

EMULSIFICATION AND EMULSION STABILITY OF SILICA-CHARGED SILICONE OILS

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4.1 New triggers for stability/unstability and texture control in emulsions

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1/ Aim of the study

The emulsification of oils containing hydrophobic solid particles of high concentration (between 5 and 30 wt %) is important for several technologies. However, this process presents a serious technological challenge, because the particles modify the bulk and surface properties of the oily phase in a way that impedes emulsification. For example, the silica-charged silicone oils (so-called "compounds") show much higher viscosity and non-Newtonian behavior when compared to the oils, from which these compounds are prepared (1,2). The high viscosity and the yield stress of the compounds impedes the deformation and break-up of the compound drops during emulsification. In addition, the hydrophobized silica particles adsorb on the oil-water interface and protrude into the aqueous phase (3,4), thus facilitating the drop-drop coalescence during emulsification. Therefore, both the modified bulk and surface properties of the oils by the silica particles, lead to difficult emulsification of the silica-silicone oil compounds.

The major aim of the current study is to find appropriate conditions for emulsification of such compounds. To achieve this aim we performed experiments to find: (1) Appropriate conditions for drop breakup, in the absence of drop-drop coalescence. In these experiments we used very viscous silicone oils without particles. (2) Appropriate conditions for preventing drop-drop coalescence, despite the presence of silica particles in the compounds.

2/ Materials and methods.

2/1. Materials. The studied oils were: vinyl terminated polydimethylsiloxane Rhodorsil 621V100, 621V600, 621V1500, 621V10000, 621V60000 and 621V100000 with dynamic viscosity of 0.1, 0.6, 1.5, 10, 60 and 100 Pa.s, respectively. The following compounds were studied: RTV 1556

based on oil 621V600, and RTV HPM based on oil 621V1500. These compounds contain around 30 wt % hydrophobized silica. To clarify the effect of silica particles on the emulsification process, in some of the experiments we diluted the original compound with the silicone oil used in its preparation. In this way, we prepared compounds with different silica concentrations, varied between 5 and 25 wt %.

Two low-molecular mass surfactants were used as received: anionic sodium dodecyl sulfate (SDS, product of Sidobre Sinnova) and nonionic polyoxyethylene-8 tridecyl ether (C13EO8, product of Rhodia). As polymer emulsifier we used polyvinyl alcohol (PVA) with a commercial name Rhodoviol® 25/140 ($M_n \approx 12600$, $M_w \approx 63000$, degree of hydrolysis $\approx 88\%$). All studied oils, compounds, and surfactants were kindly supplied by Rhodia Silicones Europe (currently Bluestar Silicones).

The procedure for preparation of the PVA solutions was as follows: Water was heated up to 80 °C and the desired amount of PVA was added under stirring until complete PVA dissolution. These solutions contained also 0.01 wt % of the antibacterial agent NaN_3 (Riedel-de Haën). Sodium chloride (NaCl) was added to some of the solutions to adjust the ionic strength.

2/2. Emulsion preparation. Emulsions were prepared by using a three-step procedure. Initially, 25 mL of the aqueous phase and 25 mL of the compound were subjected to mild shear agitation for preparing a premix (coarse emulsion). The second homogenization step was accomplished by intensive stirring of this premix by rotor-stator homogenizer Ultra Turrax T25 (IKA) operating at 9 500 rpm. The duration of this homogenization step was fixed at 5 min. In the last homogenization step, intensive stirring for additional 5 min at 20 500 rpm was applied.

2/3. Optical observations of emulsions. The drop size distribution and the type of the formed emulsions were determined by optical microscopy. The mean volume-surface diameter, d_{32} , was calculated from the size-distribution histogram.

2/4. Measurement of interfacial tension. The oil-water interfacial tension was measured by drop-shape-analysis to pendant oil drops on DSA 10 instrument (Kruess, Germany).

2/5. Foam films in capillary cell. Foam films of micrometer size were formed and observed in reflected light by using the method of Scheludko (5) to determine the equilibrium film thickness and to compare it to the protrusion depth of the silica particles. The film is formed from a biconcave drop placed in a short capillary (i.d. 2.5 mm, height 3 mm) by sucking out liquid through a side orifice. The films are observed in reflected light by optical microscope, equipped with long-distance objective, CCD camera, video-recorder and monitor. The interference of the light, reflected from the two surfaces of the foam film, leads to the appearance of dark and bright interference fringes when using a monochromatic light for illumination, or to fringes of different colors when white light is used. A given fringe appears as a result of the interference of light, reflected from film areas of the same thickness (5). From the intensity of the reflected light and from the order of the respective interference fringe, one can determine precisely the local thickness of the film.

