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SHORT COMMUNICATION

Investigation of Some Food Industrial vegetable Oil-Based Nonionic Surfactants

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Abstract

Nowadays the surfactants are used in many areas of everyday life and industry, thanks to their diverse and favourable properties. They have been used as detergents, wetting agents, emulsifiers, foaming or dispersing agents, from the food industry, through the cosmetics industry, to the heavy industry. Among surfactants, nonionic surfactants form one of the most diverse groups. Since the hydrophobic and hydrophilic parts of the non-ionic surfactant are formed due to the different polarities of the molecular parts, countless raw materials become suitable for the production of such surfactants, depending on their polarity and reactivity. In the world of surfactants, in addition to application efficiency, environmental friendliness also plays an important role. In order for a surfactant to be environmental friendly, it is necessary to strive for the best solution the conditions of production and application. In this study it was set ourselves the goal of investigating nonionic surfactants, which based on their properties, may be suitable for industrial application, while also contributing to sustainable development.

Keywords Vegetable oil · Additives · Nonionic surfactants · Used cooking oil

Introduction

There are many types of surfactants available today, with a wide range of prices. Accordingly, the raw materials are extremely diverse and can come from countless places, and their production methods can range from simple hydrolysis to multi-step, high-pressure syntheses. With some exceptions, the raw materials market does not depend on the surfactant production industry. As a result, raw material prices can change significantly due to external factors that are not dependent on the production of surfactants. This volatile situation has brought changes and competition in the surfactant industry [1–3].

For the sake of simplicity, it was grouped the raw materials required for the production of surfactants according to their origin. They can be of natural or petroleum-based, synthetic origin [1, 4].

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After reviewing a lot of literature, it was found that the market for surfactants has been secure for a long time, and they will be indispensable ingredients in many products for a long time to come, whether we are looking at the food industry, the cosmetics industry, or any other industry, since its field of application is almost limited by the imagination [5, 6].

Within surfactants, nonionic surfactants also have many other advantages, which is why their sales volume is expected to increase in the future as a result of continuous research and due to growing market demands. Due to their diverse molecular composition, they can be changed according to individual goals, so it is easy to find the most suitable type [7]. It is important to mention, however, that these are expected to always be mixtures of molecules of several sizes, because the selectivity of their production methods is not 100% [8, 9].

The diverse composition also entails the diversity of the raw material base. In addition to synthetic, mainly petroleum-derived raw materials, there are also natural, so-called bio-based materials, which also comply with the environmental protection aspect. Therefore, surfactants, including nonionic surfactants, represent a diverse scientific field full of opportunities nowadays [10–12].

The aim of this study is to investigate a biodegradable nonionic surfactant using natural vegetable oil available in Hungary and used vegetable (cooking) oil raw materials, and to perform qualification tests from the point of view of the petroleum industry.

The experimental work was based on the literature review. I was set ourselves the goal of investigating non-ionic surfactants using organic raw materials of natural origin, vegetable oil and used vegetable oil. Our goal was to investigate the use of used cooking oil as a valuable raw material. It was determined the physical–chemical properties of the synthetized surfactants through analytical testing, as well as their potential applications with impact testing methods. The aim of this study was to produce nonionic surfactants from raw materials that are environmentally friendly, easily biodegradable, from renewable sources, or recyclable waste [13, 14].

Materials and Methods

Materials

The synthesis of the surfactants was a transestherification reaction between two of the raw materials with the help of a base catalyst. To improve the turbidity and composition properties of the product afterwards a stripping step was applied.

Synthesis of monoglycerides from vegetable oils through glycerolizes reactions with glycerol as a nucleophile electron donor is also known as transesterification. Edible vegetable oil (EU Regulation 1129/2011) and glycerol (Merck G7757) were used for the synthesis. This transesterification reaction between triglycerides and glycerol is performed in the presence of a base catalyst or lipase enzyme catalyst to produce new ester compounds, monoglycerides and diglycerides. The reaction scheme of the glycerolizes of vegetable oil is shown in Fig. 1 [15].

The aim is that the surfactants are clear, shiny and sediment-free. Surfactants made using glycerol are shiny, but dark in colour. For this reason, the qualification tests were performed only on surfactants with a homogeneous appearance, glossy, light or dark colour. During the synthesis all technological parameters were unchanged, only the vegetable oil reactant changed. After the synthesis, the appearance of the synthetized surfactant was examined.

The data of surfactants were summarized in Tables 1.

Vegetable oils from household (S-2) and restaurant (S-4) collections were used for the synthesis of surfactants.

After the synthesis, the appearance of the synthetized surfactant was examined. The appearance of the synthesized surfactants is shown in Fig. 2.

They were found to be clear, shiny, without any sedimentation.

Methods

A set of mature analytical methods is available for the qualification of surfactants, which have been used by mankind for decades and are constantly being developed. Those properties of the surfactant are measured and determined, which are related to a field of application. Such an area can be as an emulsifier, wetting agent, foaming agent, etc. application. I describe the methods I used in the following subsections [16, 17]).

