

Article

In-Situ Continuous Monitoring of the Viscosity of Surfactant-Stabilized and Nanoparticles-Stabilized Pickering Emulsions

Upinder Bains and Rajinder Pal *

Department of Chemical Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada;
usbains@uwaterloo.ca

* Correspondence: rpal@uwaterloo.ca; Tel.: +1-519-888-4567 (ext. 32985)

Received: 7 July 2019; Accepted: 25 September 2019; Published: 27 September 2019



Abstract: An in-situ method of measuring the viscosity of unstable and stable emulsions on a continuous basis under agitation conditions was developed and utilized to investigate the viscous behaviour of surfactant-stabilized and nanoparticles-stabilized oil-in-water (O/W) emulsions at different volume fractions of the dispersed phase (oil). The stability characteristics (droplet size and phase-separation) of emulsions under quiescent conditions were also determined with the aging of emulsions. Emulsions are Newtonian at low volume fractions of the dispersed phase. At high concentrations of the dispersed phase, emulsions behave as non-Newtonian shear-thinning fluids. The nanoparticles-stabilized (Pickering) emulsions are unstable in comparison with the surfactant-stabilized emulsions. The droplet sizes of Pickering emulsions increase rapidly with aging, whereas the droplet sizes of surfactant-stabilized remain nearly the same over a period of 24 h. However, Pickering emulsions are much more viscous than the surfactant-stabilized emulsions when comparison is made at the same volume fraction of the dispersed phase.

Keywords: emulsion; nanoparticles; Pickering; rheology; viscosity; emulsion stability; non-Newtonian; droplet size; phase separation

1. Introduction

Emulsions are dispersions of two immiscible liquids. They are of interest in many important practical applications in the food, cosmetic, oil production, agriculture, and several other process industries [1–6]. There are two types of emulsions: Oil-in-water (O/W) type, where oil forms the dispersed (droplets) phase and water forms the continuous phase; and water-in-oil (W/O) type, where water forms the dispersed (droplets) phase and oil forms the continuous phase. Without an effective interfacial stabilizer, emulsions are unstable systems and they readily separate out into oil and water phases as the mechanical agitation is stopped. As emulsions are created by increasing the interfacial area between the two immiscible phases, they possess a high interface free energy. Given the chance, the droplets tend to coalesce to decrease the interfacial area and, hence, the interfacial free energy. There are a number of methods available to improve the thermodynamic and kinetic stabilities of emulsions. One such method is to add a surfactant to the system. The presence of a surfactant at the interface lowers the interfacial tension between the two phases and hence improves the thermodynamic stability. The surfactant also provides a steric barrier to intimate contact between two approaching droplets and thus improves the kinetic stability. Surface-active polymers and amphiphilic solid nanoparticles can also improve the thermodynamic and kinetic stabilities of emulsions by lowering the interfacial tension and creating a steric barrier between the approaching droplets. The kinetic stability of emulsions can further be enhanced by reducing the rate of sedimentation or creaming of droplets by

decreasing the average droplet size of the emulsion and by increasing the viscosity of the continuous phase. Figure 1 shows a schematic diagram of the surfactant-stabilized and nanoparticles-stabilized oil droplets in an O/W emulsion.

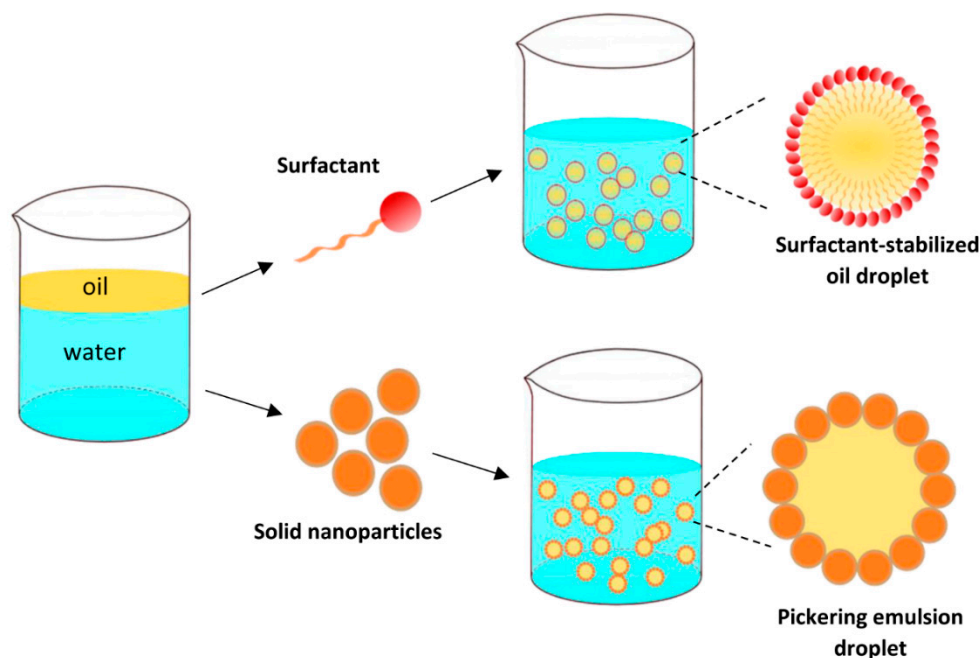


Figure 1. A schematic diagram of surfactant-stabilized and nanoparticles-stabilized oil droplets in an oil-in-water (O/W) emulsion.

Emulsions stabilized with solid nanoparticles, referred to as Pickering emulsions, are becoming increasingly important due to their widespread applications [3]. The physical properties of Pickering emulsions can be easily manipulated by changing the nature and number of nanoparticles added to the emulsion. Furthermore, the solid nanoparticles used in the Pickering emulsions are environment-friendly, natural materials such as starch nanoparticles.

In the formulation, mixing, and pumping of emulsions, the most important physical property to be considered is viscosity. Thus, accurate measurement of the viscosity of emulsions is important. The key factors affecting the viscosity of oil-water emulsions are the viscosity of the continuous phase, the ratio of dispersed phase viscosity to continuous phase viscosity, and the volume fraction of the dispersed phase [7]. The droplet size and droplet size distribution also affect the viscosity, especially at high-volume fractions of the dispersed phase [8].

Rheological characteristics of emulsions can be determined using off-line and on-line methods. In the off-line methods, samples of emulsion are extracted from the process and sent to the laboratory for analysis and characterization. As emulsions are heterogeneous fluids, sampling of emulsion from the process itself may pose problems. As discussed by Pal [9], even when the emulsion upstream of the sampling device is well dispersed (pseudo-homogeneous), the collected sample may not be representative of the actual emulsion in the process. Thus, special care is required to ensure representative sampling.

As emulsions are prone to creaming, sedimentation, and coalescence of droplets, it is important to develop an in-situ method of measuring the viscosity of emulsions under mixing conditions. The in-situ measurement of the viscosity of emulsions under mixing conditions is especially important when emulsions are unstable in nature. Unlike off-line measurements in which the samples are manually collected (subject to sampling errors) and studied in a viscometer, in-situ measurements have the additional advantage of data collection on a continuous basis without any time delays, leading to better quality control of the emulsion product. This is especially significant in processes where emulsions

are prone to phase inversion. When phase inversion of an emulsion takes place, an abrupt change in viscosity occurs resulting in processing problems of emulsion-based fluids.

