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Influence of methanol on the phase behavior of nonionic fluorinated surfactant: Relation to the structure of mesoporous silica materials

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ABSTRACT

We have investigated the effect of methanol addition on the $R_8^F(EO)_9$ and $R_7^F(EO)_8$ surfactant-based systems. While upon the addition of methanol the L_1 micellar phase grows, the direct hexagonal (H_1) and the lamellar (L_α) liquid crystals progressively melt with the increase of alcohol content. Phase behavior and SAXS measurements proved that methanol molecules interact with the oxyethylene units of the surfactant. This involves a folding up of the hydrophobic chains in the liquid crystal phases. Moreover, for the $R_7^F(EO)_8$ surfactant, the cloud point curve is shifted to high temperatures upon addition of alcohol. Starting from these systems, we have prepared mesoporous materials. Results show that due to the hydrogen bonds between the alcohol and the EO groups, the hexagonal structure of the mesostructured silica obtained from $R_8^F(EO)_9$ is lost when the content of CH_3OH is increased. In contrast, for the compounds prepared from the $R_7^F(EO)_8$-based system, the pore ordering occurs in the presence of alcohol. This phenomenon has been related to the moving of the cloud point curve toward high temperatures with the addition of methanol. Our study reveals also that under our conditions the methanol released during the hydrolysis of the silica precursor does not affect the self-assembly mechanism in a positive or negative way.

1. Introduction

Since their discovery in the early 1990s, surfactant-templated mesoporous materials have attracted much research attention due to a number of remarkable properties, such as adjustable pore size, high surface area and pore volume, and ease of surface modification [1–9]. The synthesis of these compounds combines sol–gel chemistry and the use of assemblies of surfactant molecules as framework templates. Depending on the surfactant concentration, two main pathways have been proposed to explain their formation. When mesoporous materials are prepared from a micellar solution, i.e., at low surfactant content, it is now admitted that the synthesis occurs through the cooperative templating mechanism (CTM) [8–12]. For example, using nonionic fluorinated surfactants $[R_m^F(EO)_n]$, which are the fluorinated analogues of the hydrogenated polyoxyethylene alkyl ethers $[R_m^H(EO)_n]$, we have synthesized mesoporous materials with a hexagonal channel array via a CTM-type mechanism in a wide range of surfactant concentrations (5–20 wt%) [13]. The second approach to the preparation of ordered mesostructures is based on the direct liquid crystal templating (LCT) pathway [12,14–17]. In this case, the surfactant concentrations are much greater and the structure of the recovered materials can be designed, a priori, based on the corresponding liquid crystal phase. Nevertheless, whatever the synthesis pathways, the characteristics of the recovered materials, such as the structure and the pore diameter, are strongly related to the properties of the surfactant used for their preparation. One of the main parameters that should be taken into account in the design of mesoporous materials is the behavior of the surfactant in solution, which can be affected by the presence of additives [18–24]. As a consequence, the properties of the mesoporous materials can be modified [25–28]. Indeed, in the literature, some papers deal with the influence of alcohol, used as a cosolvent, on the structural ordering and morphology of mesoporous silica [29–35]. For instance, by increasing the amount of alcohol, such as ethanol, propanol, or methanol, in the synthesis mixture of mesoporous materials prepared from the CTMABr-surfactant based system, Cool and co-workers [35] have observed the following transition mesophase sequence: hexagonal → cubic → lamellar → radially arranged hexagonal close-packed mesophase. To explain the phase transition, the authors consider a variation of the surfactant packing parameter. They claim that at the lower concentration, alcohol molecules penetrate into the surfactant micelles and act as a cosurfactant. However, they have not performed a study to understand the effect of alcohol addition on the surfactant phase behavior.

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The synthesis of a mesoporous silica material requires a silica precursor, generally an alkoxide. In aqueous solution the alkoxide is hydrolyzed and condensed to form polymeric species composed of Si–O–Si units, and during the hydrolysis step, alcohol is formed. As mentioned above, the presence of alcohol can strongly affect the characteristics of the recovered mesostructure. In this study, we try to shed some light on the role played by methanol in the pore ordering of mesoporous materials prepared from nonionic fluorinated surfactants belonging to the polyoxyethylene fluoroalkyl ether family [$C_mF_{2m+1}C_2H_4(OC_2H_4)_nOH$, labeled as $R_m^F(EO)_n$]. This methanol is produced during the hydrolysis of tetramethoxysilane (TMOS), used as the silica precursor. We have investigated the effect of methanol addition on the surfactant phase behavior in water and we have determined the structural parameters of the liquid crystal phases.

2. Materials and methods

The fluorinated surfactants, which were provided by DuPont, have average chemical structures of $C_8F_{17}C_2H_4(OC_2H_4)_9OH$ and $C_7F_{15}C_2H_4(OC_2H_4)_8OH$. They are respectively labeled as $R_8^F(EO)_9$ and $R_7^F(EO)_8$. In both cases the hydrophilic chain moiety exhibits a Gaussian chain length distribution and the hydrophobic part is composed of a well-defined mixture of fluorinated tails.

2.1. Phase diagram determination

The samples were prepared by weighing the required amounts of surfactant, methanol, and water in well-closed glass vials to avoid evaporation. They were left at controlled temperature for some hours in order to reach equilibrium. The phase diagrams were established at 20 and 40 °C in the whole range of water–surfactant composition. The methanol concentration was varied from 0 to 20 wt%. Liquid crystal phase domains were identified by their texture, observed with an optical microscope equipped with cross polarizers. To find the exact limits of these domains, additional SAXS measurements were also performed.

