



## Influence of salt and HPAM on the emulsion stability and TOG

Vinicius Ferraz<sup>1\*</sup>, Paulo Rocha<sup>1</sup>, Edilson Silva<sup>1</sup>, Rita Nunes<sup>1</sup>, Michele Frota<sup>1</sup>, and Elizabete Lucas<sup>1,2</sup>

<sup>1</sup>Universidade Federal do Rio de Janeiro, IMA/LMCP, Rio de Janeiro, Brazil, \*vinicferraz@ima.ufrj.br

<sup>2</sup>Universidade Federal do Rio de Janeiro, COPPE/PEMM/LADPOL, Rio de Janeiro, Brazil

### Abstract

The formation of w/o emulsions is undesirable for the oil industry, as they directly impact extraction, transport and consequently the cost of oil production. Emulsions are heterogeneous systems, thermodynamically unstable, consisting of at least two immiscible liquids where one is dispersed as droplets within the other. Resins and asphaltenes are considered the main interfacially active natural components responsible for the stability of the emulsion. Nevertheless, other parameters can also affect such stability. In this work a sample of heavy oil was used to prepare w/o emulsions without and with 450 ppm of HPAM (partially hydrolyzed polyacrylamide) in brine and without and with 650 ppm of demulsifier in oil phase. The influence of the salts concentration on the stability of the w/o emulsions and on the TOG (total oil and grease) of the separated water was evaluated by bottle test and fluorimetry, respectively. The stability decreases as increasing the water content in the emulsion and the demulsifier concentration. Increasing salinity in the range of ~ 35,000 ppm and ~ 90,000 ppm, both emulsion stability and TOG of separated water decreased. HPAM and demulsifier provoked a decrease in the emulsion stability, although the effect of both together is not additive. HPAM provoked an increase in TOG of the separated water.

### Keywords

Water in oil emulsion; emulsion stability; total oil and grease

### Introduction

Approximately 80% of exploited oils are obtained as water in oil (w/o) emulsions [1]. The formation of w/o emulsions is undesirable for the oil industry, as they directly impact extraction, transport and consequently the cost of oil production [2, 3, 4]. The formation of an emulsion occurs by mixing two liquids that are immiscible. One of these liquids will be in the form of microdroplets suspended in the other component of the mixture. In a w/o emulsion, water (brine) will be found as microdroplets, suspended in the oil phase (petroleum). The oil phase impairs the mobility of the droplets, hampering droplets collision and the coalescence process. However, emulsions are thermodynamically unstable systems, so aqueous and oil phases tend to separate to reduce the interfacial area [4, 5, 6, 7]. This separation can take a long time, and it is not advantageous for the oil industry to wait for it, therefore demulsifiers are used to accelerate the emulsion destabilization [8, 9].

Considering that reservoirs present oils with different characteristics, it is necessary to study the factors that lead to the emulsions formation, to apply methods that destabilize them [4, 10, 11]. There are some factors that will impact the stability of w/o emulsions, such as: surface tension, oil composition, salt concentration, temperature, pH,

water content, oil and grease content, size and size distribution of droplets, speed and time of shearing, presence of solid particles, nanoparticles or amphiphilic polymers [1, 3, 7, 8, 12]. Regarding the crude oil composition, asphaltenes are considered the main responsible for the emulsions stability, as they form a resistant viscoelastic interfacial film at the water oil interface, hindering the process of droplet coalescence and making the emulsion more stable [4, 8, 13].

Water in oil emulsions, likewise, can be stabilized by salts, which are present in the formation water (connate water) or in the injected water (used in primary recovery). However, its effect generates contradiction among researchers. Some studies indicate that the increase in the salt concentration in the aqueous phase tends to destabilize it. On the other hand, there are data suggesting the stability due to the presence of salt in the aqueous phase [2, 11].

Another agent that can affect the stability of w/o emulsions is the amphiphilic polymers used for advanced oil recovery [4, 7]. This class of polymers promotes interaction between aqueous and organic environment, which may or may not contribute to the increasing of the emulsion stability [14, 15]. Depending on the water content, amphiphilic polymers can hinder the formation of emulsions. The most common amphiphilic polymer

used in enhanced oil recovery is the partially hydrolyzed polyacrylamide (HPAM) which is used due to its low cost and its thickening power, that provokes the increase in oil transport to the production well, consequently, increasing oil productivity [1, 4, 15, 16].

Due to the controversy in the literature and the difficulty to deal with heavy oils, this work aims to evaluate the influence of salt concentration on the stability of w/o emulsions and on the TOG (total oil and grease) of the separated water by using bottle test and fluorimetry, respectively. Moreover, the influence of the addition of HPAM and/or demulsifier was evaluated. All study was conducted using synthetic emulsions prepared with a heavy oil.

