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The Effects of Capillary Forces on the Flow Properties of Glass Particle Suspensions in Mineral Oil

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The effect of water on the flow behavior of glass microspheres dispersed in mineral oil was investigated for various levels of water, particle volume fractions, and particle sizes. The addition of small amounts of water leads to large increases in viscosity due to the formation of water bridges between particles that give rise to capillary forces between the particles. The capillary forces between the particles also make the flow profile highly shear-thinning across the range of particle volume fractions that were studied (0.10 to 0.25). The presence of water leads to a significant effect of particle size, and the viscosity of dispersion goes through a maximum as the amount of water is increased. Two hydrophobic surfactants, Span 80 and Arquad 2HT, were found to reduce the viscosity of the dispersions with added water, but the mechanism and extent of viscosity reduction differed. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2334–2340, 2011

Keywords: capillary force, hydrates, anti-agglomerants, surfactants, rheology

Introduction

The rheological properties of suspensions and slurries are of great importance for many applications, but there has been little work to understand how capillary forces between particles can influence the behavior of the fluid or how surfactants affect this behavior.[1] One important application is the control of hydrate formation during the production of natural gas. In subsea natural gas pipelines, the presence of oil and water combined with low temperatures and high pressures allows dispersions of gas hydrates to form. The hydrate particles can adhere together and to the pipe walls and lead to a blockage of the pipe. It is believed that the strong adhesion is primarily due to capillary forces from liquid water bridges between particles.[2–7] Additives called anti-agglomerants are being studied for their ability to control blockage formation. These additives are typically surfactants that can affect hydrate adhesion and dispersion.[2,5,8] They also will then affect the flow behavior of the hydrate suspension. Thus, a fundamental understanding of how capillary forces and surface-active materials influence the flow properties of a suspension containing liquid bridges is of great interest.

When a second, insoluble liquid phase is added to a suspension where the second liquid preferentially wets the dispersed solid, liquid bridges should form between particles. Capillary forces arise due to liquid bridges connecting particles. Figure 1 shows a schematic of such a liquid bridge. The capillary force is approximately given by[9,10]

$$\frac{F_{\mathrm{cap}}}{\sigma R} = -2\pi \sin\theta_{\mathrm{s}} \sin\left(\theta_{\mathrm{s}} + \theta_{\mathrm{p}}\right) - \pi R \sin^2\theta_{\mathrm{s}}\left(\frac{1}{\rho} - \frac{1}{x_{\mathrm{p}}}\right), \quad (1)$$

where x_{p}, ρ, and θ_{s} are defined in Figure 1, σ is the interfacial tension between the two liquid phases, R is the particle radius, and θ_{p} is the contact angle of the liquid bridge phase on the

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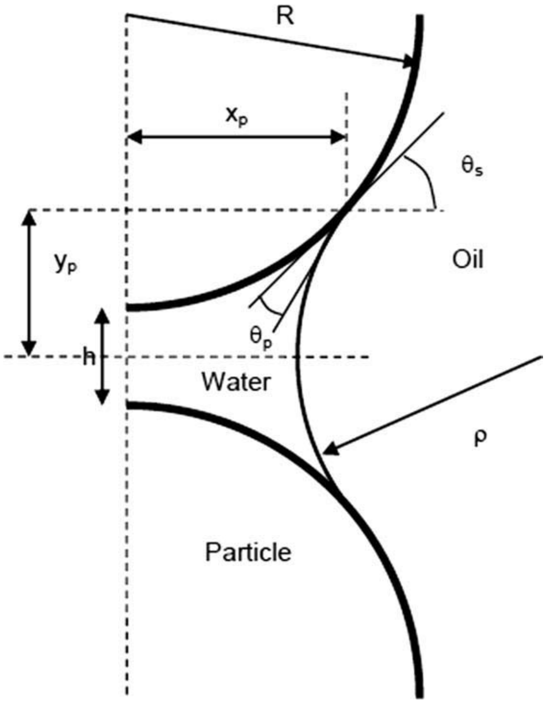

Figure 1. Liquid water bridge connecting two spherical particles dispersed in oil.

