

SURFACE ACTIVITY OF SOME FATTY ACID MONOGLYCERIDES

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Monoglycerides of some saturated and unsaturated fatty acids were prepared, and their surface activity was investigated.

INTRODUCTION

One of the most important group of emulsifiers are the fatty acid monoglycerides. Thanks to their nontoxicity they found wide use in food, pharmacy and cosmetic industries [7].

Their importance as emulsifying agents depends on the possibility to form the w/o and o/w emulsions in a wide pH range. As it is known, the fundamental activity of emulsifiers is to lower the interfacial tension existing at the interface between two immiscible liquids. Namely, high interfacial tension makes impossible to form fine dispersion during production of emulsions.

The lowering of the interfacial tension is not the sole result of the monoglycerides adsorption at the water oil interface. The other consequence is the formation of a protective surface film, which resists the deemulsification process. Above a certain concentration the adsorption process is not continued. In this time there are in the solution as well individual surfactant molecules as the micelles, which are the aggregates of the individual molecules. The micelles are in thermodynamic equilibrium with individual molecules and that is why they influence the surface activity of a certain emulsifying agent.

It is assumed in literature [15] that the beginning of the concentrations region — where sudden changes of some physicochemical properties of surface active agents solutions appear, is convergent with the beginning of formation of greater amount of micelles.

This concentrations region was named critical micelle concentration (CMC). CMC is of great importance from the practical point of view, because it determines the concentration of surface active compound, above which the change of surface properties of the solution does not occur. The scope of our work was: the synthesis of the pure monoglycerides of some fatty acids and the investigation of their surface activity.

EXPERIMENTAL PART

The glycerides of lauric, miristic, palmitic, stearic and erucic were obtained.

The first four acids of 99⁰/₀ purity were made by "Reachim" and the erucic acid of 98⁰/₀ purity was obtained by saponification of rapeseed oil and then by crystallization of obtained acids from acetone [12, 15].

From many glyceride synthesis [2, 6, 7, 11, 14] the method elaborated by Fischer [9] and modified by Hartman [10], Quinn and Sampugna [14] was chosen. It consists in esterification of fatty acids by isopropylidene glycerol.

Blocking of hydroxyl groups in glycerol with acetone and the next stage of synthesis — the esterification — occur at presence of acid catalyst. In that case it was p-toluenesulphonic acid. Esterification was carried out in a homogenous system using benzene as a solvent. At both stages of our synthesis the indicator, of reaction and was the stopping of reaction water exudation.

The obtained products are characterized in Table 1.

Table 1

The characterization of products

| Monoglyceride of | Form of the product | Colour of the product | Mass of the product g | Synthesis yield (%) |
|------------------|---------------------|-----------------------|--------------------------|------------------------|
| Lauric acid | greasy | white | 63.2 | 92.0 |
| Miristic acid | crystals | white | 67.0 | 90.0 |
| Palmitic acid | crystals | white | 71.0 | 81.6 |
| Stearic acid | crystals | white | 80.0 | 80.4 |
| Erucic acid | greasy | cream-coloured | 86.7 | 49.3 |

All obtained monoglycerides were in crystalline or greasy forms, white or creamcoloured.

The yields of the esterification processes diminished with increasing hydrocarbon chain length of the esterified fatty acids.

The synthesis products were qualitatively analyzed by the thin layer chromatography method [9]. The chromatograms were developed by benzene:ethyl ether (17:4) mixture and visualised by 50% H_2SO_4 at the temperature of 473 K.

Chromatogram is presented in Figure 1.

