Optimization of non-ionic surfactants for removing emulsified oil from gas condensate oil–water emulsion in N oilfield

Peng Lv1 · Yigang Liu1 · Yunbao Zhang1 · Limei Sun2 · Xianxing Meng3 · Xianghai Meng1 · Jian Zou1

Received: 4 February 2020 / Accepted: 30 June 2020 / Published online: 7 July 2020
© The Author(s) 2020

Abstract
The aim of the present study was to obtain effective and economical chemical agents for treatment of oily water from N oilfield. Component characterization of crude oil from N oilfield was carried out with gas chromatography–mass spectrometry. Optimization of non-ionic surfactants combined with dissolved air flotation (DAF) for oil removal was investigated. The results show that the crude oil consisted of nine major components which counted for 96.4% of the total composition, and the first four compounds made up 50% of the total composition. For the first four compounds, the density difference between water and each individual compound is smaller than the difference between water and normal alkanes with the same number of carbon atoms, while the solubility of these four compounds in water is greater than that of normal alkanes with the same number of carbon atoms. The characteristic of both density and solubility of the crude oil increased the oil water separation difficulty in DAF progress. The oil content in oily water from N oilfield without any treatment was 5285.95 mg/L. The oil content after treatment of DAF without any chemicals was 895.53 mg/L. Non-ionic surfactants NIS1, NIS2 and NIS3 all were effective for removing emulsified oil in oily water in DAF progress. 1200 mg/L NIS1 combined with DAF was the optimized formulation by the view of efficiency and economy. The formulation could be successfully used as a commercial product in N oilfield.

Keywords Oily water · Crude oil · Emulsified oil · Non-ionic surfactants · GC–MS

Introduction
Oily water is produced in the petroleum industry process, such as drilling, oil recovery, oil gathering and transportation and oil refining. Since unqualified oily water generates pollution to surface and underground, discharging oily water is getting more and more attention (Abdol et al. 2008). Oily water is a special liquid-in-liquid colloidal dispersions classified as O/W emulsions (Raya et al. 2020). The dispersion, aggregation (Mozaffari et al. 2015) and the adsorption (Darjani et al. 2017) phenomenon are the main aspects which related the colloidal kinetic stability. Generally, the solids (Darjani et al. 2019; Mozaffari et al. 2016a, b, 2019), surfactants or functional molecules such as asphaltenes and resins are contributed to the stabilized emulsion (Raya et al. 2020). As an O/W emulsions in a specific oilfield, the factors affecting its stability include the pH of the wastewater, the temperature, the oil/water content, functional molecules such as asphaltenes and resins, solid content and the kind and concentration of the surfactant. These factors mainly affect the interfacial tension between the oil and water, and the thickness and rheological property of interfacial film (Mozaffari 2015; Mozaffari et al. 2016a, b). The efficient and cost-effective methods for oily water treatment have been focused on to satisfy the stringent regulatory standards implemented in different countries (Ahmadun et al. 2009; Masuelli et al. 2009; Nandi et al. 2010; Amani and Kariminezhad 2016; Lv et al. 2017; Klymenko et al. 2017; Huang et al. 2018; Darvishzadeh et al. 2018; Nguyen et al. 2019; Thaís et al. 2019). DAF combined with chemicals is effective to remove low-density particles from oily water (Leonie and Sarubbo 2018). Generally, it is believed that chemical pretreatment is essential for a high efficiency in
DAF (Al-Sabagh et al. 2015; Leonie and Sarubbo 2018). Non-ionic surfactants were often used in oily wastewater treatment (Abedi and Nekouei 2011; Zhang et al. 2014; Souza et al. 2017), especially for removal of emulsified oil from gas condensate oil–water emulsion (Al-Sabagh et al. 2015). Certain characteristic properties of non-ionic surfactants for instance, its non-volatility, temperature and environment-friendly surfactant (Sarmah et al. 2020) and stable at high salinity (Lawson 1978) make it more efficient and feasible for field application.

