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# Some Methods for Characterization of Crude Oil-Water Emulsions Breaking

Rebeka Bejczi*, Roland Nagy

University of Pannonia, Faculty of Engineering, Department of MOL Hydrocarbon and Coal Processing; Egyetem srt. 10., Veszprém, H-8200, Hungary
bejczi.rebeka@mk.uni-pannon.hu

Gas and petroleum recovery operations often produce oil-in-water (O/W) emulsions with varying stabilities. Analyzing the composition of these emulsions is crucial for subsequent crude oil processing, requiring effective flocculation and demulsification processes. The efficiency of emulsion breakdown is influenced by numerous factors. This study evaluated several commercially available flocculants by analyzing interfacial tension, zeta potential, and conducting phase separation tests. Our objective was to identify the most effective flocculant for the model emulsion system and determine the optimal dosing concentration.

## 1. Introduction

Demulsification and flocculation play pivotal roles in crude oil recovery from oil-in-water (O/W) emulsions in petroleum extraction. The stability of these emulsions in oil recovery processes is influenced by various factors. Notably, emulsion breaking stands as a critical process in the petroleum industry (Wong et al., 2015; Nagy et al., 2018).

Ortiz et al. employed sealed glass tubes containing 10 ml of crude oil emulsion mixed with graphene-based nanosheets. Following a 15-minute agitation period at room temperature, they measured the remaining oil content in the treated water using a UV–VIS spectrometer (Shimadzu UV2600). Demulsification efficiency in the treated water was then calculated using Equation (1) as follows:

$$E = \frac{(C_0 - C_i)}{C_0} * 100 \quad (1)$$

where E is the efficiency (%), $C_0$ and $C_i$ were the initial and residual oil content respectively in the treated water (ppm) (Ortiz et al., 2019, Liu et al., 2015).

Ye et al. (2022) produced stable water-in-oil (W/O) emulsions by homogenizing crude oil and deionized water. The process involved heating an iron cup containing 150 grams of crude oil and 350 grams of deionized water in a water bath set at 60°C for 20 minutes. These emulsions, with variations in pH and salinity, exhibited stability for several days. Demulsification efficiency was assessed by measuring the separated water volume (Ye et al., 2021).

In Li et al.'s (2018) investigation, the interfacial tension (IFT) between aged crude oil and a demulsifier solution was determined using a spinning drop interfacial tension meter. This measurement was conducted at a constant rotation speed of 8000 rpm and 70°C.

Nguyen et al. (2013) evaluated the apparent viscosity of synthetic emulsions using a Brookfield viscometer immediately after preparation. The measurements were performed at room temperature with a rotation speed of 100 rpm.

Onaizi et al. (2022) employed dynamic light scattering to analyze zeta potential and droplet size in formulated crude oil/water nanoemulsions. Measurements were conducted promptly after sonication to minimize potential aging effects on these characteristics, following Huang et al.'s (2019) recommendation.

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## 2. Materials and methods

### 2.1 Flocculants

Various types of flocculants, each with distinct chemical structures, were utilized for the tests. Detailed information regarding these flocculants, including their chemical compositions and characteristics, can be found in Table 1.

*Table 1: Data of flocculating agents*

| | F-1 | F-3 | F-3 |
|---|---|---|---|
| Components | poly aluminium chloride | flocculants mixtures | hydrolyzed polyacrylamide |
| Apperance | opalescent liquid | opalescent liquid | opalescent liquid |
| Density, g/cm³ | 1,24-1,30 | 1,01-1,15 | 1,02-1,10 |
| pH value | 2,5-3,5 | 6,5-7,5 | 7,0-8,0 |
| Solubility | good in water | partially in water | partially in water |

The flocculants were tested using different concentrations.

### 2.2 Preparation of model emulsion

To prepare the model emulsion, the initial step involved creating the model crude oil and model brine. The model crude oil consisted of 50/70 bitumen, n-heptane, and toluene, with a n-heptane to toluene ratio of 60:40 (v/v%). The concentration of bitumen in the model crude oil was maintained at 5 g/l. For the model brine, salts such as NaCl, $CaCl_2 \cdot 2H_2O$, $NaHCO_3$, and $CH_3COONa$ were dissolved in distilled water. The concentrations of these salts are summarized in Table 2.