A number of on-line techniques are available for the measurement of fluid viscosity [10]. They can be broadly classified into three groups: (1) Rotational-type devices such as co-axial cylinder viscometers; (2) tube or capillary viscometers; and (3) vibrational-type devices. The rotational-type on-line viscometers available commercially are generally suitable for viscous fluids. The tube or capillary devices and vibrational devices are generally single-point (one flow or shear rate) devices suitable for viscous Newtonian fluids.

The objectives of this work are as follows: (a) To develop an in-situ method of measuring the viscosity of emulsions over a broad range on a continuous basis under agitation conditions; (b) to study the viscous behavior of surfactant-stabilized O/W emulsions using the in-situ measuring device; (c) to study the viscous behavior of nanoparticle-stabilized (Pickering) O/W emulsions using the in-situ measuring device; and (d) to investigate the stability of surfactant-stabilized and nanoparticles-stabilized O/W emulsions.

2. Experimental Setup

Figure 2 shows a schematic drawing and photograph of the experimental setup. The emulsions were prepared in a cylindrical glass vessel of capacity approximately 20 L with the following dimensions: Inside diameter = 29 cm, height = 29.5 cm, and glass wall thickness = 7 mm. The glass vessel was equipped with a variable-speed Gifford-Wood homogenizer (model 1-L; rotor-stator type) to provide the necessary shear and mixing of fluids, a dual channel electrical conductivity probe (range 0–200 mS/cm) with a built-in temperature sensor connected to a Thermo Orion 3 Star conductivity meter to continuously monitor the conductivity and temperature of the emulsions, and a Brookfield viscometer for in-situ monitoring of the viscosity of emulsions under agitation conditions.

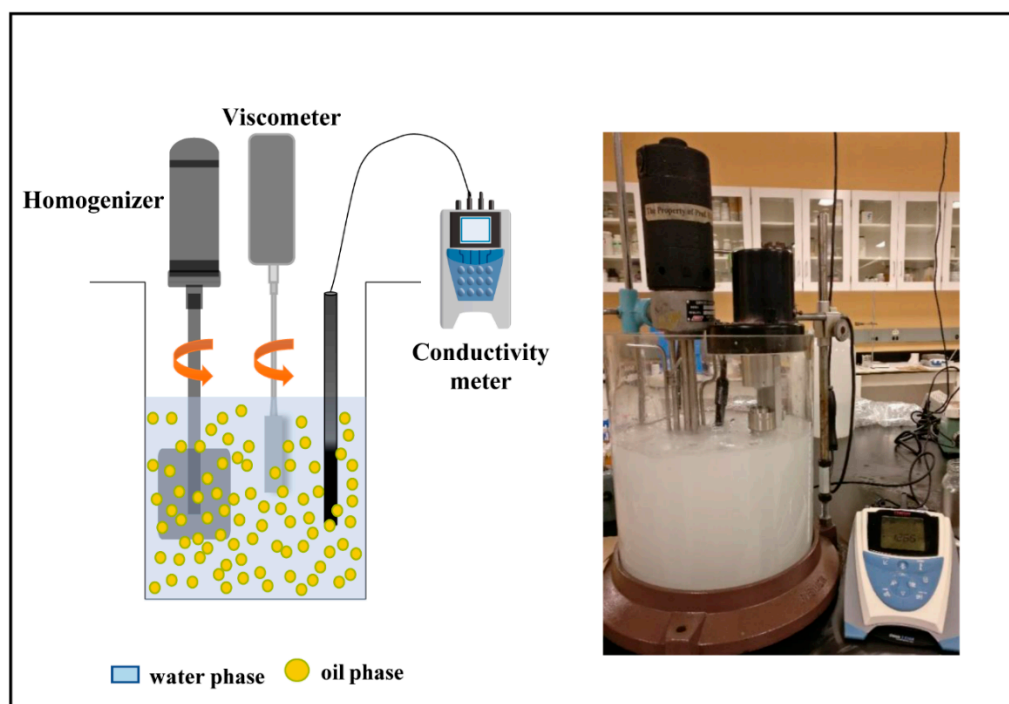


Figure 2. Schematic diagram and photograph of the experimental set-up for the in-situ measurement of the viscosity of emulsions.

2.1. In-Situ Measurement of the Viscosity of Emulsions

An enhanced Brookfield UL adapter connected to a Brookfield model LVT viscometer was used for the in-situ monitoring of the viscosity of emulsions under agitation conditions. The enhanced UL adapter of the viscometer consists of a solid cylindrical spindle that rotates inside a cylindrical tube chamber. The spindle can be rotated at eight different speeds, ranging from 0.3 to 60 rpm. Figure 3 shows the schematic diagram and photograph of the UL adapter assembly. The diameter of the inside solid spindle is 25.15 mm and the inside diameter of the outer cylindrical tube chamber is 27.62 mm. Thus, the gap width in which the emulsion is sheared is 1.235 mm. The height or length of the spindle is 92.37 mm. The spindle was immersed in the tank and the viscous drag exerted by an emulsion was measured at different rotation speeds (rpm). To confirm the reproducibility, measurements were repeated at least three times for each rpm and the average value was reported.

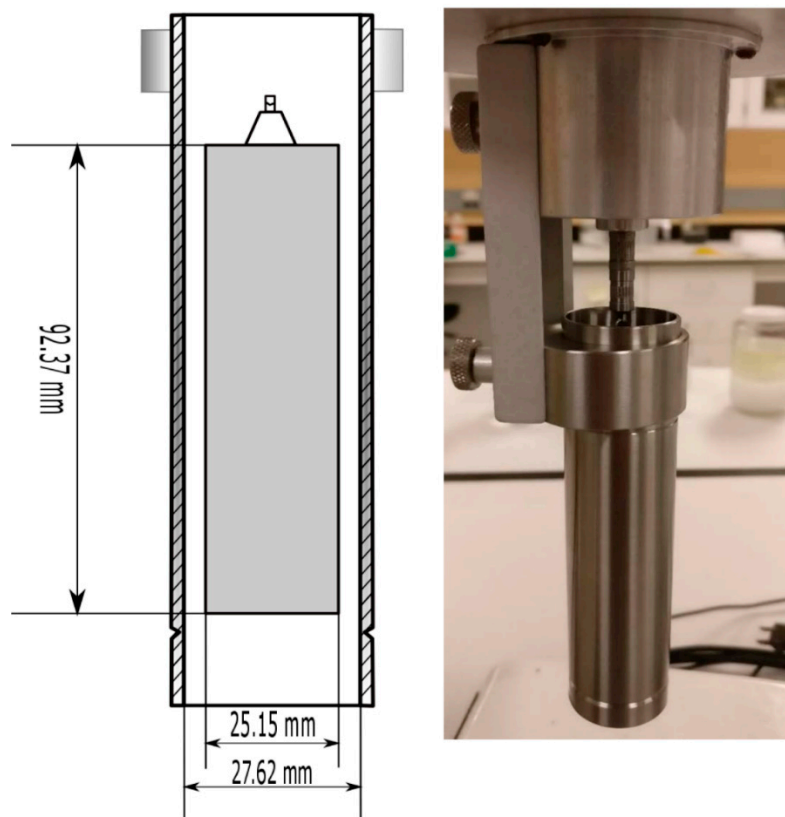


Figure 3. Schematic diagram of the enhanced UL adapter spindle assembly (left) and photograph of the enhanced UL adapter spindle assembly attached to the Brookfield LVT viscometer (right).

