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Emulsifiers from renewable materials: an eco-friendly synthesis and properties

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The focus of this study was the preparation of novel bio based polyglycerol emulsifiers characterized by a one pot synthesis, thus by modified properties with respect to interfacial activity and effectiveness as emulsion stabilizers. The final products of the esterification process, carried out in the presence of carboxylates were used directly as emulsifiers (without purification or fractionation). Polyglycerol emulsifiers obtained in proposed conditions can be tailored to stabilize the defined emulsion system. The modification of the surface activity of emulsifiers may be obtained by programming the fatty acid acyl group in the polyglycerol ester as well as the hydrocarbon chain length in sodium soap and concentration of this compound in the reaction mixture.

Keywords: fatty acid esters, polyglycerols, nonionic surfactants, emulsifiers, renewable fatty raw materials.

INTRODUCTION

Natural fats and oils have proven to be a valuable raw materials for the surfactant manufacturer on a cost, performance and environmental basis. Utilization of renewable resources, combined with recycling, is thought to be an important approach to Green Chemistry. Fats and oils are typical of these resources. However, in many cases the resulting surfactant is only realized through reaction of the natural component with petroleum – based chemical such as ethylene oxide. An attractive alternative to ethoxylation, from an environmental point of view, is the possibility of use natural glycerol as the hydrophilic part of the fatty acid surfactant.

Glycerol in its pure chemical form is a versatile base chemical that has been used for several decades to manufacture a variety of products. Besides this, glycerol is a green feedstock because of its bioavailability and is today a base chemical for the production of plenty of value-added products in chemical industries. Research on glycerol as a chemical platform for the production of bulk chemicals has been heavily stimulated by the increasing biodiesel production in recent years. A growing interest in the biodiesel industry has arisen because of the environmental implications of this "non-fossil" based fuel. This is the basic reason for an increasing quantity of glycerol in the market. For example, the European Union has set a target of 5.75% for the percentage of total transport fuel sales to come from biofuel by 2010, which will increase to 10% in 2020[1]. Consequently, it can be concluded that the production of crude glycerol resulting from biodiesel will be increase in different regions of the world.

Surfactants, which are synthesized through esterification of polyols (e.g. glycerol and polyglycerol) with fatty acids constitute an important group of derivatives, which are used as emulsifiers in food, cosmetic, pharmaceutical and chemical industries or as specific ingredients where a controlled release is the goal. Polyglycerol fatty acid esters (PGFE) have a wide field of applications due to their behaviour as nonionic surfactants, biodegradability, huge range of properties (liquids, solids, etc.) and the different raw materials available (vegetal, saturated, unsaturated, etc.)[2]. In the food industry, the use of these esters as additives in the E.U. is regulated in the European Directive 95/2/EC.

The PGFE produced through a condensation reaction of fatty acids or partial glycerides with glycerol have merits derived from the easy modification of their lipophilicity and hydrophilicity by changing the degree of polymerization of glycerol groups, and/or by modifying the degree of esterification with fatty acid moieties and the chemical structures of fatty acid moieties. Because of their characteristic interfacial activity and/or tendency for molecular self-assembly, PGFE can control and modify both the physical and chemical properties of the phase boundary between different phases such as liquid (water)–liquid (oil)[3].

PGFE are mainly obtained in a two step synthesis: the first one is glycerol polymerization in the presence of catalyst and the next one is the esterification of the mixture of polyglycerol with fatty acids. The direct esterification of polyglycerols leads to a mixture with a broad range of different compounds owing to the large number of hydroxyl group. Because after the polymerization of glycerol the reaction mixture contains some part of the unreacted substrates, the product of esterification (emulsifier) may contain mono- di- or even triacylglycerols[4]. Several works have been published on the esterification of glycerol and polyglycerol with fatty acids, looking for selective processes with high region-selectivity in which the catalyst can be easily recovered and, therefore, the energy consumption reduced[5–7].

