

# Investigation the Solubility of Vegetable Oil-Based Nonionic Surfactants for the Petroleum Industry

Máté Hartyányi<sup>a,\*</sup>, Roland Nagy<sup>a</sup>, László Bartha<sup>a</sup>, Sándor Puskás<sup>b</sup>

<sup>a</sup>Department of MOL Hydrocarbon and Coal Processing, University of Pannonia, H-8200 Veszprém, Hungary

<sup>b</sup>Oilfield Chemicals and Technologies, MOL Plc, H-6701 Szeged, Hungary

[hartyanyi.mate@mk.uni-pannon.hu](mailto:hartyanyi.mate@mk.uni-pannon.hu)

In the present day, surfactants find extensive use across various industries owing to their versatile and advantageous characteristics. They serve as detergents, wetting agents, emulsifiers, foaming agents, and dispersants, spanning from the food and cosmetic sectors to heavy industrial applications. Among surfactants, nonionic surfactants constitute a highly diverse category. Efficiency of application, environmental considerations, and sustainability are increasingly significant factors in the surfactant industry. To enhance these attributes, the adoption of natural and recycled raw materials presents a viable solution. Notably, surfactants derived from vegetable and animal oils, or their derivatives, with hydrophobic groups are among the largest subcategory within the realm of naturally sourced surfactants.

In our work, surfactant compositions developed for tertiary oil recovery using naturally sourced surfactants was examined. During our research, a connection between the solubility of these surfactant compositions and other properties was sought to establish.

## 1. Introduction

Various industries, including oleo-chemistry, cosmetics, energy, and food, utilize vegetable oils. In contemporary times, the industrial extraction of vegetable oils from oilseeds and nuts commonly involves mechanical extraction and hexane extraction. (Nagy et al. 2014). Mechanical extraction is typically acknowledged as the most effective method for recovering virgin oil from seeds with a high oil content (>20 wt%) (Bogaert et al., 2018).

Surface-active agents, commonly known as surfactants, reduce the Interfacial Tension (IFT) due to their amphiphilic structure, which allows them to adsorb to the oil/water interface. Despite the novelty and significance of this concept, the implementation of this extraction method poses considerable challenges as several constraints must be taken into account. One primary challenge is identifying the appropriate surfactant molecule capable of solubilizing vegetable oils in water at a sufficiently high level. Vegetable oils are primarily composed of triglyceride molecules, consisting of three fatty acids bound to a glycerol molecule. Triglycerides exhibit high hydrophobicity owing to the medium to long alkyl chains (8 to 22 carbons) of their constituent fatty acids, coupled with a dual light hydrophilicity associated with the glycerol region. Additionally, within the same oil species, fatty acids can be saturated or unsaturated, branched or unbranched, resulting in a diverse array of molecular structures. In essence, vegetable oils consist of various bulky molecules that are not easily soluble in water. (Gagnon et al., 2021).

Because of their diverse chemical structure and bulkiness, triglycerides exhibit less readily interaction with the tails of surfactants compared to short-chain oils, such as alkanes. (Ab Raman et al., 2003).

Traditional surfactants are amphiphilic molecules composed of a lipophilic hydrocarbon chain (typically consisting of 10 to 20  $-\text{CH}_2-$  units) directly linked to a hydrophilic polar head group (Figure 1a). The classification of surfactants is based on the charge of the polar head, resulting in nonionic, anionic, cationic, or zwitterionic types. In contrast to conventional surfactants, extended surfactants feature intermediate polar groups, such as polypropylene oxide (PO)<sub>y</sub> and/or polyethylene oxide (EO)<sub>z</sub>, inserted between the hydrophilic head and the lipophilic tail, as illustrated in Figure 1b. (Gagnon et al., 2021).

