CHEMICAL ENGINEERING TRANSACTIONS
VOL. 110, 2024
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Marco Bravi, Antonio Marzocchella, Giuseppe Caputo

ISBN 979-12-81206-10-6; **ISSN** 2283-9216
DOI: 10.3303/CET24110023

Study on Surfactants Based on Vegetable Oil by Emulsification Effect

Roland Nagy[a,*], Máté Hartyányi[a], László Bartha[a], Sándor Puskás[b]

[a]Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, H-8200 Veszprém, Hungary
[b]Oilfield Chemicals and Technologies, MOL Plc, H-6701 Szeged, Hungary
nagy.roland.dr@mk.uni-pannon.hu

Nowadays, the crude oil demand increasing with the growing the energy and plastic product demand, nevertheless the crude oil stocks are finite. The main part of crude oil content in reservoir in not recoverable with commercial recovery methods (primary and secondary). Widespread method of enhancing the crude oil production recovery is the tertiary crude oil recovery where many times use chemical agents. One of these methods when surfactants and surfactant mixtures are used in polymer-surfactant flooding. In this case the effective surfactant selection is required. An important step of the selection is the investigation of emulsification effect.
There are lot of variable and human factor in the classic manual emulsifying effect measurements what can cause mistakes. Our aim was decreasing the possible inaccuracy. To achieve this goal, the standardised (ISO 6611 and ASTM D1401) application in crude oil – surfactants – brine system was investigated, what used in case of crude oil derivatives. Surfactants/surfactant mixtures based on vegetable oil was used to investigate the emulsifying effect with the classic manual method and a new automated method. These results were compared and the conclusions to applicability the automatic method in surfactant selection was drew.

1. Introduction

Nowadays, as demand for energy and various plastics increase, so does the demand for crude oil, while the world's oil reserves are limited. With conventional (primary and secondary) oil recovery methods, a significant portion of the oil in the reservoirs cannot be recovered. The so-called enhanced oil recovery methods, one of the variants of which is the use of chemical auxiliaries, are becoming more and more widespread to increase oil production and its efficiency. These methods include surfactant-polymer flooding by using different surfactants, also known as surfactants/surfactant mixture, therefore the effective selection of the used surfactants is essential for their development (Rellegadla et al. 2017; Green and Willhite 1998).
Surfactants are special materials whose molecular structure can be divided into two functional groups according to their solubility. They contain a polar (hydrophilic) group, which may be ionic or nonionic, and an apolar (hydrophobic or lipophilic) group. These molecules adsorb at the water-oil interface and form micelles above the critical micelle formation concentration (Olajire 2014; Malahov et al. 2022; Schram 2009). The purpose of the surfactants used is to greatly reduce the interfacial tension and forming emulsion between the crude-brine and thereby increase the capillary number (Farooq et al. 2021; Luan et al. 2022).
One of the proposed key oil recovery enhancement mechanisms during chemical flooding is the emulsification and carryover of crude oil with the injected aqueous surfactant solution (Adil and Onaizi 2022). The formulation of ex-situ emulsions and their subsequent injection into oil wells have started to gain research interest, and the few published studies in this regard have reported better oil recovery using the ex-situ emulsions (Jalilian et al. 2019; Mandal et al. 2010).
The experiments were conducted in closed glass tubes with lids by Ortiz et al. (2019). These tubes contained 10 ml of crude oil emulsion and a certain amount of graphene oxide and amine-modified graphene nanosheets.

