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RHEOLOGY OF OIL-IN-WATER SILICONE OIL EMULSIONS

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Abstract. *Emulsions are found in numerous industrial sectors, such as pharmaceuticals, food, cosmetics, petroleum, among others. Due to their widespread applications, understanding the rheological properties of this type of fluid is of utmost importance due to their direct influence on industrial processes. In terms of emulsion rheology, it is understood that the rheological behavior is dependent on different conditions, such as the concentration of the dispersed phase and droplet size distribution. In this study, oil-in-water (o/w) emulsions with large droplet sizes (D90 approximately 80 μm) and low concentrations of synthetic silicone oil were analyzed. Due to the large droplet sizes, these emulsions did not exhibit significant temporal stability. However, in scenarios where droplet size is more critical than stability, this configuration can be interesting. The study evaluated the rheological behavior of emulsions, examining dependencies of viscosity on shear rate and shear time. Additionally, a comparison was made between rheometric tests and analytical models proposed in the literature to assess emulsion viscosity. As a complementary analysis, the presence of droplet breakage or coalescence during flow in the rheometer was investigated. Based on the results obtained, it was observed that the analyzed emulsions exhibit simultaneous rheopetic and pseudoplastic behavior. Furthermore, there was no tendency for droplet breakage or coalescence during the flow. These findings provide valuable insights into the rheological characteristics and stability of the studied emulsions, which are crucial for various industrial applications.*

Keywords: *Emulsion, Rheology, oil-in-water, Viscosity, Silicone oil.*

1. INTRODUCTION

An emulsion is a dispersion of two or more immiscible liquids, where one phase, called the continuous phase, contains droplets of other liquids, known as dispersed phases. In this dispersion, one of the phases is hydrophilic, and the other is lipophilic. The formation of these emulsions occurs when the liquids come into contact in the presence of a surfactant and sufficient energy for droplet generation (Sousa *et al.*, 2022). Emulsions can be classified in a simplified manner as oil-in-water (o/w), where the continuous phase is aqueous, or water-in-oil (w/o), where the continuous phase is oily (Bibette *et al.*, 2003).

An important characteristic of these emulsions is stability, which is a subjective concept that refers to the ability of an emulsion to resist changes in its properties over time. Additionally, the droplet size of an emulsion is inversely proportional to its stability, and surfactants play a crucial role in emulsion stabilization. The presence of surfactants at the interface exerts a fundamental role in reducing interfacial tension, forming an efficient barrier against coalescence, and significantly contributing to the system's stability (McClements, 2015).

It is common for emulsions to be produced with small droplet sizes since, in most cases, the main focus is to maximize their stability. However, in some cases, such as in this study, larger droplet size is more important than emulsion stability.

The presence of emulsions is highly significant in a wide range of industries, including the pharmaceutical, petroleum, food, cosmetics, and others. From the perspective of the cosmetic and pharmaceutical industries, the use of silicone oils, similar to the ones used in this study, is considered highly advantageous due to the wide range of sensory benefits they offer. These advantages include reducing the viscosity of products (KRAMBECK, 2009).

Due to the wide range of applications of this type of fluid, obtaining the rheological properties of these emulsions becomes essential, which is the main focus of this study. Furthermore, it is well known that the rheological properties of these emulsions will depend on their concentration (Pal, 2000).

Previous studies have shown that the viscosity of oil-in-water emulsions is dependent on the shear rate, exhibiting pseudoplastic behavior, which becomes more pronounced with increasing volumetric fraction of oil in water (Otsubo and

Prud'homme, 1994). Additionally, apart from the pseudoplastic behavior, concentrated oil-in-water emulsions exhibit rheopetic behavior, meaning their viscosity may vary with shear time (Torlopov *et al.*, 2022).

2. METHODOLOGY

For this study, oil-in-water (o/w) emulsions were prepared using the Ultra-Turrax IKA equipment, which was used to disperse Silicone oil with a kinematic viscosity of 49.73 cSt and a density of 0.967 g/mL at 25 °C, in water containing the surfactant STEOL® 23-2S.30 CP-F. Additionally, deionized water with a dynamic viscosity of 0.963 mPas, at 25 °C, was used as the continuous phase.

In several situations, it became necessary to determine the droplet size distribution (DSD) of the emulsions, which was accomplished using a laser particle size analyzer Bettersize St.