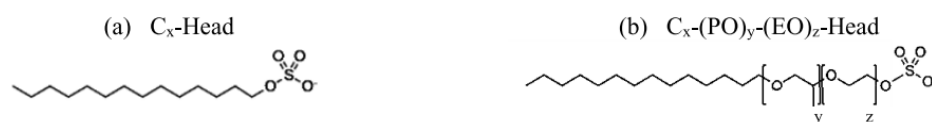


Figure 1. Typical formulas of conventional (a) and extended (b) surfactant molecules. Case of sulfate headed  $C_{12}$  surfactants (Gagnon et al., 2021)

The solubility of a surfactant in water is influenced by its type, structure, and operational conditions such as temperature, pressure, and salinity. Anionic surfactants exhibit solubility dependence on both temperature and salinity, while the solubility of nonionic surfactants is primarily affected by temperature. Structurally, the solubility of surfactants in water shows an inverse correlation with the length of the alkyl chain: longer chains result in lower water solubility for the surfactant. In light of this, the Hydrophilic-Lipophilic Balance (HLB) value has been proposed as a characterization parameter for this aspect. (Griffin, 1949).

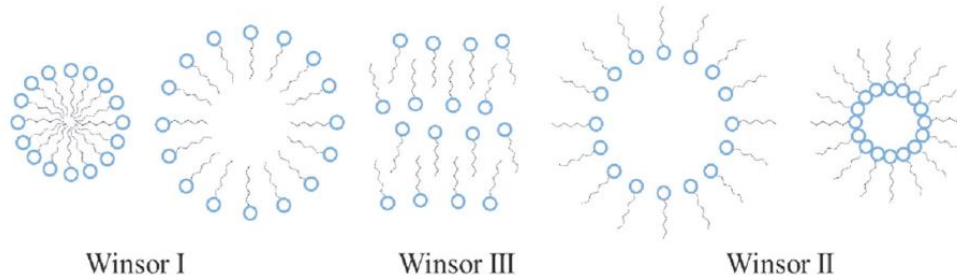


Figure 2. Schematization of the Winsor transition at one micelle scale (Gagnon et al., 2021)

Several formulation methods aim to decrease the concentration of salt, alcohol, and surfactant while achieving ultralow Interfacial Tension (IFT) ( $< 10^{-2}$  mN/m). At such low IFT levels, systems composed of oil and water are referred to as "microemulsions." (Tafur et al., 2022). Microemulsions can exist in two primary forms: oil in water (Winsor type I) or water in oil (Winsor type II). However, it's noteworthy that only under a very specific formulation of the water phase, which results in the lowest Interfacial Tension (IFT), does the oil-water system become bicontinuous. This particular state is referred to as "Winsor type III microemulsions." (Nordiyana et al. 2016).

The solubility of surfactants is a highly significant property that dictates the potential and constraints of their subsequent applications.

During our work, it was aimed to investigate the solubility properties of surfactant blended and their components. Our further goal was to investigate the relationship between the solubility of individual surfactants and the solubility of surfactant compositions.

## 2. Materials

Commercially available individual surfactants and their blended of these surfactants were used for the investigation. Both anionic and nonionic types of commercial surfactants were used, and the main characteristics of these surfactants were summarized in the Table 1 and 2.

Table 1: Main properties of used surfactants (part I.)

Name	Producer	Type	Appearance	Active component
S-1	BASF	Anionic	White or yellowish paste	Sodium Laureth Sulfate + 2 EO
S-2	MOL LUB Ltd.	Anionic	Yellow liquid	Polietheramine-DBS salt (gemini)
S-3	MOL LUB Ltd.	Nonionic	Yellow or brownish liquid	RME-DEA reaction product

Table 2: Main properties of used surfactants (part II.)

Name	Active material content (%)	pH value (5 wt% in water at 25°C)	HLB value	Density (g/cm <sup>3</sup> ) (20°C)
S-1	68-73	7-9	40	1.07-1.1
S-2	58-62	7-9	n.a.	0.996
S-3	>98	7-9	8.5	0.985

Using the surfactants presented above, surfactant compositions were prepared, and their composition is summarized in the Table 3.

Table 3: Compositions of used surfactant blended

Sign of surfactant blended	S-3, wt%	S-2, wt%	S-1, wt%
SM-1	30	50	20
SM-2	30	48	22
SM-3	30	46	24
SM-4	30	44	26
SM-5	30	42	28

Surfactants and surfactant blended were dissolved in synthetic brine. The important parameters and composition of this brine are summarized in the Table 4.