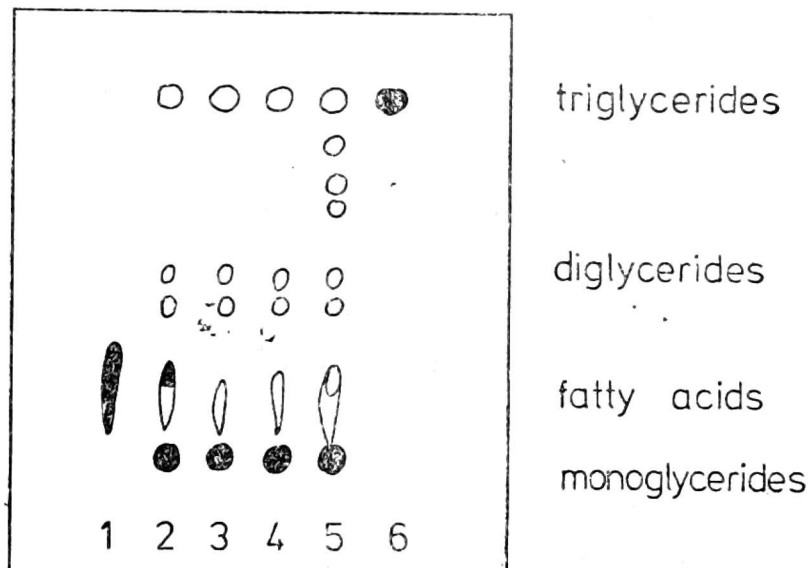


Fig. 1. Thin layer chromatogram: 1 — Palmitic acid, 2 — 40% commercial monostearate, 3 — synthesized monoglyceride of palmitic acid, 4 — synthesized monoglyceride of palmitic acid, 5 — synthesized monoglyceride of erucic acid, 6 — rape-seed oil

The chromatogram shows that the obtained synthesis products are not pure monoglycerides. Diglycerides, triglycerides and small amounts of fatty acids are present as the impurities.

The most contaminated was the monoglyceride of erucic acid, which besides of above mentioned impurities, contained others which could be formed because of the presence of double-bond in the compound.

To carry out the quantitative determination of the products composition there was undertaken the analysis by column chromatography according to Ouilin [13].

A column filled with silica gel made by Merck — 200 mesh was applied and benzene, 10% solution of ethyl ether in benzene and ethyl ether were used as eluants. The elution order was: triglycerides, diglycerides and monoglycerides.

The obtained results of our analysis are given in Table 2.

It was ascertained that by the above described method of esterification there can be obtained a product of nearly 90% concentration of monoglyceride.

By column chromatography there were separated ca. 10 g of synthesised products in aim to receive monoglycerides of 100% purity.

As a result of purification by column chromatography there were received also small amounts of diglycerides and triglycerides of indivi-

Table 2

The quantitative product composition of monoglycerides synthesis

| Monoglyceride of | Monoglycerides % | Diglycerides % | Triglycerides % | Transition fraction % |
|------------------|---------------------|-------------------|--------------------|-----------------------------|
| Lauric acid | 94.9 | 2.7 | 0.4 | 2.0 |
| Miristic acid | 95.2 | 2.3 | 0.4 | 2.1 |
| Palmitic acid | 87.6 | 7.0 | 5.0 | 0.4 |
| Stearic acid | 90.0 | 7.0 | 1.0 | 1.9 |

dual acids. But the monoglyceride of erucic acid was crystallized from petroleum ether boiling in the range of 313-333 K [4]. Purity of the product after crystallization was checked by thin layer chromatography.

THE INVESTIGATION OF THE SURFACE ACTIVITY OF SYNTHESIZED MONOGLYCERIDES

In aim to investigate the surface properties of monoglycerides the following physicochemical studies were undertaken:

- the measurement of surface tension of monoglyceride oil solutions,
- the measurement of interfacial tension at the phases boundary water-monoglyceride oil solutions.

Both kinds of measurements were carried out by the drop weight method [1, 3] at 318 K of temperature. The oil phase consisted of refined rapeseed oil with acid value = 0.2, Iodine Value = 98.6 and Saponification Value = 184.4. Total contents of mono- and diglycerides in this oil was less than 0.2%.

The measurements of surface tension were made for pure rapeseed oil and monoglyceride oil solutions. The surface tension measured for the pure rapeseed oil was 31.5 mN/m.

On the base of this Figure 2 it can be stated that the monoglycerides diminish only in a small degree the surface tension of their oil solutions.

For example — for the monoglyceride of stearic acid a surface tension value decrease of 0.15 mN/m was obtained in the concentration range of emulsifier equal 6.7 m mol/l — 27 m mol/l. Some what greater decrease of the surface tension value was obtained in the case of the monoglyceride of lauric acid equaly 0.28 mN/m. Analogously diglycerides does not effect the surface tension of the oil, too. The results of that investigations were given in Table 3.

