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# Counterion effect on the phase behavior of perfluoropolyether carboxylates: micelles and liquid crystals in water

F. Caboi <sup>a</sup>, A. Chittofrati <sup>b</sup>, P. Lazzari <sup>b</sup>, M. Monduzzi <sup>a,\*</sup>

<sup>a</sup> *Dipartimento di Scienze Chimiche, Università di Cagliari, Cittadella Universitaria Monserrato, S.S. 554 Bivio per Sestu, 09042 Monserrato-Cagliari, Italy*

<sup>b</sup> *Ausimont-CRS, Bollate, Milano, Italy*

## Abstract

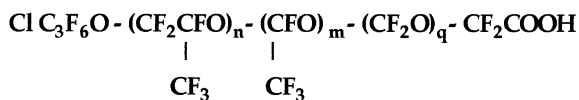
Perfluoropolyether carboxylates having sodium, potassium or ammonium counterions, and hydrophobic chains, mostly Cl–C<sub>3</sub>F<sub>6</sub>O– terminated, have been investigated in aqueous binary systems, with the focus laid upon the counterion effect on the major self-assembly features. Micellization and liquid crystal formation have been detected via surface tension, conductivity, optical microscopy and NMR. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** PFPE surfactants; Self-assembly; Counterion effect; NMR; Surface tension; Conductivity

## 1. Introduction

The self-assembly features of various ammonium salts of perfluoropolyether (PFPE) acids, having average molecular weight in the range 400–900, have been reported in several papers [1–6]. Micellar solutions and diluted dispersions of liquid crystals have been studied by ESR [1,2], whereas liquid crystalline phases have been investigated by NMR [3,4]. Very limited work on counterion, other than ammonium, is available for this class of surfactants, only the case of the micellization of a PFPE sodium carboxylate of average MW of 430 being reported [5,6].

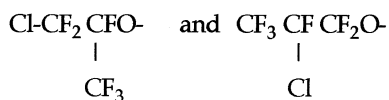
The previous studies on these PFPE surfactants focused on the carboxylic salts obtained by purification and distillation of raw acidic mixtures produced via photooxidation of hexafluoropropene [7], so to have perfluoroalkyl terminated hydrophobic tail. Another process [8], based on the co-oxypolymerization of chlorotrifluoroethylene and hexafluoropropene [8–10], leads to acidic mixtures of the following general structure:



where  $n \gg m$ ,  $q \approx 0$  and the ClC<sub>3</sub>F<sub>6</sub>O group is both in the form:

\* Corresponding author. Tel.: +39-70-6754385; fax: +39-70-6754388.

E-mail address: monduzzi@vaxca1.unica.it (M. Monduzzi)



These mixtures (Cl-PFPE-H) may contain a small quantity (<10%) of perfluoroalkyl-terminated chains. To obtain the Cl-PFPE-H mixtures of narrow MW distribution (MWD), purification and distillation steps have been used.

In the present work, the ammonium, potassium and sodium salts (ClPFPE-X), from a narrow MWD acidic mixture of formula I, are investigated with the aim to examine the effect of counterion on the self-assembly of the aqueous binary systems, in terms of hydration and counterion binding.

## 2. Experimental

### 2.1. Materials

The acidic mixture of formula I has an average MW of  $504 \pm 1.5\%$  as determined by acid/base titration; this result was confirmed by  $^{13}\text{C}$ - and  $^{19}\text{F}$ -NMR and also by titration of the ammonium salt with hexadecylpyridinium chloride, using a Metrohm Tenside ion-specific electrode.

The GC-MS analysis of the corresponding methyl esters indicated the main components to be the terms of formula I with  $m=p=0$  and  $n=1$  (approximately 55 wt% in the mixture),  $n=2$  (20 wt%) and  $n=0$  (10 wt%).

Three types of terminal groups were identified by NMR, that is a minor amount of  $\text{CF}_3\text{O-}$  end groups (around 7%), and a  $\text{CF}_3\text{CF}(\text{Cl})\text{CF}_2\text{O-}/\text{ClCF}_2\text{CF}(\text{CF}_3)\text{O-}$  molar ratio equal to 2.

In the dry salts, prepared from stoichiometric amount of the corresponding hydroxide as described in [3], the absence of acid was ascertained via IR. The residual water in the salts was less than 1% by Karl Fisher titration.

The thermogravimetric analysis (by Perkin Elmer instrument, in the range 50–350°C, with scan rate  $10.0^\circ\text{C min}^{-1}$ ) of the surfactant salts has been used to provide an indirect check of surfactant purity. Similarly to the case of pe-

rfluoroalkanoates [11], the thermal stability was strongly dependent upon the counterion and increased in the order  $\text{NH}_4^+ < \text{K}^+ < \text{Na}^+$  [10].

The surfactant/water samples were prepared, as previously reported [3,4], using distilled water purified through a MilliQ apparatus. The surface tension of water at 25°C was  $72 \text{ mN m}^{-1}$ . For the NMR studies,  $\text{D}_2\text{O}$  (Carlo Erba, 99.8% enriched) was used.

To define the binary phase diagram in the liquid crystalline regions, each sample, in flame sealed glass tubes, has been homogenised through back and forth centrifugation cycles. Prior to observation, each sample has been aged at 25°C for 3 months at least. The occurrence of anisotropic phases was detected by crossed polarizers and optical microscopy.