In an initial stage, with the aim of conducting studies on emulsions with larger droplet sizes and maximum temporal stability, a matrix of experiments was performed to determine the optimal production point (mixing time and rotation speed on the Turrax). In this matrix, emulsions with Silicone oil were produced with mixing times of 300, 600, and 900 seconds, mass concentrations of 1% and 10%, and the following rotation speeds: 3000 rpm, 6000 rpm, and 9000 rpm. The matrix results, discussed in the next section, guided the production of other emulsions with different mass fractions. These results revealed that the optimal configuration for production was a time of 300 seconds and a rotation speed of 3000 rpm. This configuration will be used for the production of all emulsions used in the rheological tests.

Following the production standards described earlier, emulsions with oil mass fractions of 20% were produced. Additionally, to maintain the emulsions stability during the rheological tests, they were kept under mechanical agitation using the Fisatom Mod. 752 A magnetic stirrer throughout the testing period. This ensured consistent mixing and prevented any significant temporal instability in the emulsions.

For each produced emulsion, rheological characterization was carried out through tests using the Haake Mars 60 Rheometer. The tests involved applying constant shear rates over a period of 10800 seconds, with the temperature controlled at 25 ± 0.1 °C using a Thermo Scientific HAAKE A10 thermal bath. The applied shear rates were 1000, 2000, 3000, and 3800 s^{-1}. The tests used a geometry of concentric cylinders (Double Gap), as depicted in Figure 1, which allowed obtaining the required rheological properties.

With the aim of estimating the viscosity of emulsions, several mathematical models have been proposed. Firstly, the Einstein equation Eq. (1) can be used to estimate the viscosity of an emulsion as a function of the viscosity of its continuous phase. In this equation, η represents the viscosity of the emulsion, η_0 is the viscosity of the continuous phase and ϕ is the volumetric fraction of the dispersed phase. The Einstein model assumes the droplets to be perfect solid spheres, which implies some modeling errors compared to the real system. However, the Einstein equation is only validated for volumetric fractions equal to or lower than 2%, where the interactions between the droplets can be neglected. In this regard, to estimate the absolute viscosity of an emulsion with volumetric fractions greater than 2%, various empirical correlations have been proposed, such as the Thomas equation presented in Eq. (2), which has been found effective for volumetric fractions below 25% (Breslau and Miller, 1970). The Eq. (2) assumes that the emulsion exhibits Newtonian behavior and is typically applied when the droplet size is not significantly large (Schramm, 1992).

$$\eta = \eta_0(1 + 2.5\phi) \tag{1}$$

$$\eta = \eta_0(1 + 2.5\phi + 10.5\phi^2 + 0.00273exp(16.6\phi)) \tag{2}$$

As depicted in Eq. (1) and Eq. (2), an increase in the concentration of the dispersed phase leads to an increase in the viscosity of the fluid. However, the increase in the concentration of the dispersed phase can also cause an escalation of non-Newtonian effects in this emulsion, meaning that the viscosity can become dependent on the imposed shear rate (Derkach, 2009).

3. RESULTS AND DISCUSSION

The graph presented in Fig. 2, for emulsions with 10% oil mass fraction, shows the behavior of the droplet size with the rotation speed and time parameters mentioned above in the methodology, with instantaneous measurements, 1 hour and 4 hours after the emulsion production. In these results, the statistical diameter D90 was used, which represents a diameter below which 90% of the diameters are contained.

The matrix of results indicated good droplet size stability up to 4 hours after production. Moreover, it revealed that the best production configuration, aiming to maximize droplet size while maintaining reasonable temporal stability, was achieved with a rotation time of 300 seconds on the mechanical stirrer at a rotation speed of 3000 rpm. This combination of parameters resulted in emulsions with the desired droplet size and acceptable temporal stability, making it the better choice. It is worth noting that for different mass fractions, the obtained D90 values may vary, but the underlying concept remains similar to that applied for the test matrix. Therefore, the configuration obtained from the initial tests is still utilized as a representative reference, recognizing that slight adjustments in the D90 values may occur for different mass fractions.

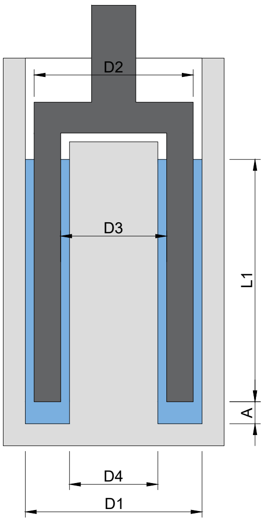

Figure 1: Diagram of the rotating geometry formed by concentric cylinders - DG41. Dimensions: D1 = 43.4 mm; D2 = 42.804 mm; D3 = 36.004 mm; D4 = 35.5 mm; A = 5.1 mm; L1 = 55.01 mm.

