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RHEOLOGY OF WATER-IN-OIL EMULSIONS

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Abstract. *In this paper, we study the rheology of water-in-oil emulsions. These emulsions can be used as model fluids, which, with the addition of certain components (e.g. Cyclopentane), are able to form hydrates at atmospheric pressure. Hydrate formation is a major issue in the oil industry; therefore, it is of great interest the study of the phenomena. The emulsions were prepared with water cut ranging from 20 to 40% and with two different oils: mineral oil Morlina S2 BL 10, reported viscosity of 10 mm²/s at 40°C, and Morlina S2 B 150, reported viscosity of 150 mm²/s at 40°C. In all cases, a surfactant blend, composed by Span 80 and Dioctyl sodium sulfosuccinate (AOT), was added, with two different concentrations: 1% and 5 wt% surfactant mixture in respect to the total emulsion weight. The best composition of the surfactant mixture was determined experimentally using the HLB system, with Span 80 fraction ranging from 100 to 75% and AOT fraction ranging from 0 to 25%, totaling 1 wt % surfactant mixture. The water-in-oil emulsions were stirred by hand and with a high-speed homogenizer. The rheology characterization was performed using Physica MCR 501 rheometer. The results obtained show the stability of the water-in-oil emulsions through time, and the effect of water cut, oil viscosity and emulsifier concentration on the viscosity. The analysis of the experimental data allows the correct choice of the model fluid to be used in future hydrate formation experiments.*

Keywords: *rheology, water-in-oil emulsion, hydrate*

1. INTRODUCTION

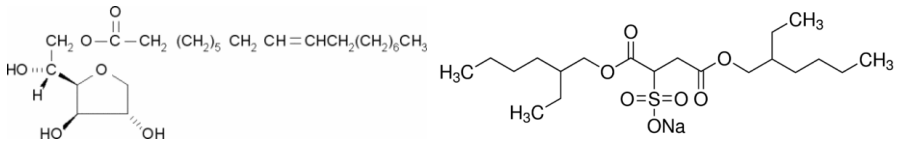
Once the oil and gas industry expand into deeper and colder waters, the formation of clathrate hydrates in water-in-oil (w/o) emulsion should be highly considered. Hydrates (natural gas hydrates or clathrate hydrates) are crystalline icelike solids composed of water and gas, in which small molecules are encaged in water cavities that are composed of hydrogen-bonded water molecules (Sloan and Koh 2008). The guest molecules include light hydrocarbons such as methane, ethane, propane, as well as hydrogen and carbon dioxide. Usually, natural gas hydrates are formed under high pressure (1-10 MPa) and temperatures below 4°C. (Morris, *et.al*, 2010). Nevertheless, not all guest molecules need to work at high pressure in order to form hydrate, such as cyclopentane, which is liquid at standard conditions. Therefore, it's possible to work with hydrate-forming systems without elevated pressure and all difficulties that bring on with it.

Recent studies of Lee *et.al*, 2008, Morris *et.al*, 2010 and Gong *et.al*, 2007 have already worked with hydrate-forming systems at atmospheric pressure. Sum *et.al*, 2013 have developed a model water-in-oil emulsion with high stability and reproducible results. This study follows the idea of preparing a stable water-in-oil emulsion and then making an emulsion characterization in order to establish a well-defined hydrate forming system.

1.1 Materials

Water-in-oil emulsions were prepared with two different types of oil: mineral oil Morlina S2 BL 10 (Morlina 10, Shell), reported viscosity 10 mm²/s at 40°C and density of 0.881 g/cm³ at 15°C; and mineral oil Morlina S2 B 150 (Morlina 150, Shell), reported viscosity of 150 mm²/s at 40°C and density of 0.887 g/cm³ at 15°C. In all cases, the water cut of the emulsions ranged from 20 to 40 wt % and employed a mixture of two surfactants, Span 80 and AOT.

Span 80 (Sorbitan monooleate) is a nonionic surfactant with a hydrophilic lipophilic balance (HLB) value of 4.3, density of 0.986 g/cm³ at 25°C and a molecular weight of 428.62 g/mol. Its empirical formula is $C_{24}H_{44}O_6$. It is an oil soluble, yellow liquid, generally used for formation of water-in-oil emulsion. AOT (Dioctly sulfosuccinate sodium salt) is an anionic surfactant with a HLB equal to 13.8 (Ge, 2009), density of 1.1 g/cm³ and a molecular weight of 444.56 g/mol. Its chemical formula is $C_{20}H_{37}NaO_7S$. It is water-soluble, white solid, and is widely used to reduce the surface tension between two phases. Both chemicals structures are shown in Fig. 1.