The following glyceride oil solutions were examined:

1% glyceride solutions mixture of 1: w/w monoglyceride and di-

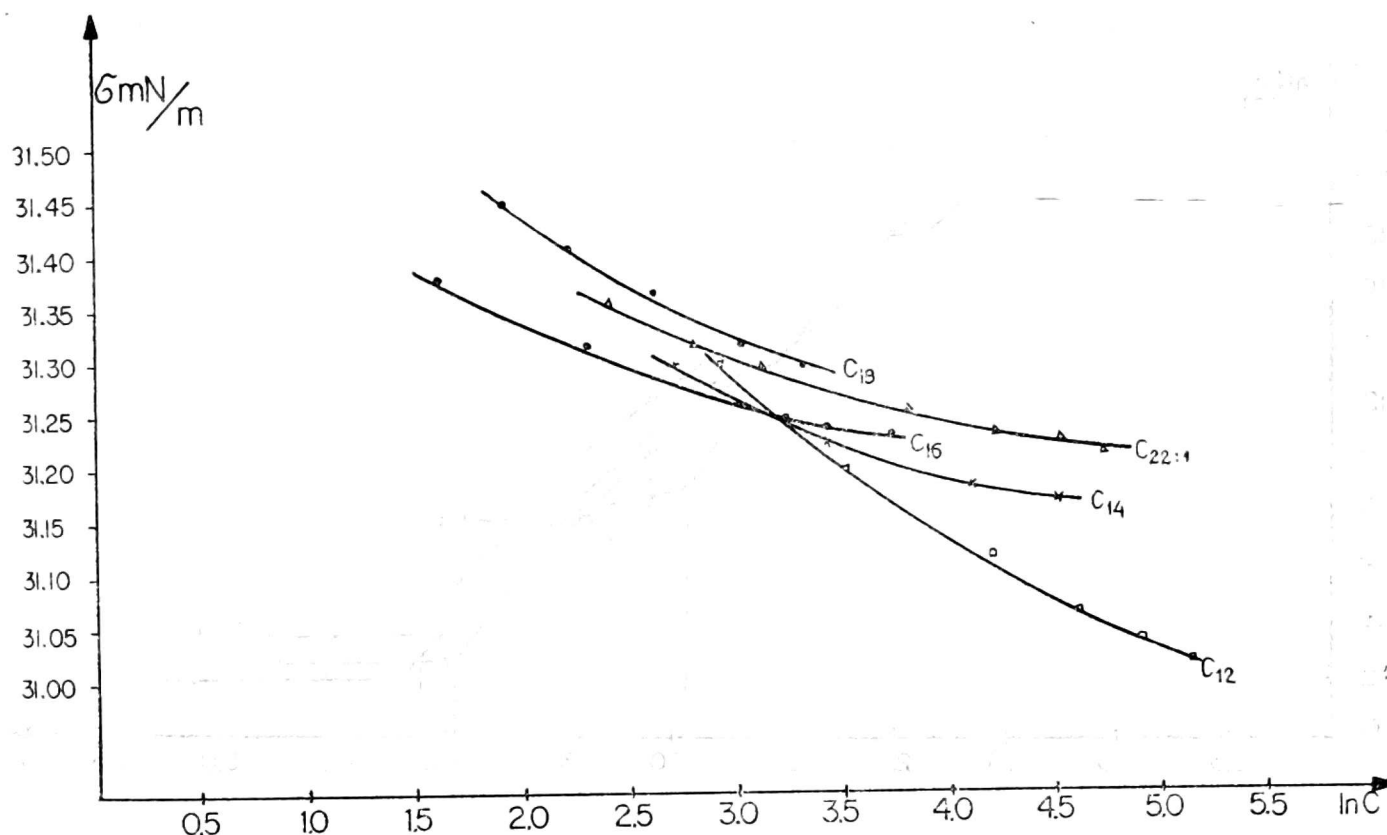


Fig. 2. The dependence of surface tension of monoglyceride oil solutions on their concentration

glyceride, and 1% glyceride solutions mixture of 9:1 w/w monoglyceride and diglyceride.