Table 4: Main properties of synthetic brine

Properties	Value
pH-value at 25 °C	6.07
Conductivity at 25 °C, mS/cm	189
Density at 25 °C, g/cm <sup>3</sup>	1.132
Dissolved salt	
NaCl, ppm	59600
KCl, ppm	1079
CaCl <sub>2</sub> , ppm	9706
MgCl <sub>2</sub> , ppm	2811
TDS, ppm	73196

Analytical purity, water free salts were used for the preparation of synthetic brine. The main properties of the crude oil used for the measurements are summarized in the Table 5.

Table 5: Main properties of crude oil

Properties	Value
Kinematic viscosity at 25 °C, mm <sup>2</sup> /s [ASTM D7042]	22.5
Dynamic viscosity at 25 °C, mPas [ASTM D7042]	19.7
Density at 25 °C, g/cm <sup>3</sup> [ASTM D4052]	0.8779
Acid number, mg <sub>(KOH)</sub> /g [ASTM 664]	0.61
IBP (ASTM D86), °C	47

Based on its properties, the crude oil used for the measurements can be considered as a light intermediate type of crude oil. For the preparation of the surfactant solutions used in the measurements, the surfactants were dissolved in synthetic brine at a concentration of 1 g/L in each case.

### 3. Methods

Detailed physical and physical-chemical investigation of the surfactant solutions were used the following methods:

- Appearance [Visual]

The measure of the solubility of the surfactants was initially conducted visually. Precipitation formation, floating, and incomplete solubility were examined in the solutions of the surfactants.

- Solubility in water

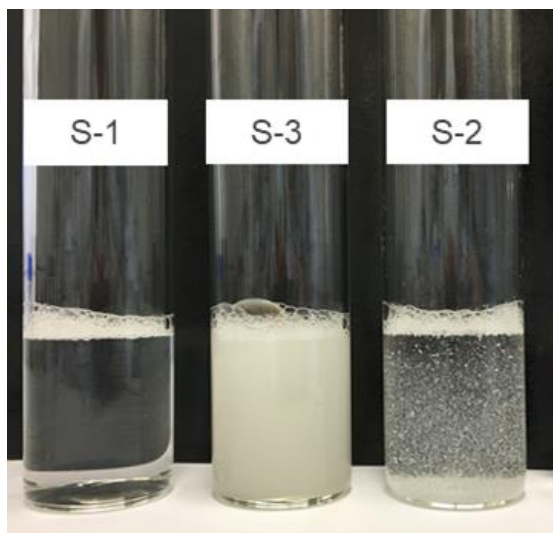
Solubility of surfactants was measured by WTW TURB 400IR turbidity meter. The turbidity determination based on nephelometric measurements.

- Determination of IFT value

The interfacial tension between the aqueous phase of the surfactant blended solution and the crude oil was measured using the spinning drop method. The measurement was carried out in a Krüss SDT tensiometer. While the rotation of the cylinder exerts a centrifugal force on its wall, the drops of the lower density fluid are deformed in an elongated form. The interfacial tension between the two fluids can be calculated from the form of the drops using the Young–Laplace-fit method (Nagy et al., 2022). All measurement was carried out in 25 °C temperature.