solid. In Eq. 1, the force is negative if attractive. The first term on the right hand side is from the interfacial tension forces acting tangentially to the interface along the contact line, and the second term gives the force arising from the capillary pressure across the curved interface (a lowered pressure between particles in most cases). Comments about the approximation used in Eq. 1 can be found in Refs. 9 and 11. The radii of curvature, x_p and ρ, are related by

$$\rho = \frac{(h/2) + 1 - \left(R^2 - x_\mathrm{p}^2\right)^{1/2}}{\cos\left(\theta_\mathrm{p} + \theta_\mathrm{s}\right)}, \tag{2}$$

with

$$\theta_\mathrm{s} = \arctan\left(\frac{x_\mathrm{p}}{\left(R^2 - x_\mathrm{p}^2\right)^{1/2}}\right) = \arcsin\left(\frac{x_\mathrm{p}}{R}\right), \tag{3}$$

where h is smallest distance between particles. For the work described here, the liquid bridges are water and the surrounding fluid is an oil phase.

The network that arises due to capillary forces being added between particles should give rise to an increase in viscosity and a shift from nearly Newtonian (for moderate volume fractions) to pseudoplastic behavior.[1] However, it is unclear to what degree viscosity will increase with the addition of capillary forces and how this increase is affected by the relative amount of bridging liquid, the size of particles, or the concentration of particles. Previous work suggests that changes in the amount of bridging liquid has only a small effect on viscosity and that the presence of a bridging liquid can give rise to an apparent yield stress.[1] Surfactants are expected to affect the capillary forces in a number of ways. Most directly, the addition of surfactant could lead to a reduction of interfacial tension between the two fluids and a change in contact angle. Surfactants may also affect the dynamics of wetting (e.g., when two particles are in contact, how quickly a liquid bridge would form). The effects of surfactants on equilibrium interfacial tension and contact angle can be determined from direct measurements. However, the overall effect of surfactants on the flow properties of a suspension is not so easily predicted. Thus, the purpose of this article is to examine how capillary forces influence the flow properties of a suspension and how some hydrophobic surfactants (as may be used as hydrate anti-agglomerants) may affect these properties.

Experimental

Suspensions were made by dispersing glass microspheres in mineral oil (Acros Organics) at various volume fractions (V_f). The viscosity of the mineral oil was 0.14 Pa sec. The glass microspheres were manufactured by Whitehouse Scientific, and a sieve fraction of 38–45 μm was used for most experiments unless otherwise noted. Particles with sieve fractions of 63–75 μm and 90–106 μm were used to examine the effects of particle size. Early tests showed that effects of washing the particles appeared to be negligible, so in this study the particles were used as received. The suspensions were made by first adding a known mass of the particles to a plastic sample tube. Deionized water was then added where the amount of water that was added was quantified by the ratio of water volume to the volume of the microspheres (V_r). Mineral oil (with or without added surfactant) was then added to the sample tube, and the contents were mixed using a vortex mixer. For the surfactants, Span 80 (sorbitan monooleate) from Sigma-Aldrich and Arquad 2HT-75 (75% dehydrogenated tallow dimethylammonium chloride in water/isopropyl alcohol) from Fluka were used as received.

Viscosity measurements were made using a Merlin II viscometer (ATS RheoSystems) with a parallel plate geometry (30 mm plates with a gap of 1.0 mm) at 25°C. The samples were pre-sheared for 2 min at 150 RPM before each test began. At each shear rate the viscometer would run for 8 sec to allow the sample to reach a steady-state and then would collect 5 sec of data. For each dispersion the viscosities of five samples were measured. The reported values in this work are the average viscosities of the five measurements at each shear rate along with a 95% confidence interval (error bars on the viscosity plots). Due to the instrument accuracy, only viscosity values corresponding to a torque value above 200 μN·m were reported. Particle settling was observed to have a significant effect (viscosity decreasing over time at a moderate shear rate) using a concentric cylinders geometry for dispersions of the glass particles in mineral oil with no added water. But settling did not have a significant effect at moderate shear rates using the parallel plates geometry for the 38–45 μm particles dispersed in mineral oil with no added water. More details on settling effects are given in the next section.

