

유화제로서 실리카를 이용한 유중수형 에멀전의 안정성에 미치는 수상부 조성의 영향

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Effect of Aqueous Phase Composition on the Stability of a Silica-stabilized Water-in-oil Emulsion

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요약 실리카 입자의 표면이 실란올(silanol, SiOH)그룹과 트리메틸실록실(trimethylsiloxy, $-\text{OSi}(\text{CH}_3)_3$)그룹으로 이루어진 양친매성 고체입자를 이용하여 유중수형(water-in-oil, W/O)의 에멀전을 제조하는데 있어서, 안정한 에멀전을 제조하기 위해서 수상에서의 pH, 전해질 화합물, 고분자의 영향을 연구하였다. 에멀전의 안정성은 실리카의 응집(flocculation) 정도를 조절함으로써 향상시킬 수 있었으며 수상의 pH 조절 및 전해질 화합물 첨가를 통해 에멀전의 안정성을 증진시킬 수 있었다. 70%의 내상을 가지는 W/O 에멀전을 제조하였을 때, 실리카 입자의 함량이 1%까지 증가함에 따라 에멀전 입자의 크기는 감소하였으나, 너무 높은 농도의 실리카는 오히려 유상의 점도를 상승시켜 작은 유화입자의 형성을 방해하였다. 제조된 에멀전의 입자 크기를 이용하여 이론적으로 계산해 볼 때, 많은 양의 실리카 입자가 외상인 유상에 존재함을 알 수 있으며, 에멀전의 안정성을 증진시키기 위해서는 실리카 입자를 계면에 위치하도록 하는 것이 보다 중요함을 알 수 있다. 내상인 수상부에 전해질 화합물을 첨가하지 않은 상태에서 내상의 pH가 증가할수록 실리카 입자의 (-)전하가 증가하여 입자간 응집 촉진에 의해 에멀전의 안정성이 증가하였다. 산성 및 중성 pH에서 전해질 화합물($0.083 \text{ mol dm}^{-3} \text{ MgSO}_4$)의 첨가는 에멀전의 안정성을 증가시킨 반면, 알칼리성 pH에서 전해질 화합물의 첨가는 에멀전의 안정성을 저하시켰다. 레오미터를 이용하여 에멀전의 물성 변화를 관찰한 결과, 전해질 화합물 첨가시 내상인 수상의 pH에 관계없이 산성 및 알칼리성에서 모두 에멀전의 탄성이 급격히 증가하였다. 이는 수상의 pH가 알칼리성인 경우 더욱 현저하였음을 볼 때, 알칼리에 의해 더욱 응집하를 띄게 된 실리카 입자와 전해질 화합물의 양이온간의 전기적 결합에 의한 것으로 사료된다. 수용성 고분자인 잔탄검의 첨가에 의해 에멀전 입자의 평균 입자 크기가 약 $2.8 \mu\text{m}$ 인 안정한 에멀전을 제조할 수 있었다. 이상의 연구를 통하여 계면활성제를 함유하지 않는 고내상의 안정한 W/O 에멀전을 제조하여 보다 피부에 안전한 유화물의 제조가 가능하였다.

Abstract: The extent of silica flocculation can be modified by varying the silica concentration, aqueous phase pH, salt and polymer concentration. High volume fraction W/O emulsion stabilized by hydrophobic silica was established with various aqueous phase conditions for cosmetic application. By increasing the silica concentration up to 1.0 wt%, the size of droplet decreased. A high silica concentration increased the viscosity of continuous oil phase by network formation, which resulted in larger size of droplet. The stability of W/O emulsion is improved as increasing the aqueous phase pH. At low and intermediate pH, the emulsions became more stable by adding salt ($0.083 \text{ mol dm}^{-3} \text{ MgSO}_4$). At high pH, the presence of salt caused significant destabilization. The gelation behavior of the emulsion indicates that the effect of salt on silica-stabilized emulsion is derived from an electrostatic attraction. The addition of xanthan gum in aqueous phase increased the mono-dispersity of the W/O emulsion by making water more hydrophobic and hindering the recombination of droplets. In conclusion, these results indicate that very stable emulsifier-free, finely dispersed W/O emulsion can be achieved for cosmetic application by changing the aqueous phase composition.