#### 4. Results

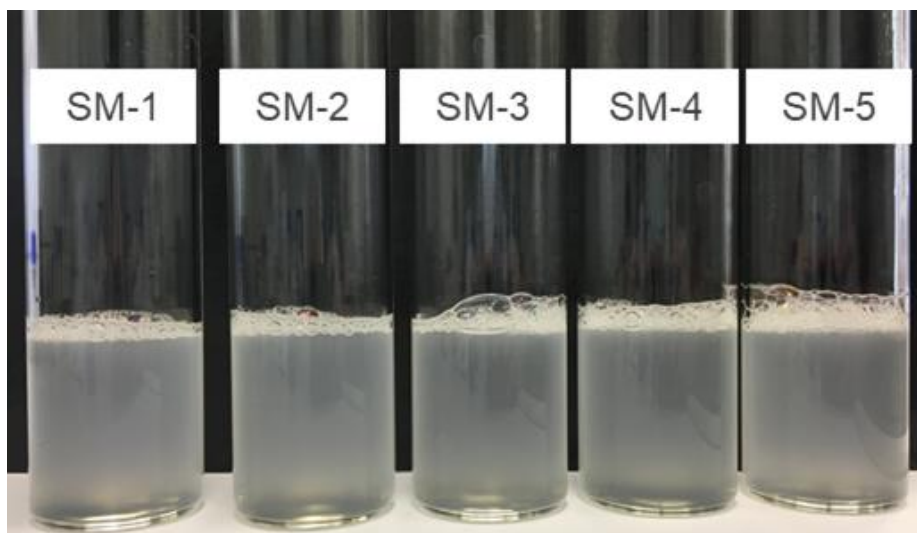
During the examinations, the solubility of surfactants and surfactant blended was initially investigated. The appearance of the surfactant solutions can be seen in Figure 3.



*Figure 3: Appearance of surfactants solution*

Among the three surfactant solutions, the marked S-1 had a transparent appearance. The surfactant marked S-2 did not dissolve in the brine; precipitation was observed. The solution of surfactant S-3 had a strongly opaque appearance, and separation was observed shortly after standing.

The appearance of the solutions of the surfactant compositions can be seen in Figure 4.



*Figure 4: Appearance of surfactant blended solution*

No visual difference was observed among the solutions of the surfactant blended. The appearance of each solution was slightly opaque.

The results of the turbidity tests for the solutions of surfactants and surfactant blended are summarized in Table 6.

*Table 6: Turbidity of surfactants and surfactant blended solution*

Surfactants and their blended	Turbidity NTU
S-1	3.56
S-2	Non-measurable
S-3	667
SM-1	78.0
SM-2	74.6
SM-3	73.1
SM-4	70.5
SM-5	68.5

Among the individual surfactants, the one marked S-2 was not measurable due to precipitation formation. The turbidity of the solutions of surfactant compositions ranged from 78.0 to 68.5 NTU. Increasing the proportion of the surfactant marked S-1 improved the solubility of the surfactant blended.

The values of interfacial tension of the solutions of surfactant blended against crude oil are provided in Table 7.

*Table 7: IFT values of surfactants and surfactant blended solution*

Surfactants and their blended	IFT, mN/m
SM-1	0.6093
SM-2	0.6680
SM-3	0.6956
SM-4	0.7313
SM-5	0.7717

The interfacial tension values of the surfactant blended against crude oil ranged from 0.6093 to 0.7717 mN/m. Increasing the proportion of the surfactant marked S-1 led to an increase in the IFT value.

## 5. Conclusions

Our goal was to enhance the solubility of surfactants that had previously performed well under low-salinity conditions. These surfactants did not dissolve on their own in the tested brackish formation water; for the anionic surfactant marked S-2, precipitation was observed, while for the S-3 surfactant, solution instability was noted. By investigated these surfactants in combination with a third anionic surfactant (S-1) that dissolved well in the tested formation water, we successfully formulated a mixture whose solubility posed no issues. Based on the examination of the turbidity of these surfactant blended, we concluded that their solubility is suitable for use in enhanced oil recovery (EOR) applications. The results led us to the conclusion that increasing the proportion of the surfactant marked S-1 improved the solubility of the surfactant blended. During the investigation of the interfacial tension of the surfactant blended in the presence of crude oil, it was determined that increasing the proportion of the surfactant marked S-1 led to an increase in the interfacial tension (IFT) value. These correlations can significantly facilitate and contribute to the successful surfactant selection and screening process.

### Nomenclature

DBS – dodecyl benzenesulfonic acid  
 EO – ethylene oxide  
 EOR – Enhanced Oil Recovery  
 HLB – Hydrophilic–lipophilic balance  
 IBP –Initial boiling point, °C  
 IFT – Interfacial tension

PO – propylene oxide  
 RME-DEA – Rapeseed methyl ester -  
 diethanolamine  
 TDS – Total Dissolved Salt

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