests that the lower interfacial tension results in a smaller energy for emulsification, but the mixed adsorbed layers of alcohols and surfactants cannot stabilize the emulsion effectively. However, the increase in the PFPE concentration compensates for the instability of the macroemulsions caused by the addition of the alcohols (Figs 14(c) and 14(d)). The concentration of PFPE in the experiments shown in Figs 14(c) and 14(d) was very high, and hence some structuring of PFPE micelles or its reverse micelles between droplets might be in part responsible for the stabilization [34,35].

Another interesting observation, following from the data presented in Fig. 14 is the inversion of the type of the emulsion upon increasing the co-surfactant concentration. Bearing in mind that PFPE is preferentially soluble in the FA phase and the fluorinated alcohol in the PFMD phase, a correlation could be made between the present system and the ordinary oil-in-water emulsions. It is well known [36,37] that mixtures of two emulsifiers with different solubilities can be used for stabilizing either oil-in-water or water-in-oil emulsions. The emulsion type depends on whether the hydrophilic or the lipophilic surfactant prevails. In fact, this is one of the basic presumptions of the so-called "hydrophilic-lipophilic balance" (HLB) concept [36,38]. Although the HLB classification of surfactants is widely used in the literature and has proved to be useful in practice, the mechanisms responsible for its manifestation are still under discussion [39]. The experimental results shown in Fig. 14 indicate that this concept can be expanded to some extent over non-aqueous oil-in-oil dispersions.
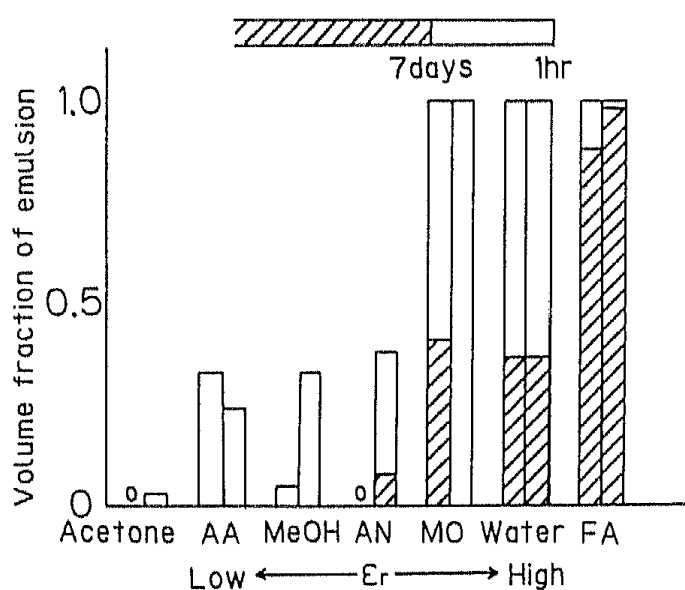

Fig. 13. Stability of oil-in-oil macroemulsions: left-hand column, 1 wt.% PFPE in NFO; right-hand column, 5 wt.% PFPE in NFO; unhatched, after 1 h; hatched, after 7 days.

