



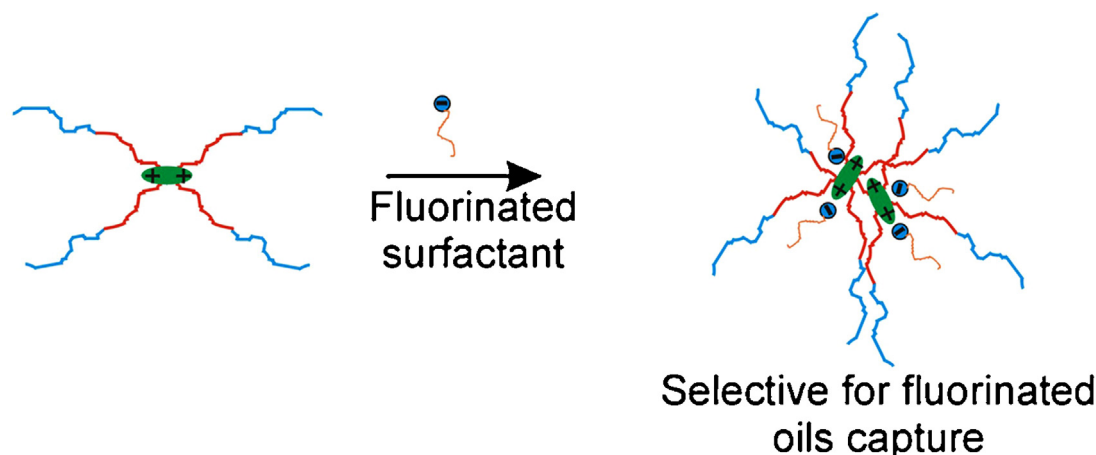
## Mixed aggregates based on tetronic-fluorinated surfactants for selective oils capture



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### GRAPHICAL ABSTRACT



### HIGHLIGHTS

- Tetronics-perfluoro carboxylic acids showed lipophobic and hydrophobic character.
- Temperature could be used to trigger the complexes formation equilibrium.
- The mixed structures incorporated selectively hydrogenated or fluorinated oils.

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### ABSTRACT

An aqueous star-like copolymer solution was titrated with perfluoro carboxylic acids at various compositions to prepare a polymeric surfactant composed of fluorinated nano-domains. The copolymer is X-shaped where each arm contains ethylene oxide and propylene oxide repetitive units linked to a central ethylenediamine group. The aggregation behavior of the hybrid macromolecule was studied from the physico-chemical point of view by changing parameters like temperature and composition. The solubilization of perfluorinated and hydrogenated alcohols in mixed self-assembled structure revealed that a selectivity toward the fluorinated moiety can be done. The self-assembled structures are promising for applications where the coexistence of nano-domains with dual lipophobic and hydrophobic character is required. Therefore, they are tools to incorporate selectively hydrogenated and fluorinated oils sparingly soluble in water.

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## 1. Introduction

The design of supramolecular structures can be done by exploiting several routes and combining different components. The issue of enhancing solubilization of compounds sparingly soluble in water is still a significant matter. Within this topic, novel inorganic micelles, composed of nanotubes properly functionalized, were designed [1,2]. They were revealed efficient tools for entrapping compounds for specific purposes. Notwithstanding, the micelles preparation through the conventional self-assembly method still remains a remarkable challenge. Under particular conditions, amphiphilic molecules may aggregate to form nanostructures responsive to external factors like pH, temperature, light, concentration, etc. Within this issue, block copolymers, with hydrophobic and hydrophilic repetitive units, allow us to obtain a variety of organized structures. Poly(ethylene oxide)-poly(propylene oxide)-poly-(ethylene oxide) (PEO-PPO-PEO) so called Pluronics were extensively investigated in water as well as in the presence of a third component. Recently, they have been used as dispersant to prepare microparticles for drug delivery [3].

Tetronics are X-shaped polyethers with four PPO-PEO arms bonded to a central ethylene diamine linker. Sequential copolymers possess hydrophobic PPO groups into the core and hydrophilic PEO chains extended outward. The tertiary amine bridging elements makes a notable difference rendering the tetronics sensitive to the pH. Compared to Pluronics, they have been less investigated; the pH effect on the aggregation process and the capability of the resulting micelles in incorporating various solutes [4–6] was analyzed; moreover, they have been used to extract single-walled carbon nanotubes [7].

Both classes of block copolymers are disposable in a large number of different structures tuned through independent and systematic control of hydrophilic and hydrophobic moieties. They are biocompatible and this explains the continuous scientific interest addressed to them.