(a) (b)

Figure 1. Molecular structure: (a) Span 80; (b) AOT.

1.2 Emulsion preparation with 1 wt % of surfactant blend

The emulsions were prepared by dissolving the emulsifiers in the phases with higher solubility. Therefore, AOT was solubilized in water and Span 80 in mineral oil at room temperature (~22°C). To determine the best composition of the surfactant blend, several trial runs were done following the HLB system. According to ICI Americas Inc., 1980, the HLB required for forming a water-in-oil emulsion using mineral oil is equal to 6 ± 1, making possible to calculate how much AOT (HLB = 13.8) to blend with Span 80 (HLB = 4.3), to achieve a HLB of 6. (Eq. (1).) Table 1 shows the HLB blend for each sample.

$$HLB_{blend} = \frac{HLB_{AOT}\,\%_{AOT} + HLB_{Span\,80}\%_{Span\,80}}{100} \quad (1)$$

Table 1. HLB blend for trials runs

Sample No.	Emulsier blend		Calculated HLB
	Span 80	AOT	
1	100 %	0 %	4,3
2	95 %	5 %	4,8
3	90 %	10 %	5,3
4	85 %	15 %	5,7
5	80 %	20 %	6,2
6	75 %	25 %	6,7

It is worth recalling that these trials were made using mineral oil Morlina 10 and Morlina 150, for three water cuts (20, 30 and 40 %). The sample was stirred by hand and with a high-speed homogenizer. In the first case, the AOT dissolved in water was added to the mineral oil with Span 80 and then, the mixture was manually stirred for 2 minutes. For the second case, the mixture was stirred with a high-speed homogenizer at 8000 rpm for 10 min, while the AOT's solution was slowly added during the first minute.

1.3 Emulsion preparation with 5 wt % of surfactant blend

The emulsions with 5 wt % were prepared following the proceeding optimized for emulsions with 1 wt % of surfactant blend. Therefore, only those formulations that successfully formed w/o emulsions at 1 wt % of surfactant blend were prepared at 5 wt % of surfactant blend. Due to the greater amount of AOT used in the system, it was necessary to dissolve the AOT in water in an oven at 70°C, until all the AOT was solubilized. The mixture of mineral oil and Span80 was also heated at approximately 70°C for 30 minutes. The emulsions were stirred with a high-speed homogenizer, as described in section 2.2.

1.4 Emulsion Characterization

2.4.1 Drop Test

Phase inversion was monitored by the drop test at room temperature. Phase inversion refers to a phenomenon that occurs when water-in-oil emulsion reverts to oil-in-water, and vice versa. Since the focus of this study was to obtain w/o emulsions, an emulsion's drop was put in beakers containing water and oil, phase inversion was detected when the drop was readily dispersed in the aqueous media.

2.4.2 Stability Test

Phase separation was monitored by visual observation for three days at room temperature.