2/6. Asymmetric thin films - protrusion depth. These experiments were performed to observe the penetration of the silica particles from the compound drops into the aqueous phase and to determine the respective protrusion depth of silica particles. Asymmetric aqueous film was formed by pressing a drop of compound against a glass substrate in surfactant solution. The drop was formed on the tip of a glass capillary which was mounted on X-Y-Z positioning stage and was connected to system for pressure control. Thus, the diameter of the compound drop (and the film diameter) could be controlled either by moving the capillary in vertical direction or by blowing/sucking compound through the capillary. The film was observed in reflected monochromatic light from below, by means of an inverted optical microscope. Digital camera, connected to video-recorder and monitor, was used to observe and record the film formation and thinning. One can easily distinguish changes in the film thickness on the order of 50 nm (bright to gray, gray to dark, and so on). The lower measurable film thickness is about 10 nm, which allows us to see

protruding particles from the compound drops, when their penetration depth is larger than ca. 15 nm.

2/7. Contact angle measurement. The contact angle of sub-millimeter sized glass beads attached at the oil-surfactant solution interface was measured by the procedure described in ref. (6). The water and oil are poured in a glass cuvette with optically clean front and back windows. A spherical glass bead is placed at the top of the oil phase and allowed to sediment. The contact angle measurement starts after the particle appears on the oil-water interface. This procedure provides the "advancing" contact angle, as defined through the aqueous phase, i.e. larger values of θ correspond to more hydrophobic particles and vice versa.

3/ Experimental results and discussion.

3/1. Drop breakup for viscous oils in inertial turbulent regime of emulsification. In the inertial turbulent regime of emulsification the drops are larger than the size of the smallest turbulent eddies in the flow (7,8) and deform under the action of pressure fluctuations, created by the turbulent eddies. The size of the smallest eddies can be estimated by the Kolmogorov theory (7,8):

$$\lambda_0 = \epsilon^{-1/4} \eta_c^{3/4} \rho_c^{-3/4} \quad (1)$$

where η_c is the viscosity and ρ_c is the mass density of the aqueous phase (the continuous phase), and ϵ is the average density of power dissipation per unit mass. To ensure emulsification in inertial turbulent regime, i.e. small turbulent eddies, we used emulsifier solutions with low viscosity: 1 wt % PVA ($\eta_c = 2.3$ mPa.s, corresponding to $\lambda_0 = 3.3$ μm at $\epsilon = 10^5$ J/kg.s) and 10 wt % SDS + 10 mM NaCl ($\eta_c = 1.7$ mPa.s, $\lambda_0 = 2.6$ μm). All experiments were performed at low oil volume fraction, between 3 and 5 %, to reduce the possible effect of drop-drop coalescence during emulsification. As oil phase we used viscous silicone oils with viscosity between 100 and 100 000 mPa.s. The obtained experimental results are presented in Table 1.

Table 1. Results for the mean drop-size, d_{32} [μm], from emulsification experiments of viscous silicone oils in different emulsifier solutions: 1 wt % PVA ($\eta_c = 2.3$ mPa.s; $\sigma_{ow} = 21$ mN/m; $\lambda_0 \approx 3.3$ μm) and 10 wt % SDS + 10 mM NaCl ($\eta_c = 1.7$ mPa.s; $\sigma_{ow} = 7$ mN/m; $\lambda_0 \approx 2.6$ μm). The mean drop size, d_{32} , is larger than λ_0 for all systems, i.e. the emulsification occurs in inertial turbulent regime.

η_D , Pa.s	0.1	0.6	1.5	10	60	100
1 wt % PVA	19±4	24±6	Millimeter sized drops + Non-emulsified oil			
10 wt % SDS	10±2	13±3				

For both studied emulsifiers, millimeter sized drops and non-emulsified oils were observed at the end of the emulsification process, when silicone oil with viscosity $\eta_D \geq 1.5$ Pa.s was used as oily phase. The explanation of this result is that the drops are unable to deform into a sufficiently long, capillary unstable threads, upon their collisions with the small turbulent eddies. In other words, the emulsification of very viscous oils is inefficient in the inertial turbulent regime, due to the very long deformation time of the viscous droplets.

