

Self-assembly of latex particles at droplet interface to prepare monodisperse emulsion droplets

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Received 9 September 2006; received in revised form 12 November 2006; accepted 6 December 2006

Available online 10 December 2006

Abstract

Monodispersed Pickering emulsion droplets were prepared by self-assembling of sulfonated polystyrene (SPS) latex particles at droplet interface. The stability of emulsion was obviously improved by pre-dispersing the latex particles in oil–water two phase and then mixing them into emulsion. For oil-in-water emulsion, the optimal stability was obtained by pre-dispersing 0.33 weight fraction of the latex particles in oil phase initially. Several parameters were considered during the preparation, including sulfonation time of the SPS latex particles, the dispersed percent of the latex particles in oil–water two phases, the pre-dispersion time of water phase dispersate and oil–water volume ratio. When sulfonation time of the latex particles was close to 60 h, the stability of the particles stabilized emulsion droplets was the best. The increase of pre-dispersion time of water phase dispersate and oil–water volume ratio could obviously decrease the dispersity of emulsion droplets. Finally, monodisperse emulsion droplets were obtained with average droplet diameter 7.4 μm and standard deviation 0.37. The emulsion droplets could re-assemble into ordered array.
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Keywords: Self-assembly; Latex particles; Droplet interface; Monodisperse; Pickering emulsion

1. Introduction

It is now well established that solid particles of colloidal dimensions can act as excellent emulsifiers alone for both oil-in-water (O/W) and water-in-oil (W/O) emulsions [1]. These so-called Pickering emulsions can be remarkably stable to coalescence due, in part, to the very high energies of attachment for particles held at liquid–liquid interfaces. A wide variety of solid materials has been used as stabilizers of either O/W or W/O emulsions including iron oxide, hydroxides, metal sulfates, calcium carbonate, silica, clays, and carbon black [2–7].

Pickering emulsions play a crucial role in many industrial applications, such as crude oil recovery and oil separation. Stabilization of oil/brine emulsions encountered during oil recovery processes, which must be broken before crude oil refining, is brought about by clays, asphaltenes, and other dispersed particles [8]. The others include pharmaceuticals, agrochemicals, waste water treatment, cosmetic preparation, home and personal care products, etc.

Systematic studies of such emulsions have been performed by Binks and co-workers [1,9–14]. These authors showed that the use of commercial hydrophobic silica particles as particulate emulsifiers enabled the preparation of submicrometer-sized water-in-oil emulsions and particles wettability is an important parameter for the process. Recently, Weitz and co-workers demonstrated that thermal annealing of the adsorbed monolayer of latex particles enabled the permeability of the so-called “colloidosomes” to be controlled and a number of controlled-release applications have been suggested for such systems [15].

Similar to the character of surfactant systems, the droplet sizes of Pickering emulsions is usually polydisperse. However, for the purpose of study and application, it is often required the use of solid-stabilized emulsions with a well-defined droplet size. Giermanska-Kahn et al. [16] reported a new method to prepare monodisperse Pickering emulsions. They started with classical surfactant-stabilized O/W emulsions, which were sheared and size fractionated to attain monodispersity. Then, the surfactant was removed by a dialysis method and simultaneously replaced by solid particles. In the way, they obtain stable Pickering emulsions of the same size distribution as the initial surfactant-stabilized emulsion.

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In this paper, the stability and dispersity of Pickering emulsion was studied by controlling the influential factors, including the sulfonation time of the SPS latex particles, the dispersed percent of the latex particles in oil–water two phases, pre-dispersion time of water phase dispersate and oil–water volume ratio. Monodisperse emulsion droplets were prepared and the packed-droplets could easily re-assemble into ordered array.