### 2.2. Methods

Either surface tension ( $\gamma$ ) and specific conductivity ( $\kappa$ ) of the surfactant salt solutions have been determined, at  $25.0 \pm 0.1^\circ\text{C}$ , in the concentration range  $0.01\text{--}20 \text{ mmol l}^{-1}$ .

The equilibrium surface tension was measured by De Nouy method (Harking-Jordan factors) via Lauda TE1C. Each equilibrium value is the average of five to six measurements with experimental deviation within  $0.2 \text{ mN m}^{-1}$ . Each measurement refers to the plateau of the curve  $\gamma$  versus time, at the concentration under examination, where  $\gamma$  was typically constant within  $0.05 \text{ mN m}^{-1}$ .

The specific conductivity was measured by a Metrohm MH660 with Pt electrodes having cell constant of  $0.98 \text{ cm}^{-1}$ . The measurements were carried out in a tapped cell up to the equilibrium values.

The liquid crystalline phases were observed in polarised light by an optical microscope Zeiss Axioplan 2.

The  $^2\text{H}$ - and  $^{13}\text{C}$ -NMR were performed by a Varian VXR-300 (7.05 T) spectrometer at 46.05 and 73.43 MHz, respectively. The accuracy on the temperature control was within  $0.5^\circ\text{C}$ .  $^2\text{H}$ -NMR spectra were recorded without lock and the error in the quadrupolar splitting measurements was around 5%. The spectra were periodically recorded to verify the achievement of equilibrium.

The samples were stored at the temperature selected for each experiment, heated for 1 h at temperature 5°C higher and left for 30 min in the NMR probe to ensure thermal equilibrium and alignment in the magnetic field, before recording the spectra.

### 3. Results and discussion

#### 3.1. Micellar solutions: surface tension and conductivity

Preliminary conductivity studies, at constant surfactant concentration close to cmc, ascertained the Krafft point of each surfactant salt to be lower than 25°C and much lower than those of the corresponding perfluoroalkanoates [11–14] in the range of similar MW. This fact may be rea-

sonably due to the CF<sub>3</sub>– branching and to the MOOD.

Fig. 1 displays the variation of equilibrium surface tension at 25°C as a function of concentration. The break points relate to the cmc of each surfactant salt. Surface tension data for Cl–PFPE–X surfactants are reported in Table 1 together with literature data for perfluorooc-tanoates (PFO–X) having the same counterions [11–13]. The dependence of cmc on the counterion is negligible for both Cl–PFPE–X and PFO–X series although the much lower cmc values for the Cl–PFPE–X surfactants should be remarked. Moreover, these Cl–PFPE–X salts display a slightly superior capacity of reducing the surface tension with respect to the linear perfluoroalkanoates. In Table 1, the minimum surface tension,  $\gamma_{\min}$ , achieved in micellar solution of the Cl–PFPE–X surfactants, can be compared with those reported for the corresponding PFO–X.

It should be mentioned that PFPE ammonium carboxylates of the same class and similar average MW, but having perfluoroalkyl-terminated PFPE tail, have been found to reach even lower values of  $\gamma_{\min}$  [15]. Reduced cmc and enhanced hydrophobicity for PFPE surfactants, compared to linear perfluoroalkanoates, have also been reported for high purity PFPE carboxylates from a different synthesis pathway [14]. These peculiarities had been early suggested on the basis of a comparative small-angle X-ray diffraction study of liquid crystals [16]. Although the (CF<sub>3</sub>)<sub>2</sub>CF– or ClCF<sub>2</sub>– end groups have been shown to increase the critical  $\gamma_{\min}$  values, measured for linear perfluoroalkyl chains in the solid state [17], the branching along the PFPE chain and the Cl-termination still promote in our case the slightly superior performance shown in Table 1. The lower  $\gamma_{\min}$  may be due either to the surfactant mixture composition or to the larger cross-sectional area of the Cl–PFPE chain. Such area may be estimated from the slope of the linear decrease of  $\gamma$  (at concentration below 0.8 mmol l<sup>–1</sup>, see Fig. 1) via Gibbs adsorption isotherm as modified by Shinoda [12]:

$$-(d\gamma/d \ln c)_T = RT\Gamma(1 + K_g/z) \quad (1)$$

Assuming  $K_g$  of 0.5, as used by Shinoda for perfluoroalkanoates, the average area for ad-

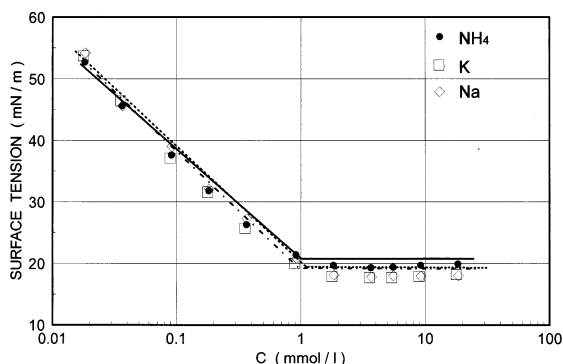


Fig. 1. Surface tension (mN m<sup>–1</sup>) versus surfactant concentration (mmol l<sup>–1</sup>) for Cl–PFPE–X salts in water. Na (■), K (●) and NH<sub>4</sub> (▲).