Keywords: pickering emulsion, emulsifier-free, w/o emulsion, silica

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1. Introduction

In a various field of industry, surfactants, polymers, solid particles or mixture of these have been used to stabilize the emulsions, e.g., foodstuffs, paints and cosmetics. Colloidal particles have been known to stabilize both o/w and W/O emulsions since early 20th century and the emulsion stabilized by particles is called Pickering emulsion after the name of the author who discovered this emulsion technology. Current experiments have shown that one characteristic of Pickering emulsion is that the solid particles are arranged at the interface between two liquid phases, where they form a mechanical barrier against the combination of the liquid droplets. In particular, it is well known that solid particles are efficient as a stabilizing agent when they are partially wetted by both aqueous and oil phases. Recent studies have summarized a wide variety of solid materials to stabilize O/W and W/O emulsions[1-7] and proved that the effectiveness of the solid in stabilizing emulsions depends on particle size, shape, concentration, wettability and the interaction of them[6,9-14].

In a series of studies, small silica particles of varying hydrophobicity have been shown to be effective emulsifiers in various oil-water systems[9-12]. Silica particles are partially flocculated by forming interparticle hydrogen bonds between silanol groups. Many studies concluded that stable emulsions can be formed when the silica particles are flocculated to some extent[5,7,8]. Less stable emulsions can be induced when the particles are completely flocculated or not flocculated at all. Recent work by Binks and coworkers has shown that the charge on the particles and their extent of flocculation can be modified by pH control and addition of simple electrolytes[7,14]. Midmore[15] reported the effect of strong acid and strong alkali on gelation properties of silica stabilized water-in-oil emulsion.

An application of emulsions in cosmetic and pharmaceutical fields requires non-hazardous surfactants. The use of reduced amount of surfactants is desirable. For example, it is known that mild dermatoses are triggered by certain emulsifier. The reduction in the required amount of surfactants can be achieved by taking an advantage of Pickering emulsion.

In the present study, we describe here emulsifier-free finely dispersed systems of silica-stabilized high volume

fraction water-in-oil emulsion, preferably as cosmetic preparations. The effect of pH control and salt, addition of polymer (xanthan gum) on the extent of flocculation and emulsion stability was investigated. To improve emulsion stability at neutral pH, the extent of flocculation was controlled by changing the concentration of silica, pH, salt and polymer.

2. Materials and Methods

2.1. Materials

Water was passed through a reverse osmosis unit and then a Milli-Q reagent water system. Cyclomethicone, cetyl 2-ethylhexanoate, Xanthan gum were purchased from Dow Corning (U.S.A), Kokyu alcohol (Japan), and CP Kelco (U.S.A), respectively. All other chemicals were analytical grade. The hydrophobic silica powder with a primary particle diameter around 7 nm has a BET surface area of $260 \pm 30 \text{ mg}^2 \text{ g}^{-1}$ and contains 0.456 OH groups/nm i.e. 22.8% of the surface contains silanol (-OH) groups and 77.2% contains trimethylsilyloxy (-O-Si(CH₃)₃) group. The primary particle can aggregate into larger units of about 460 nm in diameter.

2.2. Preparation, Stability and Characterization of W/O Emulsions.

The W/O emulsion was prepared using the following formulation: aqueous phase 60 wt% water, 10 wt% 1,3-butylene glycol; Oil phase 22 wt% cyclomethicone, 8 wt% cetyl 2-ethylhexanoate. Emulsions were prepared varying the pH of aqueous phase using HCl and NaOH. The ionic strength was also varied using MgSO₄. Known mass of hydrophobic silica was dispersed in oil phase and then aqueous phase ($\Phi_w=0.7$) was added slowly to the oil phase operating the homo mixer (Model. Robotics. Tokushu KIKA, Japan) at 3500 rpm for 5 min. After all the aqueous phase was added, the emulsification was made at 5000 rpm for further 10 min. Emulsified droplet size distribution was determined using a Malvern MasterSizer MS20 employing Fraunhofer diffraction. Emulsions were diluted with its own continuous phase not to affect the size distribution. The microscopy image of emulsion were obtained using Leica DMRP (type 301-371, Germany) fitted with a digital camera (Canon Power shot, S40). Images were processed using Canon remote capture (ver.2.4) soft ware.