2. Experimental

2.1. Materials

Styrene (St) monomer was purchased from Shanghai Chemical Reagents Corporation (China) and was purified by vacuum distillation before used. Poly(vinylpyrrolidone) (PVP) was purchased from Shanghai Chemical Reagents Company (China). *N*-Butyl acetate (nBA), with a relative density of 0.88 and solubility in water of 7 g/L at 20 °C, was purchased from Yixing Reagents Company (Jiangsu, China). Methyl methacrylate (MMA), with a relative density of 0.94 and solubility in water of 16 g/L at 20 °C, was purchased from Shanghai Chemical Reagents Corporation (China). Concentrated sulfuric acid (98%) was purchased from Beijing Chemical Reagents Corporation (China). Ethyl alcohol was purchased from Zhenxing Chemical Company (Shanghai, China). All the solvents were analytical grade and were used as received. Deionized water (resistivity > 18.2 MΩ cm⁻¹) prepared by Milli-Q 185 system (Millipore, USA) was used for all experiments.

2.2. Preparation of sulfonated polystyrene latex particles

Polystyrene (PS) particle powder with 2.13 μm in diameter was prepared by dispersion polymerization as described elsewhere [17]. The polystyrene particles were sulfonated in concentrated sulfuric acid at 40 °C. The degree of sulfonation could be controlled by the reaction time. After diluting, the sample was repeatedly centrifuged and washed with ethanol–water, then dried in vacuum at 50 °C.

2.3. Preparation of emulsion stabilized by sulfonated polystyrene latex particles

Dispersions of sulfonated polystyrene particles, respectively, in deionized water and *n*-butyl acetate were prepared by a high-intensity ultrasonic vibracell processor operating at 20 kHz and up to 10 W for 2 min to form homogeneous systems. Then the two parts were mixed using a magnetic agitator operating at 1000 rpm. The mixture changed from turbid into creamy-white

in appearance gradually. The emulsification took about 5 min to complete.

2.4. Characterization

The morphology and size of emulsion droplet were examined by OLYMPUS BX41 optical microscopy (OM) equipped with a Nikon COOLPIX4500 high-resolution digital CCD camera and the average droplet diameters were measured from at least 300 droplets on the OM photos by using Adobe Photoshop 7.0 software. The dispersity of droplet diameter is characterized by standard deviation defined as:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (X_i - \bar{X})^2}$$

where n is sample number, X_i is sample size and \bar{X} is the mean. The standard deviation is a measure of how spreads out the droplet diameter are. The stability of emulsion at 25 °C was evaluated in graduated vessels by monitoring the just arisen time of the oil–emulsion and emulsion–water interfaces, which represents the ability of emulsion to withstand creaming and coalescence. The content of SO₃H group at particle surface was measured by alkali titration. In order to simulate contact angles of particles at oil–water interface, the method reported by Gayle and John was adopted [18]. The sulfonated polystyrene slides were immersed in methyl methacrylate contained in a silica rectangular cell (cube of internal dimension 10 × 10⁻³ m). A drop of water with 10 μl volume was injected into and then formed at the interface of oil and PS slide. The contact angles, measured through water (θ_{ow}), at the oil–water-sulfonated polystyrene substrate interface were measured using a JY-82 contact angles analyzer at ambient temperature.

3. Results and discussion

3.1. Effect of sulfonation time of PS latex particles

It is well known that solid particles are efficient self-assembly at droplet interface only if they are partially wetted by both the aqueous and oil phases. The wettability of PS particles was adjusted by controlling the sulfonation time, therefore, the density of chemigrafted SO₃H group on the particle surfaces. A series of sulfonated PS latex particles were fabricated and the relevant properties are summarized in Table 1. It was found that with the increase of sulfonation time, the area of per SO₃H group and the contact angles θ_{ow} decreased, meaning the increase of hydrophilicity. When sulfonation time was close to 60 h, the particles contact angle was about 90°.

