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Predictive synthesis of ordered mesoporous silica with maltoside and cationic surfactants based on aqueous lyotropic phase behavior

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ABSTRACT

Self-assembled nonionic alkyl glycoside surfactants are of interest for creating functional adsorption and catalytic sites at the surface of mesoporous sol–gel-derived materials, but they typically impart poor long-range order when they are used as pore templates. Improved order and control over the functional site density can be achieved by mixing the alkyl polyglycoside surfactant with a cationic surfactant. Here, we investigate the rarely reported lyotropic liquid crystalline (LLC) phase behavior of aqueous solutions of a nonionic disaccharide surfactant, n-dodecyl-β-D-maltoside ($C_{12}G_2$/DM), and cetyltrimethylammonium bromide (C_{16}TAB) by low-angle powder X-ray diffraction (XRD) and polarized optical microscopy (POM). An approximate ternary phase diagram of the C_{16}TAB–$C_{12}G_2$–water system is developed at 50 °C, which includes 2-D hexagonal (P6mm symmetry), bicontinuous cubic ($Ia\bar{3}d$ symmetry), lamellar, and rectangular (cmm symmetry) LLC phases. By replacing the volume of water in the phase diagram with an equivalent volume of silica, ordered mesoporous materials are prepared by a nanocasting technique with variable $C_{12}G_2$/C_{16}TAB ratios. For large regions of the phase diagram, this approach is predictive. However, silica materials synthesized with comparatively high $C_{12}G_2$/C_{16}TAB ratios are only poorly ordered in a way that does not correspond to their lyotropic liquid crystalline phase behavior. Also, in contrast with our previous study of mixed C_{16}TAB/n-octyl-b-D-glucopyranoside templating [37] the boundary between hexagonal and bicontinuous cubic materials is shifted towards higher surfactant content than in the aqueous LLC system.

1. Introduction

Since the discovery of surfactant templated mesoporous materials possessing long-range order and narrow pore size distributions by Mobil researchers in 1992, [1,2] a tremendous amount of research has been directed towards synthesizing different mesostructured silicas with various surfactant templates for applications in the areas of separation, adsorption, catalysis, drug delivery, electronic devices, etc. [3–12]. Classes of surfactants employed include cationic, [1] anionic, [3,13] nonionic, [4,14–17] cationic/anionic mixtures, [18,19] cationic/nonionic mixtures, [20–23] and anionic/nonionic mixtures [24,25]. Despite this range of investigations, sugar-based surfactants (mainly alkyl glycosides) have been largely neglected. Sugar surfactants are a novel class of nonionic surfactants synthesized from renewable resources and are of increasing interest for industrial applications and academic research as an alternative to other types of surfactants.

Composed of a sugar head group with multiple hydrophilic hydroxyl groups and a hydrophobic hydrocarbon chain, alkyl glycoside surfactants are of interest because of: (a) their ability to form liquid crystalline phases [26–29], (b) the possibility of forming chirally discriminative ordered mesoporous inorganic materials by transferring the chiral information from its headgroup into sol–gel-derived materials, [30–32] and (c) their appealing "green" characteristics of being nontoxic, biodegradable, and synthesized from renewable resources [33,34]. Despite their advantages as detergents, these sugar-based nonionic surfactants can be difficult to assemble into well-ordered materials [35] because neutral surfactants (N^o) and weakly charged inorganic precursors (I^o) interact only by relatively short-ranged hydrogen bonding forces, often resulting in disordered mesostructures [4,36].

Here, the commercially available disaccharide surfactant n-dodecyl β-D-maltoside ($C_{12}G_2$/DM) is selected for the second of a series of studies [37] of isothermal lyotropic phase behavior of alkyl glucosides mixed with the widely used cationic surfactant cetyltrimethylammonium bromide (C_{16}TAB) in water. Good ordering of materials and control over the functional site density at the material surface can be gained by mixing a cationic surfactant (which interacts strongly with silica but without molecular specificity) with the nonionic but highly functional and chiral $C_{12}G_2$ surfactant. The maltoside surfactant $C_{12}G_2$ has advantages compared to a glucose-based surfactant such as octyl-β-D-glucopyranoside

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(C_8G_1) because its larger headgroup should increase the curvature of the micellar aggregates to favor cylindrical micelles over lamellar aggregates, and it should provide more hydroxyls for selective binding to the metal oxide matrix [38]. The only example of using $C_{12}G_2$ alone as a surfactant template for the synthesis of mesoporous material is from Hüsing et al. but resulted only in thin films of hexagonal mesophase over a narrow composition range [39,40]. Pang et al. described the preparation of $Ia\bar{3}d$ cubic silica particles by evaporation-driven assembly with CTAB and $C_{12}G_2$ [41]. In their case, the sugar surfactant was introduced to stabilize the mesophase during surfactant removal rather than to systematically investigate mesoporous materials synthesis with this mixed template system.