Table 1  
Surface tension data for Cl–PFPE–X and PFO–X series

	cmc (mmol l <sup>–1</sup> )	$\gamma_{\min}$ (mN m <sup>–1</sup> )	$A_{\text{surf}}$ (Å <sup>2</sup> )
<i>Cl–PFPE–X</i>			
NH <sub>4</sub> <sup>+</sup>	1.1	17.8	74
K <sup>+</sup>	0.9	17.7	71
Na <sup>+</sup>	1.0	19.3	77
<i>PFO–X</i> [11–13]			
NH <sub>4</sub> <sup>+</sup>	33	19.0	48
K <sup>+</sup>	26.3–27	20.6	43
Na <sup>+</sup>	32–36	24.6	42

sorbed Cl–PFPE–X surfactant molecule ranges between 71 and 77 Å<sup>2</sup>. These values are much higher than those of 42–48 Å<sup>2</sup> reported for the corresponding PFO–X [12].

As for the PFO–X, slightly higher  $\gamma_{\min}$  and cross sectional area are observed for Cl–PFPE–Na with respect to the other Cl–PFPE salts. This trend may be related to the higher hydration of Na<sup>+</sup> with respect to K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> (see below).

The degree of binding,  $\beta$ , can be obtained from the variation of conductivity with surfactant concentration.  $\beta$  is given by the ratio between the slopes of the conductivity in the micellar region ( $c > \text{cmc}$ ) and in the premicellar region ( $c < \text{cmc}$ ) [18,19], as shown in Fig. 2.  $\beta$  values of 0.23 for Cl–PFPE–Na, 0.31 for Cl–PFPE–K, and 0.40 for Cl–PFPE–NH<sub>4</sub> are obtained. Generally a strong hydration favors the dissociation of the counterion. As a result, the trend of counterion binding is inversely related to the trend of counterion hydration, Na<sup>+</sup> > K<sup>+</sup> > NH<sub>4</sub><sup>+</sup>.

Conductivity data give much higher cmc values with respect to those determined by surface tension (Fig. 1). Indeed the counterion binding strongly influences the conduction properties, particularly in the proximity of cmc. It is worth noticing that a  $\beta$  value of 0.48 (close to the value for Cl–PFPE–NH<sub>4</sub>) and almost coincident cmc values by conductivity and surface tension, have been obtained for PFO–NH<sub>4</sub> by Hoffmann [19]. Among the several reasons for the deviations observed for Cl–PFPE–X, it seems reasonable that the MWD would play a significant role in the partitioning of the surfactant mixture between aqueous bulk and air/water interface. This leads to an enrichment of the terms with higher MW in the surface film whereas the bulk enriches with the low MW terms. This partition can justify the higher cmc values by conductivity.

Turning the attention to perfluoro-terminated PFPE carboxylates, a cmc of 1.19 mmol l<sup>−1</sup> has been determined by conductivity and light scattering for a PFPE–Na surfactant having narrow MWD around 430 [5]. In addition a molar conductivity  $\lambda^-$  of the surfactant anion of 23.5 S cm<sup>2</sup> mol<sup>−1</sup> has been estimated using the literature  $\lambda^+$  value for Na<sup>+</sup> at 25°C [20], and assuming the

surfactant salt as monomeric species in dilute solution. The same approach has been applied to the conductivity measured at  $c < \text{cmc}$  (Fig. 2), with the three Cl–PFPE–X surfactants. Thus, using the  $\lambda^+$  value of 50.1 S cm<sup>2</sup> mol<sup>−1</sup> for Na<sup>+</sup>, and 73.5 S cm<sup>2</sup> mol<sup>−1</sup> for K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> [20], at 25°C, a  $\lambda^-$  of  $22.8 \pm 1.1$  S cm<sup>2</sup> mol<sup>−1</sup> is found, in fairly good agreement with the data previously obtained by Kallay et al. [5].

### 3.2. Binary phase diagrams: NMR and optical microscopy

The binary phase diagrams have been determined by visual inspection, optical microscopy, and NMR. D<sub>2</sub>O was used to enable <sup>2</sup>H-NMR measurements. The analysis of <sup>2</sup>H-NMR quadrupolar splittings has been selected to study the concentrated phases of the Cl–PFPE–X surfactants by virtue of the informative response of the technique, even in the presence of multiphase samples.

Nuclei with a spin quantum number  $I \geq 1$ , such as <sup>14</sup>N or <sup>2</sup>H, have an electric quadrupolar moment that can interact with non zero net electric field gradients giving multiple resonance of  $2I$  peaks [21], separated by the splitting:

$$\Delta\nu_q = (3/m)P_b\chi S_b \quad (2)$$

where  $m=4$  and  $m=8$  for the lamellar and hexagonal phase respectively,  $P_b$  is the fraction of the observed nucleus in the bound state,  $\chi$  is the quadrupolar coupling constant and  $S_b = 1/2(3 \cos^2 \vartheta_D - 1)$  is the order parameter related to the average time orientation ( $\vartheta_D$ ) of the nucleus with respect to the surfactant chain axis. For water molecules,  $P_b$  is linearly dependent on the surfactant/water ( $s/w$ ) molar ratio and thus Eq. (2) can be rewritten as [21]:

$$\Delta\nu_q = (3/m)n_b(s/w)\chi S_b \quad (3)$$

where  $n_b$  is the number of bound water molecules per polar head. The straight line of Eq. (3) would pass through the origin at low surfactant concentration. At high surfactant concentration the curve should ideally pass through a maximum.  $\Delta\nu_q$  maximum occurs at the  $s/w$  molar ratio related to the hydration number,  $n_b$ , as follows [21]:

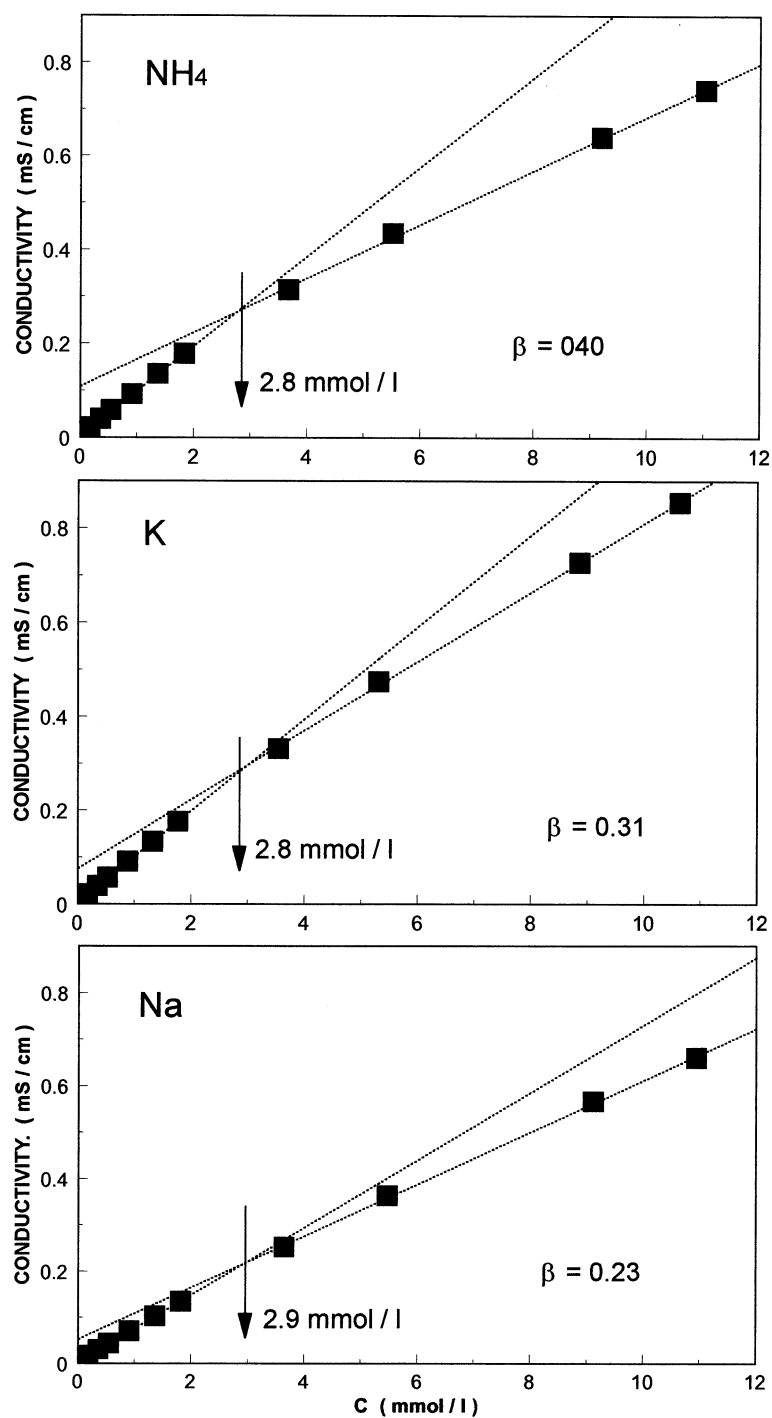


Fig. 2. Conductivity ( $\text{mS cm}^{-1}$ ) versus surfactant concentration ( $\text{mmol l}^{-1}$ ) of aqueous solutions of the Cl-PFPE-X salts at  $25^\circ\text{C}$ . (a)  $\text{NH}_4$  ( $\blacktriangle$ ); (b) K ( $\bullet$ ); (c) Na ( $\blacksquare$ ).

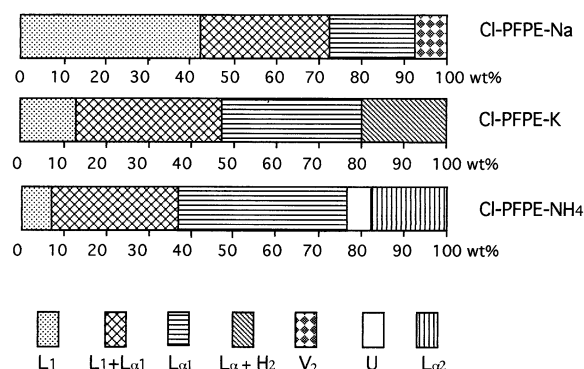


Fig. 3. Binary phase diagrams of the CI-PFPE-X/D<sub>2</sub>O systems. (a) CI-PFPE-Na; (b) CI-PFPE-K; (c) CI-PFPE-NH<sub>4</sub>. L<sub>1</sub>, isotropic liquid phase; L<sub>α1</sub>, L<sub>α2</sub>, lamellar LC; H<sub>2</sub>, hexagonal LC; V<sub>2</sub>, cubic LC; U, undefined phase.