The obtained results were compared with values of surface tension measured for 1% solutions of pure monoglycerides. No essential differences were observed.

As it was mentioned the main action of the emulsifier lies in diminishing of the interfacial tension. The interfacial tension was measured in the system: distilled water — monoglyceride oil solution. From the obtained results it was plotted the dependence of surface tensions of monoglyceride solutions on their concentration.

The interfacial tension for pure rapeseed oil-water interface was 25 mN/m. As it is seen on the figure with the increasing of the emulsifier concentration, in case of every monoglycerides, there is observed a distinct diminishing of the interfacial tension. The greatest decreases were observed in the range of lower concentrations. While analyzing the diagram a typical break down of interfacial tension — concentration curve is observed. This break down appears near such a concentration above which there does not occur the decrease of the interfacial tension value.

With the increase of the hydrocarbon chain length of the fatty acid in the monoglyceride, there is observed the shift of the break down

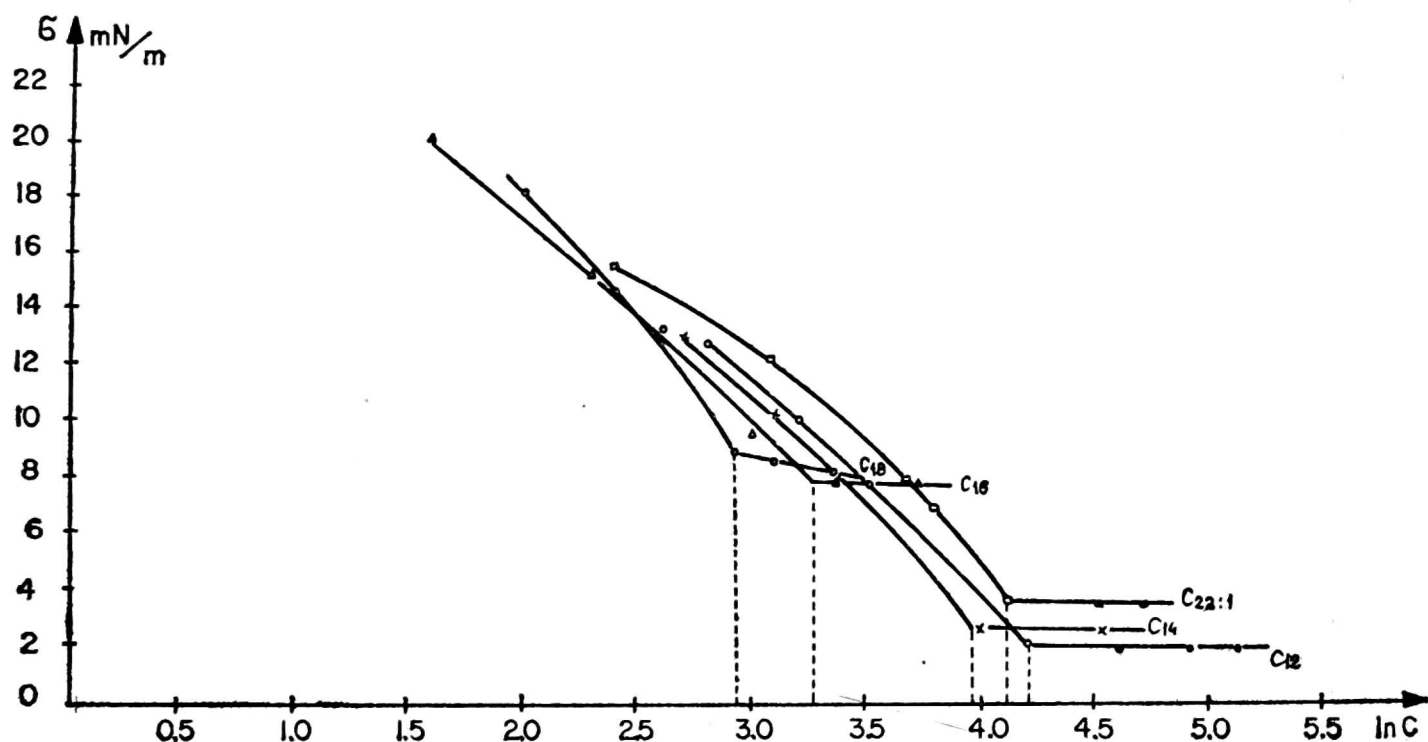


Fig. 3. The dependence of interfacial tension of monoglyceride oil solutions on their concentrations