2.2. Viscosity versus Shear Rate Behavior of Emulsions

The viscosity versus shear rate behavior of emulsions was determined from the viscometer readings at different speeds of rotation of the viscometer spindle. The shear rate in the fluid is calculated from the following expression [11]:

$$\dot{\gamma} = \left(\frac{2R_C^2}{R_C^2 - R_B^2} \right) \left(\frac{2\pi}{60} \right) N = (1.226)N \quad (1)$$

where R_C and R_B are the radii of the outer tube chamber and inner spindle, $\dot{\gamma}$ is the shear rate, and N is the speed of rotation of spindle in rpm. The shear rate ranges from 0.368 to 73.56 s⁻¹. The shear stress in the fluid, in units of Pa, is calculated from the viscometer dial reading as follows:

$$\tau = \left(\frac{M}{2\pi R_B^2 L} \right) (DR/100) = (7.34 \times 10^{-3}) DR \quad (2)$$

where L is the length of the spindle, M is the torque factor, and DR is the dial reading.

3. Experimental Work

3.1. Materials

Surfactant-stabilized and nanoparticles-stabilized O/W emulsions were prepared using the following materials: Deionized water, high-purity NaCl, starch nanoparticles (SNPs), non-ionic water-soluble surfactant Triton X-100 (polyethylene glycol), and ultrapure food grade white mineral oil. The SNPs were provided by EcoSynthetix Inc. The mean diameter of the SNPs was approximately 21 nm as reported in our earlier study [12]. The oil was supplied by Petro-Canada under the trade name Purity FGWO-15. Its viscosity was 26.4 mPa.s at 21 °C.

3.2. Preparation of Starch Dispersions

The dispersions of starch nanoparticles were prepared by slowly sprinkling SNPs (2 wt.%) onto 0.01 mol/L NaCl aqueous solution used as a continuous phase for the emulsions and ensuring that no clumps of nanoparticles were formed during dispersion. For better mixing conditions and faster dispersion, a high shear Gifford-Wood homogenizer (model 1-LV) was used. To ensure a complete dissolution of nanoparticles, the solution was homogenized at 5000–6000 rpm for a duration of 60 min at room temperature $22 \text{ }^{\circ}\text{C} \pm 2 \text{ }^{\circ}\text{C}$. The SNP concentration of 2 wt.% was selected based on our phase inversion study [12] where it was observed that no further improvement in the stability of emulsion occurs with starch nanoparticle concentration greater than 2 wt.%.

3.3. Preparation of Emulsions

Two different sets of oil-in-water (O/W) emulsions were prepared using the white mineral oil (Purity FGWO-15). In one case, a non-ionic, water-soluble surfactant Triton X-100 was used as a stabilizer at a concentration of 0.5 vol.% based on the aqueous phase containing 0.01 mol/L NaCl. The concentration of 0.5 vol.% Triton X-100 is much higher than the critical micelle concentration (CMC) of Triton X-100 (about 0.03%). Thus, O/W emulsions produced with 0.5% surfactant concentration were expected to have a good stability. The emulsions were prepared by adding the known volume of oil to a known volume of aqueous phase while maintaining the homogenizer mixing. These emulsions are referred to as “surfactant-stabilized emulsions”. The other set of O/W emulsions were prepared using 2 wt.% SNPs dispersion as the continuous phase. These emulsions, stabilized by starch nanoparticles, are referred to as “Pickering emulsions” or “nanoparticles-stabilized emulsions”. The nanoparticles-stabilized emulsions were prepared by adding the known volume of oil to a known volume of 2 wt.% SNPs dispersion while maintaining the homogenizer mixing. Further details about the preparation of emulsions can be found in [10]. The viscosity measurements were made after 10 min of homogenizer mixing and the mixture was kept homogenized during the measurements. The total volume of oil-in-water emulsions was maintained at 11 L. The concentration of the dispersed phase (oil) of emulsion was increased by withdrawing the existing O/W emulsion and adding a known amount of oil while maintaining the total volume constant. For the surfactant-stabilized emulsions, off-line viscometer (Fann co-axial cylinder viscometer) was also used to obtain the viscosity data for comparison purposes. The in-situ viscosity measurements were repeated three times for each rpm to ensure the accuracy and reproducibility of the readings. Before every measurement, the UL adapter assembly was disassembled and cleaned and then immersed again into the fluid. In some experiments, readings were also recorded as a function of time at a given rpm while the spindle was rotating inside the chamber to investigate any effects of emulsion separation on the viscosity measurements.

4. Results and Discussion

4.1. Rheological Behavior of Emulsions

Figure 4 shows the transient plots of viscometer dial reading for surfactant-stabilized and nanoparticle-stabilized oil-in-water emulsions at different rpms. The plots indicate that the steady state was reached within 1 min. Also, the dial reading versus time data obtained from three separate runs at the same rpm (see Figure 4a) nearly overlapped with each other, indicating excellent reproducibility.