An EasyDrop Drop Shape Analysis System (DSA) from Kruss was used to measure the contact angles and interfacial

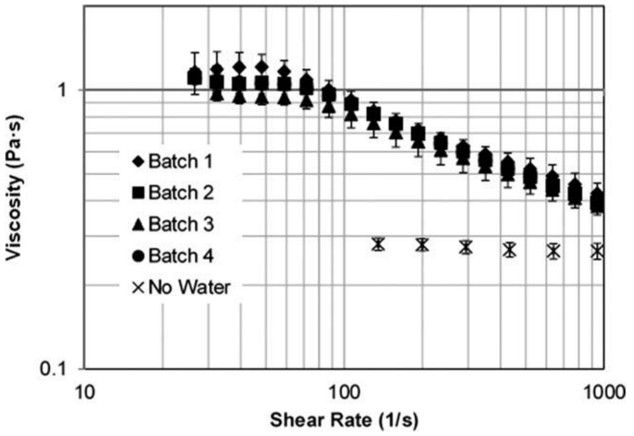

Figure 2. Viscosity versus shear rate plot showing the repeatability of measurements for four batches of glass particles (38–45 μm) dispersed in mineral oil with a particle volume fraction of 0.2 and relative water amount (V_r) of 0.05.

Viscosity measurements for a suspension of the same particle size and volume fraction but without added water are also shown.

tension values. The DSA captures an image of a pendant or sessile drop and uses image analysis to calculate contact angles and tensions. Pendant drops of water immersed in oil solutions (mineral oil with surfactant) were used to find interfacial tensions. Measurements were taken over time until an equilibrium interfacial tension value was reached. Sessile drops of water on soda lime glass (microscope slides) submerged in mineral oil solutions were used to measure contact angles. The glass was cleaned by submerging it in a Chromerge (chromium trioxide in sulfuric acid) solution for about 1 min. The slide was then rinsed multiple times with water and dried with nitrogen. The sessile drops were formed using a 0.5 mm needle attached to a syringe. The needle was adjusted so that water could be added to the very top of the drop. The contact angle measurements were taken when it was clear that the contact line was advancing or static and then again when it was receding.

Results and Discussion

Figure 2 shows that the viscosity for a dispersion of glass particles (38–45 μm) in mineral oil increases significantly with a relatively small amount of water, and the viscosity profile becomes clearly shear-thinning with the addition of water. The liquid bridging caused by the addition of water leads to an increase in particle interaction, which causes the increase in viscosity and the strong non-Newtonian behavior. Even at the high shear rates, the viscosity of dispersion with added water is greater than the viscosity in the absence of water, which means that the liquid bridges are still able to form at those shear rates. The points on Figure 2 represent the average of five viscosity measurements from a given batch, and the error bars represent the confidence interval from the measurements in one batch. Figure 2 shows that although there is some batch-to-batch variation in viscosity, the viscosity values are fairly consistent, particularly at the higher shear rates. At the smaller shear rates, there may be some effects of settling that could affect repeatability. Sampling variations within batches tended to be larger at the smaller shear rates. At 35 sec^{-1}, the viscosity was observed to drop about 6% over 5 min for a V_r (ratio of water volume to particle volume) of 0.05, but at 410 sec^{-1} viscosity remains constant over time. It may be that the settling of large flocs which are not broken up at low shear rates can lead to small decreases in measured viscosity. But as shear rate is increased and the flocs break apart, settling is no longer significant. The viscosity of the dispersion in the absence of water is comparable to what was observed by Chen et al.[12] (both in terms of magnitude and the nearly Newtonian behavior).

Viscosities were measured for dispersions with varying amounts of water for a particle volume fraction of 0.20. The amount of water that was added varied from a V_r of 0.01 to 0.20. Figure 3 shows that over this range of added water, the viscosities appear to go through a maximum near V_r of 0.05. There is little change in viscosity with added water at the lowest shear rates that were measured (about 30 sec^{-1}), and at the higher shear rates the change in viscosity between V_r values of 0.05 and 0.10 is very small (within the range of batch-to-batch variation). But there is a significant drop in viscosity when V_r is increased to 0.15 and 0.20.