$$n_b = (w/s) + 1 \quad (4)$$

The phase diagrams, shown in Fig. 3, are based on observations of the samples aged at 25°C for 10–12 months. The solubility limits, at 25°C, are approximately 42 wt% for CI-PFPE-Na, 12.5 wt% for CI-PFPE-K and 7 wt% for CI-PFPE-NH<sub>4</sub>. Hence, the extension of the L<sub>1</sub> micellar region decreases in the order Na<sup>+</sup> > K<sup>+</sup> > NH<sub>4</sub><sup>+</sup> in agreement with the trends of counterion hydration and binding to the micelles. Micellar self-assembly is indeed favored by counterion dissociation. This increases the electrostatic repulsion among the polar heads and promotes a positive curvature ( $H > 0$ ) of the surfactant interface.

At concentration exceeding the above limits wide two phase regions occur. The <sup>2</sup>H-NMR confirmed the coexistence of an isotropic micellar phase and a birefringent liquid crystalline (LC) phase. Figs. 4a and 5a show the quadrupolar splittings together with the isotropic signals for two samples of CI-PFPE-Na and CI-PFPE-K.

The identification of a monophasic lamellar LC region, in the range 72.5–92.5 wt% for CI-PFPE-Na, 47.5–80 wt% for CI-PFPE-K and 37.5–77.5 wt% for CI-PFPE-NH<sub>4</sub>, was attained by <sup>2</sup>H-NMR. Examples are shown in Figs. 4b, 5b, 6a and b. The attribution of the LC region to a lamellar phase (L<sub>α</sub>) was easily attained by optical microscopy as shown in Fig. 7a, b and c. The interpretation of <sup>2</sup>H-NMR spectra for the ammo-

nium surfactant, particularly at high surfactant concentration (see Fig. 4b and c) is complicated by the occurrence of slow exchange between am-

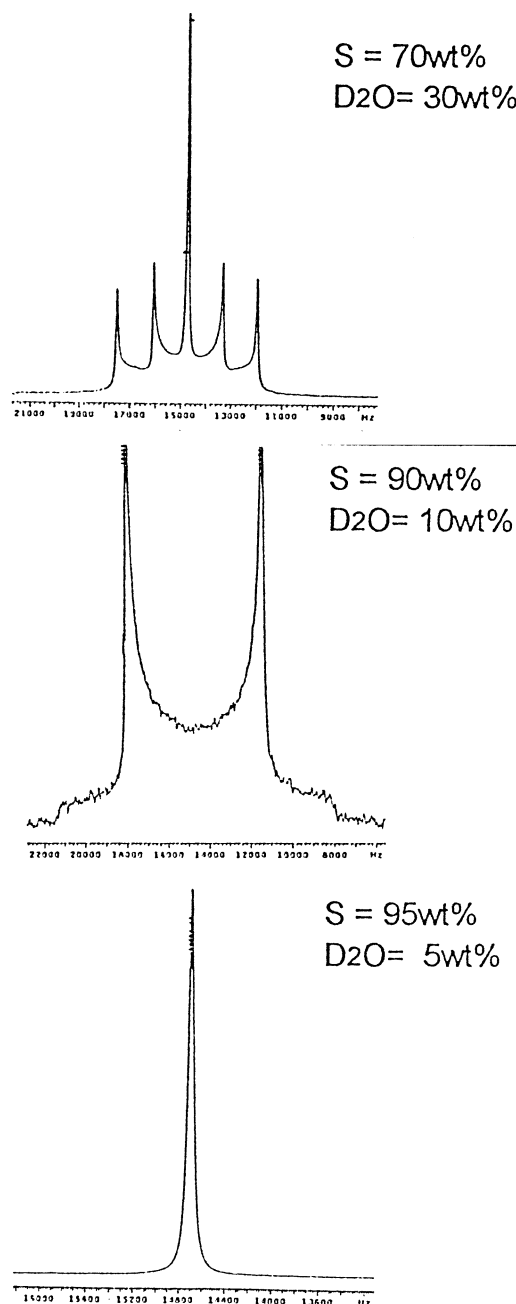


Fig. 4. <sup>2</sup>H-NMR spectra of CI-PFPE-Na/D<sub>2</sub>O system at various compositions. (a) S/D<sub>2</sub>O = 70/30 wt%, L<sub>1</sub> + L<sub>α</sub>; (b) S/D<sub>2</sub>O = 90/10 wt%, L<sub>α</sub>; (c) S/D<sub>2</sub>O = 95/5 wt%, V<sub>2</sub>.