3/2. Effect of the viscosity of the aqueous phase on the emulsification process. To change the regime of emulsification in favor of drop deformation (9), we increased the solution viscosity by using PVA solutions with higher concentration (up to 10 wt % PVA which corresponds to viscosity of 610 mPa.s). The results from this experimental series are shown in Figure 1. One sees that the size of the droplets decreases significantly with the increase of the viscosity of the aqueous

phase. Note that this high viscosity of the continuous phase corresponds to viscous regime of turbulent emulsification (the droplets are smaller than the smallest turbulent eddies). Furthermore, the emulsification of extremely viscous oils (100 Pa.s) becomes possible and rather efficient when the viscosity of the aqueous phase is above 35 mPa.s.

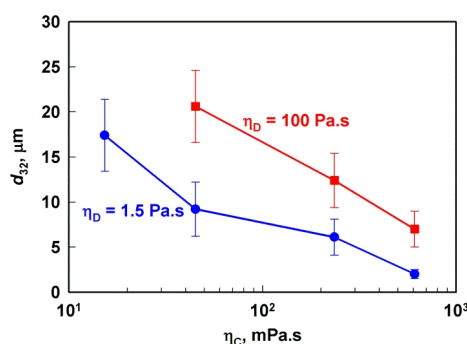


Figure 1. Mean volume-surface diameter, d_{32} , as a function of the viscosity of the aqueous phase for emulsions formed in PVA solutions with different concentrations. Silicone oils with $\eta_D = 100$ Pa.s and $\eta_D = 1.5$ Pa.s are used as oil phases. Here the emulsification occurs in the viscous turbulent regime, $d > \lambda_0$, due to the higher viscosity of the aqueous phase.

3/3. Emulsification in presence of silica particles. To clarify the effect of silica particles on the emulsification of silica-charged oils in the viscous turbulent regime, we performed emulsification experiments in solutions of three different emulsifiers. In all these cases the viscosity of the continuous phase was high, $\eta_c > 35$ mPa.s, to ensure efficient drop breakup. Namely, solutions of 10 wt % C13EO8 + 40 wt % Glycerol (67 mPa.s), 5 wt % PVA (50 mPa.s), and 10 wt % SDS + 40 wt % glycerol (45 mPa.s) were used. The obtained experimental results are summarized in Table 2. Note that the silicone oils without silica are very well emulsified in all these viscous solutions, forming O/W emulsions. However, when silica particles were present in the oily phase, different results were observed, depending on the specific emulsifier. The SDS could not suppress completely the coalescence between the compound drops with particle concentration $C_p \geq 5$ wt %. As a consequence, non-emulsified oil was observed at the end of the emulsification process. The emulsification in 10 wt % C13EO8 solution led to the formation of inverse water-in-oil (W/O) emulsions, certainly related to intensive coalescence of the oily drops during the emulsification process. The emulsions formed in PVA solution were of oil-in-water type (O/W), which means that this emulsifier efficiently suppressed the coalescence between the oily compound drops during emulsification.

Table 2. Results from emulsification experiments of silica-silicone oil compounds with different silica concentrations. O/W = oil in water emulsions; W/O = water in oil emulsion; O/W+O = oil in water emulsion plus non-emulsified oil.

C_p , wt %	Viscosity of the oily phase, Pa.s	C13EO8 + Glycerol	SDS + Glycerol	5 wt % PVA
		$\eta_c = 50$ mPa.s		
0	0.6	O/W		
5	0.6	W/O	O/W + O	O/W
10	1.5			
15	5.0			
30	50			
0	60	O/W		

3/4. Model experiments to clarify the effect of silica particles on the emulsification process. It is well known that mixed silica-silicone oils act as very effective antifoams, which is related to the so-called “pin-effect” of silica particles (10,11). This term is used to describe the bridging of the two opposite surfaces of a liquid film by solid particles, which may lead to a rapid film rupture, if the particles have proper hydrophobicity, size, and shape. Similar pin-effect of particles could be expected for the oil-water-oil films, formed between two drops in the emulsion during and after emulsification, see Figure 2. The experiments and theoretical analysis show that, if two emulsion drops are pushed against each other by certain hydrodynamic force, the solid particles would come in direct contact with the other drop and will form solid bridges between the film surfaces, at much lower in magnitude force, as compared to the film rupture in the absence of solid particles. Note that this effect is possible only if the protrusion depth of the particles into the aqueous phase is larger than the thickness of the aqueous film, formed between two colliding oil droplets during emulsification (11).

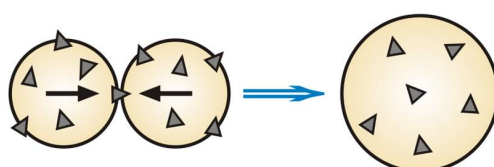


Figure 2. Schematic presentation of the drop-drop coalescence due to the pin effect of silica particles.