It is not surprising that the amount of water has an effect on the dispersion viscosity. The volume of a single liquid bridge between two spheres has a significant effect on the magnitude of the capillary force and on the distance over which the force may act (see for e.g., Refs. 9 and 10). Figure 4 shows how the capillary force for a single liquid bridge varies with particle separation for a contact angle (θ_p) of 10° (this value is based on the measurements given below) for various V_{rel} values, where V_{rel} is the volume of the liquid bridge relative to the particle volume. The force mapping in Figure 4 uses Eqs. 1–3 and is based on the method of Megias-Alguacil and Gauckler[9] using the correction from

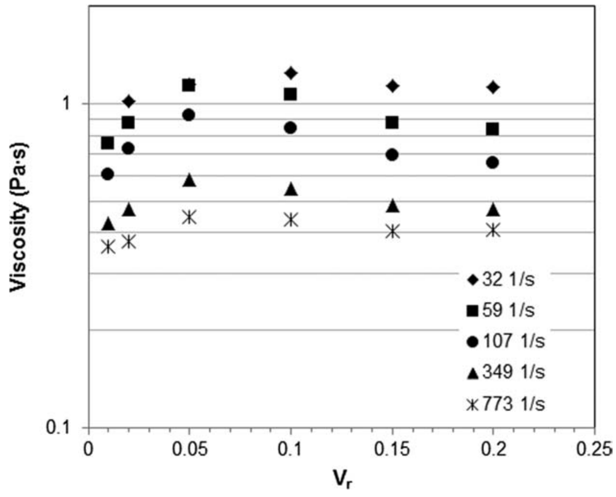

Figure 3. Viscosity versus relative water amount (V_r) for glass particles (38–45 μm) dispersed in mineral oil with a particle volume fraction of 0.2 and at shear rates as indicated in the legend.

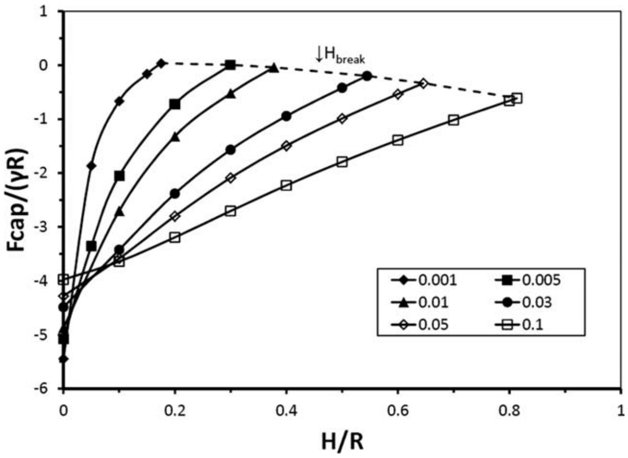

Figure 4. Dimensionless capillary force as a function of the dimensionless separation between particles for the relative liquid volumes indicated in the legend at $\theta_p = 10^\circ$.

Bakken et al.[10] The curve for H_{break} is the theoretical point where the liquid bridge would break.[9] Figure 4 shows that when V_{rel} is decreased from 0.1 to 0.01, the attractive force at contact increases by about 20–25% and the maximum separation between two particles with a liquid bridge (i.e., the particle separation over which the capillary force will act) decreases by more than 50%. In addition to affecting the volume of individual liquid bridges, a change in the amount of water added to dispersion could affect the number of liquid bridges. It may be that as the amount of water is increased, the number of liquid bridges increases until a threshold V_r of somewhere around 0.05. Above this value, additional water might only increase the volume of liquid bridges and actually cause the number of bridges to decrease (essentially causing a coalescence of smaller bridges). A maximum in viscosity versus water content has also been observed for electro-rheological fluids.[13]