Gas condensate oil reservoirs are an important source of oil and gas supply in China. The work for removing emulsified oil from gas condensate oil–water emulsion from N oilfield is important and necessary to satisfy the stringent regulatory standards implemented in China. In order to obtain effective and economical chemical agents for treatment of oily water from N oilfield, the paper studied the effects of oil composition and its characteristics (density, solubility) on removing emulsified oil from gas condensate oil–water emulsion for the first time. The component characterization of N oilfield crude oil was carried out with gas chromatography–mass spectrometry. The density and solubility in water for some components were figured out to explain the extreme difficult for oil removal. Optimization of non-ionic surfactants combined with DAF for oil removal was investigated.

Materials and instruments

Artificial brine

The composition of formation brine in N oilfield is shown in Table 1. The artificial simulation water based on the composition of the formation brine in N oilfield was prepared and used for preparing the simulated solution in this research.

Dehydrated crude oil

The dehydrated crude oil from N oilfield was used as the oil phase in the oil–water emulsion. The density of dehydrated crude oil at 56 °C was measured by DMA 45 densitometer made by Anton Paar Company, Austria. The density of the oil is 0.8571 g/cm³ at 56 °C.

Chemicals

The chemicals used in the experiment such as NaOH (≥ 99.5%), NaHCO₃ (≥ 99.5%), Na₂CO₃ (≥ 99.5%), NaCl (> 99.5%), KCl (> 99.5%), CaCl₂ (> 96%), MgCl₂·6H₂O (> 99%) and n-Hexane (> 99.5%) are provided by Beijing Modern East Fine Chemical Co..

Non-ionic surfactants: NIS₁, NIS₂ and NIS₃.

Instruments

Gas chromatography–mass spectrometry (GC–MS) 7890B-5977 (Agilent Technologies Inc., USA), TD-500D Oil Analyzer (Turner Designs, USA) and WPB05 Waring Blender (Waring Commercial, USA) were hired in experiments. Dissolved air flotation instrument was a self-made device. The parameters (e.g., chemical concentration, feed rate and working pressure) effecting on the flotation efficiency for removing of the oil can be adjusted by the experimenter.

Experiments

Gas chromatography–mass spectrometry of crude oil

Component characterization of N oilfield crude oil was carried with GC–MC.

GC conditions

The oven temperature was programmed from 80 °C (isothermal for 3 min), with an increase of 5 °C/min, to 230 °C (isothermal for 1 min), then 4 °C/min to 280 °C, ending with a 4 min isothermal at 280 °C. The temperature of the injector was 250 °C. Helium was the carrier gas, and split ratio was 20:1.

MC conditions

The spectrometers were operated in electron-impact (EI) mode, the scan range was 20–600 amu, the ionization energy was 70 eV and the scan rate was 3.8 scan/s. The ionization source temperature was 230 °C, and the solvent delay was 2 min.

| Ions          | K⁺+Na⁺ | Ca²⁺  | Mg²⁺  | CO₃²⁻ | HCO₃⁻ | SO₄²⁻ | Cl⁻   | Total  |
|---------------|--------|-------|-------|-------|-------|-------|-------|--------|
| Concentration (mg/L) | 2288.12 | 28.74 | 55.48 | 227.7 | 1314.99 | 117.34 | 2620.24 | 6652.62 |
Oil removal from oily water

Similar to the experimental method in previous studies (Lv et al. 2017), the oil was extracted from oily water with n-Hexane and then measured by TD-500D oil analyzer to get oil content for individual oily water. The oil content for oily water from N oilfield without any treatment, for that from treatment of DAF without any chemicals, and for that from treatment of DAF combined with chemicals was measured, respectively. The effect of three non-ionic surfactants (NIS1, NIS2 and NIS3) with the same concentration of 600 mg/L on removing the emulsified oil in the DAF progress was studied. The concentration influence of the best surfactant on removing the emulsified oil was studied with different concentration (600 mg/L, 800 mg/L, 1000 mg/L, 1200 mg/L and 1500 mg/L).

Artificial brine and N oilfield crude oil were used to prepare oily water. The artificial brine and dehydrated N oilfield crude oil were heated in a water bath at 56 °C, respectively. Initial artificial oily water was prepared by adding crude oil to the artificial brine according to the oil content predetermined above, and then the mixture was blended at 5000 r/min for 15 min in waring blender shear emulsifier.