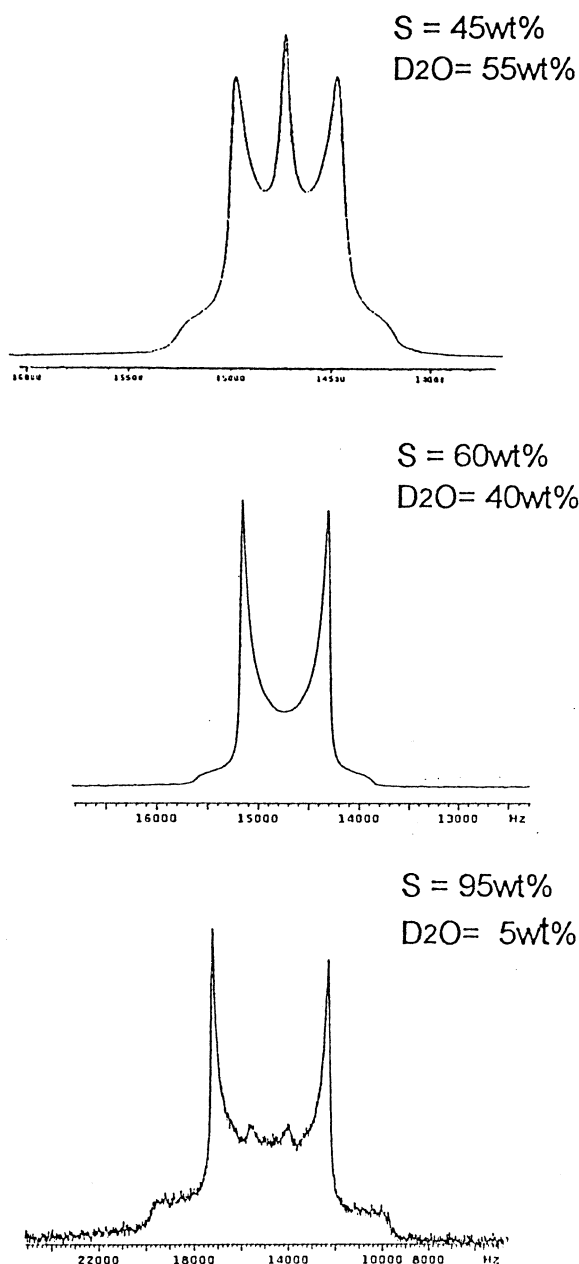


Fig. 5.  $^2\text{H}$ -NMR spectra of Cl-PFPE-K/ $\text{D}_2\text{O}$  system at various compositions. (a)  $S/\text{D}_2\text{O} = 45/55$  wt%,  $L_1 + L_\alpha$ ; (b)  $S/\text{D}_2\text{O} = 60/40$  wt%,  $L_\alpha$ ; (c)  $S/\text{D}_2\text{O} = 95/5$  wt%,  $L_\alpha + H_2$ .

monium and water deuterons. However, the separation of the two splittings is easily accomplished on the basis of the different chemical shifts, as demonstrated in previous papers [3].

The achievement of the equilibrium was a crucial point for all the samples in the concentrated regions of the binary phase-diagrams, since con-

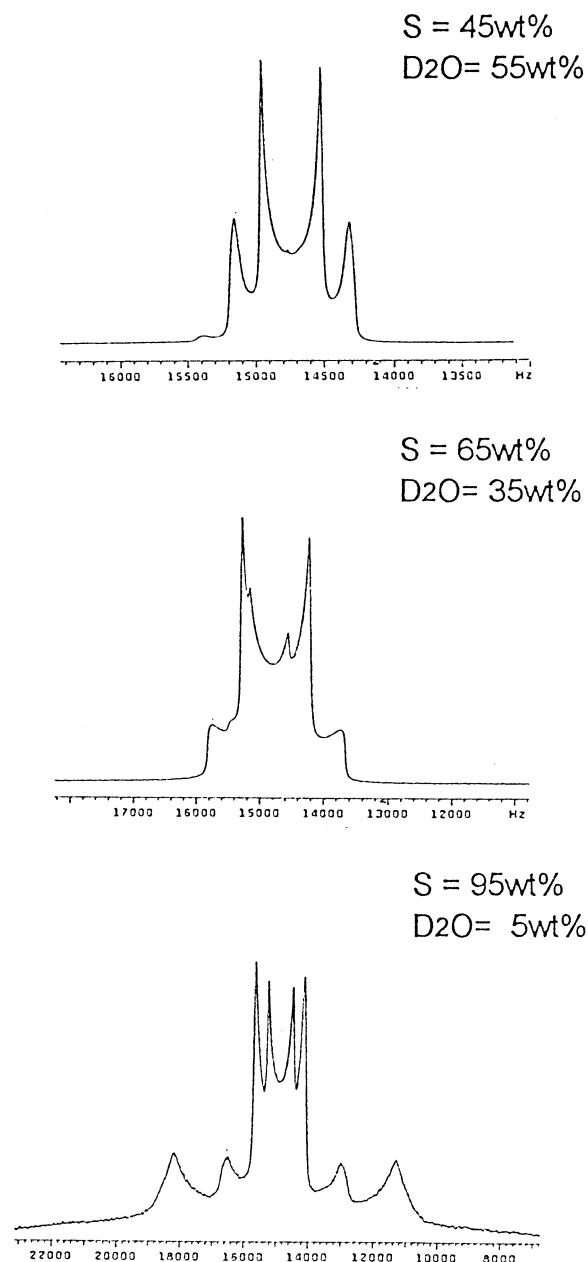
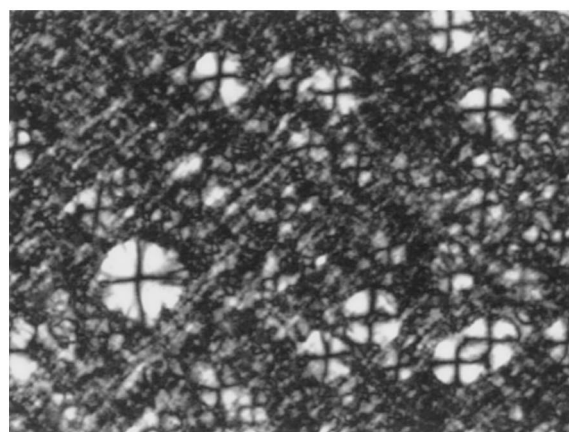
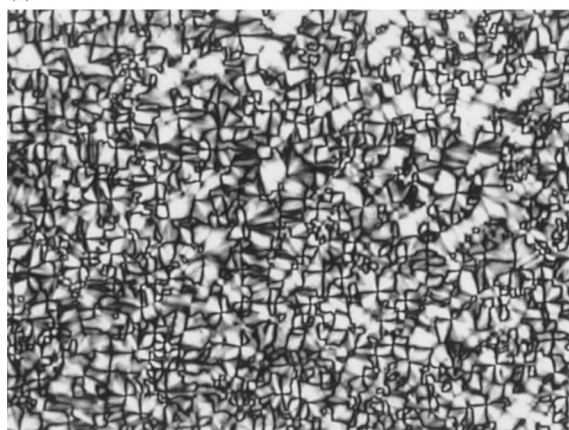