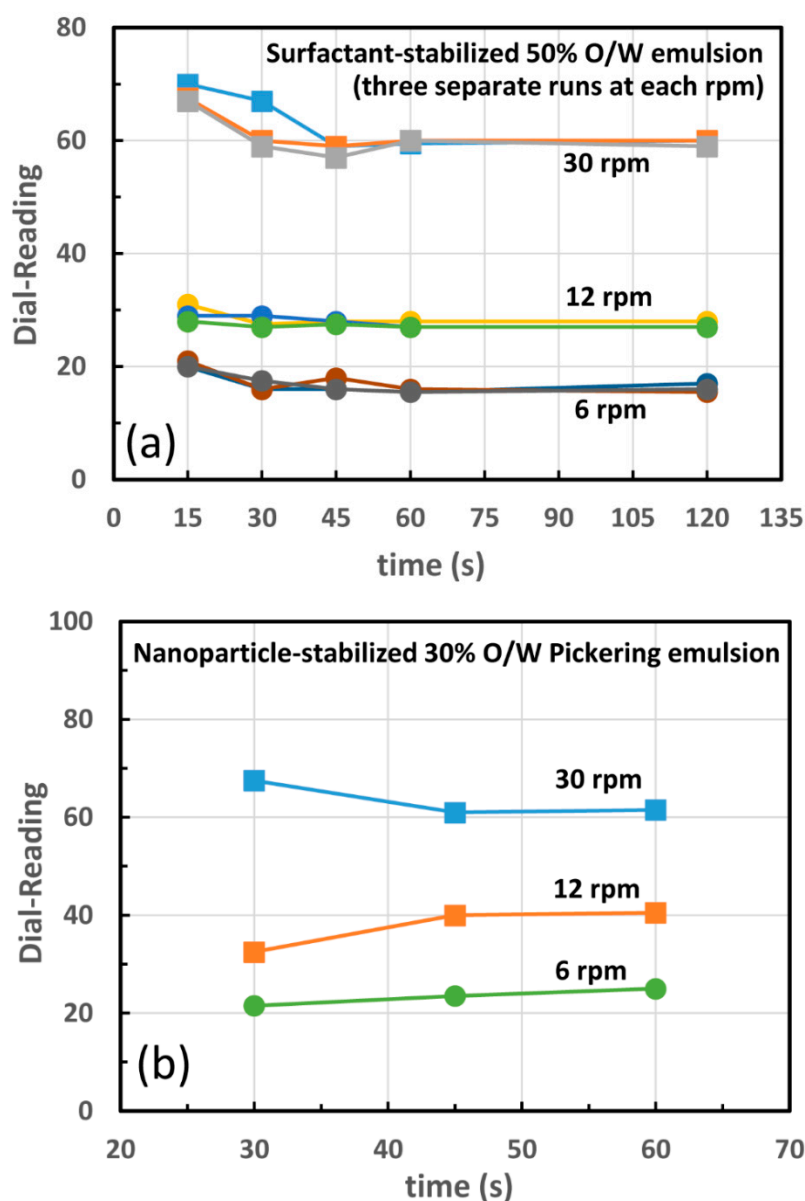


Figure 4. Transient plots of viscometer dial reading for (a) surfactant-stabilized and (b) nanoparticle-stabilized (Pickering) O/W emulsions at different rpms.

The variations of temperature and electrical conductivity with the increase in the dispersed phase (oil) concentration of emulsion are shown in Figure 5 for both surfactant-stabilized and nanoparticle-stabilized emulsions. The temperature was nearly constant from one concentration to another, but the electrical conductivity of emulsion decreased with the increase in the nonconductive oil concentration of the emulsion as expected. No phase inversion of O/W emulsion to W/O emulsion was observed in surfactant-stabilized and nanoparticle-stabilized Pickering emulsions. Note that phase

inversion of emulsion is characterized by sharp changes in the electrical conductivity [12]. When an O/W emulsion inverts to W/O emulsion, a sharp drop in the electrical conductivity is expected as the nonconductive oil phase forms the continuous phase in W/O emulsion

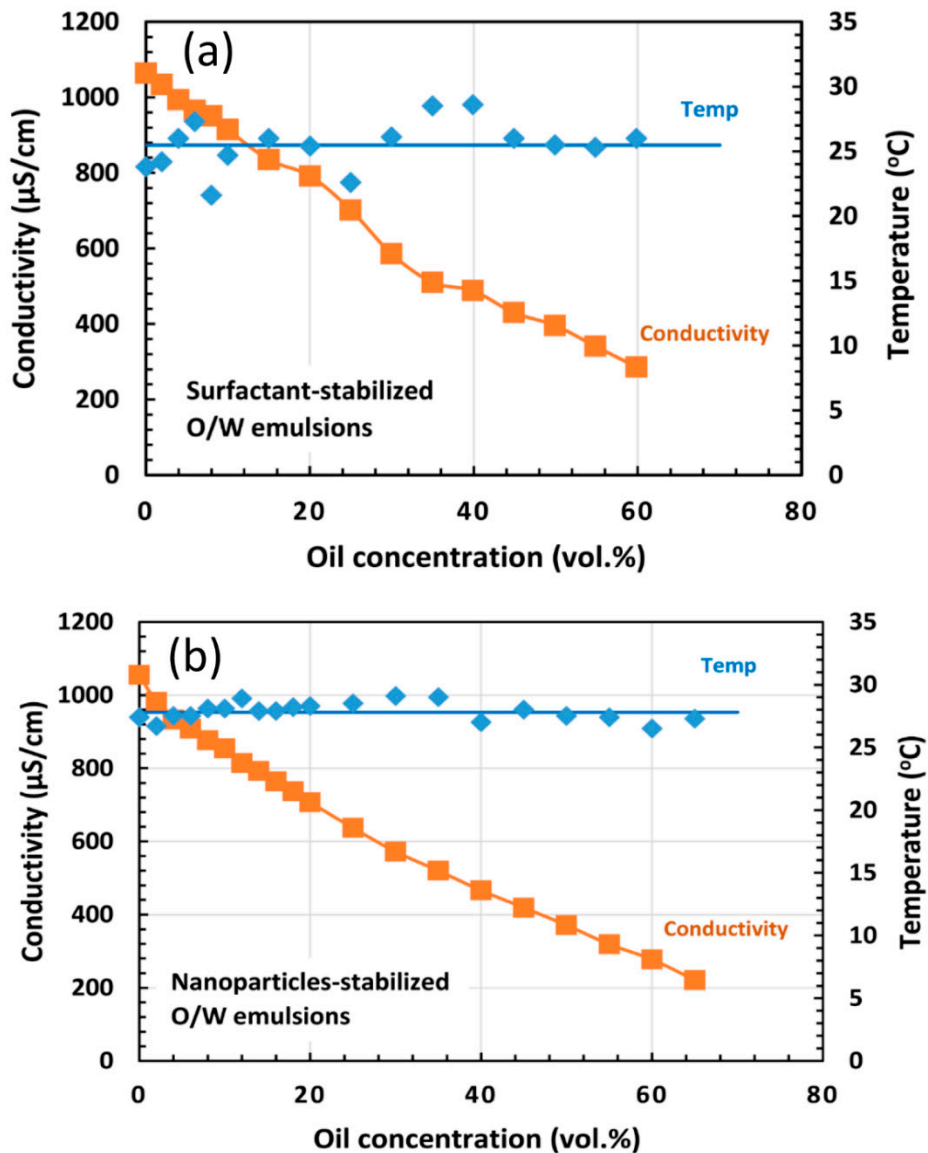


Figure 5. Variations of temperature and electrical conductivity of (a) surfactant-stabilized and (b) nanoparticle-stabilized O/W emulsions with the increase in oil concentration.

Figure 6 shows the rheograms of surfactant-stabilized and nanoparticle-stabilized O/W emulsions for different concentrations of dispersed-phase (oil). For the surfactant-stabilized O/W emulsions (Figure 6a), the data at low shear rates ($\leq 73.56 \text{ s}^{-1}$) were obtained from the in-situ device (Brookfield UL adapter connected to a Brookfield model LVT viscometer), whereas the data at high shear rates were obtained using an off-line device (Fann co-axial cylinder viscometer). The data obtained at high shear rates using the off-line device are consistent with the data obtained at low shear rates using the in-situ device in that they fall on the same line. For the nanoparticle-stabilized Pickering O/W emulsions (Figure 6b), all the data were obtained using the in-situ device (Brookfield UL adapter) while maintaining the homogenizer mixing. These emulsions were not sufficiently stable to carry out the off-line measurements.