*Table 2: Salt concentrations of the model brine*

| Salt | Concentration, g/l |
|---|---|
| NaCl | 0,5 |
| $CaCl_2 \cdot 2H_2O$ | 0,2 |
| $NaHCO_3$ | 2,6 |
| $CH_3COOHNa$ | 2,6 |
| Total (TDS) | 5,9 |

After preparing the model brine and model crude oil, a mixture of Na-dodecyl benzenesulfonate and coconut fatty acid diethanolamide in a 1:1 ratio was dissolved in 5 g/l of model brine. Subsequently, 6 g/l of 2-butoxyethanol was added to the solution. The resulting emulsion was a dispersion containing 10% (v/v) model crude oil and 90% (v/v) model brine containing surfactant.

### 2.3 Emulsion stability (Phase separation tests)

The experiments were carried out in graduated cylinders equipped with caps. Each cylinder contained 20 ml of the model emulsion. Various quantities of flocculant were introduced into the emulsion, followed by manual shaking of the cylinders. Subsequently, the samples were maintained at 40°C, and the separation of water and oil was examined at 15, 30, 45, and 60-minute intervals.

### 2.4 Determination of interfacial tension

The interfacial tension (IFT) between the aging model crude oil and an aqueous demulsifier solution was measured using a Spinning Drop Tensiometer (SDT) from Krüss. The demulsifier solution was added to the glass tube, and then, an oil droplet was injected into the center of the water phase. The experiment was conducted at a temperature of 25°C.

### 2.5 Determination of zeta potential and size

The zeta potential and size of the formulated model emulsion were measured using dynamic light scattering (DLS) technique. Specifically, these measurements were performed with a Zetasizer Nano ZS size analyzer from Malvern.

## 3. Results

Our investigations commenced with phase separation tests conducted at 40°C. The stability assessments were performed at 15, 30, 45, and 60-minute intervals, with the quantities of separated oil, emulsion, and water measured and expressed as volume percentages (v/v%). Flocculant concentrations ranged from 500 to 3000 ppm. Despite being time-consuming, we deemed the phase separation test as the most illustrative method for presenting our findings. The emulsion stability results are summarized in Table 3.

*Table 3: Investigation of the emulsion stability (O: oil, v/v%%, E: emulsion, v/v%, W: water v/v%)*

| Temperature | | 40°C | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flocculation time | | 15 min | | | 30 min | | | 45 min | | | 60 min | | |
| | | Phases (v/v%) | | | | | | | | | | | |
| Flocculant sign | Conc. (ppm) | O | E | W | O | E | W | O | E | W | O | E | W |
| F-1 | 500 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 |
| | 1000 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 |
| | 1500 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 |
| | 2000 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 5 | 50 | 45 | 5 | 50 | 45 |
| | 2500 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 5 | 50 | 45 | 5 | 50 | 45 |
| | 3000 | 2,5 | 75 | 22,5 | 2,5 | 75 | 22,5 | 5 | 50 | 45 | 5 | 50 | 45 |
| F-2 | 500 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 |
| | 1000 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 |
| | 1500 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 |
| | 2000 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 |
| | 2500 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 |
| | 3000 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 | 10 | 0 | 90 |
| F-3 | 500 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 |
| | 1000 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 |
| | 1500 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 |
| | 2000 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 |
| | 2500 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 |
| | 3000 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 | 0 | 100 | 0 |

The separation of the the emulsion with different flocculants after 15, 30, 45, and 60 minutes is depicted in Figures 1 to 3.