Table 1
Properties of PS latex particles with different sulfonation time

No.	1	2	3	4	5	6	7	8
Sulfonation time (h)	3	9	11	13	23	30	60	120
Area per SO ₃ H (nm ²)	9.65	5.16	5.04	3.88	3.65	3.51	3.37	2.95
θ_{ow} /Degree	122.5	107.1	104.0	99.1	95.4	92.7	90.6	84.5

Pickering emulsions can be remarkably stable to coalescence due, in part, to the very high energies of attachment for particles held at liquid–liquid interfaces. The energy is most strongly for particle contact angles $\theta_{ow} = 90^\circ$. Either side of 90° , the energy falls rapidly. Furthermore, stabilizing colloids tend to be small compared to the emulsion droplet size. For preparing monodispersity emulsion droplets, stability is a prerequisite. So PS latex particles sulfonated for 60 h were the best.

3.2. Effect of dispersed percent of latex particles in oil–water two phases

Although much is known about the properties of composite surfactants improving on the stability in surfactant systems, scarcely any work has been undertaken regarding latex particles dispersed in oil–water two phases behaving on the stability in solid-stabilized emulsions. So a total of 0.65 wt% sulfonated polystyrene particles, starting with between 0 and 0.65 wt% particles in water and between 0.65 and 0 wt% particles in oil (*n*-butyl acetate), respectively, were used to prepare emulsions. After mixing the two phases, the characters of the obtained emulsion, including average droplet diameter, emulsion stability, and dispersity varying with the weight fraction of particles in aqueous phase (ϕ_{wp}), were summarized in Fig. 1 and the weight fraction of water in system (ϕ_w) is 0.79. It was shown that with the increase of the weight fraction of particles in the aqueous

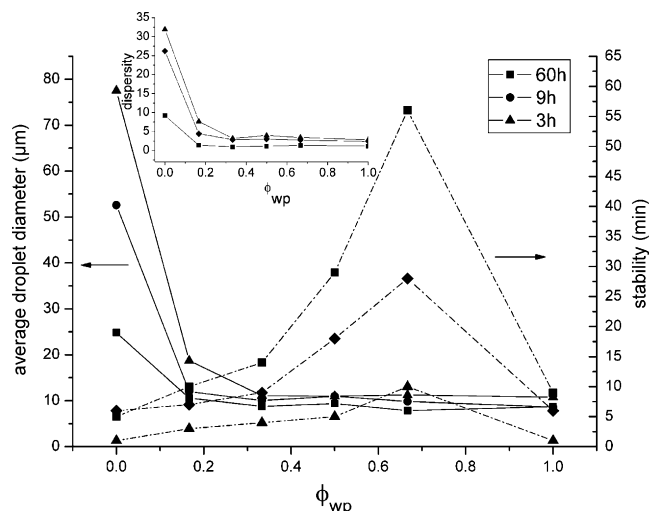


Fig. 1. Effect of the weight fraction of SPS latex particles (sulfonated for 60 h, 9 h, 3 h) in water phase on average droplet diameter, stability and dispersity (the top left inserted figure) of *n*-butyl acetate in water emulsions ($\phi_w = 0.79$) with a fixed particles concentration of 0.65 wt% in system.

phase and a concomitant decrease of particles in the oil phase the average droplet diameter decreased initially, and then leveled off. The dispersity had same trend. The initial big size was due to form emulsions containing a mixture of O/W droplets and W/O/W globules as shown in Fig. 2.

