



## Preparation of cyclohexanone/water Pickering emulsion together with modification of silica particles in the presence of PMHS by one pot method



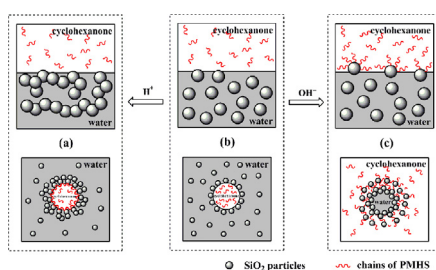
Wei Wu, Hongling Chen\*, Chang Liu, Yanjia Wen, Yongbing Yuan, Yu Zhang

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China

### HIGHLIGHTS

- The addition of PMHS made it possible to form emulsions under alkaline conditions.
- A phase inversion from o/w to w/o can be observed as the aqueous pH grows.
- The particles were chemically modified by PMHS under alkaline conditions.
- Emulsions stabilized by particles and PMHS can be stored for 3 months.
- Pickering emulsions and modified particles were prepared by one pot method.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 29 July 2013

Received in revised form 15 January 2014

Accepted 10 February 2014

Available online 18 February 2014

#### Keywords:

Pickering emulsions

Silica sol

Ball milling

Poly(methylhydrosiloxane)

Phase inversion

### ABSTRACT

Pickering emulsions prepared from cyclohexanone and silica sol with equal volumes have been investigated in this article. The aggregation of particles in the sols at different pHs was mainly attributed to the weak electrostatic repulsion in accordance to the classical DLVO theory. The emulsions stabilized solely by sol particles were unstable to creaming and coalescence after a period of storage, and phase separations were observed at aqueous pH > 7. In the presence of PMHS, the emulsion stability increased dramatically, and droplets began to form under alkaline conditions. At pH = 11, emulsions stabilized by PMHS and particles inverted from o/w to w/o. The causality was investigated by using Fourier transform infrared (FT-IR) spectroscopy, thermal analysis (TGA and DTG) and  $^{29}\text{Si}$  CP MAS NMR to characterize the surface nature of particles around the dispersed droplets. It was summarized that the acid conditions were just contributed to the particle aggregation, and no reaction between PMHS and particles was observed. However, alkaline conditions were tested to be responsible for the chemical grafting of PMHS onto particle surfaces, which increased the hydrophobicity of particles and inverted the type of emulsions from o/w to w/o. As a result, stable emulsions and modified particles were prepared simultaneously by one pot method through ball milling.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

It is well known that the so-called emulsion is a heterogeneous system, in which a liquid phase is dispersed as droplets in another

\* Corresponding author. Tel.: +86 25 83587206; fax: +86 25 83587206.

E-mail addresses: [hlchen@njut.edu.cn](mailto:hlchen@njut.edu.cn), [profchen@163.com](mailto:profchen@163.com) (H. Chen).

immiscible or partially miscible liquid phase. An additive, usually a surfactant is used to achieve temporary dispersion of the droplets in the continuous phase [1]. At the beginning of the twentieth century, particles with colloidal size were found to be an effective alternative to traditional surfactants in the respect of enhancing the stability of emulsions. The obtained ones were named “Pickering emulsions” after the discovery [2].

Generally, emulsion systems are thermodynamically unstable, and the droplets in emulsions will coarsen over a period of time. In an oil–water system, if the emulsion droplets are small and the dispersed phase has a finite solubility in the continuous phase, some small droplets of emulsion will shrink, while the large ones will grow, resulting in the increase of droplet size as time evolves. This phenomenon is referred to “Ostwald ripening” or “disproportionation” [3]. To date, scholars have always taken precautions against Ostwald ripening, using oil phases such as toluene [4,5] and alkanes [6–8], which are almost immiscible in water. However, few of these studies paid attention to the utilization of partially miscible reagents, such as cyclohexanone and ethyl acetate. As described previously, the strong package of particles at the oil–water interface leads to preminent stability against coalescence and Ostwald ripening of droplets [9–11]. Furthermore, compared with surfactant-stabilized systems, the attachment energy of particles to the oil–water interface is much larger than that of surfactants, often up to several thousands of  $kT$  [12]. So, in order to stabilize such systems containing partially water-soluble oils, enhancing the package of particles at the oil–water interface is a suitable method in theory.