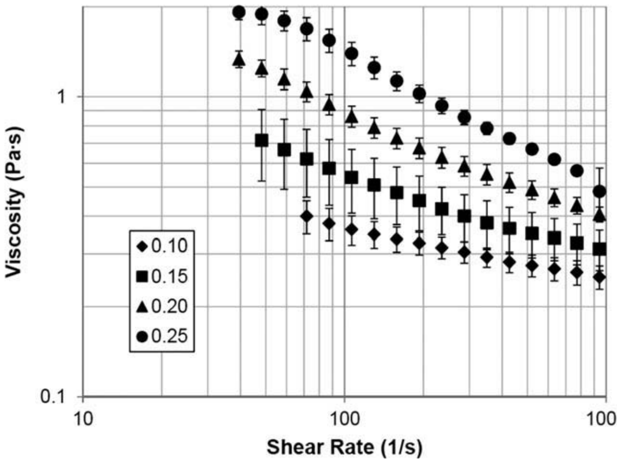

Figure 5. Viscosity versus shear rate for glass particles (38–45 μm) dispersed in mineral oil with a relative water level (V_r) of 0.1 and particle volume fractions as indicated in the legend.

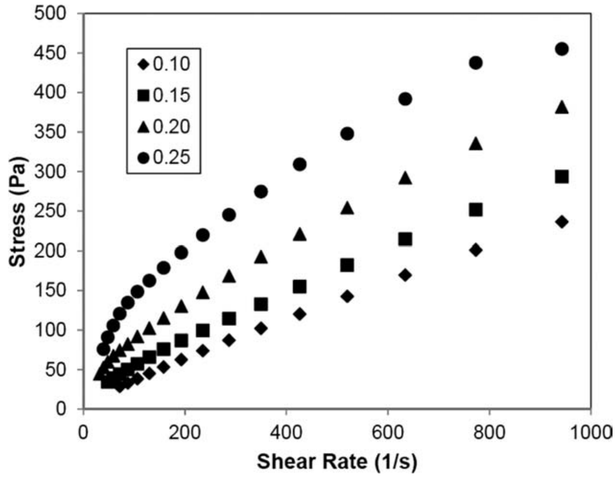

Figure 6. Stress versus shear rate for glass particles (38–45 μm) dispersed in mineral oil with a relative water level (V_r) of 0.1 and particle volume fractions as indicated in the legend.

Figure 5 shows the effect of particle volume fraction on viscosity. Particle volume fractions were varied between 0.10 and 0.25, where a V_r value of 0.10 was used for all dispersions. As expected, viscosities increase as the volume fraction of particles increases, and the flow is clearly shear-thinning for the volume fractions that were tested. Figure 6 shows shear stress as a function of shear rate for these same systems. At the lowest shear rates measured, the stresses appear to be converging on the origin. This suggests that unlike previous observations,[1] the addition of liquid bridges for this system does not seem to lead to an apparent yield stress.

Figure 7 shows the effects of particle size on viscosity when water is present. As particle size decreases, the viscosity increases significantly. This is very different from what is observed for dispersions of glass particles in mineral oil with

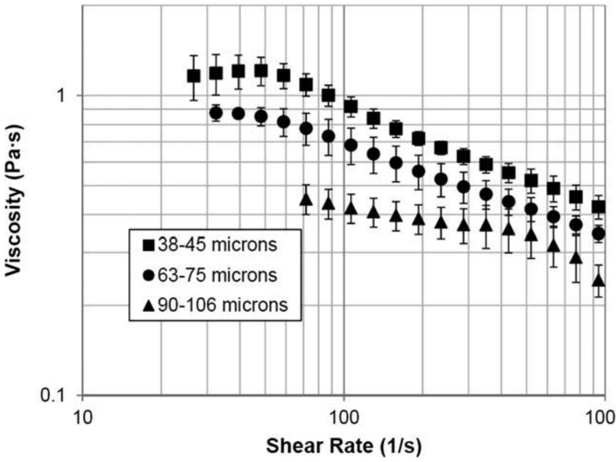

Figure 7. Viscosity versus shear rate for glass particles dispersed in mineral oil with a relative water level (V_r) of 0.05, particle volume fraction of 0.2, and particle sizes as indicated in the legend.