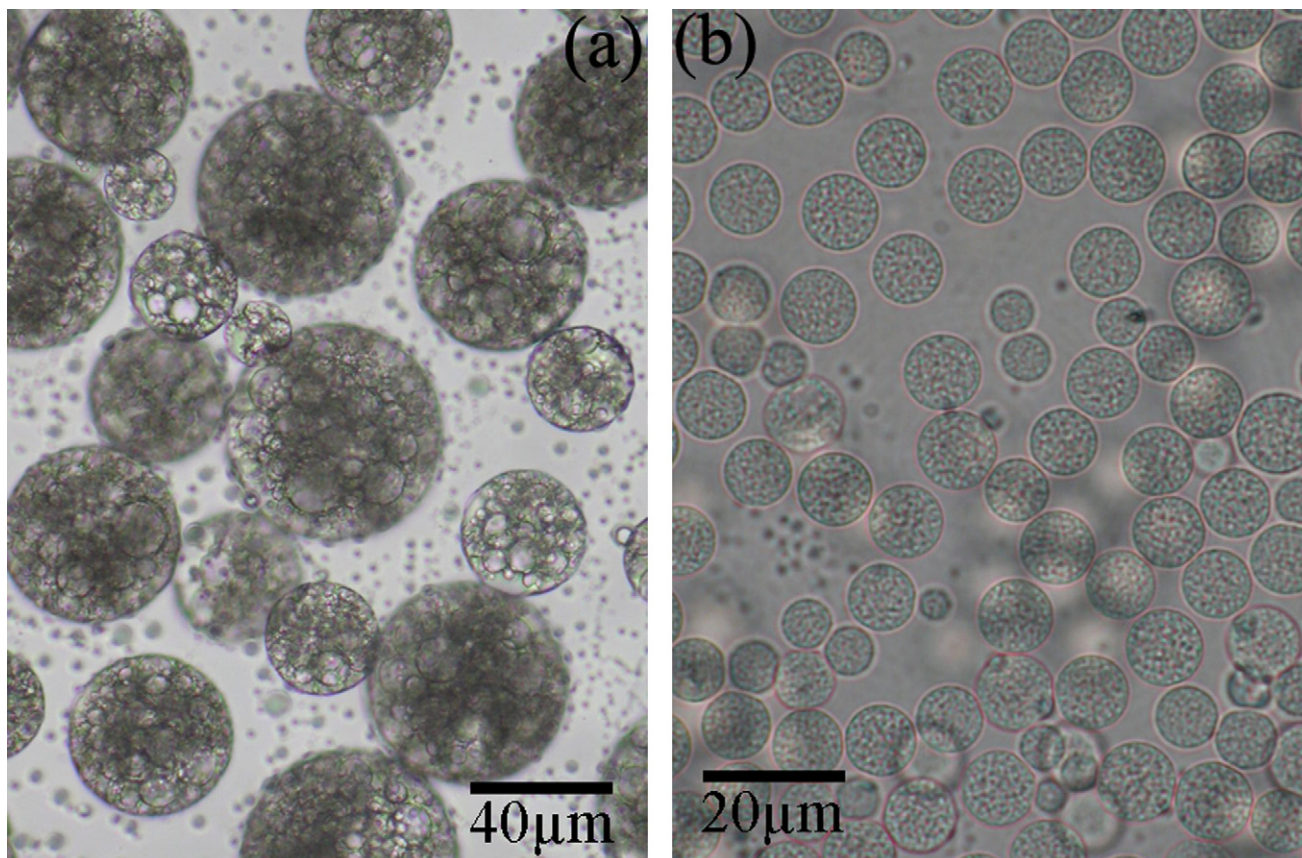


Fig. 2. Optical microscopy images of emulsion stabilized by 60 h SPS latex particles with a fixed particle concentration of 0.65 wt% in emulsions and $\phi_w = 0.79$: (a) W/O/W and O/W emulsion at $\phi_{wp} = 0.17$; (b) O/W emulsion at $\phi_{wp} = 0.67$.

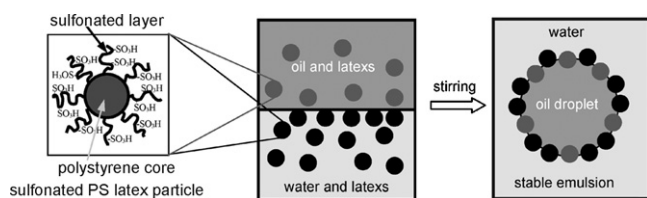


Fig. 3. Schematic illustration of the formation of a composite particles layer around droplet by using the same SPS latex particles.

The existence of multiple emulsions has been associated with the coalescence of drops with inclusion of the continuous phase during the mixing process as a result of insufficient coverage of freshly formed interfaces [14]. When ϕ_{wp} exceeded 0.33, the average droplet diameter approximately kept constant, which implied the disappearance of multiple emulsion. Then the behavior of particles in two phases is thus dominated by the behavior of the aqueous-based dispersion.