There is a general agreement that a compact package of particles around the droplet surfaces was mainly attributed to the aggregation degree and wettability of particles. The attachment energy of a single particle to an oil–water interface passes through a maximum at the contact angle  $\theta_{o/w} = 90^\circ$ , only those particles with moderate wettability and weakly flocculated structure are able to prepare stable emulsions [13,14]. Particles in silica sol without addition of other electrolytes are always small enough to undergo Brownian motion and collisions with one another. Especially in the case of uncharged silica particles, coagulation and aggregation will be induced by the van der Waals attraction force and the building of the siloxane bonds between surface silanol groups [15]. On the contrary, the silica sol will be permanently stable because of the strong electrostatic repulsion between particles. In this case, the negatively charged particles are always too discrete to stabilize the Pickering emulsions. Sometimes, some co-stabilizers are employed to induce the aggregation or flocculation of silica particles, such as surfactants and salts [6,16,17]. In some cases, regulating the ratio of co-stabilizer to particles or the aqueous environments can also reverse the wettability of particle surfaces and trigger the phase inversion of emulsions [16,18].

In this paper, cyclohexanone was selected as a partially water-soluble oil phase, the solubility of which in water is 0.5488 mol/L at 25 °C [19]. Instead of adding co-stabilizers such as surfactants and salts to induce the aggregation or flocculation of particles in aqueous dispersion, the effects of poly(methylhydrosiloxane) (PMHS) on the aggregation of particles to form network structure at oil–water interface have been investigated. As we know, PMHS containing plenty of highly active –Si–H groups, is an effective modifying agent to alter the wettability of particle surface by forming a highly complex silicone network [20,21].

Emulsions were prepared from commercial silica sol and cyclohexanone by high-energy ball milling (HEBM) in this paper, differing from traditional ultrasound or mechanical shearing. Previous literatures have proved that the HEBM is not only a mixing device, but also a special reactor for modification. A predominant increase in the number of active sites on the particle surfaces can be

realized by the shearing and impacting actions of milling medium [22]. What is more, the decomposition of modifying agents under special condition such as sonication usually can be exempted during milling process [23]. PMHS was added into cyclohexanone as an active particle modifier and emulsion co-stabilizer. The particle modification occurred concurrently with the emulsifying process. To our most surprise, a phase inversion of cyclohexanone/water emulsions was observed by appending PMHS and changing the pH of aqueous phase.

## 2. Experimental

### 2.1. Materials

In this study, silica sol W-25 (25 wt% in water,  $\text{Na}_2\text{O} < 0.01\%$ ,  $\text{pH} = 7\text{--}7.5$ ) was purchased from Jiangyin Saiwei Chemicals and Trade Co., Ltd., China. The mean particle diameter was determined by dynamic light scattering using a Zetasizer 3000HSA. Cyclohexanone (A.R), acetone (A.R) and petroleum ether (A.R) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. Poly(methylhydrosiloxane) (PMHS, hydrogen content, 1.56 wt%) was kindly supplied by Dow Corning (Shanghai) Co., Ltd., China. Hydrochloric acid and sodium hydroxide, all of analytical grade, were used to adjust the aqueous pH. Deionized water was employed in all of the experiments.

### 2.2. Preparation of emulsions stabilized by silica particles alone

The silica sols with 5 wt% silica particles diluted from W-25 were mixed with cyclohexanone to prepare emulsions with equal volumes of 15 mL each. The silica sols at pH from 2 to 13 were stored over night. 100 mL agate tin, 60 g  $\text{ZrO}_2$  balls (1.0–5.0 mm) and a QM-3SP04 milling apparatus from Nanjing Nanda Instrument Plant were used to conduct the emulsification with 650 rpm for 4 h at room temperature, leaving the equipment to rest 10 min every 20 min to ensure the exhaustion of heat generated during the milling. A TG20-WS benchtop high-speed microcentrifuge was used subsequently to separate silica particles and droplets from emulsions. 25 mL of emulsion sample was centrifuged in a 50 mL polypropylene centrifuge tube for 10 min. The revolution number was fixed at 10,000 rpm, corresponding to the relative centrifugal force (RCF) of 9940 g.

### 2.3. Preparation of emulsions stabilized by particles and PMHS

Another batch of cyclohexanone/water emulsions stabilized by silica particles and PMHS was prepared. PMHS was dissolved in cyclohexanone and the mass ratio of PMHS to nano- $\text{SiO}_2$  in silica sol was conducted at 0.4:1. The pH values of particle dispersions were changed from 2 to 13. The preparation process was the same as above.

### 2.4. Characterization of the emulsions

The stability of emulsions to creaming, sedimentation and coalescence was assessed by observing the appearances over time, normally after 72 h. Photographs of emulsion samples were taken by a Canon EOS 450D digital camera. Drops of emulsions were imaged with an optical microscope GaleIV-3 from Cambridge instruments. The emulsion type was determined immediately after emulsification by a conductivity meter DDS-11A. The drop size distributions of emulsions after 3 days storage were measured by a light scattering Microtrac S3500.

Download English Version:

<https://daneshyari.com/en/article/593130>

Download Persian Version:

<https://daneshyari.com/article/593130>

[Daneshyari.com](https://daneshyari.com)