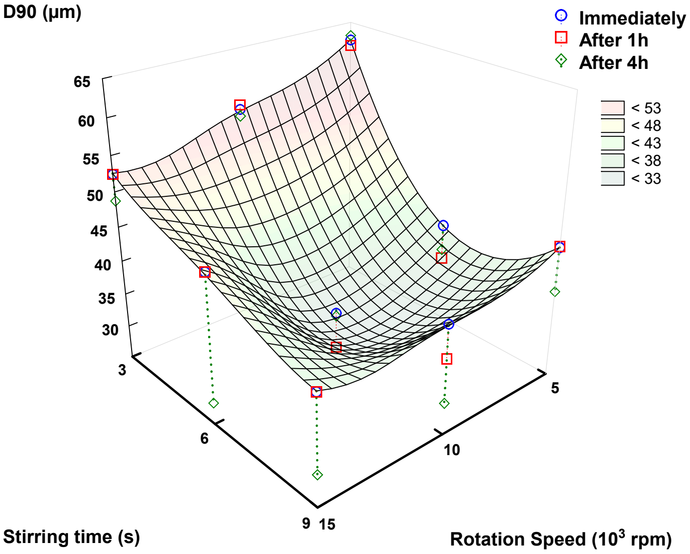

Figure 2: D90 as a function of stirring time and rotation speed.

Initially, starting with the rheological results of apparent viscosity as a function of shear time at a fixed applied rate, the obtained results are displayed in Fig. 3. In this figure, it can be observed that the analyzed emulsion exhibits a pseudoplastic behavior, with a decrease in apparent viscosity in the initial moments of the test with the shear rate. Moreover, it is noted that this emulsion shows a considerable increase in apparent viscosity with the shear time, which characterizes the rheopexy of the emulsion. Finally, the results also indicate that for shear rates of 3000 and 3800 s^{-1}, a plateau region of apparent viscosity is reached at the end of the test, which suggests that the entire rheopetic effect occurred during the earlier moments of the test.

Due to the dependence of apparent viscosity on both shear rate and shear time, it becomes convenient to visualize these results simultaneously, as shown in Fig. 4. Analyzing this figure, it is evident that the graphs fit considerably well to the plotted surface, suggesting that it could be a good representation of the rheological behavior of this emulsion. Additionally, upon a general analysis, the two behaviors described in the previous paragraph are clearly discernible.

Another notable analysis is regarding the magnitude of the increase in apparent viscosity with time concerning the applied shear rate. From a visual perspective, by examining Fig. 3 and Fig. 4, it is evident that this increase is much more pronounced at lower applied rates, as reported in previous studies (Torlopov *et al.*, 2022). This result is further confirmed by calculating the variation in apparent viscosity during the test ($\Delta\eta$), which can be expressed as the ratio between the difference of the maximum apparent viscosity and the maximum viscosity and the minimum apparent viscosity, as shown in Eq. (3). These results are presented in Tab. 1, and demonstrate that, for shear rates of 1000 and 2000 s^{-1}, the percentage

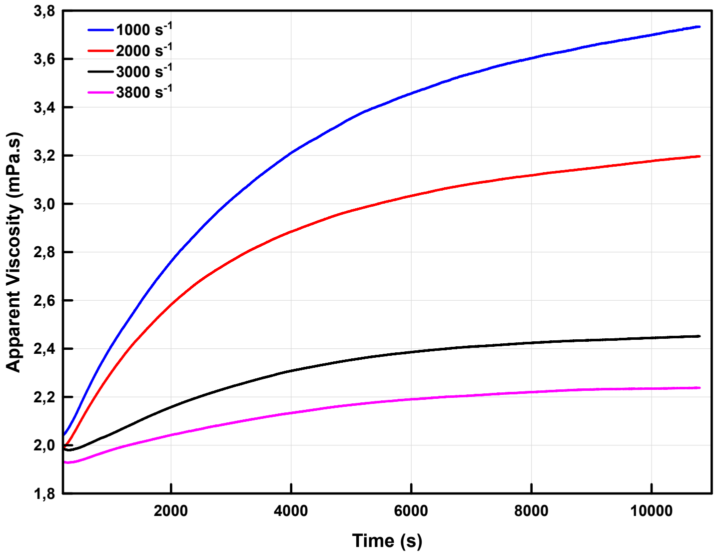

Figure 3: Apparent viscosity as a function of shear time for constant applied shear rates.