The influence of the latex particles dispersed in both aqueous phase and oil phase on improving emulsion stability is obvious. Regardless of the difference of sulfonation time of PS particles, the stability of emulsion all had a maximum at $\phi_{wp} = 0.67$. With the increase of hydrophilicity of the PS particles, the increase of stability is more evident. The phenomenon is possibly due to a composite particles layer form around the dispersed droplets as shown in Fig. 3. Since the same particles exhibit the receding contact angle or the advancing contact angle, respectively, with the oil–water interface when particles originate in water or oil phase and the former is smaller than the latter normally [14,19], the composite particles layer will be constituted by the same particles with slightly different wettability. By more adequately hydrated by water on one side and solvated by oil on the other, the composite layers increased stability of emulsion. The stability was maximal when the hydration and solvation reach balance.

3.3. Effect of homogenization time of water phase dispersate

In accordance to the contact angles experiment of water drops on planar, Binks and co-workers indicated that particle–fluid interactions are important prior to the introduction of the second fluid phase [20]. For the dispersate of SPS latex particles in water, before adding oil phase, the homogenization time of the dispersate possibly affect final emulsion droplets size and dispersity. Keeping a particle concentration in the emulsions of 0.65 wt% and $\phi_w = 0.79$, the effect of homogenization time of water phase dispersate on average droplet size and dispersity was shown in Fig. 4. Obviously, the average droplets size and dispersity decreased with extending of the homogenization time.

The reason was possibly due to hysteresis caused by particle surface roughness. For the SPS particles dispersed into water phase, the ionization equilibrium of the sulfogroup at particles surface needs time due to the surface roughness. With prolonging homogenization time, the surface charge of different particles will tend to coincidence. The time dependence of the ionization equilibrium was also observed during the process of alkali titra-

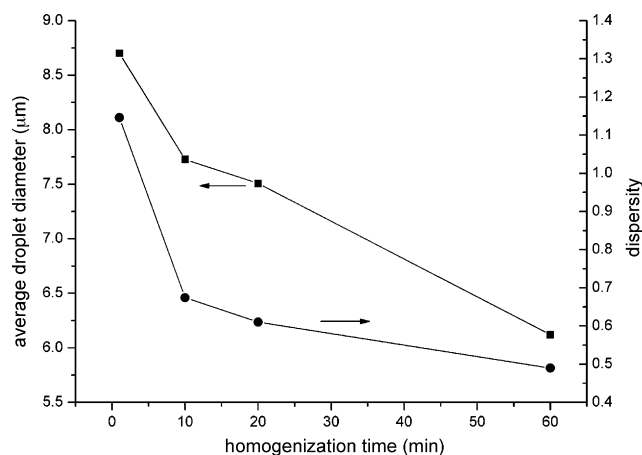


Fig. 4. Effect of homogenization time of water phase dispersate on the average droplet diameter and dispersity of *n*-butyl acetate in water emulsions ($\phi_w = 0.79$) with a fixed particle concentration of 0.65 wt% in emulsions.

tion, which shown the additive quantity of base to equivalence point increasing with time.

3.4. Effect of oil–water volume ratio

Fixing water phase volume and increasing oil phase volume, the average droplets size and dispersity of emulsions varying with ϕ_w are plotted in Fig. 5. The samples were prepared by dispersing 60 h SPS latex particles of 0.02 g and 0.04 g in oil and water phases, respectively, and the water phase dispersate was pre-homogenized for 60 min then mixing with the oil phase. It was indicated that the average droplet diameter decreased gradually from 8.3 μm to 7.4 μm with a concomitant decrease in the dispersity. Monodisperse emulsion was formed at low ϕ_w as shown in Fig. 6.