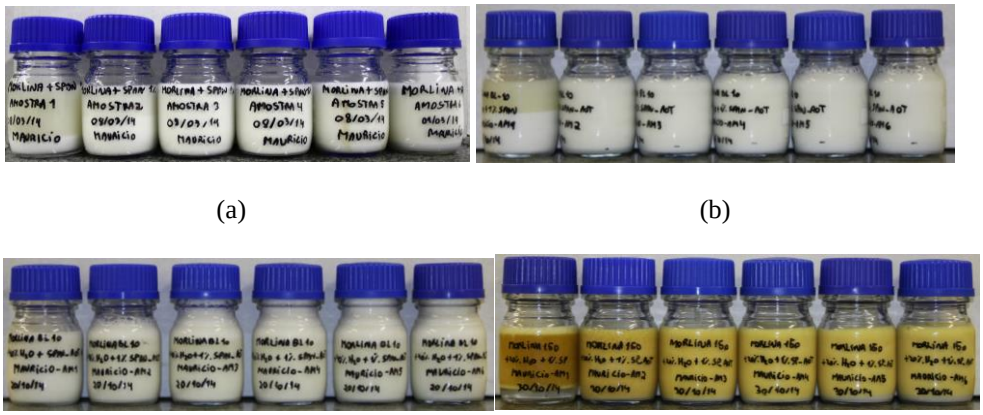
2.4.1 Rheology

The rheological data were obtained using MCR 501 rheometer, from Anton Paar. The Couette geometry was used, with a cup diameter of 28.920 mm, cylinder diameter of 26.665 mm and cylinder length of 40.017 mm. The sample volume used in each test was approximately 19 mL, and the sample was allowed to rest at 2°C for 45 min prior to the measurement. It was also used the Double Gap geometry, with a cup internal diameter of 23.818 mm, cup external diameter of 27.590 mm, cylinder internal diameter of 24.654 mm, cylinder external diameter of 26.664 mm and cylinder length of 40 mm. The sample volume used in each test was approximately 4 mL, and the sample was allowed to rest at 20°C for 30 min prior to the measurement. In both cases, the temperature was stabilized using a cooling bath, and in each test, 6 points per decade on a log scale were taken, and each point at a steady state.

2. RESULTS AND DISCUSSION

2.1 Phase Inversion and Emulsion Stability

Visual observation confirmed that almost all emulsions prepared with mineral oil Morlina 10 and Morlina 150 and with 1 wt % of emulsifier blend (water cut ranging from 20 to 40 % and manually stirred) were not stable, showing droplet coalescence one day after preparation (Fig. 2). Because of the high viscosity of Morlina 150, samples did not mixture quite well at the moment of the preparation, showing phase separation in the next day. As a result, the emulsions were not prepared using this oil with 30 and 40 % water cut. Only one emulsion (1 wt % surfactant, water cut of 20 %) prepared with Morlina 10 did not show droplet coalescence and phase inversion, which was confirmed by the drop test (Fig. 3). The composition of this surfactant mixture corresponds to 85 wt % Span 80 and 15 wt % AOT.



(a) (b)

(c) (d)

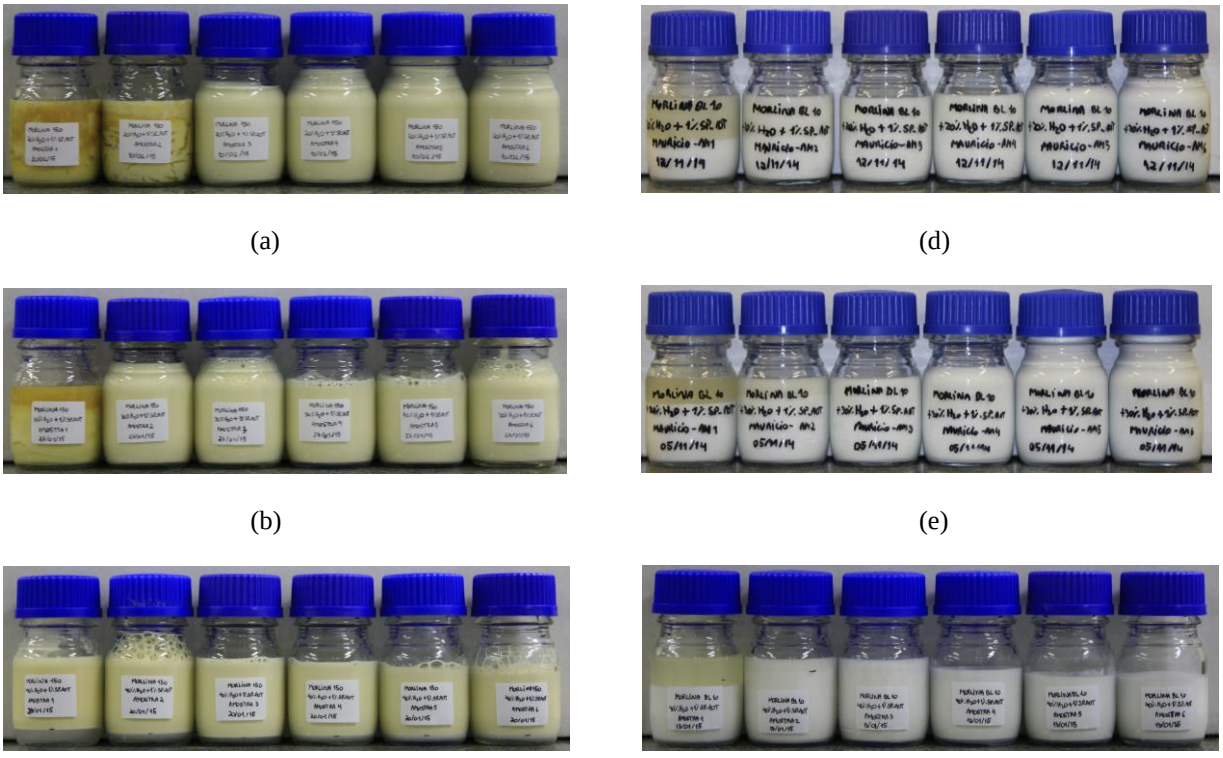
Figure 2. Emulsions samples stirred by hand: (a) Morlina 10, 20 % water cut; (b) Morlina 10, 30 % water cut; (c) Morlina 10, 40 % water cut; (d) Morlina 150, 20 % water cut.