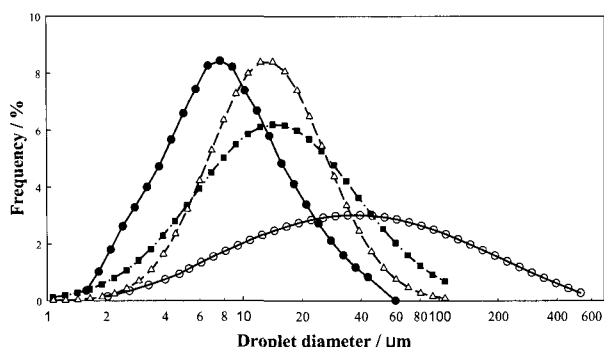


Figure 1. Effect of silica concentration on the droplet diameter volume distribution of the water-in-oil emulsion ($\phi_w=0.7$) with the aqueous phase pH 6. The silica concentrations used in wt% are (○) 0.3, (■) 0.5, (●) 1.0, and (△) 1.5.

To obtain a SEM image, small amount of the emulsion was taken on the top of an aluminum mounting pin and quickly put into slush nitrogen (60 K). The frozen emulsion was instantaneously mounted on a sample stage cooled by liquid nitrogen in a cryo transfer system (Alto 2100, Gatan, U.K.). After fracturing with a knife, the frost on the specimen surface was sub-

limed by etching and the surface was coated with gold. Then coated specimen was transferred to a sample stage cooled by liquid nitrogen in a SEM (JEM 6360V, JEOL Ltd.). The observation was performed at accelerating voltage of 5 kV. As a guide to emulsion stability (droplet size and distribution), the intensity of backscattering was measured using a Turbiscan Lab (Formulation Co., France) based on multiple light scattering method[16,17]. The detection head is composed of a pulse near-infrared light source ($\lambda=850$ nm). Emulsion was placed in a flat-bottomed cylindrical cell (25 mm diameter, 55 mm height) and the average intensity of backscattering from 30 mm to 32 mm height of the cell was collected. At various pH and $MgSO_4$ concentration, backscattering was measured immediately after preparation. The rheological measurements on the emulsion were performed using a HAKKE RS50 RheoStress (Germany). Stress sweep experiments at 1 Hz from 1 Pa to 200 Pa was done to measure G' (Storage modulus) and G'' (loss modulus) of the emulsion. Cone and plate sensor system was used in this experiment.