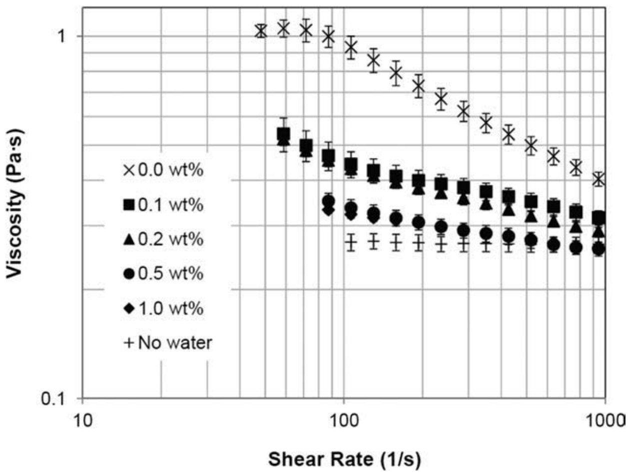

Figure 8. Viscosity versus shear rate for glass particles (38–45 μm) dispersed in mineral oil with a relative water level (V_r) of 0.05 and a particle volume fraction of 0.2 with Span 80 concentrations as indicated in the legend.

Viscosity measurements for a suspension of the same particle size and volume fraction but without added water or surfactant are also shown.

no added water. Chen et al.[12] found that over these shear rates and for particle sizes in essentially this same range, viscosity did not change with particle size for glass particles dispersed in mineral oil. In the absence of water, there is very little particle-particle interaction for these particle sizes beyond hydrodynamic interactions. Thus particle size has little effect. The addition of water gives rise to strong attractive forces between particles. As particle size decreases and interfacial area increases, the number of liquid bridges and the extent of particle interactions can increase. This leads to the viscosity increase.

For the larger particle sizes, there may also be some effect from particle settling. Although settling did not have a significant effect at moderate shear rates (410 sec^{-1}) for the smaller particles, there was a small decrease in viscosity over time (5–10% over about 5 min) for the larger particles. This may account for the fairly large drop in viscosity at the highest shear rates for the large particles. However, sedimentation alone cannot explain the large differences in viscosity for the various particle sizes. If sedimentation alone were responsible for the particle size effects, the viscosities would be comparable at low shear rates (when the viscosity measurements begin) and would gradually diverge as shear rates (and time) increase.

Two surfactants, Span 80 and Arquad 2HT, were studied to see to what extent they would affect the capillary forces and thus the viscosities of the dispersions. Both surfactants are relatively hydrophobic, and they (or surfactants with similar chemistry) have been studied as hydrate anti-agglomerants. Span 80 has been found to provide some hydrate-inhibition behavior[14] but is not considered a highly effective inhibitor (it does not work well at relatively low concentrations and high subcooling). Arquad 2HT is a hydrophobic quaternary ammonium surfactant, and surfactants with this chemistry have been found to be much more effective as inhibitors.[8,15] It was thought that a better understanding of how surfactants like these affect capillary forces from water bridges between hydrophilic particles in a nonaqueous medium may provide some insight into how hydrate inhibitors prevent the adhesion of hydrate particles.

Figure 8 shows the effects of various concentrations of Span 80 on the dispersion viscosity. The particle volume fraction was held at 0.20, and the V_r value was 0.05. In the preparation of all of these dispersions, water was added to the glass particles prior to the oil/surfactant mixture. This would allow the particles to be initially wetted with the water. As the concentration of Span 80 increases from 0.1 to 1.0 wt % in mineral oil, the viscosity of the dispersion gradually decreases. However, even at 1.0 wt % surfactant, the viscosity of the dispersion at lower shear rates is still higher than that for a dispersion with no added water, and the dispersion is more shear-thinning than the dispersion without water. Thus Span 80 appears to reduce the magnitude of the capillary forces between particles and reduce the particle-particle interactions; but at 1.0 wt %, it is not capable of preventing liquid bridges. It should be noted that the concentrations of Span 80 were all well above the critical micelle concentration (CMC)—CMC values for Span 80 in many aliphatic hydrocarbons are on the order of 0.001 wt %.[16] However, no solubilization of water into the reverse micelles was observed during the interfacial tension experiments (the volumes of water drops did not significantly change over time), and the viscosity of mineral oil solutions did not significantly change with increases in Span 80 concentration over the concentration range used for this work.

