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Multi-phase equilibrium microemulsions and synthesis of hierarchically structured calcium carbonate through microemulsion-based routes

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Abstract

Middle-phase microemulsions (MPMs) in two systems of a cationic surfactant, tetradecyltrimethylammonium bromide (TTABr)/*n*-butanol/iso-octane/Na_2CO_3 or $CaCl_2$ and an anionic surfactant, sodium dodecyl sulfate (SDS)/*n*-butanol/iso-octane/Na_2CO_3 or $CaCl_2$, were used to synthesize nanostructured calcium carbonates. MPMs provide a simple and versatile reaction media, i.e., upper-phase W/O, BC, and O/W structured equilibrium microemulsions to be used for synthesizing hierarchically structured $CaCO_3$ at the nanometer scale. On the basis of the investigations on the phase behavior of the MPMs, hierarchically structured calcium carbonates with dendrites, ellipsoids, square-schistose cubes, and spheres were synthesized through the MPM-based routes.

Keywords: Calcium carbonate; Microemulsions; Surfactants; Scanning electron microscope

1. Introduction

Nanostructured inorganic materials with novel morphologies have been intensively researched because of their unique properties and intriguing potential applications in many fields [1–8]. A rich array of morphologies including fibers, wires, rods, belts, tubes, spirals, and rings [9] have been synthesized by a wide variety of methods. Surfactant-based templates, i.e., self-assembled structures, such as reverse micelles [2,9], water-in-oil (W/O) microemulsions [2,10], and vesicles [11], allow control of the size, shape, and crystallinity of inorganic nanocrystals. Microemulsion-based templates have provided a general route to produce a wide range of thermally stable nanostructured composite materials with large surface-to-volume ratios [10]; however, only single-phase equilibrium reverse microemulsions, i.e., water-in-oil (W/O microemulsions), have been used to synthesize nanostructured inorganic materials [10]. Pileni [2] studied different W/O microemulsion systems and concluded that the size of the particles was determined by the molar ratio of water and surfactant (r), $r = [H_2O]/[\text{surfactant}]$.

Middle-phase microemulsions (MPMs) are multi-phase equilibrium systems comprising the microemulsions and residual water or residual oil, i.e., a lower-phase oil in water (O/W, Winsor I) microemulsion with excess oil upper-phase or an upper-phase water in oil (W/O, Winsor II) microemulsion with excess water lower-phase or MPMs with bicontinuous water and oil are called BC (Winsor III) microemulsion. MPMs have important applications in the chemical industry, chemical reactions, and especially in ternary oil recovery [12], because the MPMs can solubilize oil as well as water, and the interfacial tensions of the MPMs and residual water or residual oil reach ultralow values (lower than 2.0×10^{-3} mN m^{-1}). However, inorganic nanomaterials produced though multi-phase equilibrium microemulsions are rare [13]. The biomimetic synthesis of calcium carbonate ($CaCO_3$), one of the most abundant biominerals, has been intensively investigated [9]. Langmuir monolayers, self-assembled monolayers, crystal-imprinted polymer surfaces, and cross-linked gelatin films have been used as templates or matrices to control the growth of $CaCO_3$ crystals.

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Macromolecular additives have been shown to greatly influence $CaCO_3$ crystallization [14].

In this article, we studied the phase behavior of middle-phase equilibrium microemulsions in two systems of a cationic surfactant, tetradecyltrimethylammonium bromide (TTABr)/*n*-butanol/iso-octane/Na_2CO_3 or $CaCl_2$ and an anionic surfactant, sodium dodecyl sulfate (SDS)/*n*-butanol/iso-octane/Na_2CO_3 or $CaCl_2$, then used them as microreactors to synthesize $CaCO_3$ nanoparticles, the various interesting morphologies of $CaCO_3$ were observed in the multi-phase microemulsion microreactors.

Considering the novel properties of middle-phase microemulsions, such as the simple confection, thermodynamic stability, as well as the easily thermodynamic equilibrium at room temperature, we herein employed the multi-phase equilibrium W/O and BC microemulsions-based routes to synthesize the calcium carbonate ($CaCO_3$). The multi-phase equilibrium microemulsions for the synthesis of inorganic particles should open up a new interesting method to synthesize nanoscale building blocks. The detailed investigations should provide regarding the mechanism of particle formation through the media of MPMs.

