

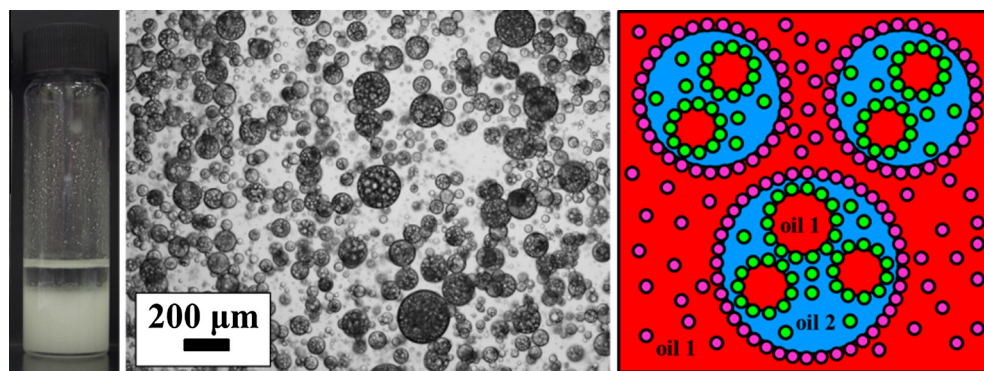


Regular Article

Double oil-in-oil-in-oil emulsions stabilised solely by particles

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GRAPHICAL ABSTRACT



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ABSTRACT

The stability of vegetable oil-in-100 cS silicone oil-in-vegetable oil V/S/V emulsions to sedimentation and coalescence has been studied. The emulsions contained two types of silica particle of different surface silanol content, 70% and 20% SiOH, which prefer to stabilise 100 cS silicone oil-in-vegetable oil S/V and vegetable oil-in-100 cS silicone oil V/S emulsions respectively, in systems containing equal proportion of the oils. The emulsions were prepared in a two-step process and were characterised using the drop test and optical microscopy. The emulsions were completely stable to coalescence for over a month. However, they underwent sedimentation which decreases as the concentration of 70% SiOH silica particles stabilising the silicone oil globules increases. The gravity-induced sedimentation halted at a relatively high particle concentration (2 wt.%) and negligible amount of the vegetable oils was released even after a month. Their average droplet diameter also decreases as the concentration of 70% SiOH silica particles increases. Values of oil-oil-solid particle contact angles θ_{oo} , measured on microscope glass slides composed of the particles, are in good agreement with the type of simple emulsions and hence double emulsions formed by the particles.

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1. Introduction

Small solid particles may be surface-active at certain fluid interfaces and are able to stabilise related materials upon adsorption as

realised by the pioneering work of Ramsden [1] and Pickering [2]. Such materials are kinetically ultra-stable compared with their surfactant-stabilised analogues [3]. For emulsions and foams, the stability to Ostwald ripening and coalescence, important for stability to phase separation, is due to both the ability of the particle-coated surface to resist expansion and shrinkage and due to steric hindrance resulting from the protrusion of adsorbed solid particles on the droplets and gas bubble surfaces [4]. Also, because the

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amount of energy ΔG_d needed to remove an adsorbed particle is very large (several magnitudes of thermal energy $k_B T$), particles are considered to be irreversibly adsorbed compared with surfactant molecules which are usually in dynamic equilibrium adsorbing and desorbing from the fluid interfaces [3,5]. As a result, particle-coated droplets and gas bubbles are less prone to coalescence than the surfactant-coated ones. ΔG_d for a spherical solid particle of radius R making a contact angle θ with a fluid interface of interfacial tension γ is given as [5]:

$$\Delta G_d = \pi R^2 \gamma (1 - |\cos \theta|)^2 \quad (1)$$

The types of materials obtained from a particle-stabilised system depend on the extent to which a small solid particle protrudes into the fluid phases upon adsorption as illustrated in Fig. 1. This is also known as particle wettability and it is quantified in terms of the three-phase contact angle (measured through the more polar phase) the particles make with the fluid interfaces [5]. For air-liquid interfaces, hydrophilic particles which protrude more into the water phase resulting in a water (w)-air (a)-solid (s) contact angle θ_{wa} value of around 40–80° form aqueous foams [6,7]. Aqueous liquid marbles [8,9] and dry water [10,11] are formed by hydrophobic particles which protrude more into the air phase giving rise to $\theta_{wa} \gg 90^\circ$. Similarly, oleophilic solid particles which protrude more into the oil phase giving rise to an oil (o)-air-solid contact angle θ_{oa} value of $<90^\circ$ are required to stabilise oil foams [12,13]. Oil liquid marbles and dry oils are stabilised by oleophobic solid particles which protrude more into the air phase leading to $\theta_{oa} \gg 90^\circ$ [14,15]. In the case of oil-water (1:1) systems, particles that protrude more into the water phase leading to an oil-water-particle contact angle $\theta_{ow} < 90^\circ$ give oil-in-water o/w emulsions [16]. However, particles that protrude more into the oil phase such that $\theta_{ow} > 90^\circ$ give water-in-oil w/o emulsions [16]. For the case of $\theta_{ow} \sim 90^\circ$ where the particles protrude equally into the oil and water phases, either o/w, w/o or multiple emulsions can be obtained [16]. In cases where θ_{ow} is 0 or 180°, no stable emulsion or foam can be prepared. Using these concepts, double emulsions containing oil and water have been prepared using a combination of small solid particles which prefer to stabilise different emulsion types [17]. Similarly, in non-aqueous systems consisting of say two different immiscible oils (o_1 and o_2) of equal proportion, particles that protrude more into oil 1 give oil 2-in-oil 1 (o_2/o_1) emulsions whilst those that protrude more into oil 2 give oil 1-in-oil 2 (o_1/o_2) emulsions [18]. Again either o_1/o_2 or o_2/o_1 can be obtained in cases where the particles protrude equally into the two oil phases giving rise to $\theta_{oo} \sim 90^\circ$. Based on this idea, it has been reported [18] that double emulsions containing two oils can also be obtained using a combination of small solid particles that prefer to stabilise different emulsion types just like in particle-stabilised double emulsions of oil and water [19]. Although Dyab and