Figure 9 shows that Arquad 2HT affects the dispersion viscosity differently than Span 80. Again, the particle volume fraction was held at 0.20, and the V_r value was 0.05.

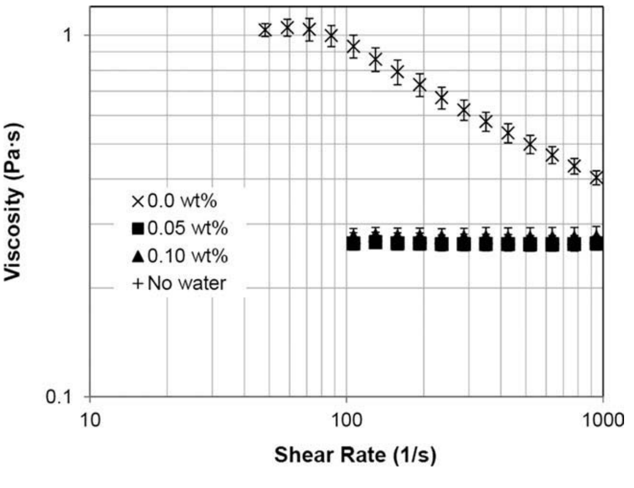

Figure 9. Viscosity versus shear rate for glass particles (38–45 μm) dispersed in mineral oil with a relative water level (V_r) of 0.05 and a particle volume fraction of 0.2 with Arquad 2HT concentrations as indicated in the legend.

Viscosity measurements for a suspension of the same particle size and volume fraction but without added water or surfactant are also shown.

Even at 0.05 wt %, the viscosity of the dispersion is essentially the same as that with no added water. Thus the Arquad surfactant appears to completely prevent particle interactions by capillary forces, even at very low concentrations.

To further study the effects of the two surfactants on capillary forces, interfacial tension and contact angle measurements were made. Table 1 shows that the interfacial tension between mineral oil and water (as measured using pendant drops) decreases significantly at a concentration of 0.05 wt % Span 80 in mineral oil. The interfacial tensions remain more or less constant as surfactant concentration is increased to 1.0 wt %. Thus, for the range of Span 80 concentrations used in the viscosity measurements in Figure 8, the equilibrium interfacial tensions should have remained unchanged (except for the dispersion with no added surfactant).

Figure 10 shows that static or advancing contact angles (measured using a sessile drop) are affected by Span 80, but, interestingly, it appears that receding angles are not significantly affected. The addition of Span 80 leads to an increase in the advancing contact angle, presumably due to surfactant adsorption at the oil/solid interface since the decrease in oil/water interfacial tension alone should lead to a decrease in contact angle. However, the receding angles, which are the relevant angles when considering the capillary force between two particles that are being pulled apart by shear, change very little when Span 80 is introduced–they consistently remain under 20°.

From Eq. 1, Table 1, and Figure 10, it would be expected that the capillary force between two glass particles (for a constant amount of water in the liquid bridge) should be about 95% less with 0.05 wt % Span 80 as compared with pure mineral oil–equilibrium interfacial tension is reduced about 95% and receding contact angle remains virtually unchanged. Also, this capillary force would not change significantly as the Span concentration is increased if the volume of the liquid bridge remains unchanged and the system is allowed to reach equilibrium (and thus the interfacial tension values reach equilibrium). The fact that the receding contact angle remains relatively small helps to explain why the dispersion viscosity is still shear-thinning at a concentration of 1% in Figure 8–water bridges can still form between particles at low shear rates. However, it is interesting that there is a somewhat gradual reduction in dispersion viscosity as the Span 80 concentration is increased. Since the liquid bridges would be forming and breaking rather quickly, the interfaces may not have time to reach equilibrium, and higher surfactant concentrations may allow for lower dynamic (effective) tensions. Also, the surfactant may be doing more than just reducing the capillary force for a bridge between particles. Since the advancing contact angle increases with the addition of Span 80, the surfactant may be producing a barrier that hinders the formation of water bridges. It also may be reducing the amount of water that is effectively available to form liquid bridges (i.e., the water is emulsified). Thus, as the surfactant concentration is increased, the number of liquid bridges and/or the rate at which new bridges can be formed are decreased. For Span 80 concentrations above 0.5 wt %, the viscosity of the dispersion at high shear rates is the same as that for dispersions without added water. Most likely at these shear rates the liquid bridges cannot form rapidly enough to create any additional interactions between particles.