Table 3

Influence of the diglycerides on the surface tension value of monoglyceride oil solutions

| Examined glycerides of | 1% monoglyceride solution | 1% glyceride solutions | |
|------------------------|---------------------------|-------------------------------|-------------------------------|
| | | 1:1 monoglyceride diglyceride | 9:1 monoglyceride diglyceride |
| surface tension mN/m | | | |
| Lauric acid | 31.20 | 31.20 | |
| Miristic acid | 31.23 | 31.30 | |
| Palmitic acid | 31.26 | 31.30 | |
| Stearic acid | 31.30 | | 31.34 |
| Erucic acid | 31.30 | | 31.34 |

in the direction of lower concentrations. This regularity is not observed in case of the monoglyceride of erucic acid.

It can be explained by the presence of the double bound in the molecule. The break down point of every curve determines the critical micelle concentration (CMC).

In the concentrations range 14-24 mole/l there can be observed the following dependence for a monoglyceride of a long hydrocarbon chain acid a greater decrease of the interfacial tension takes place.

There was also plotted the influence of the hydrocarbon chain length on the critical micelle, concentration value of monoglycerides.

The points lay on a straight line. The investigation to determine the effect of the diglycerides presence on the interfacial tension were carried out, too.

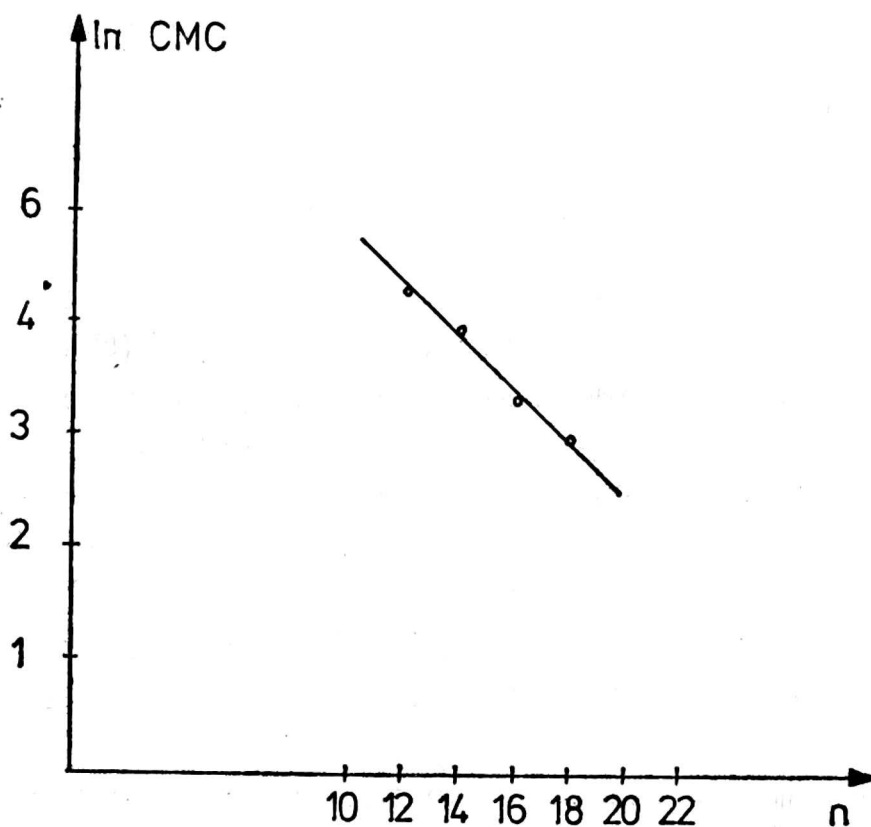


Fig. 4. Influence of hydrocarbon chain length on the CMC value of monoglycerides

Table 4

Influence of the diglycerides on the interfacial tension value at the interface water-monoglyceride oil solutions

| Examined glycerides of | 0.5% monoglyceride solution | 1% monoglyceride solution | 1% glyceride solutions | 1% glyceride solutions |
|--------------------------|-----------------------------|---------------------------|-------------------------------|-------------------------------|
| | | | 1:1 monoglyceride diglyceride | 9:1 monoglyceride diglyceride |
| interfacial tension mN/m | | | | |
| Lauric acid | 12.79 | 7.80 | 11.56 | |
| Miristic acid | 13.10 | 7.90 | 12.72 | |
| Palmitic acid | 13.98 | 9.54 | 13.00 | |
| Stearic acid | 13.20 | 6.97 | | 7.22 |
| Erucic acid | 15.06 | 12.16 | | 12.78 |