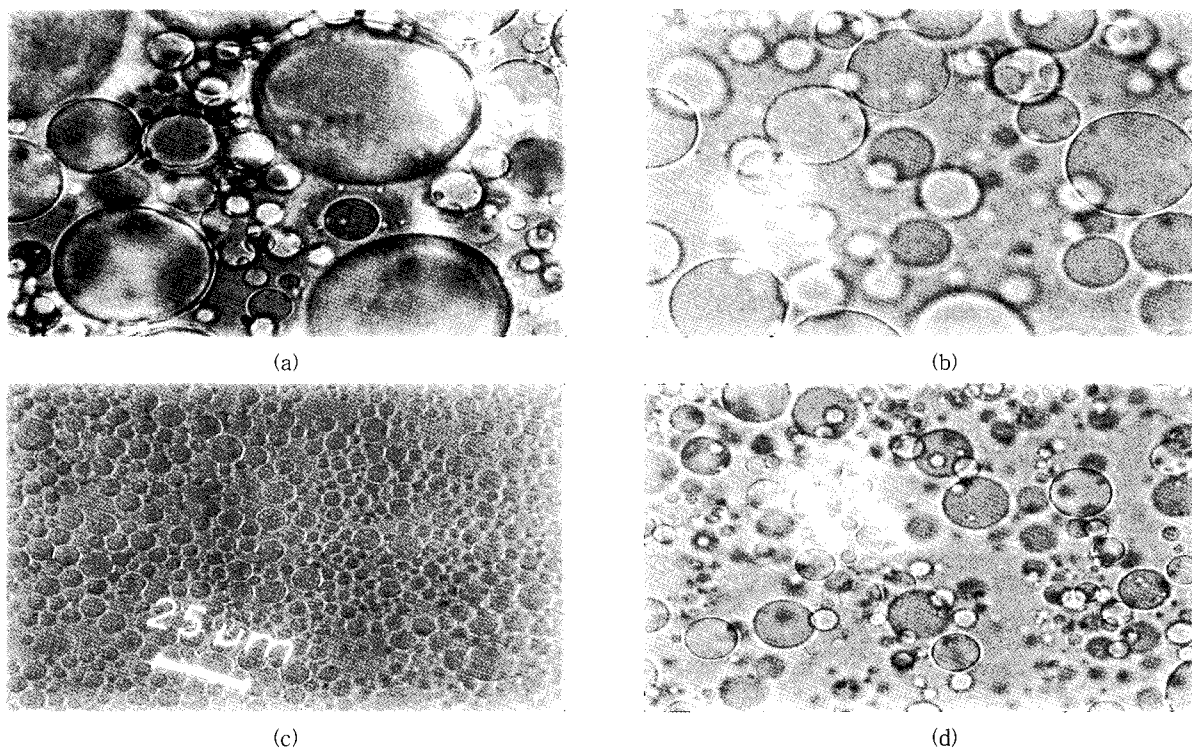
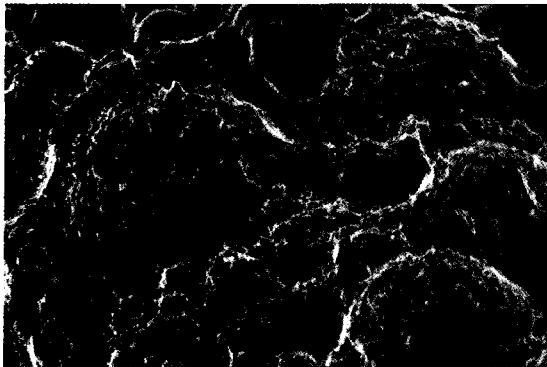
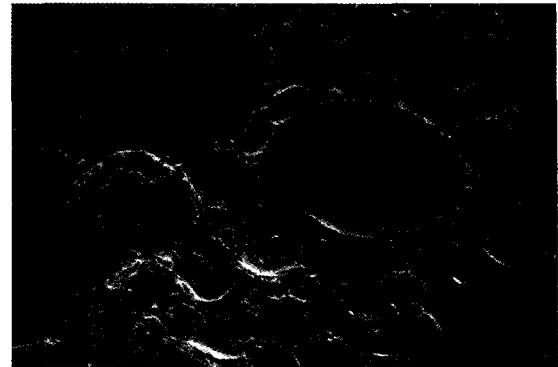


Figure 2. Optical micrograph of the silica stabilized water-in-oil emulsion ($\phi_w=0.7$). The wt% of silica concentrations are (a) 0.3, (b) 0.5, (c) 1.0, and (d) 1.5.



(a)



(b)

Figure 3. Cryo-SEM images of the silica stabilized water-in-oil emulsion ($\phi_w=0.7$) (a) the surface of the droplets, (b) the cut face of the droplets. The Bar represents 10 μm in length.

3. Result and Discussion

3.1. Effect of Silica Concentration on the Droplet Size Distribution

The effect of particle concentration on droplet size distribution was investigated. High volume fraction emulsions ($\phi_w=0.7$) were prepared at the aqueous phase pH around 6. Figure 1 shows that the droplet size distribution as silica concentration was varied. At silica content below 0.3 wt%, a stable emulsion was not formed. By increasing the silica concentration up to 1.0 wt%, more finely dispersed emulsion was obtained. In contrast, a high content of silica particle caused a relatively larger droplet formation which is clearly visible in the microscope image (Figure 2). By increasing the concentration of silica particles, a continuous reduction in average size was observed accompanying with a gradual increase of flocculation. Stabilization by solid particles depends on their ability to migrate to the interfacial region to form a film, which inhibits coalescence of the droplets. By increasing silica concentration, a high viscosity of the oil phase produced by network formation with the silanol group decreases the rate of silica particle diffusion to the droplet surface. As a result, coalescence occurs more readily, which explains more larger droplet size distribution at high silica content. Figure 3 shows the calculated (theoretical) value of droplet surface area enclosed with particle at various silica concentration when the droplet was assumed to have the size and density of 10 μm , 1 g cm^{-3} each and contact angle of 120°. The coverage of droplet surface is over 100% at 1.0 wt% silica