## Methodology

It was used an oil sample with 13.2 °API (by densimeter), water content of 2.8 w/t% (by Karl Fischer) and asphaltenes content (C71) of 12.9 w/t% (by oil precipitation in n-heptane and solubilization in toluene). Preliminarily, 20/80 and 40/60 w/o synthetic emulsions were evaluated in terms of stability by bottle test at 100 °C: the aqueous phase was prepared using brine at 55,000 ppm (NaCl: CaCl<sub>2</sub> 10:1), and without and with 450 ppm of HPAM; in the oil phase, the demulsifier concentration was varied (0, 50, 350 and 650 ppm). The second set of analyses were performed using 40/60 w/o emulsions: oil phase without and with 650 ppm of demulsifier; and aqueous phase without and with 450 ppm of HPAM, varying salinity as ~ 35,000 ppm, ~ 63,000 ppm and ~ 90,000 ppm using a mixture of salts. In these set of analyses, it was verified emulsion stability by bottle test and the TOG of the separated water was determined by fluorimetry.

## Experimental Procedure

### Preparation of synthetic w/o emulsions

Procedure established for w/o emulsion preparation using a heavy oil: (1) brine was previously prepared at room temperature and magnetic stirring for 30 minutes; (2) brine and oil were put in the oven for 30 min at 80 °C; (3) brine was slowly added in the oil under stirring with glass stick at room temperature; (4) the mixture was stirred in Polytron at 15000 rpm with external heating of 60 °C for 6 min.

### Bottle test

The fresh prepared w/o emulsion was poured into graduated conic glass flasks, which was put into the thermostatic bath until test temperature is reached. Then, the demulsifier was added using micropipette and the glass flask was shaken manually for 1 minute. After that, the glass flask was put into the thermostatic bath again and the test was started. For the first 30 min, at every 5 min the glass flask was removed from the bath and the volume of separated water was read. From 30 to 60 min test, the volume was read at every 10 min.

This generated a kinetic curve of percentage of separated water in function of time or simply the percentage of separated water at the end of the test, that is, after 60 min. The separated water was used to determine TOG.

### Determination of TOG by fluorimetry

To obtain enough amount of water for TOG determination, the bottle test was conducted in triplicate for the same system. At the end of the bottle test, the oil was removed from the conical tube using pipette and then the water was removed also using a clean pipette. Water separated from the three tests was mixed, and 45 mL were poured into a separation funnel, followed by the addition of 5 mL of n-hexane to proceed the oil extraction. After centrifugation, the organic phase was analyzed by fluorimetry (TD-3100, Turner Design) to determine TOG.

## Results and Discussion

### Preliminary results

As expected, it was observed that the emulsion with the highest water content (40/60) was the one with the lowest stability. As increasing demulsifier concentration the emulsion stability decreased: at 20/80 w/o, it was observed 0.0, 2.5, 10.5 and 15 % of separated water by the addition of 0.0, 50, 350 and 650 ppm of demulsifier, respectively; and at 40/60 w/o, it was observed 12.5, 37.5, 62.5 and 70 % of separated water by the addition of 0.0, 50, 350 and 650 ppm of demulsifier, respectively. The same effect was observed when the demulsifier was added to emulsions containing HPAM in the aqueous phase, that is, the emulsion stability decreased as increasing demulsifier concentration. The addition of 450 ppm of HPAM in the aqueous phase also influenced the emulsion stability, even without adding demulsifier: the percentages of separated water were 15.75 and 43.75 % for the 20/80 and 40/60 w/o emulsions, respectively. All emulsion stability tests presented in this section were performed using brine containing only NaCl:CaCl<sub>2</sub> (10:1) at 55,000 ppm.

### Influence of HPAM and salt on emulsion stability and TOG of separated water

To verify the influence of salt concentration on the emulsion stability and TOG of the separated water, brines with three different concentrations were used ~ 35,000 ppm, ~ 63,000 ppm and ~ 90,000 ppm using a mixture of salts. The test was carried out only for the 40/60 w/o emulsion without and with the addition of 650 ppm of demulsifier. These conditions were selected because they presented large volume of separated water without complete separation.

The influence of HPAM and demulsifier added together and individually, using as brine 55,000 ppm of NaCl:CaCl<sub>2</sub> (10:1), was confirmed for all brine concentrations using mixture of different salts.

Concerning the influence of brine concentration on the emulsion stability and TOG of separated water, it was observed a decrease of both as increasing the salinity in the range between ~ 35,000 ppm and ~ 90,000 ppm. Such behavior may be related to the salting out effect, that is, when the brine concentration increases, the phase separation is induced and the oil content in the water becomes lower, because it becomes more difficult to mix the oil in water containing ions.

TOG of separated water after bottle test was around 10 ppm when using only demulsifier (650 ppm of emulsifier) for all salinities tested (from ~35,000 to ~90,000 ppm). With the addition of 450 ppm HPAM, without adding demulsifier, the TOG was significantly influenced by the salinity of the brine: for 35,000 ppm of salts, TOG is close to 40 ppm, decreasing to ~14 ppm when using higher salinity (~90,000 ppm). The addition of HPAM (450 ppm) and demulsifier (650 ppm) together provoked a significant increasing in TOG, when compared with the addition of demulsifier and HPAM separately, in all salinities tested: at ~35,000 ppm of salts, the TOG values were 12.28, 41.27 and 55.31 ppm, respectively, with the addition of demulsifier, HPAM and demulsifier+HPAM; at ~63,000 of salts, the TOG values were 6.28, 17.63 and 29.85 ppm, respectively, with demulsifier, HPAM and demulsifier+HPAM; and, at ~90,000 ppm salts, the TOG values were 8.64, 14.22 and 32.70 ppm, respectively, with demulsifier, HPAM and demulsifier+HPAM.