1. Determination of saponification number (ISO 3657:2013)
2. Determination of total acid number (ASTM D974-21)
3. Water number determination [18].)
4. Determination of kinematic viscosity at 40 °C and 100 °C (ASTM D 445-04e2)
5. Determination of surfactant composition [8]
6. Determination of transmittance [19, 20]
7. Definition of interfacial tension [21]
8. Determination of emulsifying effect [22, 23]

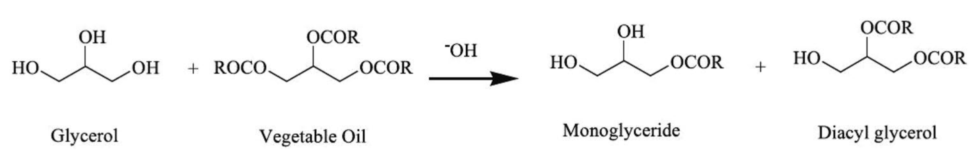

Fig. 1 Base catalysed glycerolizes of vegetable oil

Table 1 Characteristics of the investigated surfactants

Surfactant	S-1	S-2	S-3	S-4	S-5
Vegetable oil raw material	Sunflower oil	Used sunflower oil (Household)	Elain Fatty acid mixtures	Used sunflower oil (Restaurant)	Rapeseed oil
Alcohol raw material	Glycerol	Glycerol	Glycerol	Glycerol	Glycerol
Appearance	Gel like, brown	Clear, brown	Clear, yellow	Clear, orange	Clear, brown

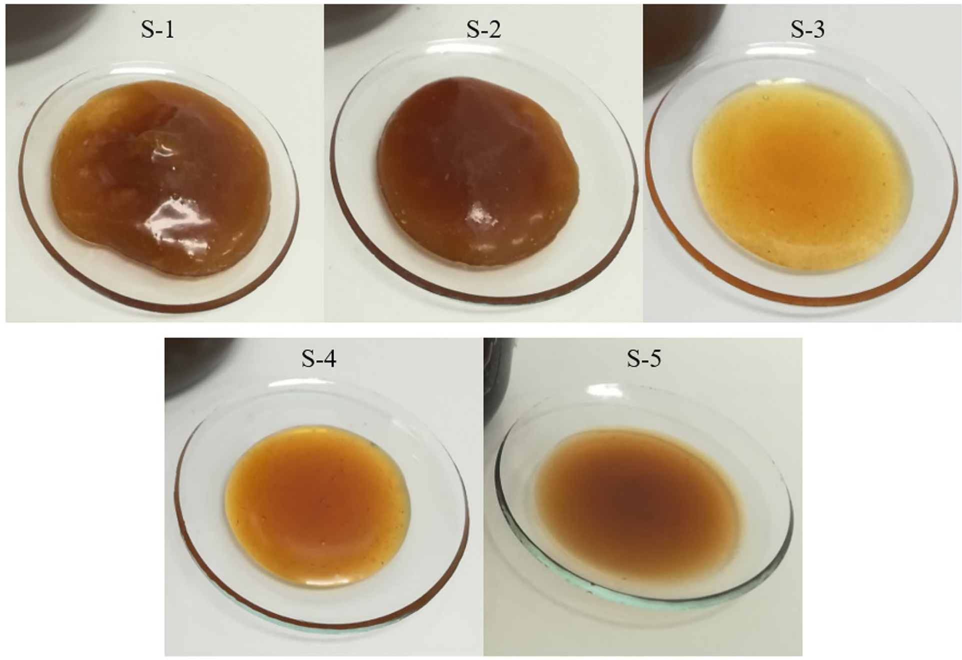

Fig. 2 The appearance of the synthetized surfactants

Results

The goal of this work is to investigate some vegetable oil-based surfactants primarily for petroleum industrial application. Furthermore, whether it is possible to use used cooking oil as a raw material was investigated.

Investigation of Surfactants

After that, surfactants were examined from physical and physicochemical properties point of view. These are the saponification number, the total acid number, water number, the kinematic viscosity measured at 100 °C, and the active ingredient content. The results were summarized in Tables 2.

The most common value of the saponification number was ~ 140 mg KOH/g. The higher the value, the greater the number of free acid and saponifiable ester groups to be neutralized.

The water number of most of the investigated surfactants is between 3.2–6.8 cm^3/g. Based on the HLB value calculated from the water number, the applicability of surfactants can be inferred. According to this, the tested surfactants with a water number of 3–7 cm^3/g can be suitable W/O emulsifiers, and those with a higher water number and HLB value can be wetting agents [24].

The active ingredient content varied in a wide range: from 24.9 to 79.8 w%. It should be noted that components other than the active ingredient have also surface-active characteristic.

Investigation of Surfactants in Water Solution

After that, 1 m/m% solutions of surfactants prepared with distilled water were investigated. These are the measurement of transmittance and interfacial tension (Table 3.).

The interfacial tension of the surfactants measured with Hungarian stabilized crude oil varied within a relatively wide interval, the lowest value was given by the surfactant marked S-2, while the highest, unfavourable value was obtained by testing the surfactant marked S-1.