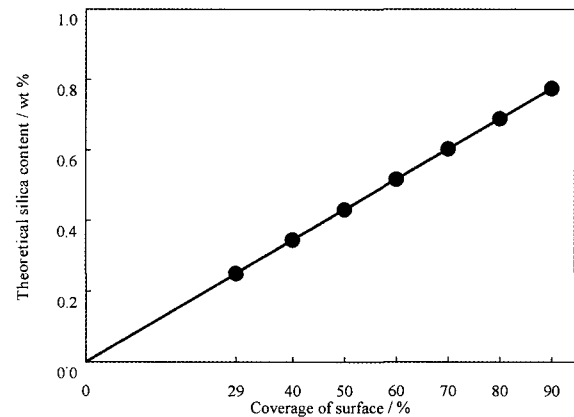


Figure 4. Plot showing the theoretical value of droplet surface area enclosed with particles at various silica concentrations.

concentration theoretically. It involves that not all the silica particles locate at the interface. Some portions of the silica still remain at the oil phase to thicken the emulsion outer phase. Even though this could enhance the emulsion stability to sedimentation, more importantly, the concentration of the silica particle located at the interfaces should be reinforced to gain excellent emulsion stability. As seen in Figure 4, we observed the droplet coated with silica by the cryo-SEM image.

3.2. Effect of pH and Salt Concentration on the Emulsion Stability

Silica-stabilized emulsion is known to be stable to coalescence although it shows a strong flocculation among droplets. Emulsions prepared at this study remain stable for a week at 50°C without creaming or

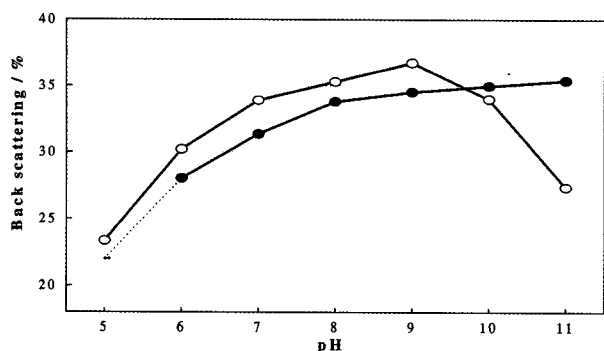


Figure 5. The effect of pH and ionic strength on water-in-oil emulsion ($\Phi_w=0.7$) stability. The concentration of silica particles in all emulsion is 1.0 wt% without MgSO_4 (●); with MgSO_4 , $0.083 \text{ mol dm}^{-3}$ (○).

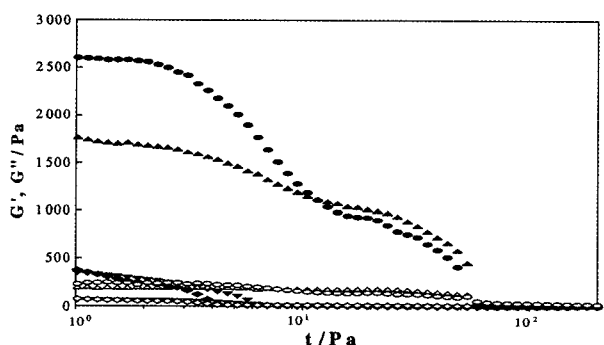


Figure 6. The effect of ionic strength on the storage modulus, G' (closed symbols), and loss modulus, G'' (open symbols) on water-in-oil emulsion ($\Phi_w=0.7$). The concentration of silica particles in all emulsion is 1.0 wt%. pH 6 without MgSO_4 (∇ , \blacktriangledown), pH 9 without MgSO_4 (\diamond , \blacklozenge), pH 6 with $0.083 \text{ mol dm}^{-3}$ MgSO_4 (\triangle , \blacktriangle), pH 9 with $0.083 \text{ mol dm}^{-3}$ MgSO_4 (○, ●).

sedimentation. Therefore, to estimate a long-term stability of emulsion, the size and distribution of the droplets were measured immediately after preparation using a light scattering method. Several studies concluded that stable emulsions could only be formed if the particles are flocculated to some extent[4,6,7,15]. The effect of charging the particle surface was investigated. By changing the aqueous phase pH, the point of zero charge of silica is at pH 2. Above this pH, silanol groups dissociate to be negatively charged. By increasing the aqueous phase pH, dissociation of uncharged silanol groups to negatively charged SiO^- groups could increase the flocculation. As shown in Figure 5, by increasing the pH, more stable emulsions (droplet size