Paper Received: 02 March 2024; Revised: 26 April 2024; Accepted: 19 May 2024
Please cite this article as: Nagy R., Hartyányi M., Bartha L., Puskás S., 2024, Study On Surfactants Based On Vegetable Oil By Emulsification Effect, Chemical Engineering Transactions, 110, 133-138 DOI:10.3303/CET24110023

They were shaken for 15 minutes in an orbital shaker at room temperature. The residual oil content in the treated water was determined by absorbance using a UV–VIS spectrometer (Shimadzu UV2600) (Ortiz et al. 2019). Halim et al. performed formation and observation of emulsion stability by bottle test for each crude oil is performed in the lab following the inhouse standardized protocol (Halim et al. 2023):

- Place 50 cm^3 of crude oil (dehydrated by centrifugation) and 50 ml of laboratory grade DI water (with pH adjusted to 8.0 using weak sodium hydroxide solution and warmed to 60 °C) in a 100 ml centrifuge tube.
- Shaking the test tube in a vortex mixer devise for 1 min to create homogeneous emulsion.
- Place the test tube in a water bath maintained at 60 °C.
- Visually observe, photograph and physically record volume of emulsion left at 3, 5, 10, 15, 20, 30, 40, 50, and 60 min.

The tests aimed to explore the possibility of improving the measurement method and investigate the quality and quantity of emulsions prepared with surfactants used in enhanced oil recovery (EOR) with an automatic device for the characterization and selection of surfactants for petroleum industrial applications. The emulsifying effect and the phase behaviour test as a function of mixing time and mixing speed were investigated for crude oil-brine-surfactant systems.

2. Materials and methods

2.1 Crude oil

Crude oil from the Algyő (Hungary) oil field was used as the oily phase. The key properties of this crude oil are summarized in Table 1.

Table 1: The most important properties of the crude oil used for the tests.

Property	Value
Density, g/cm^3 (d^{25}_4)	0.8242
API density	38.7
Dynamic viscosity, mPas (25 °C)	45.0
Kinematic viscosity, mm^2/s (25 °C)	51.5
Kw (Watson)	12.8
Characteristic	Paraffinic
Approx. mean average boiling point (°C)	410

Based on the values presented in the table, the crude oil used for the tests was considered to be a light, paraffinic crude oil.

2.2 Brine

Synthetically produced brine was used as the aqueous phase for the experiments which were based on the brine of the Algyő (Hungary) oil field. The ion concentrations of synthetic brine are summarized in Table 2.

Table 2: Composition analysis of the synthetic brine.

Parameter	Value (ppm)
Na^+	1638
Ca^{+2}	72
Cl^-	431
HCO_3^-	1888
CH_3COO^-	1870
TDS	5900

Each of the salts used to produce the brine was a technical grade, water-free salt. The salts were dissolved individually and each solution was mixed, firstly the sodium salt solutions and the solution of calcium salt were added in the end. The appearance of the solution was transparent.

2.3 Surfactants

For the investigations, we utilized fatty acid-diethanolamine surfactants produced using various individual fatty acids and diethanolamine. The key properties of the surfactants used in the studies are summarized in Table 3.

Table 3: Properties of the emulsification device (ADEM).

Mark of surfactants	Used fatty acid	Appearance of surfactants	Stability of surfactants
S-1	Lauric acid	Pale yellowish/ brownish, liquid	Stable, phase separation was not observed
S-2	Myristic acid	Pale yellowish/ brownish, paste	Stable, phase separation was not observed
S-3	Palmitic acid	Pale yellowish/ brownish, solid	Stable, phase separation was not observed
S-4	Oleic acid	Dark brown, liquid	Stable, phase separation was not observed
S-5	Stearic acid	Pale yellowish/ brownish, solid	Stable, phase separation was not observed

The surfactants used were dissolved in the synthetic brine and thus prepared at a concentration of 15 g/l.

2.4 Determination of emulsification capacity

The investigation of the emulsifying effect was conducted using both manual and automated methods. In the manual method, experiments were carried out in graduated cylinders equipped with caps. Each cylinder was filled with a 50-50 V/V% mixture of brine containing surfactant and crude oil, which was then manually shaken. Subsequently, the samples were stored at 80°C, and the separation of water and oil was analyzed after 1 hour. For the ADEM (automated) method, the Green Lab ADEM apparatus was employed. In this automated approach, the test temperature, the ratio of the water and oil phases, and the test duration were fixed at 80°C, 50-50 V/V%, and 1 hour, respectively. After mixing, the samples were left to separate without further mixing. The stirring speed was set at 1500 rpm, and the stirring time was 120 seconds.
The most important parameters of the equipment are summarized in Table 4.

