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Regular Article

A surfactant-free microemulsion consisting of water, ethanol, and dichloromethane and its template effect for silica synthesis

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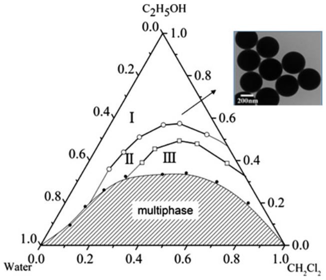
GRAPHICAL ABSTRACT

The phase behavior and properties of a surfactant-free microemulsion (SFME) containing water/ethanol/dichloromethan were investigated. Solid silicananoparticles (SSNs) were synthesized in the O/W region of the SFME, and the factors influencing the synthesis were also discussed.



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ABSTRACT

A new type of surfactant-free microemulsion (SFME) containing water/ethanol/dichloromethane was constructed, and three microregions water-in-dichloromethane (W/O), bicontinuous (B.C.) and dichloromethane-in-water (O/W) regions were identified. The polarity environment of the SFME was investigated. Solid silica nanoparticle (SSN) was selected as a model nanomaterial to investigate the feasibility of the water/ethanol/dichloromethane SFME for the preparation of nanomaterials. In the O/W SFME region of the microemulsions, uniform spherical solid silica nanoparticles (SSNs) were synthesized. Under the same experimental conditions, they are of smaller particle size and have narrower range of diameter distribution, than the SSNs synthesized from ethanol and water mixture. The effects of tetraethylorthosilicate concentration (C_{TEOS}), ammonia hydroxide concentration ($C_{NH_3 \cdot H_2O}$) and dichloromethane content on the size and morphology of the SSNs were investigated. The average diameters of the SSNs increased with increasing C_{TEOS} and$C_{NH_3 \cdot H_2O}$. However, the effect of increasing $C_{NH_3 \cdot H_2O}$ on the particle size is more significant. The time evolution of the morphology and diameter of the SSNs were also investigated to elucidate the growth mechanism for the SSNs synthesized in the O/W SFMEs.

1. Introduction

Microemulsions are optically isotropic, transparent, and thermodynamically stable systems containing water, oil, surfactant

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and cosurfactant [1]. Because of the unique microstructure and properties, microemulsions have been widely used in various fields, such as food technology, drug delivery, environmental science and nanomaterial preparations [2–6]. The droplets of microemulsions can be used as a template for the preparation of nanoparticles. Microemulsions have many advantages in terms of the synthesis of nanoparticles, such as excellent control over particle size, narrow size distribution and mild reaction condition, and therefore, were used to prepare high-quality nanomaterials, such as inorganic nanoparticles and organic polymer nanoparticles [7,8]. However, microemulsion method also has disadvantages and limitations, such as toxicity of surfactant, difficulty in recycling, as well as less-than-effective utilization of the nanoparticles surfaces, because active sites on the surfaces may be blocked by the surfactant used [9].

In recent years, surfactant-free microemulsions (SFMEs) have attracted much research attentions [10]. SFMEs consist of water, oil and an "amphi-solvent", and contain no surfactant (or amphiphile) which is usually considered to be a necessary component for a microemulsion formulation. The "amphi-solvent" is completely or at least partially miscible with both water and oil, such as ethanol, propan-1-ol and propan-2-ol [11–13]. Research works showed that SFMEs have similar microstructure types to those of surfactant-based microemulsions (SBMEs), namely, oil-in-water (O/W), bicontinuous (BC) and water-in-oil (W/O) structures [14–17]. As thus, SFMEs can also be used for the preparation of nanomaterials. SFMEs, used as templates for nanoparticle preparation, would possess the strengths of SBME system, that is, excellent control over particle size, narrow size distribution and mild reaction condition, and at the same time overcome its weaknesses, such as high costs due to the use of large amount of surfactants, the surface adsorption of nanomaterials and environmental pollution. Also, it can be recycled.

However, so far, there has been few reports on the preparation of nanomaterials by using surfactant-free microemulsion system as templates [10]. Hou et al. reported the synthesis of Mg_2Al-Cl layered double hydroxide (LDH) nanosheets using SFME system [18,19]. The LDH nanosheets synthesized presented a uniform lateral dimension and a small thickness. Notably, it does not contain any organic impurity and performs superior removal ability towards low concentration phosphate compared with the LDH particles synthesized using traditional co-precipitation method. This demonstrates that it is feasible and advantageous to prepare nanomaterials with surfactant-free microemulsions as templates. CdS nanoparticles were prepared by a double-microemulsion technique in butan-1-ol/olive oil/water surfactant-free microemulsion system [20]. The CdS nanoparticles synthesized have almost homogeneous spherical morphology.