(a) (b)

Figure 3. Images of emulsion's drop (Morlina 10, 20 % water cut, 1 wt % of emulsifier blend, surfactant mixture correspond to 85 wt % Span 80 and 15 wt % AOT) in two different media ((a) water; (b) oil) indicating that phase inversion did not occur.

Visual observation and drop tests confirmed that all emulsions (1 wt % surfactant) prepared with Morlina 150 (Fig. 4:a,b,c), with water cut ranging from 20 to 40 % and stirred with a high-speed homogenizer were not stable, presenting mainly phase inversion, but also strong phase separation just after a few minutes (Fig. 5).

The same results described above occurred for emulsions prepared with Morlina 10 and 20 % water cut. Nevertheless, trial runs (Fig. 4:d,e,f) for emulsions prepared with Morlina BL 10 (30 and 40 % water cut) and mixed by a high-speed homogenizer presented two good results, one for each water cut. These emulsions did not display droplet coalescence and phase inversion. The composition of emulsifier blend in these emulsions was 90 wt % Span 80 and 10 wt % AOT in both cases.

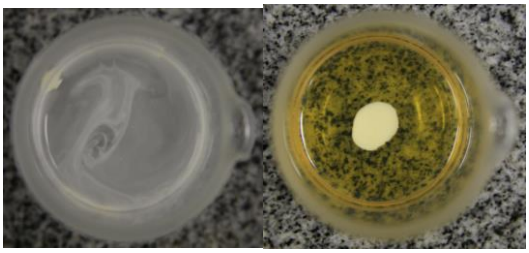


(a) (d)

(b) (e)

(c) (f)

Figure 4. Emulsions samples stirred with high-speed homogenizer: (a) Morlina 10, 20 % water cut; (b) Morlina 10, 30 % water cut; (c) Morlina 10, 40 % water cut; (d) Morlina 150, 20 % water cut; (e) Morlina 150, 30 % water cut; (f) Morlina 150, 40 % water cut.



(a) (b)

Figure 5. Images of emulsion's drop (Morlina 150, 30 % water cut, 1 wt % of emulsifier blend, surfactant mixture correspond to 80 wt % Span 80 and 20 wt % AOT) in two different media ((a) water; (b) oil) indicating that phase inversion occurred.

For better understanding, Tab. 2 and Tab. 3 resume all the described results.

Table 2. Results of trial runs for emulsions stirred by hand – 1 wt % of surfactant

	Water Cut		
Mineral Oil	20 %	30 %	40 %
Morlina 10	w/o emulsion: compositon of the surfactant mixture: 85 wt % Span 80 and 15 wt % AOT	Emulsions were not stable	Emulsions were not stable
Morlina 150	Emulsions were not stable	-	-

Table 3. Results of trial runs for emulsions stirred by high-speed homogenizer – 1 wt % of surfactant

	Water Cut		
Mineral Oil	20 %	30 %	40 %
Morlina 10	Emulsions were not stable	w/o emulsion: compositon of the surfactant mixture: 90 wt % Span 80 and 10 wt % AOT	w/o emulsion: compositon of the surfactant mixture: 90 wt % Span 80 and 10 wt % AOT
Morlina 150	Emulsions were not stable	Emulsions were not stable	Emulsions were not stable

Only three mixtures formed w/o emulsions. Considering that, emulsions with 5 wt % were prepared (section 2.3), using the same materials and percentages shown in Tab. 2 and Tab. 3. The results of these new mixtures are shown in Tab. 4. It should be noticed that all emulsions prepared with Morlina 150 were not stable against coalescence or presented phase inversion in most cases.