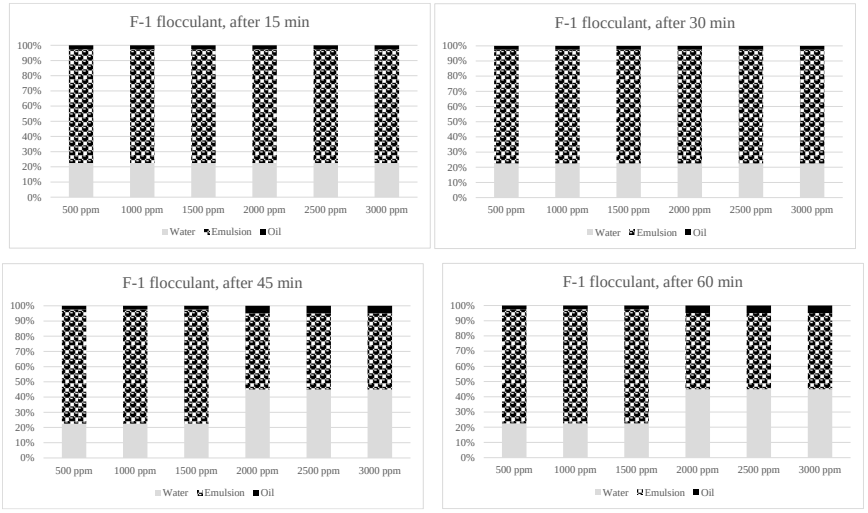


*Figure 1: The emulsion stability test with different concetration of F-1 flocculant*

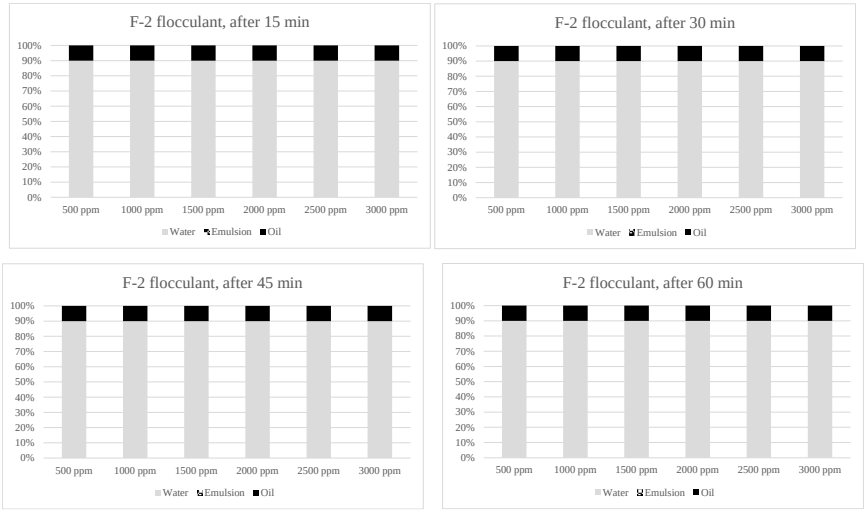


*Figure 2: The emulsion stability test with different concetration of F-3 flocculant*

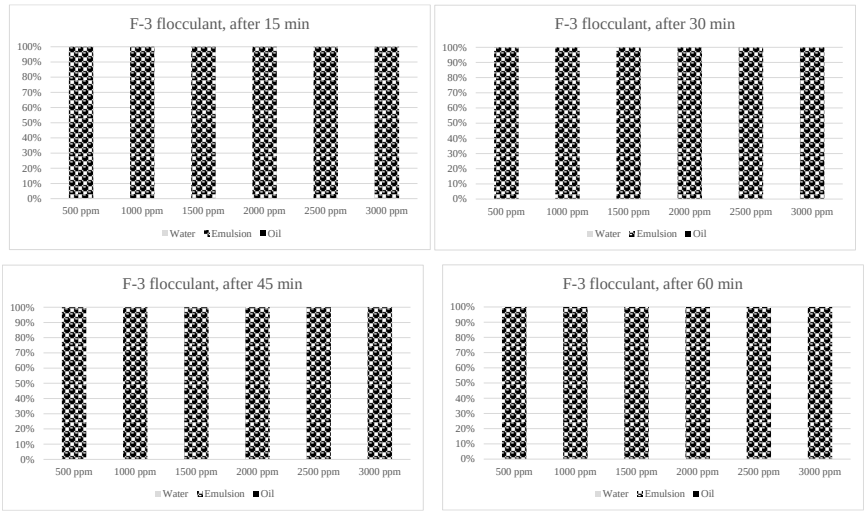


*Figure 3: The emulsion stability test with different concetration of F-5 flocculant*

It was observed that between 25-50% of the oil could be extracted after 60 minutes using the F-1 flocculant. Using the F-3 flocculant, all the crude oil had separated after 15 minutes. However, during the analysis of emulsion breakdown, the F-3 flocculant did not demonstrate effective separation of a minimal amount of oil. The interfacial tension results are shown in Table 4.