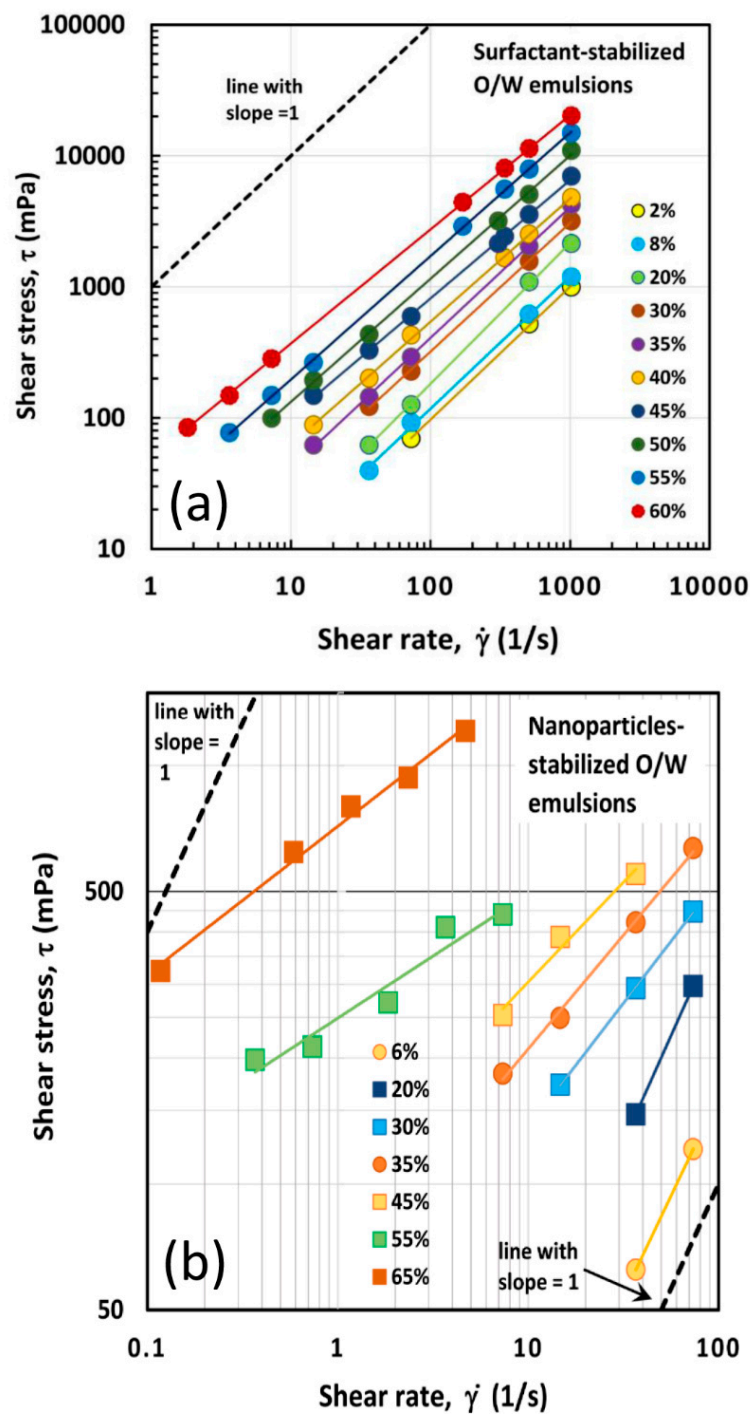


Figure 6. Rheograms of (a) surfactant-stabilized and (b) nanoparticle-stabilized O/W emulsions at different oil concentrations.

The rheograms are linear on a log-log scale, indicating that the emulsions followed the power-law behavior:

$$\tau = K\dot{\gamma}^n \quad (3)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, K is the consistency index, and n is the flow behavior index. At low concentrations of oil, the emulsions are Newtonian in nature as the flow behavior index n is unity. At high concentrations of oil, $n < 1$ indicates non-Newtonian pseudoplastic (shear-thinning) behavior.

Figure 7 shows the plots of consistency index (K) and flow behavior index (n) as functions of oil concentration for both surfactant-stabilized and nanoparticle-stabilized O/W emulsions. The consistency index K increased with the increase in oil concentration, whereas the flow behavior index n decreased with the increase in oil concentration. Thus, the O/W emulsions became more viscous and shear-thinning with the increase in oil concentration. The consistency index K rose slowly with the initial increase in oil concentration. A sharp increase in K occurred when the oil concentration was increased above about 40% by vol.

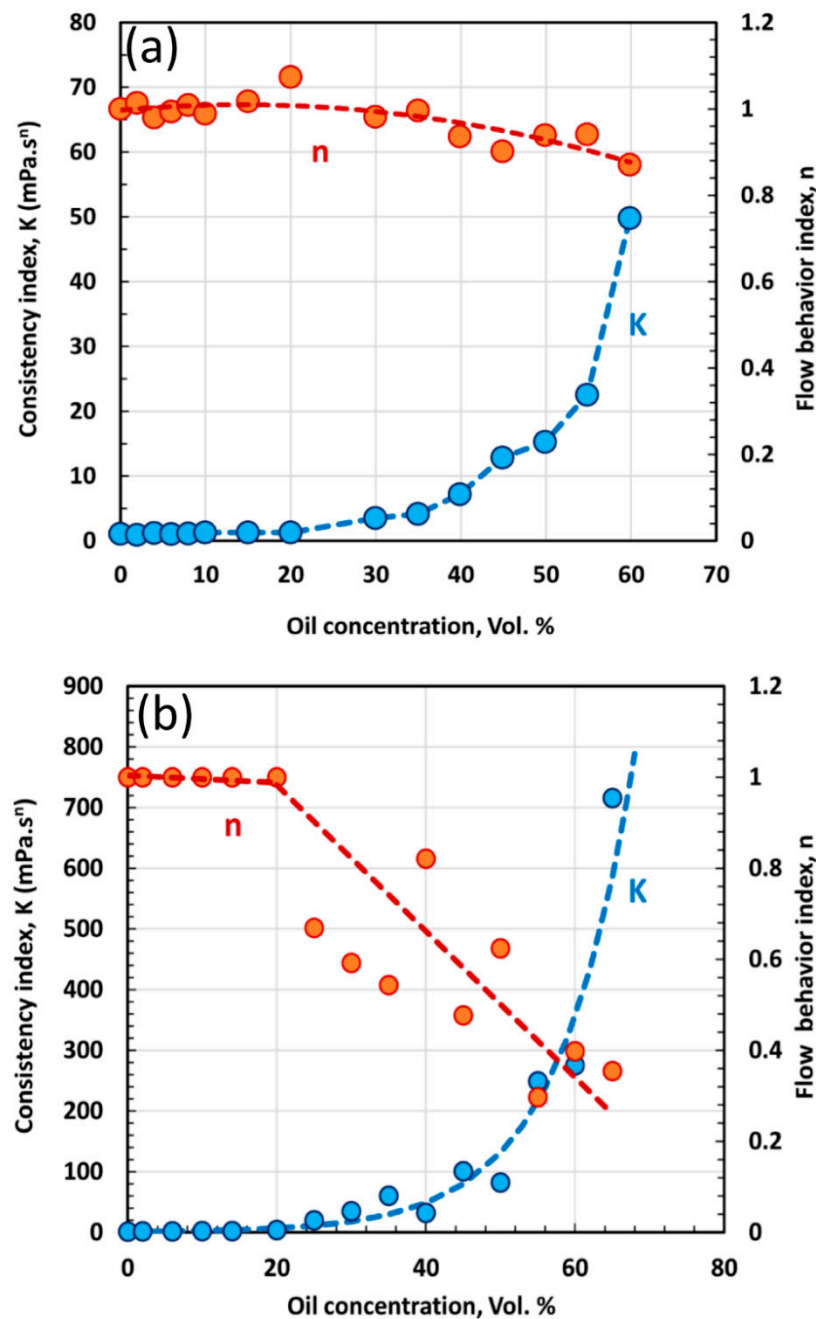
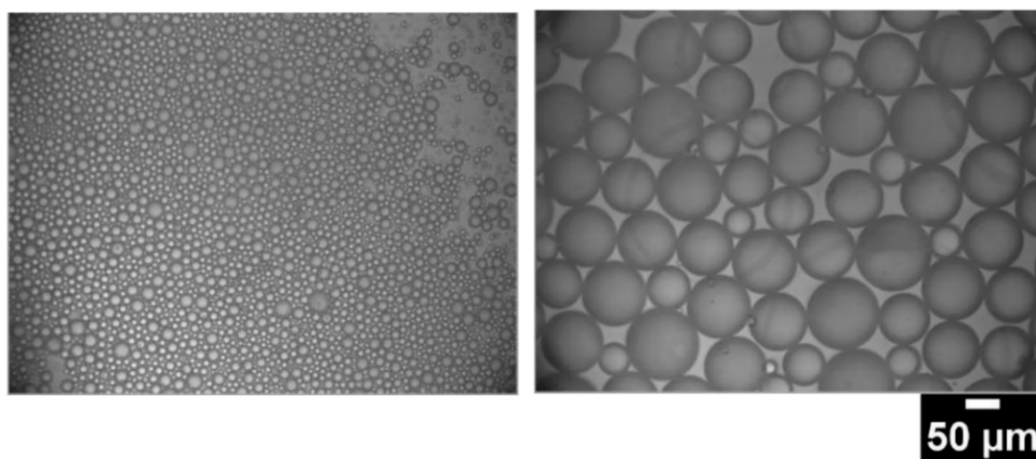