SnS nanoparticles were also synthesized in a O/W surfactant-free microemulsion system containing chlorobenzene/methanol/ethylene glycol [21]. It was found that the reactant ($SnCl_2$) concentration has a significant influence on the size of the prepared nanoparticles, while temperature has little influence.

Besides inorganic nanomaterials, SFMEs were also used to prepare organic polymer nanomaterials. Yan et al. prepared the precisely-defined shell-functionalized core-loaded nanocapsules with tunable diameters (ranging from 50 nm to 190 nm) in the surfactant-free microemulsion systems of water/oil(hexadecane or miglyol)/acetone [22].

However, the synthesis of metal oxide and nonmetal oxide nanomaterials using SFMEs as template has not been reported. Solid silica nanoparticles (SSNs) have been synthesized mainly using microemulsions method [23] and Stöber method [24], and are widely used in industrial applications, such as catalysis [25], stabilizers [26], pigments [27] and chemical mechanical polishing [28].

The size, uniformity and surface properties of the SSNs have great influence on its applications [29–32]. Due to the above-mentioned advantages displayed by SFMEs in preparation of nanoparticles, it is of important theoretical and practical significance to prepare the monodisperse and high-purity silica nanoparticles with different morphologies and sizes, and at the same time, investigate the properties of SFMEs and the effect of the microstructures of SFMEs on silica nanoparticle synthesis by adjusting the composition of the SFMEs.

This research proposes a new type of surfactant-free microemulsion template system containing water, ethanol and dichloromethane. The microstructures and the properties of the system were investigated. Solid silica nanoparticles (SSNs) were selected as model nanometerials to investigate the template effect of the SFMEs for nanoparticles. The mechanism for the growth process of SSNs was examined. This research has significant importance for expanding the areas of application of SFMEs, as well as the preparation of nanoparticles.

2. Experimental

2.1. Materials

Ethanol, dichloromethane (CH_2Cl_2), methyl orange(MO), tetraethylorthosilicate (TEOS, 99%) and ammonia hydroxide (25 wt%) were purchased from China National Pharmaceutical Group Corporation (Shanghai, China). All the chemicals were of analytical grade and used without further purification. Ultrapure water ($18.25 M\Omega \cdot cm$) was used throughout the experiments.

2.2. Apparatus

All weighing operations were conducted with a high precision electronic analytical balance (Shanghai, China). A low-frequency (50 Hz) conductivity meter (DDSJ-308A, Shanghai Precision Scientific Instrument Co., Ltd) with a DSJ-0.1 electrode of cell constant $0.096 cm^{-1}$ was used to measure the conductivity. The UV–Vis spectra were performed on a computer controlled UV–Vis spectrometer (UV-2600, Shimadzu Instrument Company). The path length of the quartz cell used in this experiment was 1 cm. Transmission electron microscopy (TEM) was carried out on a HT7700 electron microscope. The zeta potential of the sample and the sizes of both the SSNs and the O/W SFME droplets were measured by dynamic light scattering (DLS) with a Zetasizer Nano ZS system from Malvern.

2.3. Phase diagram construction

The phase diagram of the water/ethanol/ dichloromethane ternary system was constructed by visual titration as follows. A mixture of dichloromethane and ethanol with the desired mass ratio of dichloromethane to ethanol ($R_{d/e}$) was taken into test tubes. An appropriate mass fraction of ultra-pure water was slowly added to the mixture under magnetic stirring. The phase boundaries were determined by observing the phase transitions from transparency to turbidity. The same procedure was repeated for three times for each mixture, and an average of these results (the relative deviation was less than ±0.2%) was obtained. This step was repeated at other fixed $R_{d/e}$values. All the experiments were conducted in athermostatted water bath at 25.0 ± 0.2 °C and kept well covered to prevent any loss due to evaporation.

2.4. Electrical conductivity measurements

In this procedure, ultra-pure water was replaced by 0.0005 mol/L NaBr solution to provide sufficient charge carriers for a detectable signal. Preliminary experiments showed that NaBr has a sufficient