*Table 4: IFT values of applied flocculants*

| | IFT, mN/m | | | | | |
|---|---|---|---|---|---|---|
| Concetration (ppm) | 500 | 1000 | 1500 | 2000 | 2500 | 3000 |
| F-1 | 2,283 | 2,253 | 1,247 | 0,448 | 0,665 | 0,512 |
| F-3 | 1,436 | 0,826 | 0,778 | 0,166 | 0,155 | - |
| F-5 | 1,636 | 1,937 | 2,085 | 2,135 | 1,936 | 1,949 |

In Figure 4, the relationships between the interfacial tension of the flocculants and their concentrations are presented.

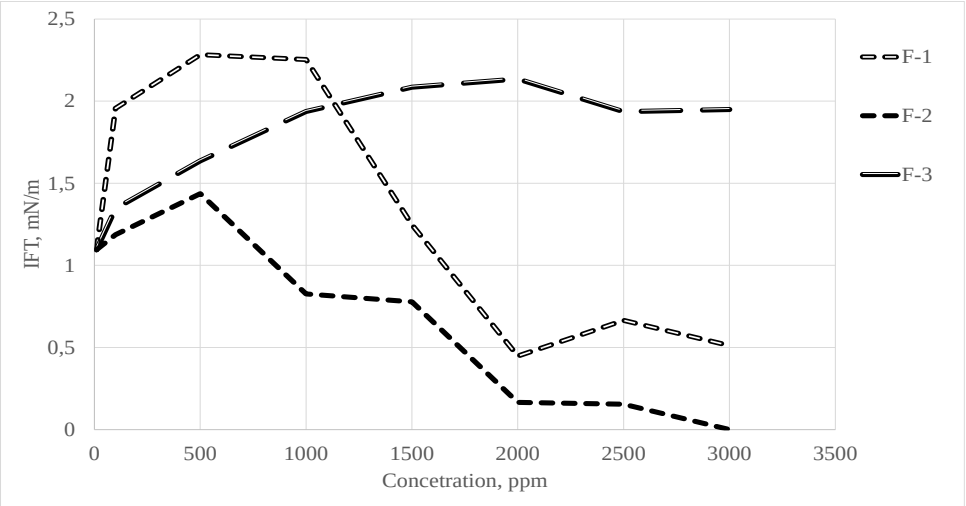


*Figure 4: IFT values of applied flocculants*

Based on the interfacial tension (IFT) results, it was determined that the flocculants 5abelled as F-1 and F-2 exhibited values below 0.65 mN/m at concentrations exceeding 2000 ppm. As a result, flocculants F-1 and F-2 were considered effective in reducing interfacial tension. Among them, flocculant F-2 demonstrated the lowest IFT value.
The zeta potential of the emulsion results are shown in Table 5.

*Table 5: Zeta potential of the emulsion using different flocculants*

| | ZP, mV | | | | | |
|---|---|---|---|---|---|---|
| Concetration (ppm) | 500 | 1000 | 1500 | 2000 | 2500 | 3000 |
| F-1 | -35 | -23,2 | -24 | -23,8 | -32,3 | -28,2 |
| F-3 | -24,8 | -71,9 | -38,3 | -35,4 | -47,1 | -29 |
| F-5 | -57,6 | -29,4 | -53,2 | -80,6 | -16,2 | -14,7 |

Figure 5 illustrates the relationship between the zeta potential of flocculants and their concentration in the emulsion.