Conclusions

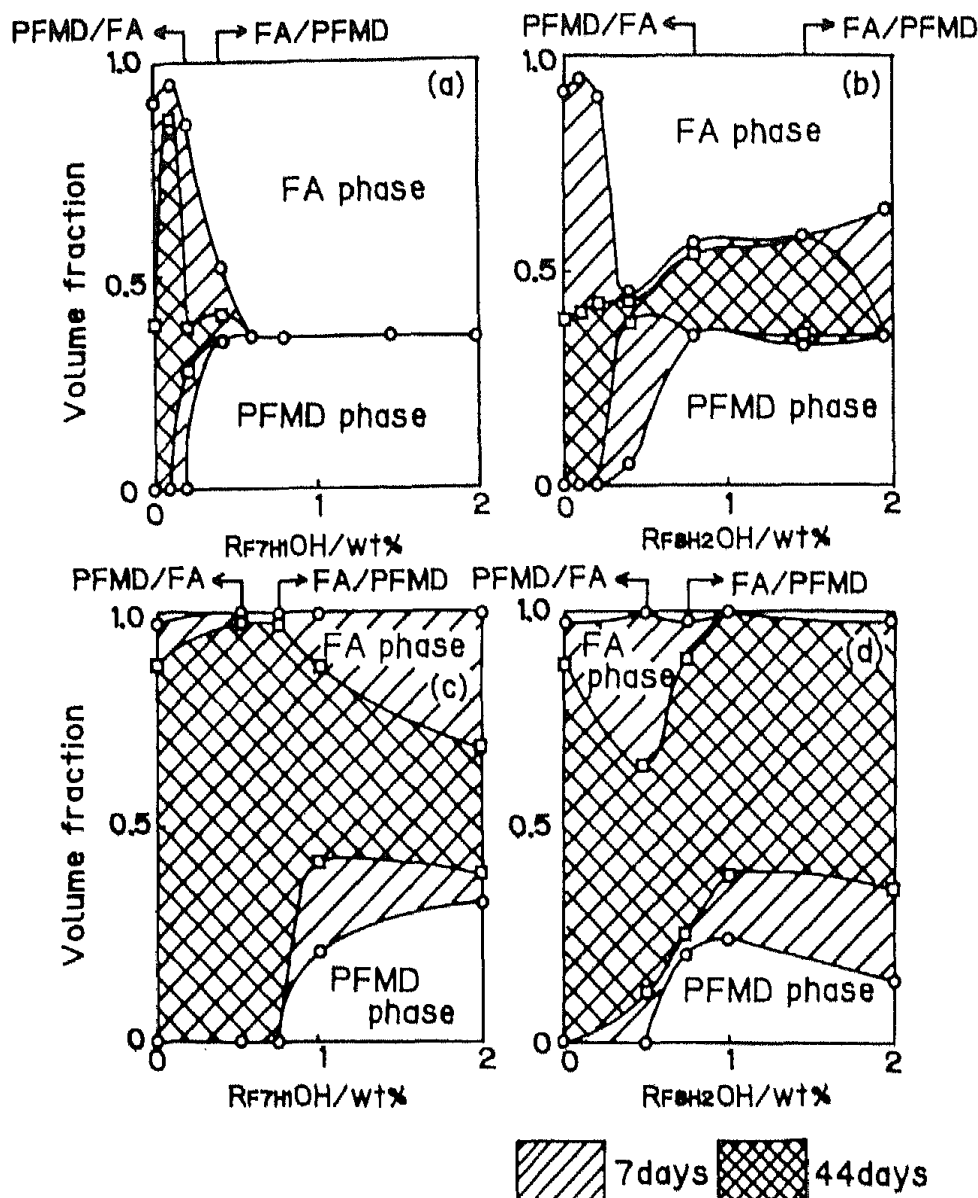The results presented above demonstrate the important role of the chemical and physical proper-

Fig. 14. Effect of the co-surfactant concentration on the formation and stability of PFMD-in-FA and FA-in-PFMD emulsions ($R_{F7H1}OH$, $C_7F_{15}CH_2OH$; $R_{F8H2}OH$, $C_8F_{17}(CH_2)_2OH$): (a) and (b), FA containing 0.5 wt.% PFPE; (c) and (d), FA containing 5.0 wt.% PFPE.

ties of the oils and surfactants on their interfacial behaviour. We showed that (1) the high values of the interfacial tension $\gamma_{1,2}$ between pure PFMD and polar liquids are entirely a result of the interactions between the polar molecules, and (2) the contribution of the dispersion interactions to $\gamma_{1,2}$ is negligible (see Fig. 2).

The comparative study of different kinds of surfactants indicated that the chemical compatibility between the "heads" and "tails" of their molecules with adjacent bulk liquid molecules determines the interfacial activity (see Fig. 3). From this viewpoint it is easy to explain why ethoxylated

perfluoroalkanol PFPE manifests such a high surfactant activity in the studied systems, while AOT does not show any. Still, the interfacial activity of PFPE strongly depends on the liquid used (Fig. 6 and Table 2). We found that the higher the polarity of non-fluorinated oils, the higher the resulting surface activity and adsorption, and the lower the CMC. This observation correlates also with the higher stability of the macroemulsions formed from polar liquids (see Fig. 13).

The investigated PFMD–non-fluorinated oil systems exhibited a large variety of phenomena, similar to those observed in non-fluorinated oil—

water systems. The appropriately chosen fluorinated alcohols acted as co-surfactants (see Figs 9 and 11). In some cases, ultra-low interfacial tension was reached and microemulsion formation was registered (see Fig. 12). During the increase in alcohol concentration the microemulsion type changed from Winsor I to Winsor II. However, we observed a large reduction on emulsion stability, indicating that the fluorinated alcohols acted as demulsifiers (Fig. 14). Bancroft's rule, which determines the emulsion type from surfactant solubility, was proved to be valid for these systems.

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