After dropping in sheet glass and simply drying in air, the SPS latex particles packed-droplet formed some ordered array as shown in Fig. 6, especially the magnified image on the top

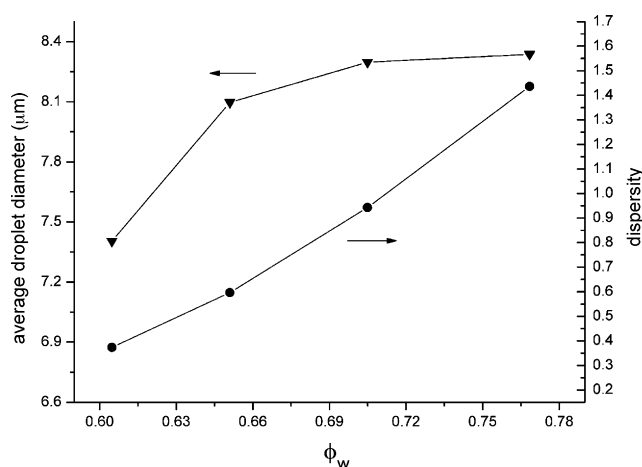


Fig. 5. Effect of the weight fraction of water on the average droplet diameter and dispersity of *n*-butyl acetate in water emulsions fabricated by dispersing 60 h SPS latex particles of 0.02 and 0.04 g in oil and water phases, respectively, and pre-homogenizing the water phase dispersate for 60 min then mixing with the oil phase.

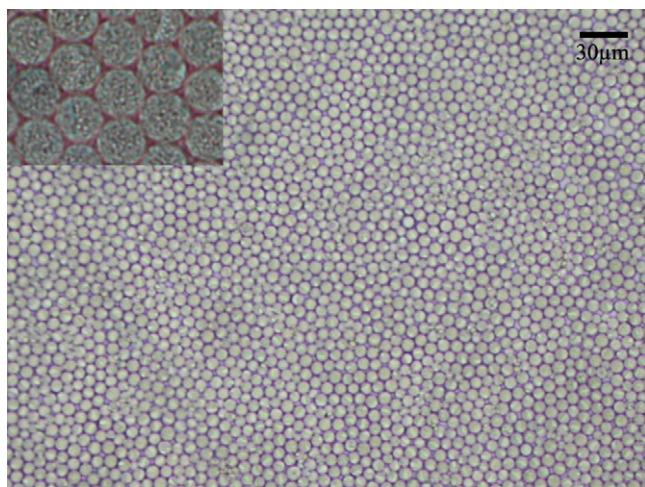


Fig. 6. Optical microscopy images of SPS latex particles packed-droplets fabricated as the point of $\phi_w = 0.60$ in Fig. 5. The top left corner is a magnified image.

left corner. The formative hexagonal close accumulate is due to a long-range repulsion which was attributed to electrostatic interactions, through the water phase, of residual surface charges at the particle packed-droplet surface. There is an extensive literature which has explored crystalline colloidal arrays (CCAs) formed spontaneously through the self-assembly of monodisperse charged colloidal spheres in low ionic strength aqueous solutions [21–23]. The use of monodisperse colloidal spheres is a prerequisite to form the ordered array. Here, the appearance of the ordered array by secondary self-assembling of the SPS particles packed-droplet also indicates the monodispersity of the emulsion droplet.

4. Conclusions

Monodispersed Pickering emulsion droplets were prepared by self-assembling of sulfonated polystyrene latex particles at droplet interface. The stability of emulsion droplets was improved by controlling sulfonation time of the PS latex particles and by pre-dispersing the latex particles in oil–water two phase and then mixing them into emulsion. For oil-in-water emulsion, the optimal stability was obtained by pre-dispersing 0.33 weight fraction of the latex particles in oil phase initially. The increase of pre-homogenized time of water phase dispersate

and the oil–water volume ratio could obviously decrease the dispersity of emulsion droplets. Monodisperse emulsion droplets could secondarily re-assemble into ordered array.

Acknowledgment

The authors thank the National Natural Science Foundation of China (No.: 50573070) for financial support of this work.

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