Table 4. Results of trial runs for emulsions stirred by high-speed homogenizer – 5 wt % of surfactant

	Water Cut		
Mineral Oil	20 %	30 %	40 %
Morlina 10	w/o emulsion: compositon of the surfactant mixture: 85 wt % Span 80 and 15 wt % AOT	w/o emulsion: compositon of the surfactant mixture: 90 wt % Span 80 and 10 wt % AOT	Phase inversion: o/w emulsion:

Therefore, there are five w/o emulsions that did not presented coalescence and phase inversion in a period of three days, confirmed by visual observation and by the drop test.

2.2 Rheology measurements

Rheological data was obtained from three of the five w/o emulsions: 20 % water cut (1 wt % surfactant), 30 % water cut (1 wt % surfactant and 5 wt % surfactant). Flow curves for these emulsions are presented in Figs. 6-8.

Tests were run for the first emulsion (20 % water cut, Fig. 6), at shear rates ranging from 10 to 1000 s^{-1} in a double gap geometry. Four different samples of the same emulsion were measured. Two of them showed Newtonian behavior, while the other two showed shear-thinning behavior (Power Law Fit). This apparent instability may be explained considering the mixing process, which is done by hand and, therefore, there is no control of the droplet size (Daltin, 2011).

For higher shear rates, it is possible to observe an increase in the viscosity of mineral oil Morlina 10. This slightly increase may be explained by the Taylor vortices.

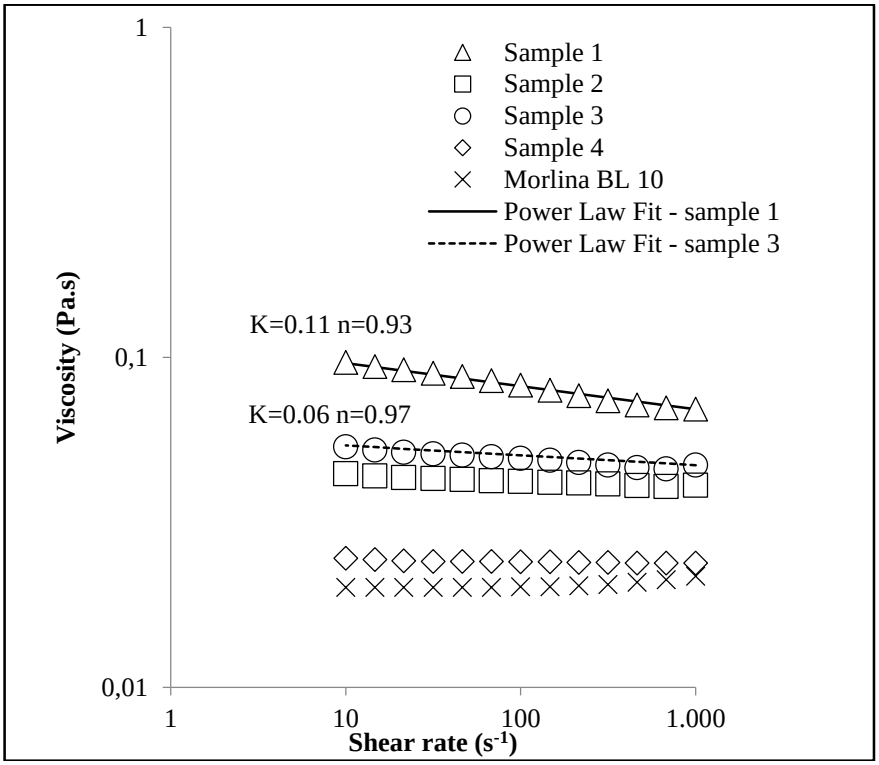


Figure 6. Viscosity profile from emulsions prepared at 20 wt % water cut, with 1 wt % surfactant (85 wt % Span 80 and 15 wt % AOT) at 20°C.