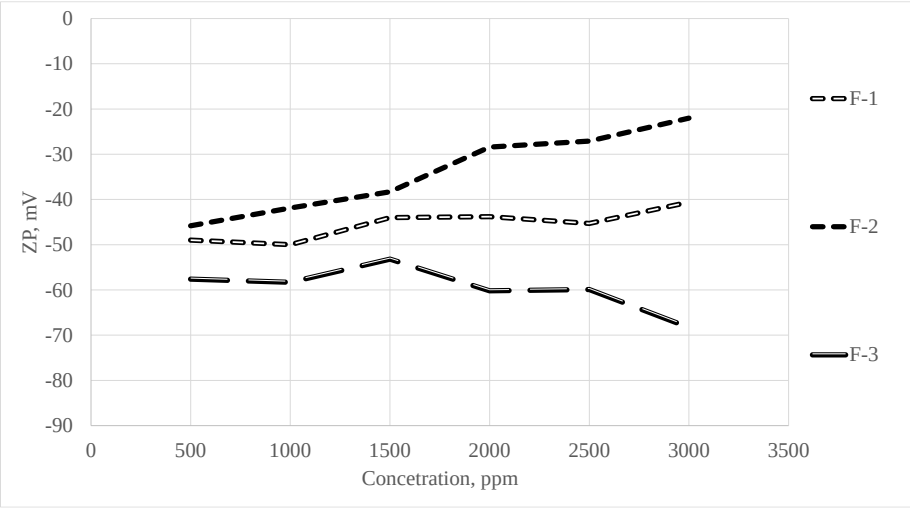


*Figure 5: Zeta potential of the emulsion using different flocculants.*

Based on the zeta potential results, flocculants labeled as F-1 and F-2 were found to be effective for the emulsion. Based on the conducted examinations, the F-2 flocculant was identified as the most effective at a concentration of 2000 ppm. The zeta potential value was found to be suitable for determining the optimal dosing concentration of flocculants during flocculation.

## 4. Conclusions

During gas and petroleum recovery, different stability oil-in-water (O/W) emulsions are produced. Achieving the separation of these emulsions is typically accomplished through flocculation and subsequent demulsification processes. Our objective was to investigate the breaking of crude oil-water emulsions, and we presented methods for characterizing demulsification and flocculation processes. The new experimental results can be summarized as follows:

- Stability tests were conducted at 40°C, and the results were recorded at 15, 30, 45, and 60 minutes to determine the quantities of separated oil, emulsion, and water. Based on the phase separation tests, it was found that the F-2 flocculant was the most effective.
- Interfacial tension values of the flocculants were determined, and the F-2 flocculant exhibited the lowest interfacial tension (IFT) value.
- The zeta potential value was found to be suitable for determining the optimal dosing concentration of flocculants during flocculation.
- The presented and applied methods were found to be suitable for assessing the effectiveness of flocculating agents in breaking emulsions.
- Based on the conducted examinations, the F-3 flocculant was identified as the most effective at a concentration of 2000 ppm.

This study makes an important contribution to improving the efficiency of various gas and petroleum recovery processes.

### References

Huang, B., Li, X., Zhang, W., Fu, C., Wang, Y., & Fu, S. (2019). Study on demulsification-flocculation mechanism of oil-water emulsion in produced water from alkali/surfactant/polymer flooding. Polymers, 11(3), 395

Li, Z., Geng, H., Wang, X., Jing, B., Liu, Y., & Tan, Y. (2018). Noval tannic acid-based polyether as an effective demulsifier for water-in-aging crude oil emulsions. Chemical Engineering Journal, 354, 1110-1119.

Liu, J., Li, X., Jia, W., Li, Z., Zhao, Y., & Ren, S. (2015). Demulsification of crude oil-in-water emulsions driven by graphene oxide nanosheets. Energy & Fuels, 29(7), 4644-4653.

Nagy, R., Lendvai, P., Kothencz, R., & Bartha, L. (2018). Application of the HLD Value in the Petroleum Industry. Papers on Technical Science, 9, 175-178.

Nguyen, D., & Balsamo, V. (2013). Emulsification of heavy oil in aqueous solutions of poly (vinyl alcohol): A method for reducing apparent viscosity of production fluids. Energy & fuels, 27(4), 1736-1747.

Onaizi, S. A. (2022). Effect of salinity on the characteristics, pH-triggered demulsification and rheology of crude oil/water nanoemulsions. Separation and Purification Technology, 281, 119956.

Ortiz, S. N. C., Cabanzo, R., & Mejia-Ospino, E. (2019). Crude oil/water emulsion separation using graphene oxide and amine-modified graphene oxide particles. Fuel, 240, 162-168.

Ye, F., Mi, Y., Liu, H., Zeng, G., Shen, L., Feng, X., ... & Yan, X. (2021). Demulsification of water-in-crude oil emulsion using natural lotus leaf treated via a simple hydrothermal process. Fuel, 295, 120596.

Ye, F., Zhang, Z., Ao, Y., Li, B., Chen, L., Shen, L., ... & Mi, Y. (2022). Demulsification of water-in-crude oil emulsion driven by a carbonaceous demulsifier from natural rice husks. Chemosphere, 288, 132656.

Wong, S. F., Law, M. C., Samyudia, Y., & Dol, S. S. (2015). Rheology study of water-in-crude oil emulsions. Chemical Engineering Transactions, 45, 1411-1416.