## Conclusions

The increase in the demulsifier concentration (0, 50, 350 and 650 ppm) provoked a decrease in the emulsion stability without and with HPAM in brine (450 ppm). The addition of 450 ppm of HPAM in the aqueous phase, without adding demulsifier, decreased the emulsion stability.

It was observed a decrease of both, emulsion stability and TOG of the separated water, as increasing the salinity in the range between ~ 35,000 ppm and ~ 90,000 ppm. Such behavior may be related to the salting out effect.

TOG of the water separated after bottle test was around 9 ppm ( $\pm$  3 ppm) when using only demulsifier (650 ppm) for all salinities tested (from ~35,000 to ~90,000 ppm). With the addition of 450 ppm HPAM, without adding demulsifier, the TOG is significantly influenced by the salinity of the brine: for 35,000 ppm of salts, TOG is close to 40 ppm, decreasing to ~14 ppm when using higher salinity (~90,000 ppm). The addition of HPAM (450 ppm) and demulsifier (650 ppm) together provoked a significant increasing in TOG (55 ppm, 30 ppm and 32 ppm for salinities of 35,000 ppm, 63,000 ppm and 90,000 ppm, respectively), when compared with the addition of HPAM and demulsifier separately.

## Acknowledgments

We gratefully acknowledge the financial support of Equinor, FAPERJ (E-26/200.974/2021) and CNPq (303583/2019-3). We acknowledge the support of ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation.

## Responsibility Notice

The authors are the only responsible for the paper content.

## References

- [1] Kang, W.; Xu, B.; Wang, Y.; Li, Y.; Shan, X.; An, F.; Liu, J. *Colloids and surfaces A: Physicochemical and engineering aspects*. 384, 555-560, 2011.
- [2] Subramanian, D.; May, N.; Firoozabadi, A. *Energy & Fuels*. 31, 8967-8977, 2017.
- [3] Yang, F.; Tchoukov, P.; Pensini, R.; Dabros, T.; Czarnecki, J.; Masliyah, J.; Xu, Z. *Energy & fuels*. 28, 6897-6904, 2014.
- [4] Umar, A.A.; Saaïd, S.B.M.; Sulaimon, A.A.; Pilusubakar, R.B.M. *Journal of Petroleum Science and Engineering*. 165, 673-690, 2018.
- [5] Kilpatrick, P.K. *Energy & Fuels*. 26, 4017-4026, 2012.
- [6] Wong, S.F.; Lim, J.S.; Dol, S.S. *Journal of Petroleum Science and Engineering*. 135, 498-504, 2015.
- [7] Kamkar, M.; Bazazi, P.; Kannan, A.; Suja, V.C.; Hejazi, S.H.; Fuller, G.G.; Sundararai, U. *Journal of Colloid and Interface Science*. 576, 252-263, 2020.
- [8] Le Follotec, A.; Pezron, I.; Noik, C.; Dalmazzone, C.; Komunjer, L.M. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 365, 162-170, 2010.
- [9] Maia Filho, D.C.; Ramalho, B.V.S.; Lucas, G.M.S.; Lucas, E.F. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 405, 73-78, 2012.
- [10] Thomas, J.E.; Correia, A.C.; Xavier, J.A.D.; De Paula, J.L.; Pitombo, N.E.S.; Carvalho, R.S.; Barragan, R.V. *Fundamentos de Engenharia de Petróleo*. Interciência, Rio de Janeiro, 2001.
- [11] Oliveira, C.B.Z.; Souza, W.J.; Santana, C.F.; Santana, C.C.; Dariva, C.; Franceschi, E.; Guarnieri, R.A.; Fortuny, M.; Santos, A.F. *Energy & Fuels*. 32, 8880-8890, 2018.
- [12] Ghannam, M.T. *Petroleum science and technology*. 23, 649-667, 2005.
- [13] Hazrati, N.; Beigi, A.A.M.; Abdouss, M. *Fuel*. 229, 126-134, 2018.
- [14] Lu, Y.; Wu, H.; Meng, Z.; Jiang, J.; Jin, Y.; Deng, Z.; Su, W.; Li, Z.; Kang, W. *Colloid and Polymer Science*. 296, 515-527, 2018.
- [15] Yang, H.; Zhang, H.; Zheng, W.; Li, X.; Wang, F.; Li, X.; Zhang, D.; Turtabayev, S.; Kang, W. *Journal of Petroleum Science and Engineering*. 204, 108713, 2021.
- [16] Lucas, E.F.; Ferreira, L.S.; Khalil, C.N. *Aplicação de Polímeros na Indústria de Petróleo*. 2 ed. Rio de Janeiro, 2015.