Table 4: Properties of the emulsification device (ADEM).

Property	Value
Number of parallelly investigated samples	6 pcs
Type of mixer	Shovel mixer
Mixing speed	500-1500 rpm
Heat transfer medium	Water
Temperature	20-85 °C
Temperature stability	≤±1 °C
Amount of sample	80 ml

The used machine is shown in Figure 1.
The emulsification effect was evaluated by calculating the ratio of the emulsion phase measured after 1 hour following the end of mixing, expressed in V/V% (Malahov et al. 2022). This measurement allows for a quantitative characterization of the efficiency of surfactants used in emulsion preparation.

Figure 1: The automated demulsibility tester (ADEM)

3. Results

In this test method, the mixing of the phases is usually done by hand. The emulsification test was tested with an automatic device to reduce the mixing error. The equipment used for the tests is suitable for testing according to different standards (according to ISO 6614 and ASTM D1401), however, these differ from the conditions we tested, so we first examined the applicability of the method.
The emulsifying effect of fatty acid diethanolamides in a crude-brine system at different mixing intensities was investigated. The results of the emulsifying effect and the separation of the phases in time were also examined (Hartyányi et al. 20.
The results of the emulsification effect obtained through the manual method are presented in the Table 5.

Table 5: Investigation of the the emulsification effect by manual method

	S-1	S-2	S-3	S-4	S-5
Oil phase, v/v%	2.5	10	30	50	50
Emulsion, v/v%	47.5	45	22.5	0	0
Water phase, v/v%	45	45	47.5	50	50

The Table 6. illustrates that, according to the manual method, S-2 and S-3 surfactants exhibit the most effective emulsification effect, while for S-4 and S-5 surfactants, complete emulsion separation occurred after 1 hour.

Table 6: Investigation of the emulsification effect by ADEM method

	S-1	S-2	S-3	S-4	S-5
Oil phase, v/v%	0	1.25	42.5	20	3.75
Emulsion, v/v%	75	68.75	57.5	80	52.5
Water phase, v/v%	25	30	0	0	43.75

It was established that the amount of the middle phases were greater in the case of the tested emulsions when the automatic method was used. The reason for this may be that the mixing efficiency of crude oil and water is higher.According to the automata method, all surfactants had effective emulsification effect especially S-4.

The Figure 2. shows a comparison of the results obtained with the manual and automatic methods.