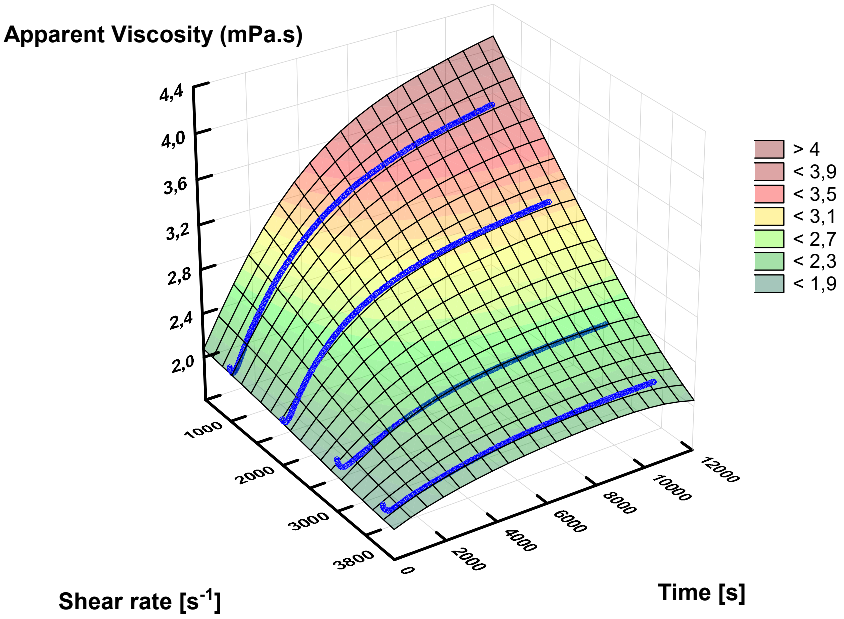

Figure 4: Apparent viscosity as a function of shear time and applied shear rate.

variation is much greater than for shear rates of 3000 and 3800 s^{-1}. Furthermore, it is noted that the variation in apparent viscosity exhibits an inverse relationship with the shear rate.

$$\Delta\eta = \frac{\eta_{max} - \eta_{min}}{\eta_{min}} \tag{3}$$

Table 1: Variation of apparent viscosity as a function of shear rate.

Shear rate $\dot{\gamma}$ (s^{-1})	η_{min} **(mPas)**	η_{max} **(mPas)**	$\Delta\eta$ **(%)**
1000	2.035	3.734	83.489
2000	1.984	3.197	61.139
3000	1.980	2.452	23.838
3800	1.928	2.238	16.079

Indeed, some previous studies have correlated the increase in viscosity with elastic deformation of droplets (Masalova, 2019) and with a higher level of droplet structural ordering under applied stress in the fluid (Derkach, 2009).

In a complementary analysis, Eq. (2) is used to estimate the theoretical viscosity of an emulsion, and it is compared with the different values observed in Fig. 4. In Fig. 5, a theoretical viscosity curve based on Eq. (2) is plotted against the volumetric fraction of the dispersed phase, it is important to highlight that the values were recalculated to a volumetric fraction of 20.5% since the emulsions were originally produced based on the mass fraction of 20%. Additionally, the figure also shows the minimum and maximum apparent viscosity points for each applied shear rate, measured through rheological tests. In this analysis it is observed that the measurements that best represent the viscosity of the sample are the apparent viscosities at high shear rate and without rheopexy effect, which are close to the viscosity η_∞, representing the plateau viscosity of infinite shear.

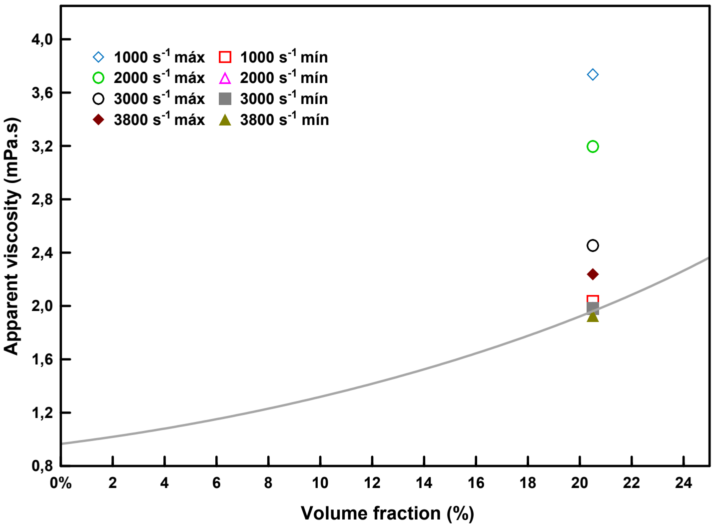

Figure 5: Comparison between the experimental apparent viscosity and the theoretical viscosity curve.