Figure 7. Variations of consistency index K and flow behavior index n for (a) surfactant-stabilized and (b) nanoparticle-stabilized O/W emulsions with the increase in the dispersed-phase (oil) concentration.

4.2. Emulsion Stability

The stability of surfactant-stabilized and Pickering O/W emulsions consisting of 50% by volume oil were monitored by visual observations over a period of seven days. The surfactant-stabilized emulsions were prepared using 0.5% (by volume) Triton X-100 (non-ionic surfactant) and the Pickering emulsions were prepared using 2% wt. starch nanoparticles, as described in the experimental work section. Photographs of the bulk emulsion samples contained in graduated cylinders were taken at different time intervals to study the phase separation behavior of emulsion under quiescent condition. The photomicrographs of emulsion samples were also taken using a Zeiss optical microscope equipped with a camera. A small quantity of an emulsion sample was diluted with the same continuous phase and was placed on a glass slide in order to take the photomicrographs.

Figure 8 compares the images of fresh surfactant-stabilized and SNPs-stabilized O/W emulsions. Clearly, the droplets of the surfactant-stabilized emulsions are much smaller than the droplets of the nanoparticles-stabilized emulsion. The Sauter mean diameters of the surfactant-stabilized and nanoparticles-stabilized emulsions are 14 and 91 μm , respectively.



Comparison of droplet sizes at time $t=0$.

Figure 8. Comparison of photomicrographs of fresh surfactant-stabilized (left photomicrograph) and nanoparticles-stabilized (right photomicrograph) O/W emulsions.

Figure 9 shows the effect of aging on the droplet sizes of emulsions over a period of 24 h. The surfactant-stabilized emulsions show a negligible change in the droplet sizes over the 24 h period (Figure 9A), while the nanoparticles-stabilized show a large increase in the droplet size over the same period of time (Figure 9B). Thus, surfactant-stabilized O/W emulsions are much more stable than the Pickering emulsions.

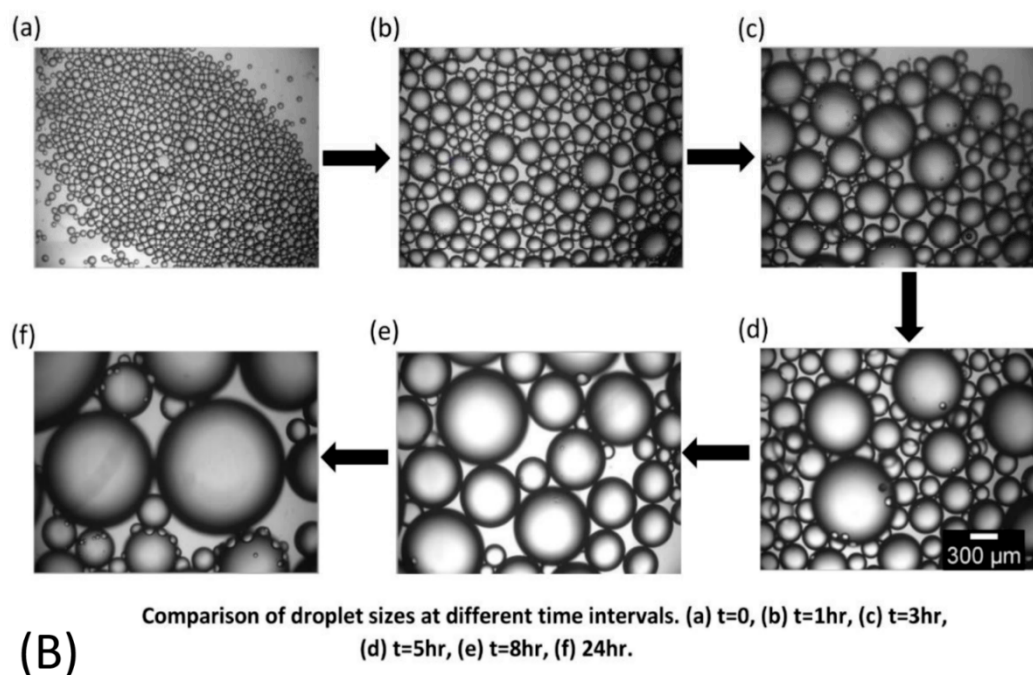
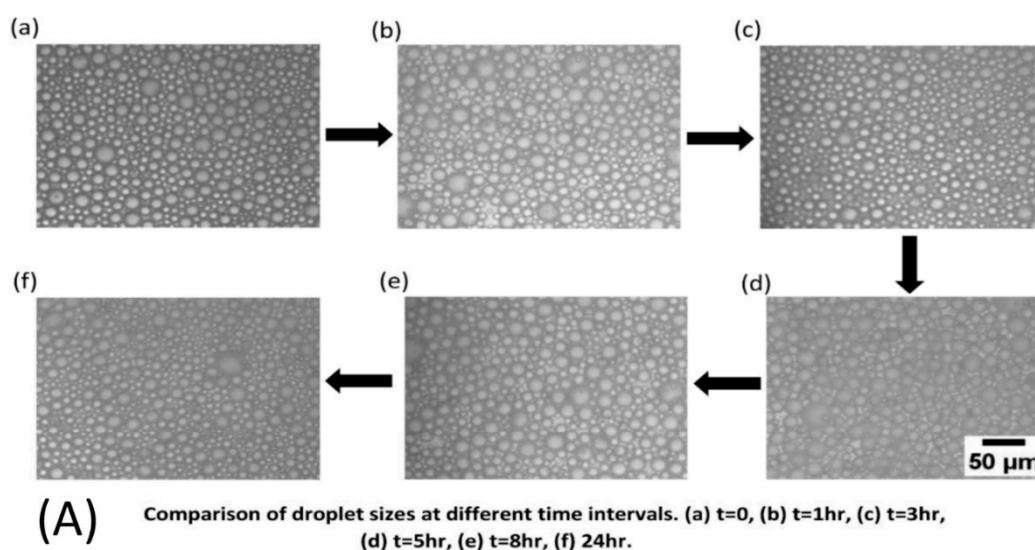