Fig. 6.  $^2\text{H}$ -NMR spectra of Cl-PFPE- $\text{NH}_4^+$ / $\text{D}_2\text{O}$  system at various compositions. (a)  $S/\text{D}_2\text{O} = 45/55$  wt%,  $L_{\alpha 1}$ ; (b)  $S/\text{D}_2\text{O} = 65/35$  wt%,  $L_{\alpha 1}$ ; (c)  $S/\text{D}_2\text{O} = 95/5$  wt%,  $L_{\alpha 2}$ .

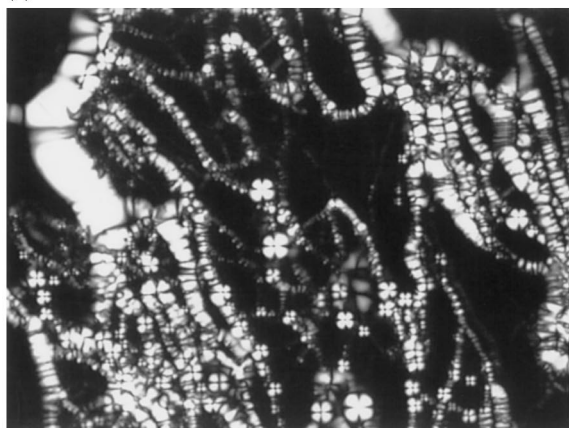




(a)



(b)



(c)

Fig. 7. Optical micrographs of the Cl-PFPE/D<sub>2</sub>O system. (a) Typical maltese crosses of  $L_\alpha$  LC in a Cl-PFPE-Na/D<sub>2</sub>O sample (60/40 wt%). (b) Mosaic pattern of  $L_\alpha$  phase in a sample of Cl-PFPE-K/D<sub>2</sub>O (55/45 wt%). (c)  $L_\alpha$  LC in the Cl-PFPE-NH<sub>4</sub>/D<sub>2</sub>O system (30/70 wt%).

stant quadrupolar splittings in the  $^2\text{H}$ -NMR spectra have been observed only after 8–10 months storage at 25°C. The  $^2\text{H}$  spectra of the samples at compositions around 80% showed anomalous shapes with respect to the spectra of samples with close compositions. It should be remarked that, before recording the spectra, these samples were left in the magnetic field while the temperature was gradually decreased from 80 to 25°C, in order to favor a slow alignment. The anomalous shapes are mainly due to the low resolution of the  $^2\text{H}$ -NMR spectra or, in other words, the samples do not easily align in the magnetic field. This behavior may be due to an anomalous increase of the viscosity reasonably induced by the occurrence of phase transitions, as demonstrated by considering the spectra of samples at higher concentration (Figs. 4c, 5c, and 6c).

Cl-PFPE-Na/D<sub>2</sub>O system, at a surfactant concentration higher than 92.5 wt%, displays another monophasic LC region, whose  $^2\text{H}$ -NMR isotropic signal (Fig. 4c) easily allows the identification of a cubic phase.

In Cl-PFPE-K/D<sub>2</sub>O system, at a composition higher than 80 wt%, the appearance of two different quadrupolar splittings in the  $^2\text{H}$ -NMR spectra (Fig. 5c) gives evidence of two coexisting anisotropic LC phases, namely a  $L_\alpha$  and, very likely, a reverse hexagonal ( $H_2$ ) phase. Indeed, the internal splitting amounts to about the half of the external one, in agreement with Eqs. (2) and (3). Optical microscopy confirms this result.

In Cl-PFPE-NH<sub>4</sub>/D<sub>2</sub>O system, at a composition around 85 wt% the  $^2\text{H}$ -NMR spectra showed well resolved quadrupolar splittings, clearly attributed to a monophasic region (Fig. 6c). Optical micrographs of these samples show the typical lamellar texture. Therefore, besides the lamellar region occurring in the range 37.5–77.5 wt%, around the 82.5 wt% of surfactant, a phase transition towards a different lamellar phase can be suggested. The occurrence of two kinds of  $L_\alpha$  phases, upon increasing surfactant concentration, has already been described for didodecyltrimethylammonium bromide in water [4]. Also, PFO-Li has been reported to form, at high concentration, two different lamellar structures, identified as a regular LCT and an intermediate phase with a

repeated layer structure. A tetragonal ( $T_1$ ) structure, closely related to the LCT self-assembly, has been proposed for that intermediate phase on the basis of X-rays and NMR studies [22].