Lastly, the droplet diameters before and after shearing were analyzed to investigate whether droplet breakage or coalescence occurred during the shearing process in this sample. For this purpose, the DSD was measured before and after the rheological tests, and the graph presented in Fig. 6 illustrates the D90 diameter before and after shearing in the rheometer. The graph demonstrates that there was some increasing variation in droplet diameters in the samples subjected to shear rate of 1000 s^{-1}, while a decreasing variation was observed in the sample subjected to a shear rate of 3000 s^{-1} and there was practically no variation with the application of a shear rate of 2000 and 3800 s^{-1}. However, based on these results, it is not possible to conclude that the shearing process induces either of the two phenomena (droplet breakage or coalescence) since there is no clear trend observed.

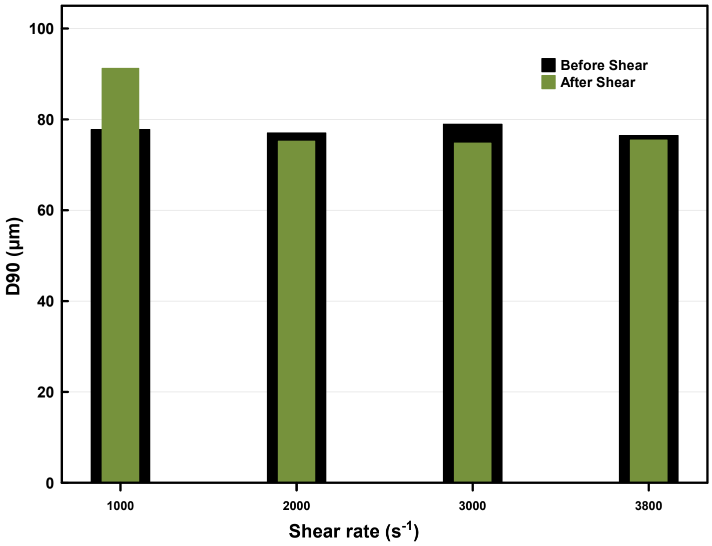

Figure 6: D90 before and after shearing for some of the samples.

4. CONCLUDING REMARKS

Based on the data obtained and the conducted analyses, it can be observed that the studied emulsions exhibit non-Newtonian rheological behavior. The viscosity of these emulsions shows a dependency on both shear rate and shear time, indicating pseudoplastic behavior, where the apparent viscosity decreases with increasing shear rate, and a rheopetic behavior, with the apparent viscosity increasing over time under shear. These results demonstrate that the rheological properties of the emulsions are complex and vary according to the applied shear conditions.

Regarding Fig. 4, it is evident that the experimental data obtained allowed for a comprehensive mapping of viscosity concerning shear rate and shear time. The three-dimensional representation provides valuable insights into how the apparent viscosity varies with different shear conditions, enabling a better understanding of the rheological behavior of the emulsions under study.

Based on the obtained results, it is observed that the energy imposed by the rheometer in these tests was not sufficient to induce a decrease in droplet size through droplet breakage mechanisms. Therefore, in order to specifically evaluate droplet breakage, future studies could involve increasing the droplet size of these emulsions and increasing the imposed shear rate.

In future steps, the intention is to repeat the tests performed for different concentrations of oil in water to investigate the influence of concentration on the rheological behavior of the emulsion. Additionally, there is a plan to cover a broader range of shear rates to improve the regression in the graph presented in Fig. 4, representing the emulsion's viscosity more accurately as a function of shear time and shear rate. By conducting tests across various concentration levels and a wider range of shear rates, researchers can gain a more comprehensive understanding of how these factors impact the rheological properties of the emulsions. This expanded investigation will provide valuable insights into the behavior and stability of the emulsion under diverse conditions, leading to a more robust understanding of its rheological behavior.

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