Figure 9. Effect of aging on the droplet size of (A) surfactant-stabilized and (B) nanoparticle-stabilized O/W emulsion.

Figure 10 shows the images of bulk samples for fresh, 24-h aged, and seven-day aged emulsions. Nanoparticle-stabilized emulsions creamed faster than the surfactant-stabilized emulsions. After seven days of aging, the surfactant-stabilized emulsions showed little change except for the upward rise or creaming of droplets. The nanoparticles-stabilized emulsions, however, showed noticeable coalescence and phase separation with aging.

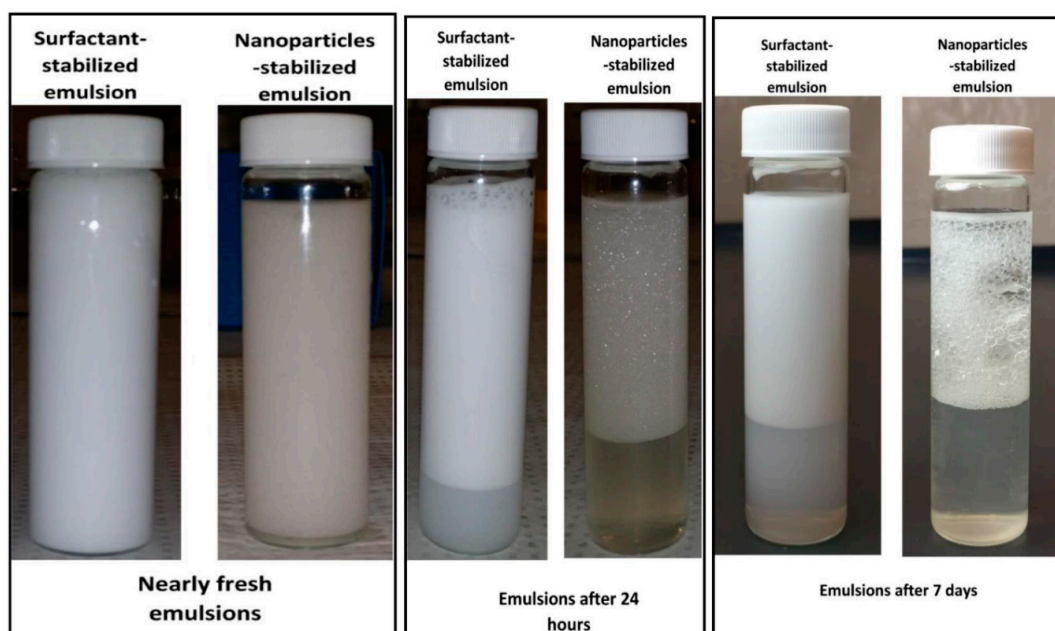


Figure 10. Images of fresh and aged surfactant-stabilized (left bottle in each box) and nanoparticles-stabilized (right bottle in each box) O/W emulsions.

4.3. Discussion

The starch nanoparticles stabilized Pickering O/W emulsions investigated in this work were relatively unstable as compared with the non-ionic surfactant stabilized O/W emulsions. If left unstirred or unagitated, the Pickering emulsions readily coalesce and separate into oil and water phases. Therefore, only in-situ measurements of viscosity under agitation conditions are reliable for Pickering emulsions. The surfactant-stabilized O/W emulsions, on the other hand, were stable with respect to coalescence and phase separation. Consequently, both in-situ and off-line measurements of viscosity are reliable and consistent.

When comparison is made at the same oil concentration, the Pickering O/W emulsions were found to be more viscous than the surfactant-stabilized O/W emulsions. The consistency index K of Pickering emulsions is significantly higher than that of surfactant-stabilized emulsions, especially at high concentrations of dispersed-phase. Figure 11 shows the comparison of the relative viscosities of Pickering emulsions and surfactant-stabilized emulsions at a fixed rpm of 30 (shear rate of 36.78 s^{-1}). Clearly, the Pickering emulsions were significantly more viscous than the surfactant-stabilized emulsions. The relative viscosity of emulsion, defined as the emulsion viscosity to matrix fluid viscosity, was consistently higher for the Pickering emulsion as compared with the surfactant-stabilized emulsion at the same volume fraction of oil.

It is interesting to note the Pickering O/W emulsions were more viscous than the surfactant-stabilized O/W emulsions despite having a much larger average droplet size. As noted earlier, the average droplet size of Pickering emulsions was about six to seven times larger than that of the surfactant-stabilized emulsions. The effect of droplet size on the rheology of emulsions has been studied in detail by Pal [8,13–16]. The influence of particle size on the rheology of suspensions has also been investigated by many authors [17–21]. In general, the dispersions (emulsions or suspensions) become more viscous upon decreasing the size of the inclusions, especially at high concentrations of dispersed phase. In the present work, we observed the opposite behavior in that the viscosity of emulsions of larger droplet size was higher than the viscosity of emulsions of smaller droplet size. There are at least three reasons for the high viscosity of large droplet size Pickering emulsions investigated in this work: 1) The viscosity of the matrix (continuous-phase) of Pickering emulsions was higher than that of the surfactant-stabilized emulsions due to the presence of starch nanoparticles

in the matrix phase. However, the higher viscosity of the matrix phase alone cannot explain the high viscosity of the Pickering emulsions, as the data plotted on a relative viscosity basis (see Figure 11) also show Pickering emulsions to be more viscous; 2) the effective volume fraction of Pickering emulsions was higher than that of the surfactant-stabilized emulsions due to the presence of a monolayer or multi-layers of starch nanoparticles at the surface of the droplets [22]; and 3) the transmission of stresses from the continuous phase to the dispersed-phase (oil) was inhibited due to the presence of starch nanoparticles at the surface of the droplets. Consequently, droplets behaved more like rigid particles without any internal circulation of fluid within the droplets.