2. Experimental

2.1. Chemicals

Tetradecyltrimethylammonium bromide (TTABr) was obtained from ACROS, sodium dodecyl sulfate (SDS) was obtained from Aldrich, and both surfactants were re-crystallized three times from mixed ethanol and acetone, 1:5 v:v. The critical micelle concentration (cmc) of SDS is 8.0 mM in water and TTABr is 3.54 mM, obtained by surface tension measurements. $CaCl_2$ and Na_2CO_3 were purchased from Chemical Factory, Shanghai, purity $\geqslant 99.9\%$, *n*-butanol and iso-octane were purchased from Chemical Factory and the purity is A.R. grade. Water was distilled three times.

2.2. Phase behavior

Stock solutions of TTABr, SDS, $CaCl_2$, and Na_2CO_3 were prepared. Phase behavior for middle-phase microemulsion systems of TTABr and SDS was studied (see Supplementary material).

2.3. Measurements of ultralow interfacial tensions

A Model 500 spinning drop interfacial tensiometer was used to determine the ultralow interfacial tensions. The measured results of ultralow interfacial tensions were put in Supplementary material.

2.4. Structures of microemulsions determined by freeze-fracture transmission electron microscopy (FF-TEM)

The experimental procedure for freeze-fracture electron microscopy comprises the following steps: microemulsion sampling, freezing of the specimen, fixing to the sample stand and cutting off, corrosion by solvent, fracturing and replication, and electron microscopic investigation of the replicas.

2.5. Synthesis of $CaCO_3$ particles

After the microemulsions had equilibrated at 25.0 ± 0.1 °C for 4 weeks, two samples with the same structure but different reaction precursors were mixed to produce $CaCO_3$ particles (detailed synthesis processes see in Supplementary material).

2.6. Characterization of $CaCO_3$ particles

The morphologies of the $CaCO_3$ products were characterized with a JEM-100 CX II transmission electron microscope (TEM, total TEM observations of $CaCO_3$ morphologies were put in Supplementary material) and a JEOL JSM6700F field-emission scanning electron microscope (FE-SEM). Powder X-ray diffraction (XRD) patterns were recorded using a X-ray diffractometer (Bruker Advance D8) with a graphite monochromator Cu$K\alpha$ ($\lambda = 0.15406$ nm) radiation (40 kV, 40 mA). Infrared spectra of KBr pellets were collected using a Nicolet Impact AVATAR 370 FTIR spectrometer.

3. Results and discussion

3.1. Phase behavior of the MPMs: Cationic TTABr/*n*-butanol/iso-octane/brine (Na_2CO_3 or $CaCl_2$)

There are 3 types of multi-phase equilibrium microemulsions: Winsor I (O/W) microemulsions with residual water phase; Winsor II (W/O) microemulsions with residual oil phase, and Winsor III (BC) microemulsions having bicontinuous structures with residual water and oil phase. In the prior work [15], by the orthogonal design, the optimal formation conditions for the MPMs in the different surfactant systems were obtained. Investigations have been made on the effects of the salt and *n*-butanol concentrations, the kinds of salts and alcohols on the formation of the MPMs. The ultralow interfacial tensions, the optimal salinity (S^*) and the length of salinity (ΔS) were measured. Some rules and data were worked out about the formation and characteristics of the MPMs, which were summarized in our previous reports [15].

The effect of salt (Na_2CO_3 or $CaCl_2$) concentration on the phase behavior of cationic 2.0 wt% TTABr/4.0 wt% *n*-butanol/iso-octane/brine (Na_2CO_3 or $CaCl_2$) was studied (Fig. 1a). The effect of *n*-butanol concentration on the phase behavior of cationic 2.0 wt% TTABr/*n*-butanol/iso-octane/brine (17.0 wt% Na_2CO_3 or 18.0 wt% $CaCl_2$) was also investigated (Fig. 1b). Table 1 lists the difference of salinity [$\Delta S = S_2$ (the salinity of the disappearance of the MPMs) $- S_1$ (the salinity of the formation of the MPMs)], the optimal salinity (S^*, the salinity for the equal interfacial tensions γ_{mo} and γ_{mw}), and the volume (V_{m}^*) at the optimal salinity of the MPMs at constant *n*-butanol concentration for the cationic TTABr system. Similar characteristic parameters of the MPMs at constant salt (Na_2CO_3 or $CaCl_2$) concentration are also listed.