The emulsifying effect of the synthesized surfactants was tested on their solution with distilled water at a concentration of 1 m/m%. 10 cm^3 of the finished solution is Hungarian

Table 2 Investigated characteristics of the synthetized surfactants

Surfactant	S-1	S-2	S-3	S-4	S-5
Saponification number, mg KOH/g (ISO 3657:2013)	142.2	141.6	134.2	147.2	116
Total acid number, mg KOH/g (ASTM D974-21)	0	0	0	0	30
Water number, cm^3 distilled water/ g surfactant	3.2	5.9	6.8	5.1	6.8
KV100°C, mm^2/s (ASTM D 445-04e2)	14.4	18.3	17.3	15.2	22.1
Active ingredient content, w%	24.9	79.8	49.4	70.1	59.6

Table 3 Transmittance and interfacial tension of the relevant surfactants

Surfactant	Transmittance, %	IFT, mN/m
S-1	64	8.25
S-2	19	1.63
S-3	20	6.60
S-4	16	3.81
S-5	20	4.51

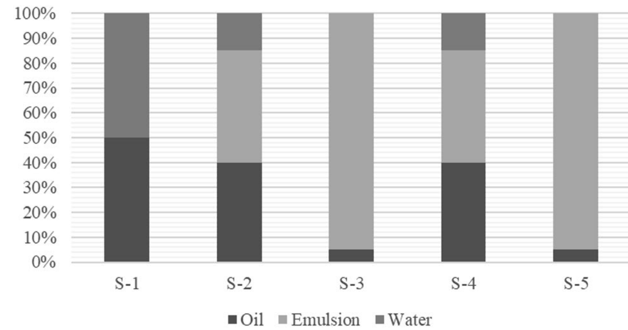

Fig. 3 Emulsifying effect of the relevant surfactants at 80 °C after 30 min

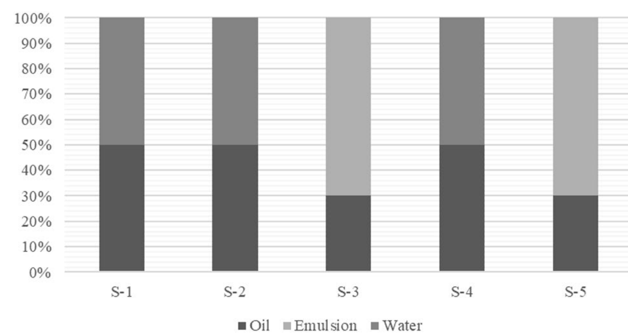

Fig. 4 Emulsifying effect of the relevant surfactants at 80 °C after 1 h

stabilized crude oil. It was mixed thoroughly with 10 cm^3 of it, and after a certain time at different temperatures, it was read the amount of the formed emulsion and the separated phases [25]. The data of emulsifying effect were summarized in Tables 4 and were shown on Figs. 3 and 4.

Surfactants that no longer form an emulsion after 30 min at room temperature are not suitable emulsifiers. The most interesting were the surfactants that were still present as a 100 V/V% emulsion after one hour at 20 °C. Among these, the surfactants that still formed a significant amount of stable emulsion after 24 h at 80 °C may be suitable even for petroleum industry application. Based on the results, the best emulsifiers are S-2, as well as S-3 and S-5.

Conclusion

In this paper, it was presented that the vegetable oil-based surfactants are promising candidate for petroleum application. The nonionic surfactants were synthesized with the help of the selected and examined vegetable oil and used vegetable oil raw materials, under laboratory conditions.

Based on the experimental studies the following conclusions can be drawn:

1. The goal was to produce bright and sediment-free, homogeneous surfactants.
2. The surfactants were subjected to typical tests used in the hydrocarbon industry: their kinematic viscosity, saponification number, water and acid number, as well as the transmittance, interfacial tension and emulsify-

Table 4 Emulsifying effect of the relevant surfactants

Time	After 30 min			After 1 h		
Phase ratio, V/V%	Oil	Emulsion	Water	Oil	Emulsion	Water
Emulsifying effect, 20 °C						
S-1	50	0	50	50	0	50
S-2	0	100	0	0	100	0
S-3	0	100	0	0	100	0
S-4	15	45	40	15	45	40
S-5	0	100	0	0	100	0
Emulsifying effect, 80 °C						
S-1	50	0	50	50	0	50
S-2	40	45	15	50	0	50
S-3	5	95	0	30	70	0
S-4	40	45	15	50	0	50
S-5	5	95	0	30	70	0

ing effect of their 1 m/m% solutions made with distilled water was determined.
3. It was found that a surfactant with a higher active ingredient content can be synthetized from used cooking oil under the used technological parameters.
4. It was found that surfactants with a higher active ingredient content have a more beneficial surface-active effect from the point of view of the petroleum industry.
5. It was found that surfactants synthesized using used cooking oil can also be effective (S-2).

Based on the results the used cooking oil has a new possibility of utilization. The synthesized additives can be equally suitable in oil industry (Metal Working Fluid, Enhanced Oil Recovery), food industry (Surfactant) and household chemical industry (Cleaning products) applications.

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Data Availability Enquiries about data availability should be directed to the authors.

Declarations

Conflict of Interest The authors have not disclosed any competing interests.

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