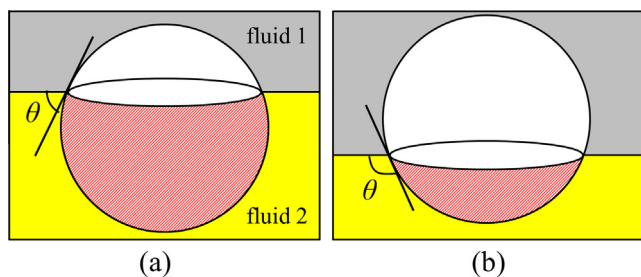


Fig. 1. Illustration of particle wettability in terms of the degree of particle protrusion into two fluid phases upon adsorption at the fluid interface. (a) Fluid 2 wets the particle more than fluid 1 leading to $\theta < 90^\circ$ and (b) fluid 1 wets the particle more than fluid 2 giving rise to $\theta > 90^\circ$. In both cases, fluid 2 is more polar than 1.

co-workers [19,20] have illustrated this using mixtures of non-polar solvents of relatively high dielectric constant ($\epsilon > 25$ at 25 °C), this is yet to be studied systematically especially in terms of the kinetic stability of the double emulsions with respect to particle concentration and also using typical oil mixtures. Typical oil mixtures here refer to relatively low dielectric constant liquids like vegetable oils ($\epsilon = 3.1$ at 25 °C) and silicone oils ($\epsilon = 2.7$ at 25 °C). Using an immiscible mixture of 100 cS silicone oil and vegetable oil and two types of partially hydrophobic fumed silica particles, we describe the preparation and stability of particle-stabilised double oil-in-oil-in-oil emulsions at different particle concentrations. This work follows from our recent [18] success in preparing simple vegetable oil-silicone oil emulsions, which are notoriously difficult to prepare with surfactants, using fumed silica particles.

As summarised in our recent paper [18], non-aqueous emulsions, be it simple or multiple, have numerous applications. They can replace their aqueous analogues in applications where the presence of water is undesirable, for example in cleaning systems that are susceptible to rust formation, in sol-gel processes with hydrolysable metal alkoxides in organised media and when incorporating drugs that are prone to hydrolysis. They can also serve as bases for topical applications, for example for dermatological drugs and as emollients in pharmaceutical and cosmetic preparations respectively.

2. Materials and methods

2.1. Materials

The triglyceride vegetable oils were olive oil (density $\rho = 0.91 \text{ g cm}^{-3}$ at 25 °C) from Sigma and rapeseed oil ($\rho = 0.92 \text{ g cm}^{-3}$ at 25 °C) from the plant *Brassica rapa* from Fluka. The oils were passed twice through a column containing basic alumina to remove polar impurities before use. The 100 cS silicone oil (polydimethylsiloxane, PDMS, $\rho = 0.97 \text{ g cm}^{-3}$ at 25 °C) was from Dow Corning and was used as received. The mutual solubility of the vegetable oils and 100 cS silicone oil is around 2 vol.% whilst the 100 cS silicone oil-vegetable oil interfacial tension is $\sim 3 \text{ mN m}^{-1}$ at 25 °C [18]. In terms of polarity, the 100 cS silicone oil is judged to be more polar than both vegetable oils [21,22].

The fumed silica particles of primary particle diameter 20–30 nm were obtained from Wacker Chemie. The particles were obtained by treating hydrophilic silica particles possessing 100% SiOH with different concentrations of dichlorodimethylsilane $\text{Si}(\text{CH}_3)_2\text{Cl}_2$. The more hydrophilic grade possessed 70% residual surface SiOH and the very hydrophobic grade possessed 20% SiOH.

2.2. Methods

2.2.1. Scanning electron microscopy of fumed silica particles

Images of the powdered fumed silica particles were obtained using a Zeiss EVO 60 scanning electron microscope (SEM). With the aid of an Edwards high vacuum coating unit, the dry particles were applied to a sticky carbon disc and coated with a thermally evaporated carbon film ($\sim 5 \text{ nm}$ thick). SEM images were taken at a voltage of 20 kV and a probe current of 70 pA. The SEM micrographs (Fig. 2) show that both particle samples are made up of partially fused and agglomerated primary particles.

2.2.2. Preparation of simple oil-in-oil emulsions

Batch oil-in-oil emulsions containing equal volumes of either rapeseed oil or olive oil with 100 cS silicone oil were prepared in screw cap glass vials (i.d. 2.4 cm and h. 7.2 cm) in the presence of either 70% or 20% SiOH fumed silica particles using the powdered particle method. The particle concentration in the emulsions

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