Feed rate, pH for oily water and working, pressure in DAF progress were 50 ml/s, 6 and 0.2 MPa, respectively, according to previous optimization. The non-ionic surfactants with different concentrations for removal of oil from oily water were performed in DAF progress by adding surfactants to oily water before DAF started working. The oily water was kept in DAF tank for 10 min before samples were taken for analysis. 15 milliliters of clarified water were collected from the middle layer, which is between the float layer and 10 cm above the base.

Results and discussion

Components of crude oil

The GC–MC spectrometry of crude oil was shown in Fig. 1. The retention time, peak area, the name of the compound and the molecular formula of the main compounds of crude oil were shown in Table 2.

The GC–MS analysis result showed the crude oil consisted of nine major components which counted for 96.4% of the total composition: toluene, 2-methylnaphthalene, naphthalene, trimethylbenzene, 1,4-xylene, 1-methylnaphthalene, 1,4-xylene, 1-methylnaphthalene, 1,4-xylene, and n-Dodecane.
n-dodecane, n-tetradecane and n-Pentadecane with proportion of 20%, 14%, 12%, 10.4%, 10%, 9%, 7%, 7% and 7%, respectively.

**Oil content of oily water before and after DAF without any chemicals**

Oil content of oily water from N oilfield before and after DAF without any chemicals was 5285.95 mg/L and 895.53 mg/L, respectively, while the later one can’t meet the requirement prescribed by the People’s Republic of China (PRC) (Lv et al. 2017). Obviously oil–water separation was hard, which can be explained from the oil density and solubility of oil in water.

The density and solubility for the first four compounds in N oilfield crude oil and normal alkanes with the same number of carbon atoms as comparison were shown in Table 3.

First, Table 3 shows the density of each compound is larger than that of each relative normal alkane with the same number of carbon atoms, so for the first four compounds which make up 50% of the total composition, the density difference between water and each individual compound is smaller than the difference between water and normal alkanes with the same number of carbon atoms. Since density difference is an important parameter affecting oil–water separation as discussed by Adewunmi (2019), the remarkable density difference between N oilfield oil and water enhanced the oil–water separation difficulty in DAF progress, which is consistent with Murakami’s work (Murakami et al. 2014). Reduced density difference between oil–water phases helps to prevent oil droplet as well as air–water surface and oil droplet from coalescence, and vice versa (Adewunmi 2019).

Second, oil can exist as free, dispersed, emulsified or soluble form in oily water. The removal methods and difficulty of these four kinds of oil are obviously different. Free oil is non-dispersed and floats on the surface, which can be skinned off. Non-emulsified dispersed oil can be removed by gravity separation (Li et al. 2015). The first two kinds of oil were removed in DAF progress without any chemicals. The removal of dissolved oil is difficult, and the commonly used methods are membrane separation method, adsorption method and biological method (Qiang 2012). It can be seen from Table 3 that the solubility of these four compounds in water is greater than that of normal alkanes with the same number of carbon atoms. The solubility properties of these four compounds enhanced the oil–water separation difficulty in DAF progress. The emulsified oil was the main target of the DAF process with chemicals (Takahashi et al. 1979). Through the combined use of DAF and chemical agents, the emulsified oil in the water is removed and the oil content in the water is reduced as much as possible.

**Non-ionic surfactants removing emulsified oil**

Effect of three non-ionic surfactants (NIS₁, NIS₂ and NIS₃) with the same concentration of 600 mg/L on removing emulsified oil in DAF progress was shown in Table 4.

According to the result in Table 4, among three surfactants, NIS₁ with 600 mg/L could get a lowest residual oil content of 69.6 mg/L, which was still higher than 10 mg/L prescribed by PRC (Lv et al. 2017).

| Chemicals                      | Chemical formula | Density (g/mL) | Solubility in water (g/100 ml, 25 °C) |
|--------------------------------|------------------|----------------|---------------------------------------|
| Toluene                        | C₆H₆             | 0.8623 (25 °C) | 5.19E−02                              |
| Neohexane                      | C₆H₁₄            | 0.6444 (25 °C) | 3.32E−03                              |
| 2-Methylnaphthalene            | C₁₃H₁₀           | 1.0058 (20 °C) | 2.50E−03                              |
| Hendecane                      | C₁₁H₂₂           | 0.7402 (20 °C) | 2.42E−04                              |
| Naphthalene                    | C₁₀H₈            | 1.1620ₜ (20 °C) | 7.00E−08                             |
| Decane                         | C₁₀H₂₂           | 0.7300² (20 °C) | 1.50E−06                             |
| Trimethylbenzene               | C₉H₁₂            | 0.8652ₜ (20 °C) | 7.00E−03                             |
| Nonane                         | C₉H₂₀           | 0.7176ₜ (20 °C) | 1.70E−05                             |