There is a wide literature, covering the last 25 years, on the self-assembling of amphiphilic molecules to form conventional micelles composed of surfactant and solute (polar and apolar ones) or surfactants of different nature (fluorinated and hydrogenated or ionic and nonionic). Recently, these mixtures have been properly manipulated by preparing surfactants, containing long hydrogenated and fluorinated chains; [8] moreover, gemini surfactants were mixed with conventional surfactant to obtain better solubilization properties [9] and conventional mixed surfactants were exploited as fragrances solubilization [10]. Within this issue, we thought it would be interesting to design nanostructures formed by hydrogenated polymeric surfactant and fluorinated conventional surfactant. Specifically, our aim was at preparing a hybrid macromolecule formed by the sequential Tetronic T1107 to which perfluoro carboxylic acids were anchored through electrostatic forces. The self-assembling of the new hybrid polymeric surfactant was tuned by changing the lipophobicity of the fluorinated acids, composition and temperature. The solubilization ability in water media was tested through perfluorinated and hydrogenated alcohols. These novel nanostructures may be efficient tools to incorporate mixtures of oils differing in the hydrophobicity (hydrogenated, fluorinated, and so on).

## 2. Experimental

### 2.1. Materials

The block copolymer (from Aldrich) is [(EO)<sub>57</sub>(PO)<sub>21</sub>]<sub>2</sub> NCH<sub>2</sub>CH<sub>2</sub>N[(PO)<sub>21</sub>(EO)<sub>57</sub>]<sub>2</sub> (T1107, 15,000 uma). Perfluoroheptanoic acid (PF7H), perfluoropentanoic acid (PF5H) and perfluorobutanoic acid (PF4H) from Fluka were crystallized from

carbon tetrachloride and dried at room temperature. 1-Hexanol (ROH), 2,2,3,3,4,4,4-heptafluoro-1-butanol (RFOH) are from Sigma.

### 2.2. Methods

#### 2.2.1. Density and sound velocity measurements

The densities ( $\pm 1 \times 10^{-6} \text{ g cm}^{-3}$ ) and the speeds of sound ( $\pm 0.1 \text{ m s}^{-1}$ ) of the solutions were determined at  $25.000 \pm 0.001 \text{ }^\circ\text{C}$  by using a density and a sound velocity meter (DSA 5000 M, Anton Paar).

The apparent molar volume of the *i*th component ( $V_{\phi,i}$ ) in a given mixture was calculated by means of the following equation

$$V_{\phi,i} = \frac{M}{d} - 10^3 \left( \frac{d - d_0}{m d d_0} \right) \quad (1)$$

where *m* and *M* are the molality and the molecular weight of the *i*th component, respectively, while *d* and *d*<sub>0</sub> are the solution and the solvent densities, respectively. In the case of the apparent molar volume of T1107 ( $V_{\phi,C}$ ) and T1107 + PFnH ( $V_{\phi,C+A}$ ) in water, in Eq. (1) *d*<sub>0</sub> refers to water. For  $V_{\phi,C+A}$  calculations the average molecular weight and the total molality were introduced in Eq. (1). For the apparent molar volume of the fluorinated acid ( $V_{\phi,A}$ ) *d*<sub>0</sub> refers to the density of the water + T1107 mixture. The apparent molar expansibility of the *i*th component ( $E_{\phi,i}$ ) was calculated by deriving  $V_{\phi,i}$  with respect to temperature ( $E_{\phi,i} = \partial V_{\phi,i} / \partial T$ ).

The isentropic compressibility coefficients of the solutions ( $\beta$ ) were computed as  $100/(u^2 \times d)$  being *u* the ultrasonic velocity of the solution. The apparent molar isentropic compressibility of the *i*th component ( $K_{\phi,i}$ ) was calculated using the following equation

$$K_{\phi,i} = V_{\phi,i} \beta + 10^3 \left( \frac{\beta - \beta_0}{m d_0} \right) \quad (2)$$

where  $\beta_0$  is the isentropic compressibility coefficient of the solvent and the other symbols have the same meaning as above. For the apparent molar isentropic compressibility of the fluorinated acid within the mixed system ( $K_{\phi,A}$ ) *d*<sub>0</sub> and  $\beta_0$  refer to the density and the isentropic compressibility of the water + T1107 mixture.

#### 2.2.2. Differential scanning calorimetry (DSC)

The experiments were done by using the micro-DSC III (SETARAM) under nitrogen flow from 10 to 60 °C with a scan rate of 0.6 °C min<sup>-1</sup>. From each DSC curve the critical micellar temperature (CMT) of the copolymer was determined as the maximum of the peak and the enthalpy of micellization ( $\Delta H_M$ ) from the integration of the peak. The baseline was subtracted according to literature [11]. The CMT and the  $\Delta H_M$  values are collected in the Appendix.

#### 2.2.3. Conductivity

Experiments were performed by means of a digital Metrohm 660 conductimeter at a frequency of 2 kHz at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ .

#### 2.2.4. Solubility

The solubility of ROH and RFOH in the aqueous copolymer and copolymer + PF7H mixtures was determined at 25.0 °C. The solubility was detected by measuring the scattering intensity at 173° ( $\lambda = 633 \text{ nm}$ ) by using a Zetasizer NANO-ZS (Malvern Instruments). The break point of the intensity versus ROH or RFOH concentration trend was taken as the solubility (some examples of these curves are reported in Supporting Information). The partition coefficient of alcohols between the micellar and aqueous phases was calculated from the slope of the relative solubility vs surfactant concentration.

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