2.2. Determination of the cloud point curve of the $R_7^F(EO)_8$ system

The cloud point was determined visually by noting the temperature at which the turbidity of the $R_7^F(EO)_8$ solutions was observed. The cloud point curve was obtained by plotting the temperature at which the solutions become unclear as a function of the surfactant concentration.

2.3. Mesoporous preparation

Before the addition of methanol, micellar solutions at 10 wt% of $R_8^F(EO)_9$ and at 25 wt% of $R_7^F(EO)_8$ were prepared. The concentration of methanol in the surfactant solution was made to vary from 0 to 15 wt%. The pH value of the solution was then adjusted to 2.0 using sulfuric acid. Tetramethoxysilane (TMOS), used as the silica precursor, was added dropwise into the micellar solution at 20 °C. The surfactant/silica molar ratio was adjusted to 0.5. The obtained samples were sealed in Teflon autoclaves and heated for 1 day at 80 °C. The final products were recovered after ethanol extraction with a Soxhlet apparatus for 48 h.

2.4. Characterization

SAXS measurements were carried out using a home-built apparatus, equipped with a classical tube ($\lambda = 1.54$ Å). The X-ray beam was focused by means of a curved gold/silica mirror on the detector placed 527 mm from the sample holder. Nitrogen adsorption–desorption isotherms were obtained at −196 °C over a wide relative pressure range, from 0.01 to 0.995, with a TRISTAR 3000 volumetric adsorption analyzer manufactured by Micromeritics. The samples were degassed further under vacuum for several hours at 320 °C before nitrogen adsorption measurements were performed. The pore diameter and the pore size distribution were determined by the BJH (Barret–Joyner–Halenda) method [36].

3. Results and discussion

3.1. Evolution of the $R_m^F(EO)_n$/water system upon the addition of methanol

Fig. 1 depicts the partial phase diagram of the ternary $R_8^F(EO)_9$/CH_3OH/water system at 20 °C (Fig. 1A) and at 40 °C (Fig. 1B). As shown in Fig. 1A, the micellar domain (L_1) detected for $R_8^F(EO)_9$ content lower than 40 wt% without methanol is progressively expanded toward higher surfactant concentrations with the addition of alcohol. For example, at 20 °C the micellar domain is extended up to 57 wt% of $R_8^F(EO)_9$ for a weight percent of CH_3OH equal to 20 wt%. When the loading of surfactant is increased from 53 to 78 wt%, a direct hexagonal H_1 phase is observed. The CH_3OH solubilization rate in the hexagonal phase is strongly dependent on the $R_8^F(EO)_9$/water ratio (noted R). Indeed, upon the addition of methanol, the surfactant range of composition belonging to H_1 is progressively reduced and the hexagonal liquid crystal phase is completely melted when the CH_3OH concentration reaches 15 wt%. The hexagonal H_1 phase is characterized by its typical SAXS profile with the relative peak positions 1, $\sqrt{3}$, 2. The distance d associated with the first peak is related to the hydrophobic radius R_H by the relation

$$\frac{V_B}{V_S+\alpha V_W+\alpha' V_M}=\frac{\sqrt{3}\pi R_H^2}{2d^2},$$

where α and α' respectively stand for the number of water and methanol molecules per surfactant molecule. V_B, V_S, V_W, and V_M respectively correspond to the molar volumes of the hydrophobic part of the surfactant ($V_B = 261$ cm^3/mol), the surfactant ($V_S = 626$ cm^3/mol), water ($V_W = 18$ cm^3/mol), and methanol ($V_M = 40$ cm^3/mol). The cell parameter a is given by the relation $a = 2d/\sqrt{3}$. Fig. 2A shows the evolution at 20 °C of the d-spacing and R_H as a function of α', for different values of R. For

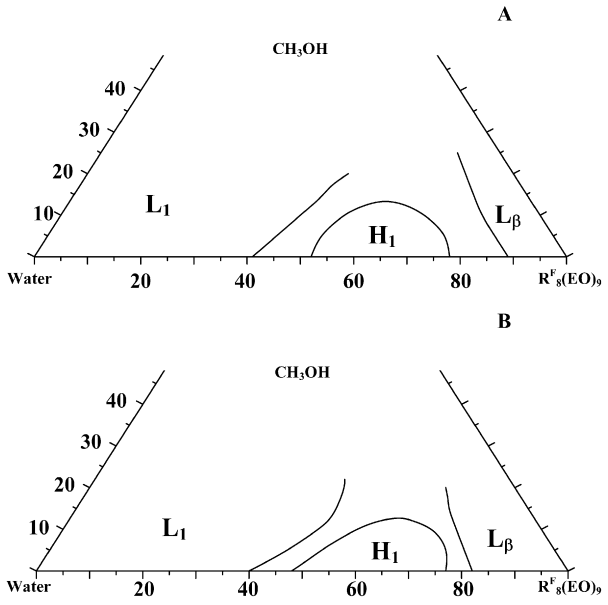

Fig. 1. Temperature–composition phase diagram (wt%) of $R_8^F(EO)_9$/CH_3OH/water system at 20 °C (A) and 40 °C (B).