Table 1. Interfacial Tension Values for Various Concentrations of Span 80 in Mineral Oil Against Water

Span 80 Concentration (wt %)	Interfacial Tension (mN/m)
0.00	49.9 ± 1.0
0.05	2.2 ± 0.3
0.20	2.3 ± 0.3
1.00	2.3 ± 0.3

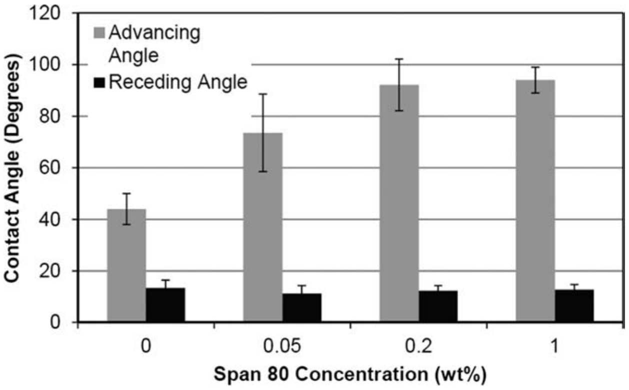

Figure 10. Contact angles of water on glass in the presence of mineral oil with various concentrations of Span 80.

Arquad 2HT is not fully soluble in mineral oil, and the mixture is hazy even at low concentrations. This prevents accurate measurements of contact angle and interfacial tension using the DSA. However, the contact angles for 0.05 wt % Arquad (both receding and advancing angles) were much larger than what was observed for Span 80, with a static contact angle about 160° and a receding contact angle above 90°. This would explain why the viscosity of dispersion with 0.05 wt % Arquad is the same as that for dispersion with no added water. The increase in contact angle above 90° would prevent liquid bridges and thus prevent the attractive capillary forces.

Conclusions

Viscosities were measured for dispersions of glass particles in mineral oil with added water. The addition of small amounts of water leads to large increases in viscosity due to the formation of water bridges between particles that give rise to capillary forces between the particles. The capillary forces between the particles also cause the flow profile to be highly shear-thinning. As the amount of water is increased, the viscosity of dispersions goes through a maximum. The presence of water also leads to a significant effect of particle size, where viscosity increases with a decrease in particle size. The increase in interfacial area that accompanies a decrease in particle size allows for a greater number of liquid bridges and increased particle interaction.

Two hydrophobic surfactants, Span 80 and Arquad 2HT, were found to reduce the viscosity of the dispersions with water added and cause the flow profile to be less shear-thinning. The increase in Span 80 concentration from 0.05 to

1.0 wt % gives rise to a fairly gradual decrease in viscosity by both lowering the interfacial tension and reducing the number of liquid bridges. The addition of Arquad 2HT at even 0.05 wt % reduces the viscosity of dispersion to the same level as that for dispersion with no water added by preventing liquid bridges from forming through an increase in the contact angle of water on glass in the presence of oil.

The effects of these surfactants on the flow behavior may give some insight as to why surfactants like Arquad 2HT (quaternary ammonium salts) are more effective anti-agglomerants of gas hydrates as compared with certain nonionic surfactants like Span 80. The effective surfactants may be able to significantly increase the contact angle of water on the solid and thus greatly reduce the ability of water to wet the hydrate particles, essentially prevent liquid bridges from connecting the particles. This could prevent strong adhesion between hydrate particles and the formation of hydrate plugs in pipelines. It would be interesting to see if model systems (such as glass spheres rather than hydrate particles) could be used to screen potential anti-agglomerants.

Acknowledgments

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