It was ascertained that the diglycerides do not decrease the interface tension in such degree as pure monoglycerides. And so for example: 1% solutions of glycerides of the following composition 1:1 w/w monoglyceride and diglyceride shows interfacial tension comparable to the value obtained for the solution of 0.5% contents of pure monoglyceride. That tension is also higher than the value for 1% solution of pure monoglyceride.

It proves weak emulsifying properties of the diglycerides and because of that it is recommended to apply emulsifiers of high contents of monoglycerides.

CONCLUSIONS

Finally, it should be stated that the absolute values of surface and interface tensions are lower for lower homologs (C_{12} - C_{14}) and the similar situation may be observed for the long chain erucic acid monoglyceride, which contains one double-bond with the configuration *cis*.

The increase of the hydrocarbon chain causes lowering of the interface tensions at lower emulgator concentration range than in case of shorter hydrocarbon chain monoglycerides.

In future, we want to investigate the influence of double-bonds configuration and their number on the surface properties of monoglycerides.

We will also try to evaluate the thermodynamical interactions between molecules of a given homolog or between two different emulgators.

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AKTYWNOŚĆ POWIERZCHNIOWA MONOGLICERYDÓW NIEKTÓRYCH KWASÓW TŁUSZCZOWYCH

Streszczenie

Otrzymano monoglicerydy kwasów tłuszczowych o różnej długości łańcucha węglowodorowego.

Syntezę prowadzono metodą kierowanej estryfikacji kwasów tłuszczowych izopropylidenglicerolem.

Otrzymane produkty analizowano jakościowo metodą chromatografii cienkowarstwowej, stosując układ: benzen: eter etylowy w stosunku (17:3). Natomiast ich skład ilościowy określono metodą chromatografii kolumnowej. Stosowano elementy: benzen, 10% roztwór eteru etylowego w benzynie oraz eter etylowy.

Własności powierzchniowe otrzymanych monoglicerydów określono przez pomiar obniżenia napięcia powierzchniowego ich olejowych roztworów oraz pomiar obniżenia napięcia międzyfazowego na granicy faz: olejowy roztwór monoglicerydu — woda. Obniżenie napięć międzyfazowego i powierzchniowego mierzono metodą ważenia kropli.

Dla poszczególnych monoglicerydów wyznaczono krytyczne stężenia (CMC) micelarne i przedyskutowano wpływ wielkości cząsteczki monoglicerydu na ich aktywność powierzchniową.

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ПОВЕРХНОСТНАЯ АКТИВНОСТЬ МОНОГЛИЦЕРИДОВ НЕКОТОРЫХ ЖИРНЫХ КИСЛОТ

Резюме

Получали моноглицериды жирных кислот с разной длиной углеводной цепи.

Синтез проводился по методу управляемой эстрификации жирных кислот изопропилиденоглицеролем.

Полученные продукты анализировали в качественном отношении по методу тонкослойной проматографии, при применении системы: бензен — этиловый эфир, в соотношении 17:3.

Количественный же состав этих продуктов определяли по методу колоночной хроматографии. Применяли следующие элементы: бензен, 10%-ный раствор этилевого эфира в бензене и этиловый эфир.

Поверхностные свойства полученных моноглицеридов определяли путем измерения поверхностного натяжения их масляных растворов и измерения межфазного натяжения на границе фаз: масляный раствор моноглицерида — вода.

Снижение межфазного и поверхностного натяжения измеряли путем взвешивания капель.

Для отдельных моноглицеридов были определены критические концентрации (СМС) и обсуждено влияние величины молекулы на их поверхностную активность.