Data without any symbol from Haynes (2016); Data with the triangle symbol (△) from “Hazardous Substances Data Bank” which obtained from the National Library of Medicine (US); Date with the square symbol (□) from Fengjun et al. (2008); Date with the star symbol (*) from Kirss et al. (2008)

| Non-ionic surfactants | Emulsified oil (mg/L) | DAF treatment | DAF treatment without any chemical |
|-----------------------|-----------------------|--------------|-----------------------------------|
| NIS₁                  | 69.6                  | 895.53       |                                    |
| NIS₂                  | 136.5                 |              |                                    |
| NIS₃                  | 101.8                 |              |                                    |
Non-ionic surfactants were often used in oily wastewater treatment (Abedi and Nekouei 2011; Zhang et al. 2014; Souza et al. 2017). These non-ionic surfactants modified the liquid/liquid and liquid/air surface properties, and served to decrease the interfacial tension between the dispersed oil phase and the oily water, and to increase the interfacial tension between the air bubbler and the oil phase. Consequently, non-ionic surfactants were effective for removal of emulsified oil in oily water in DAF progress (Al-Sabagh et al. 2015). Dai and Zhao (2018) suggested a mechanism to explain the effect of surfactants on oil–water separation, in which the surfactant molecular can replace the original adsorption film, and weaken its protection on the surface of oil droplets, make oil droplets easier to aggregate to form oil layer, and be separated from wastewater finally.

The influence of $NIS_1$ concentration on oil removal is shown in Fig. 2.

With the increase in $NIS_1$ concentration from 400 to 1200 mg/L, the residual emulsified oil content was decreased significantly from 70 to 9.6 mg/L, the latter of which can meet the requirement prescribed by PRC similar to the previous results (Lv et al. 2017). More increase of $NIS_1$ concentration only generates minor change of oil content from 8.1 to 6.5 mg/L, so 1200 mg/L $NIS_1$ was the optimized formulation for emulsified oil removal from N oilfield oily water. The effect of surfactant concentration on the residual emulsified oil content was similar to study of Mhatre et al. (2018). Mhatre studied the effect of various chemical demulsifiers to the electrocoalescence process in emulsion which determined the stability of the emulsion. They found the chemical agent gave a tremendous effect to the stability of the emulsion at the first phase. They also pointed out that demulsifiers contain concentration limit. Because when the concentration of demulsifiers reached certain value, the raising of the demulsifiers concentration did not enhance the electrocoalescence process. 1200 mg/L was the critical point of concentration in this paper which was similar to the concentration limit in the study of Mhatre.

### Conclusion

1. Based on the GC–MS analysis, the crude oil consisted of nine major components which counted for 96.4% of the total composition, and the first four compounds made up 50% of the total composition.

2. For the first four compounds, the density difference between water and each individual compound is smaller than the difference between water and normal alkanes with the same number of carbon atoms, while the solubility of these four compounds in water is greater than that of normal alkanes with the same number of carbon atoms. The characteristic of both density and solubility of the crude oil increased the oil–water separation difficulty in DAF progress.

3. Oil content of oily water from N oilfield before and after DAF without any chemicals was 5285.95 mg/L and 895.53 mg/L, respectively, while the later one can’t meet the requirement prescribed by PRC.

4. Among three surfactants, $NIS_1$ with 600 mg/L could get a lowest residual oil content, and 1200 mg/L $NIS_1$ was the optimized formulation for emulsified oil removal from N oilfield oily water.

### References

Abdol HR, Kassim WM, El HA, El-Jawashi SA (2008) Risk assessment and remediation suggestion of impacted soil by produced water associated with oil production. Environ Sci Technol 145(3):95–102

Abedi S, Nekouei F (2011) Removal of direct yellow 12 from water samples by cloud point extraction using triton x-100 as nonionic surfactant. J Chem 8(4):1588–1595