The liquid crystalline phase diagrams of pure $C_{12}G_2$ in water [26,27,42] and $C_{16}TAB$ in water [43–45] have been reported in the literature, but not for aqueous mixtures of these two surfactants. Here we report the isothermal lyotropic liquid crystalline (LLC) phase behavior of the aqueous mixtures of $C_{16}TAB$ and $C_{12}G_2$ surfactants. All previous studies of binary phase behavior of $C_{16}TAB$–water system exhibited the presence of hexagonal (H_I), cubic (Q_I), and lamellar (L_α) phases. An earlier study of Wärnheim and Jönsson [44] agrees qualitatively with a later study performed by Auvray et al. [43] which reported different phase boundaries along with a deformed hexagonal phase between the hexagonal and cubic phases identified by using small-angle X-ray scattering (SAXS). More recently, the liquid crystalline phase behavior of $C_{16}TAB$ in water was revisited by Yang and White to clarify the regions where phase transitions from hexagonal to deformed hexagonal to cubic take place [45]. The first complete binary surfactant–water phase diagram for $C_{12}G_2$ was reported by Warr et al., [42] who reported almost temperature-independent phase transitions from isotropic liquid (I) to lamellar (L_α) to solid surfactant (S) as the surfactant concentration increases. Later the phase behavior of $C_{12}G_2$ in water system was investigated by Auvray et al. [26] using SAXS. Their study suggested that phase behavior of $C_{12}G_2$ with water is more complex than was indicated in the previous study. Along with a lamellar phase that has low surface curvature, they also have found high surface curvature hexagonal (H_I, P6mm space group) phase and intermediate curvature phases such as bicontinuous cubic (Q_I, $Ia\bar{3}d$ space group) and rectangular (R). A recent study of the binary phase diagram of the $C_{12}G_2$–water system conducted by Boyd et al. [27] was not able to establish a phase boundary between the hexagonal and lamellar phases using polarized optical microscopy, and no intermediate cubic phase was observed.

The variability in observations between these three studies suggest that $C_{12}G_2$ may be very sensitive to the method of preparation of the liquid crystals, perhaps due to the rate of assembly of surfactants that have a bulky hydrated headgroup. The formation of a high surface curvature hexagonal phase by $C_{12}G_2$ can be anticipated based on its surfactant packing parameter. Without considering specific interactions, the packing parameter g is equal to $\upsilon/a_o l_c$, [38] where υ is the volume of the hydrophobic tail, a_o is the area occupied at the micelle-water interface by the surfactant headgroup, and l_c is the hydrophobic tail chain length. By taking the value of a_o as 45 Å^2 at 25 °C [27] along with the values of υ and l_c of the extended dodecyl hydrocarbon chain as 350 Å^3 and 16.7 Å respectively (calculated using Tanford's formulas [46]), the critical packing parameter value for $C_{12}G_2$ surfactant is slightly less than 0.5, which should favor cylindrical micelles. Although these calculations are over-simplified because of the dependence of a_o on temperature and degree of hydration, the ability of $C_{12}G_2$ to form a hexagonal phase is also supported by the finding of hexagonal LLC phase with other disaccharide surfactants [47,48].

Surfactant-templated materials with periodic mesostructures can be prepared from either dilute surfactant solutions [1,2] or within concentrated surfactant solutions that are in or near a liquid crystalline state [49]. The mechanism that has been proposed for the first synthetic route is known as cooperative self-assembly [50,51]. In this mechanism, the surfactant and inorganic precursor combine into a new precipitated phase, so the structure of the product is difficult to predict from LLC behavior – especially when mixed surfactants are used. The second method, proposed by Attard et al. [49] and sometimes known as nanocasting, uses a relatively concentrated surfactant solution ($\geqslant$30 wt.%) in which a preformed liquid crystalline phases acts as the template for the final mesostructure. To be more precise, the silica precursors and surfactants form a homogeneous liquid crystal upon evaporation of alcohol produced during hydrolysis and of excess water that may be needed to drive hydrolysis to completion. This second method offers the advantage of being able to predict the final mesostructure of the surfactant–silicate complex. Alberius et al. [52] outlined a general method for predictive synthesis of surfactant templated mesostructure by taking into account the effects of solvent evaporation on the final mesostructural behavior. This method is based on a hypothesis that the volume of hydrophilic inorganic species, present in the reaction system after complete hydrolysis of the ceramic precursor, can replace the water in a LLC phases to generate a material with the same structure. Another advantage of nanocasting for our system is that both surfactants are incorporated into the as-made material in the ratio initially added to the synthesis solution.

Here we report for the first time to our knowledge the lyotropic liquid crystalline phase behavior of aqueous mixtures of $C_{12}G_2$ and $C_{16}TAB$ surfactants measured by low-angle powder X-ray diffraction (XRD) and polarized optical microscopy (POM). We then use this ternary phase diagram to draw a quantitative comparison between the liquid crystal mesophases and the observed mesostructures of silica synthesized using the nanocasting (LLC templating) approach [49]. This is accomplished by replacing the volume of water in the LLC with an equivalent volume of hydrolyzed inorganic precursor [52]. The approach is similar to our prior study of the octyl-β-D-glucopyranoside/$C_{16}TAB$ system, [37] but we hypothesize here that the maltoside surfactant should expand the hexagonal and bicontinuous cubic regions of the phase diagram towards regions of high polar solvent and glycosurfactant content. However, we will show that the bulkier headgroup of $C_{12}G_2$ introduces more differences between the LLCs and silica materials than in the prior study, most likely due to the increase in the number and specificity of hydrogen bonding interactions with water.

2. Experimental

2.1. Materials

Tetramethyl orthosilicate (TMOS, 98%) and cetyltrimethylammonium bromide ($C_{16}TAB$, 99%) were purchased from Sigma–Aldrich and n-dodecyl-β-D-maltopyranoside (β-$C_{12}G_2$, $\geqslant$99%, %α < 0.2) from Anatrace. Deionized ultra-filtered water (DIUF), 0.1 N HCl, and absolute ethanol were purchased from Fisher Scientific. All chemicals were used as received.

2.2. Phase characterization

To perform phase studies, precisely weighed surfactants and DIUF water were mixed in small vials that were securely closed and sealed with Parafilm. First, the samples were homogenized by heating at a temperature of 60 °C for at least an hour. The mixture was then equilibrated at 50 °C for 3–6 days (length depending on the surfactant concentration) until an equilibrium solution