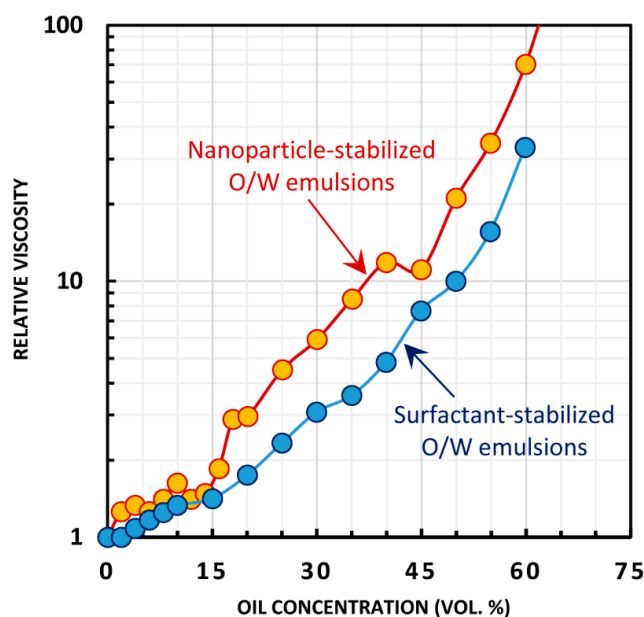


Figure 11. Comparison of the relative viscosities of Pickering emulsions and surfactant-stabilized emulsions at a fixed rpm of 30 (shear rate of 36.78 s^{-1}).

5. Conclusions

An in-situ method of measuring the viscosity of unstable and stable emulsions on a continuous basis under agitation conditions was developed. The rheology of oil-in-water emulsions stabilized with surfactant (Triton X-100) and starch nanoparticles was investigated using the in-situ technique. The stability characteristics of emulsions in terms of droplet size changes and phase separation with aging were also determined. Surfactant-stabilized emulsions were found to be more stable with respect to coalescence and phase separation. Pickering emulsions tended to separate readily into oil and water phases if left unagitated for a certain period of time. The droplet size of Pickering emulsions increased rapidly with aging. The droplet sizes of surfactant-stabilized emulsions hardly changed with aging up to seven days and no phase separation was observed in these emulsions. However, Pickering emulsions were found to be more viscous than the surfactant-stabilized emulsions despite having a much larger average droplet size compared with the surfactant-stabilized emulsions. The Sauter mean diameter of freshly prepared Pickering emulsions was about six to seven times that of the surfactant-stabilized emulsions. This observation is in contradiction with the existing literature, as fine small-sized emulsions are generally known to be more viscous than the coarse large-sized emulsions. The high viscosity of Pickering emulsions is explained in terms of the presence of a layer of nanoparticles at the surface of the droplets. The presence of nanoparticles at the surface of the droplets not only increased the rigidity of the droplets, but also increased the effective dispersed-phase concentration of the emulsion. Both surfactant-stabilized and Pickering emulsions were found to be generally Newtonian only at low values of the dispersed-phase concentration. They became non-Newtonian shear-thinning emulsions at high concentrations of the dispersed phase.

Author Contributions: This project of in-situ measurement of the rheology and phase inversion of emulsions, with and without additives such as surface-active nanoparticles and surfactants, was conceived by R.P. The design and construction of the setup was done by both U.B. and R.P. The experimental work was carried out by U.B. The manuscript was written by R.P.

Funding: The APC was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pal, R. *Rheology of Particulate Dispersions and Composites*; CRC Press: Boca Raton, FL, USA, 2007.
2. Becher, P. *Emulsions: Theory and Practice*; Krieger Publishing Co.: Malabar, FL, USA, 1977.
3. Yang, Y.; Fang, Z.; Chen, X.; Zhang, W.; Xie, Y.; Chen, Y.; Liu, Z.; Yuan, W. An overview of Pickering emulsions: Solid-particle materials, classification, morphology, and applications. *Front. Pharmacol.* **2017**, *8*, 1–20. [[CrossRef](#)] [[PubMed](#)]
4. Torrey, S. *Emulsions and Emulsifier Applications—Recent Developments*; Noyes Data Corporation: Park Ridge, NJ, USA, 1984.
5. Lissant, K.J. *Emulsions and Emulsion Technology*; Marcel Dekker: New York, NY, USA, 1974.
6. Friberg, S. *Food Emulsions*; Marcel Dekker: New York, NY, USA, 1976.
7. Pal, R. Rheology of simple and multiple emulsions. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 41–60. [[CrossRef](#)]
8. Pal, R. Effect of droplet size on the rheology of emulsions. *AIChE J.* **1996**, *42*, 3181–3190. [[CrossRef](#)]
9. Pal, R. Techniques for measuring the composition (oil and water content) of emulsions—a state of the art review. *Colloids Surf. A Physicochem. Eng. Asp.* **1994**, *84*, 141–193. [[CrossRef](#)]
10. Bains, U. In-Situ Continuous Monitoring of Catastrophic Phase Inversion and Viscosity of Pickering Emulsions. Master's Thesis, University of Waterloo, Waterloo, ON, Canada, 2018.
11. Whorlow, R.W. *Rheological Techniques*; Ellis Horwood Ltd.: Chichester, UK, 1980.
12. Ogunlaja, S.B.; Pal, R.; Sarikhani, K. Effect of starch nanoparticles on phase inversion of Pickering emulsions. *Can. J. Chem. Eng.* **2018**, *96*, 1089–1097. [[CrossRef](#)]
13. Pal, R. Viscosity and storage/loss moduli for mixtures of fine and coarse emulsions. *Chem. Eng. J.* **1997**, *67*, 37–44. [[CrossRef](#)]
14. Pal, R. Scaling of the relative viscosity of emulsions. *J. Rheol.* **1997**, *41*, 141–150. [[CrossRef](#)]
15. Pal, R. Shear viscosity behavior of emulsions of two immiscible liquids. *J. Colloid Interface Sci.* **2000**, *225*, 359–366. [[CrossRef](#)] [[PubMed](#)]
16. Pal, R. Relative viscosity of non-Newtonian concentrated emulsions of non-colloidal droplets. *Ind. Eng. Chem. Res.* **2000**, *39*, 4933–4943. [[CrossRef](#)]
17. Parkinson, C.; Matsumoto, S.; Sherman, P. The influence of particle-size distribution on the apparent viscosity of non-Newtonian dispersed systems. *J. Colloid Interface Sci.* **1970**, *33*, 150–160. [[CrossRef](#)]
18. Chong, J.S.; Christiansen, E.B.; Baer, A.D. Rheology of concentrated suspensions. *J. Appl. Poly. Sci.* **1971**, *15*, 2007–2021. [[CrossRef](#)]
19. Hoffman, R.L. Factors affecting the viscosity of unimodal and multimodal colloidal dispersions. *J. Rheol.* **1992**, *36*, 947–965. [[CrossRef](#)]
20. Rodriguez, B.E.; Kaler, E.W.; Wolfe, M.S. Binary mixtures of monodisperse latex dispersions: Viscosity. *Langmuir* **1992**, *8*, 2382–2389. [[CrossRef](#)]
21. Del Gaudio, P.; Ventura, G.; Taddeucci, J. The effect of particle size on the rheology of liquid-solid mixtures with application to lava flows: Results from analogue experiments. *Geochem. Geophys. Geosyst.* **2013**, *14*, 2661–2669. [[CrossRef](#)]
22. Pal, R. A simple model for the viscosity of Pickering emulsions. *Fluids* **2018**, *3*, 2. [[CrossRef](#)]