Emulsions with 30 % water cut (1 wt % surfactant) were measured at shear rates ranging from 1 to 100 s^{-1} in a double gap geometry, presenting shear thinning behavior. This sample fit to Herschel-Bulkley model. (Fig. 7)

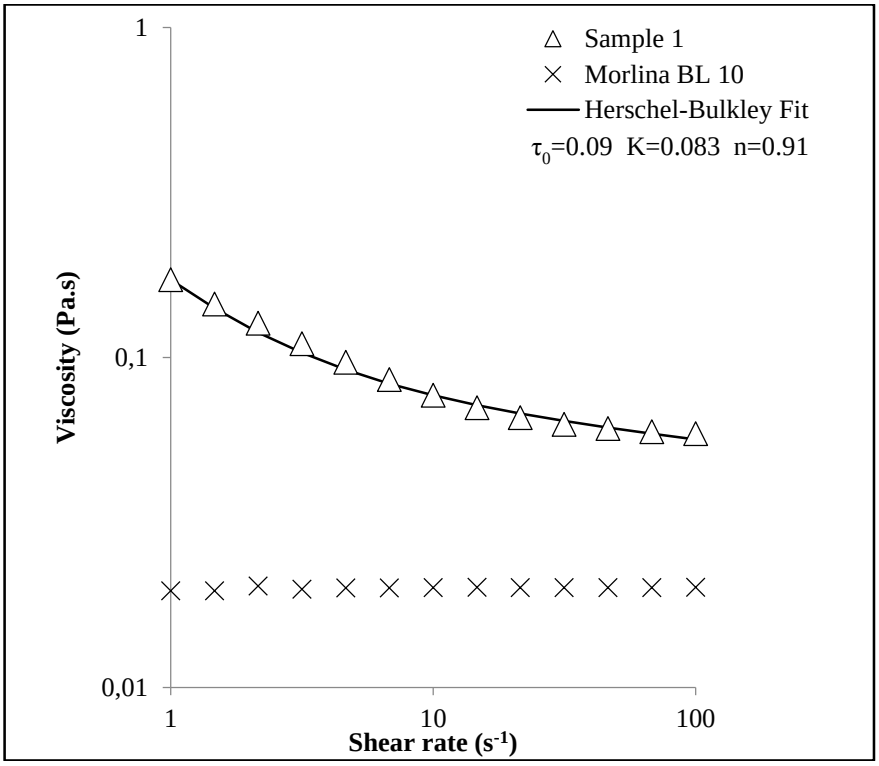


Figure 7. Viscosity profile from emulsion prepared at 30 wt % water cut, with 1 wt % surfactant (90 wt % Span 80 and 10 wt % AOT) at 20 °C.

Emulsions with 30 % water cut (5 wt % surfactant) were measured at shear rates ranging from 1 to 100 s^{-1} in a Couette geometry, presenting shear thinning behavior. Three different samples of the same emulsion were measured, showing different values of viscosity, but all of them following shear-thinning behavior. Sample 1 fit to Herschel-Bulkley model, while samples 2 and 3 fit to Power Law model. Although the mixture process is controlled with a high-speed homogenizer, there were difficult in adding AOT's solutions in the first minute of preparing, so this could explain the differences obtained.