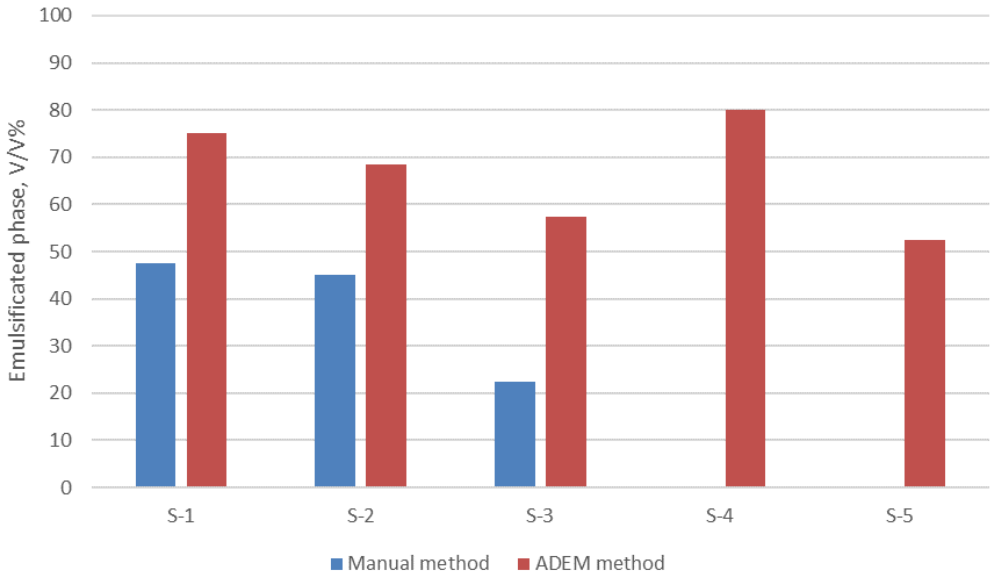

Figure 2: Comparison of manual and automatic methods

It can be seen that the emulsification results determined by the manual method differ from those determined by the automatic method. Surfactants were shown a lower emulsification effect during the manual method. The difference between the results obtained with the two methods is due to the stability of the emulsions. The phase separation in case of S-2 surfactant with automata method shown in Figure 3.

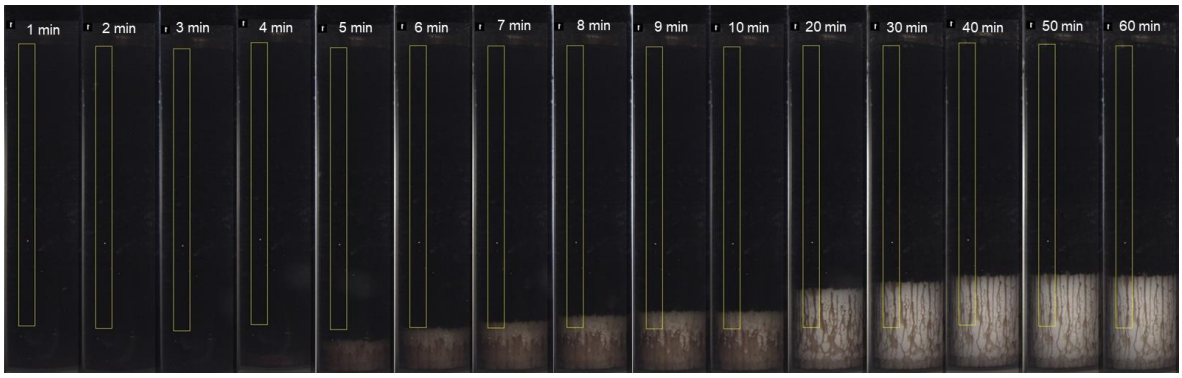

Figure 3: The phase separation in case of S-2 surfactant depended on the time of sedimention

During the above investigation (Figure 4), was found that the quantity of the emulsion stabilized after 30 minutes. Emulsions prepared by automata method were more stable and more representative of real conditions.

4. Conclusions

In our work, the emulsifying effect of fatty acid-diethanolamine type surfactants produced with various individual fatty acids using brine and light paraffin (base) oil was investigated. When examining the emulsifying effect manually, the test results were lower compared to the automatic method, which is due to the more intensive mixing during emulsion production influencing the emulsion that remained after one hour of settling. In both methods, it can be observed that with an increase in the hydrophobic chain of the applied surfactant, i.e., a decrease in the HLB value, the emulsifying effect decreased under the examined conditions. In the automatic method, the highest emulsifying effect was observed for the surfactant containing a double bond in its chain (S-4). In this case, the emulsifying effect could not be determined manually. The presumed reason for this is that

in this case, the types of emulsions also varied, and the energy required for their production was higher than the energy reported for the manual method.
The applied method may be suitable for investigating applications beyond the petroleum industry.

Nomenclature

DI – deionized
EOR – enhanced oil recovery
HLB - Hydrophilic–lipophilic balance
TDS – Total dissolved salt, ppm

Acknowledgments

Prepared with the professional support of the Doctoral Student Scholarship Program of the Co-operative Doctoral Program of Ministry of Innovation and Technology financed from the National Research, Development and Innovation Fund. Founding number: KDP-11-3/PALY-2021
Expressing gratitude to MOL Plc for their generous support of the research and providing the opportunity for publication.

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