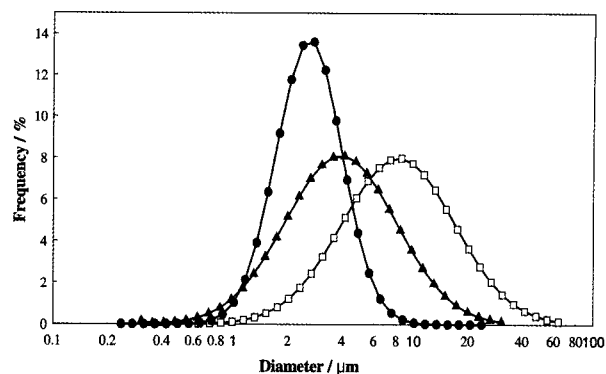


Figure 7. Effect of xanthan gum on the droplet diameter volume distribution of the water-in-oil emulsion ($\Phi_w=0.7$) containing $0.025 \text{ mol dm}^{-3}$ MgSO_4 with the aqueous phase pH 6. The concentration of silica particles in all emulsion is 1.0 wt%. The concentration of xanthan gum concentrations used in wt% are (□) 0, (▲) 0.01, and (●) 0.03.

and distribution) were obtained. At low pH ($\text{pH}<5$) without salts, a stable emulsion was not formed, indicating insufficient flocculation at acidic pH. The effect of increasing the ionic strength is also shown in Figure 3. Interestingly, an addition of $0.083 \text{ mol dm}^{-3}$ MgSO_4 to aqueous phase caused a dramatic change to form a stable emulsion at pH 5 accompanying with the small enhancement of emulsion stability up to pH 9. At low pH, the particle shows a low surface potential (insufficient charge) to locate at interface. An addition of MgSO_4 at low pH appeared to promote flocculation to form a stable dense film at oil-water interface by taking particles at interface. At $\text{pH}>9$, an addition of salt caused a destabilization of emulsion on the contrary. The destabilizing effect of MgSO_4 on the emulsion at high pH may be linked to the excessive flocculation of the aqueous colloid. An excessive flocculation caused a rigid crust of interface membrane to destabilize the emulsion.

The effect of ionic strength on G' (storage modulus) and G'' (loss modulus) at pH 6 and pH 9 has demonstrated in Figure 6 as the same emulsions in Figure 5. An addition of $0.083 \text{ mol dm}^{-3}$ MgSO_4 in each case resulted in an increase in G' . The effect of ionic strength on G' was greater at alkali pH (pH 9) than acidic pH (pH 6), which is more negatively charged. The present gelation behavior indicates that the effect of MgSO_4 on silica-stabilized emulsion is derived from an electrostatic attraction.

3.3. Effect of Polymer on Mono Dispersity of Emulsion

The effect of adding polymer (xanthan gum) to the dispersed aqueous phase on the droplet size volume distribution of the water-in-oil emulsion ($\Phi_w=0.7$) containing $0.025 \text{ mol dm}^{-3} \text{ MgSO}_4$ was investigated in aqueous phase at pH 6. Figure 7 shows that an addition of xanthan gum to aqueous phase increased the mono-dispersity of the emulsion. By adding 0.03 wt% xanthan gum, the diameter of droplet decreased effectively. Over 80 vol% of the drops were in the range of diameter between $1 \mu\text{m}$ and $3.2 \mu\text{m}$. Recent work by Midmore[7,16] described the preparation of very stable O/W and W/O emulsion with silica particles flocculated by the polymer hydroxypropyl cellulose. An aqueous phase of hydroxypropyl cellulose has been known to increase the mono-dispersity of the emulsion by making water more hydrophobic to allow the silica particle to adsorb more rapidly. Another effect of the hydroxypropyl cellulose is to increase the viscosity of the dispersed phase, which hinders the recombination of droplets. A similar argument occurs when xanthan gum is added to the aqueous phase.

4. Conclusion

By using silica as a stabilizer, finely dispersed stable W/O emulsion of high volume fraction has been successfully established. The stability of emulsion can be improved by controlling the extent of flocculation. An aqueous phase pH, salt and xanthan gum affect the emulsion stability. An application of this W/O emulsion to cosmetic formulation could provide an excellent safety and novel skin feel as well.

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