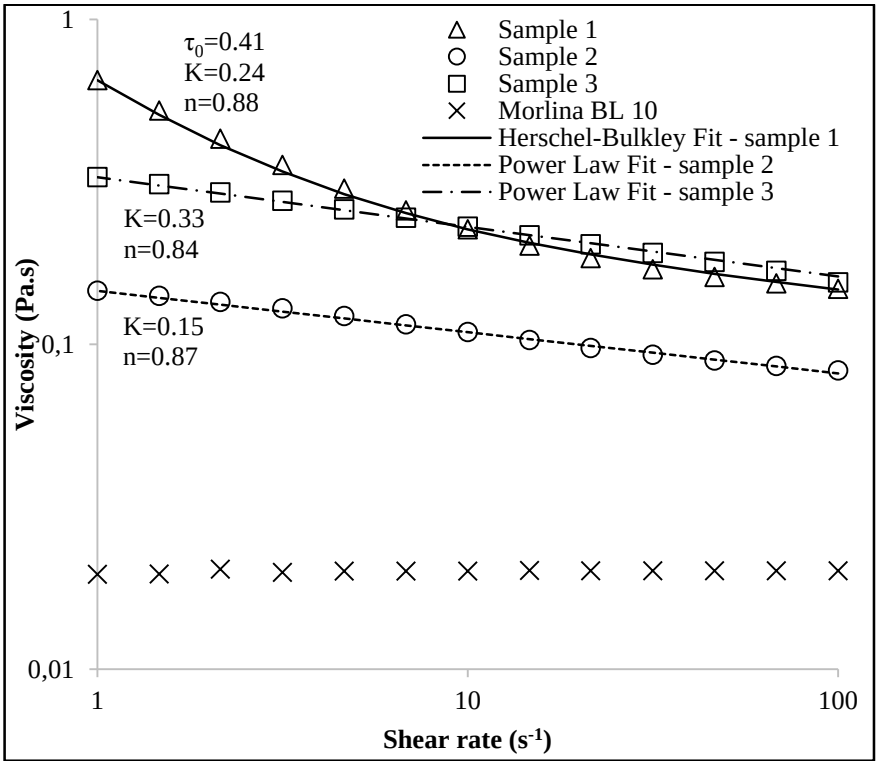


Figure 8. Viscosity profile from emulsions prepared at 30 wt % water cut, with 5 wt % surfactant (90 wt % Span 80 and 10 wt % AOT) at 20°C.

3. CONCLUSIONS

Emulsions with water cut ranging from 20 to 40 % have been prepared from mineral oil Morlina 10, mineral oil Morlina 150, Span 80, AOT and water. No mixtures prepared with Morlina 150 (by hand and with a high-speed homogenizer) formed water-in-oil emulsions. For all samples that were mixture with Morlina 10, only five of them formed w/o emulsion, as follow below:

- 20 % water cut, 1 wt % surfactant (85 wt % Span 80 and 15 wt % AOT), mixture by hand;
- 20 % water cut, 5 wt % surfactant (85 wt % Span 80 and 15 wt % AOT), mixture with a high-speed homogenizer;
- 30 % water cut, 1 wt % surfactant (90 wt % Span 80 and 10 wt % AOT), mixture with a high-speed homogenizer;
- 30 % water cut, 5 wt % surfactant (90 wt % Span 80 and 10 wt % AOT), mixture with a high-speed homogenizer;
- 40 % water cut, 1 wt % surfactant (90 wt % Span 80 and 10 wt % AOT), mixture with a high-speed homogenizer;

Rheological measurements performed on them show that the viscosity of the emulsion increases with the increasing of water cut. Rheological data also showed that, despite using the same water cut and surfactant blend, each sample's emulsion presented its own trend, what may be explain in some difficulties in adding AOT's solutions in the first minute of preparing. However, in the period of three days, visual observation confirmed that all w/o emulsions were stable against coalescence and drop test confirmed that they did not show phase inversion. Therefore, it should be said that they are suitable for posterior hydrates tests, once they remain as w/o systems.

4. REFERENCES

Daltin, Décio. "Tensoativos: Química, Propriedades e Aplicações. Editora Blucher, 2011.
Gen, Se. "Formulation of Emulsion Systems for the Preparation of Butyl Rubber Gloves". Université de Montréal. Canada. 2009.

ICI Americas Inc.. "The HLB SYSTEM a time-saving guide to emulsifier selection". Wilmington, Delaw.are. 1980.
Linares, Jose G. Delgado; Majid, Ahmad A. A.; Sloan, E. Dendy; Koh, Carolyn A.; Sum, Amadeu K.. "Model Water-in-Oil Emulsions for Gas Hydrate Studies in Oil Continuous Systems". Energy & Fuels. United States. 2012.
Lo, C.; Zhang, J. S.; Somasundaran, P.; Lu, S.; Couzis, A.; Lee, J. W. "Adsorption of Surfactants on Two Different Hydrates". United States. p. 12724-12726. 2008.
Peixinho, Jorge; Karanjkar, Prasad U.; Lee, Jae W.; Morris, Jeffrey F. "Rheology of Hydrate Forming Emulsions. Langmuir". 26 (14). United States. p.11699-11704. 2010.
Sloan, E. D.; Koh, C. A. - Clathrate Hydrates of Natural Gases. 3.ed. Boca Raton, FL. CRC Press. 758p. 2008
Yao, Hai-Yuan; Li, Qing-Ping; Chen, Guang-Jin; Gong, Jing. "An Experimental Investigation on Rheology of Condensate Oil/tetrahydrofuran Hydrate Slurry". Proceedings of the 7th ISOPE Ocean Mining Symposium. Lisbon. Portugal. July 1-6. 2007.

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