To clarify whether the effect of silica particles in the studied compounds is related to their ability to protrude out of the oil-water interface and to bridge the surfaces of the emulsion films formed between neighboring droplets, we measured the protrusion depth of the particles and compared this depth to the thickness of the films. We found that for all studied emulsifiers, the protrusion depth of the particles was around 20 nm, whereas the film thickness was strongly dependent on the emulsifier. Typical images from the microscope observations of the various foam films are shown in Figure 3. One sees that for C13EO8 and SDS solutions the film thickness is around 10 nm (i.e. smaller than the protrusion depth of silica particles), whereas for PVA solution the film thickness is around 110 nm (much larger than the protrusion depth of particles).

From these and other experiments we were able to conclude that the small film thickness for C13EO8 and SDS solutions leads to very efficient coalescence of the compound drops, due to the pin-effect of the silica particles present in the compounds. In contrast, the thick films in PVA solutions prevent the pin effect of silica particles and thus facilitate the formation of stable O/W emulsions with the studied compounds.

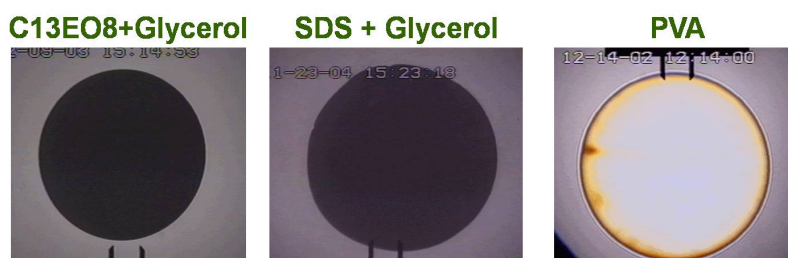


Figure 3. The foam films formed from C13EO8, SDS and PVA solutions: the equilibrium thicknesses $h_{EQ} \approx 10$ nm for C13EO8, $h_{EQ} \approx 10$ nm for SDS, and $h_{EQ} \approx 110$ nm for PVA. For comparison, the protrusion depth of the silica particles into the aqueous phase is ≈ 20 nm.

As shown in Table 2, the emulsification in C13EO8 solution leads to formation of inverse W/O

emulsions, certainly due to intensive coalescence of the oil drops during stirring. Direct measurements of the contact angle of glass particles at oil-water interface, in the presence of the various emulsifiers, showed that the hydrophobicity of these particles was strongly affected by adsorption of C13EO8 on the solid/water interface - the particles acquired contact angles closer to 90 degrees, thus favouring the particle adsorption on the interface. From these and other experiments we could conclude that the enhanced adsorption of the silica particles on the oil-water interface led to the very efficient stabilization of the W/O emulsions, by the silica particles when C13EO8 solutions were used, see Figure 4.

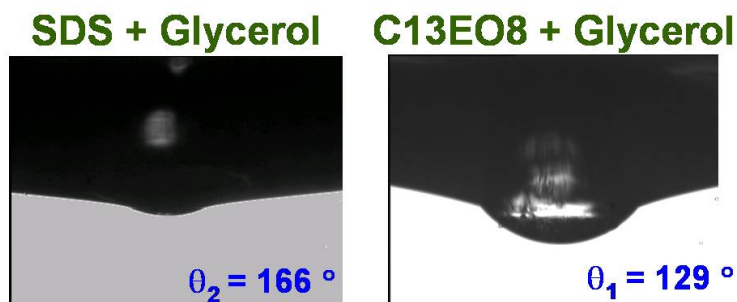


Figure 4. Contact angle of solid particle on oil-SDS and oil-C13EO8 solution interface.

4/ Conclusions

Necessary conditions for obtaining stable O/W emulsion with silica-charged silicone oils are:

- Using continuous phase with high viscosity, $\eta_c > 30$ mPa.s, to ensure efficient drop deformation and breakage, in viscous turbulent regime.
- Using emulsifier which ensures thick emulsion films between the emulsion droplets, in order to suppress the "pin-effect" of the silica particles (leading to emulsion destabilization).

Necessary condition for obtaining stable W/O emulsion in such systems is:

- Use of emulsifier ensuring better adsorption of the hydrophobic silica particles on the oil-water interface (contact angle around and below 130 degrees). In this case, the particles stabilize very efficiently the aqueous drops against coalescence.

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