The water deuterium quadrupolar splittings,  $\Delta v_q$ , plotted as a function of the surfactant-to-water molar ratio ( $s/w$ ) for the Cl-PFPE-X surfactants are shown in Fig. 8.

The quadrupolar splittings measured for Cl-PFPE-Na lay on a straight line crossing through the origin. The maximum predicted by theory [21] can be roughly identified around  $s/w = 0.2$  which corresponds to a degree of water binding per polar head  $n_b = 6$ .

The low quantity of the  $H_2$  phase, which forms at high surfactant concentration in the Cl-PFPE-K binary system, should not affect the splitting due to the  $L_\alpha$  phase. Accordingly,  $\Delta v_q$  values, measured in the diluted region, lay on a straight line. With increasing the surfactant concentration, a maximum occurs around  $s/w = 0.3$ , which leads to  $n_b = 4$ .

Data measured for the Cl-PFPE- $\text{NH}_4$  system lay over two straight lines with different slopes. This supports the hypothesis of a transition to a second lamellar phase. The maximum can be identified in the  $L_{\alpha 2}$  region at  $s/w = 0.3$ , which again leads to  $n_b = 4$ .

In the diluted region, similar  $\Delta v_q$  are observed for Cl-PFPE- $\text{NH}_4$  and Cl-PFPE-K surfactants. This implies similar arrangements of the water molecules residing at the polar-apolar interface.

The good agreement between conductivity and NMR results, in terms of counterion hydration, is

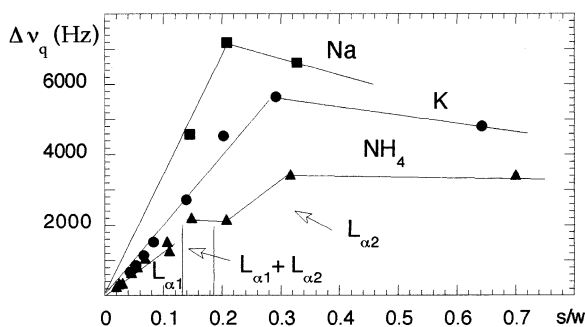


Fig. 8. Ouadrupolar splitting,  $\Delta v_q$  (Hz) versus surfactant/water molar ratio ( $s/w$ ).

to be stressed. The electrostatic interactions, which are strictly related to hydration and binding of the counterion, play a crucial role on the packing of the surfactant through the effective area of the polar head.

#### 4. Conclusion

The phase behavior of the  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  salts of a perfluoropolyether carboxylic mixture (mostly  $\text{ClC}_3\text{F}_6\text{O}-$  terminated) has been investigated in water to highlight the effect of counterion hydration and binding on the packing features.

At extreme dilution, the fully dissociated monomeric Cl-PFPE anions have the same value of molar conductivity for the three counterions. At concentration exceeding cmc, the binding of the counterion to the micelles increases in the order  $\beta_{\text{Na}^+} < \beta_{\text{K}^+} < \beta_{\text{NH}_4^+}$ . At the air/water interface, the highest value of surface tension in the micellar region is found for the sodium salt, as already observed for the PFO-X series.

The extension of the micellar solution region in the binary phase diagrams increases in the order  $\text{NH}_4^+ < \text{K}^+ < \text{Na}^+$ , though the difference between ammonium and potassium is small. In the micellar region, the higher hydration of the sodium counterion, evidenced by a lower  $\beta$  value (i.e. lower counterion binding), leads to the highest solubility of Cl-PFPE-Na in water.

The three Cl-PFPE-X surfactants form lamellar phases in the intermediate range of concentration, while the difference in the packing features due to the counterion type is particularly relevant at high surfactant concentration. Indeed, significantly different LC structures are observed, namely a cubic phase (very likely of the bicontinuous type) for sodium, a second lamellar phase for ammonium, and a reverse hexagonal phase, in equilibrium with a lamellar one, for the potassium salt. The type of LC phases can be easily related to an increase of the packing parameter  $v/al$ , as defined by Mitchell and Ninham [23], in the sequence  $\text{Na}^+ < \text{NH}_4^+ < \text{K}^+$ . This trend agrees with the higher hydration number ( $n_b = 6$ ) and with the lower binding ( $\beta = 0.23$ ) observed for

Cl–PFPE–Na. The lower hydration ( $n_b = 4$ ) and dissociation ( $\beta = 0.31$  and  $0.40$ ) observed for Cl–PFPE–K and Cl–PFPE–NH<sub>4</sub> bring about two different arrangements, despite the similarity in very dilute solution, where fully dissociated and hydrated K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> have identical molar conductivity. The presence of NH<sub>4</sub><sup>+</sup> allows a rearrangement of the lamellar self-assembly. With decreasing water content and hydration, K<sup>+</sup> counterion allows for a further decrease of the polar head area and favors a reverse curvature ( $H < 0$ ) of the surfactant interface.

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