On the other hand, the product of the synthesis can be used as an emulsifier to stabilize the defined dispersed system. In this case mainly the hydrophilic – lipophilic properties of the emulsifier are important in order to obtain a product with the desired properties and stability. The hydrophilic properties of the emulsifier, which can be expressed as the HLB value, are a function of the molecular weight of the esterified fatty acid, the degree of esterification of hydroxyl groups and the number of glycerol units forming the polyglycerol backbone. For a given hydrocarbon chain length of fatty acid and the degree of esterification, the hydrophilic properties of the emulsifier increase with the molecular weight of polyglycerol[8]. Mixed surfactant systems are used in many applications. By combining surfactants, unique performance attributes not achievable with a single surfactant can be realized. Common combination often involves nonionic surfactants with anionic surfactants or with other nonionic. In our earlier work we stated that such combinations have been shown to be more surface active than the individual components, for example having lower critical micelle concentration (cmc) and interfacial tension at the O/W interface[9, 10].

The focus of this study was the preparation of novel bio based emulsifiers by tailoring the PGFE emulsifier composition and hydrophilic properties through reaction parameters programming. The final effect is to obtain the product of the reaction carried out in the proposed conditions which may be directly used as emulsifier, e.g. without purification or fractionation.

EXPERIMENTAL

Materials

Individual fatty acids e.g. lauric ($C_{12:0,}$ dodecanoic), myristic ($C_{14:0}$, tetradecanoic), palmitic ($C_{16:0}$, hexadecanoic) and stearic ($C_{18:0}$, octadecanoic) were purchased from Sigma – Aldrich, diglycerol (99.5%) from Solvay, glycerol and sodium hydroxide (analytical grade) from POCH. All materials used in chromatographic analysis and for evaluation of the HLB of the emulsifiers were high purity products and not purified before use. To prepare emulsions paraffin oil (Shell Ondina 934, medical purity)[11] and paraffin wax (Sigma-Aldrich) were used as the oil phase. The same oil was used in the interfacial measurements.

Methods

Glycerol (G) polymerization was carried out in a thermostated reactor equipped with a mechanical stirrer (200 rpm). The molar ratio of glycerol to NaOH was 1:0.01. The syntheses were carried out at the temperature 230°C in the atmosphere of nitrogen. The reaction progress was investigated by analyzing the reaction mixture composition at 1h intervals.

Esterification of polyglycerol (PG) mixture with fatty acids was carried out at 150°C in the thermostated reactor equipped with the mechanical stirrer (200 rpm) in the atmosphere of nitrogen. At the start of the reaction, sodium hydroxide was added to the fatty acid to obtain the corresponding concentrations of fatty acid carboxylate. The pressure in the system was reduced (800 hPa) to eliminate water formed during the esterification process and to prevent the hydrolysis of the ester. The reaction progress was investigated by analyzing the reaction mixture composition at 1h intervals.

Analytical methods

The concentration of glycerol, monoacylglycerols and esters of diglycerol were determined as trimethylsilyl derivatives using programmed gas chromatography with internal standardization[12]. The composition of the polyglycerols was checked by GC and TLC GPC-HPLC (Varian 8500, RIDIK 102)[13]. Fatty acids concentrations were determined by a potentiometric titration method according to IUPAC[14].

Surface activity of emulsifiers

In order to investigate the surface properties of the synthesized emulsifiers, the isotherms of the interfacial tension of the paraffin oil solutions at the O/W interface were determined. The interfacial measurements were carried out by the ring (Du Noüy) method with K10 ST tensiometer (Krüss). The paraffin oil solutions of the emulsifiers were examined at 45 ± 0.1°C. Surface tension of the purified water (D4700 NONO BDS-Barnstead) at 20°C was 72.3 mN/m.

Calorimetric and pNMR measurements

Differential scanning calorimetry (DSC) was applied to determine melting and crystallization temperature of PGFE emulsifiers. A Mettler TA 3000 thermal analysis system, equipped with a TC 10 TA processor and DSC 30 temperature cell, was used. Determining the melting curves, the reaction product was quickly cooled to -50°C, and heated at a heating rate of 2°C/min to complete melting. Determining the crystallization curve, the sample of the emulsifier in the amount of 30 mg after melting at 80°C was cooled to – 70°C at a cooling rate of 5°C/min. An empty pan was used as a reference. The heat of fusion and crystallization was calculated using the area under the melting and crystallization peak respectively. The melting and crystallization temperature were estimated by the tangent at the point of greatest slope on the portion of the peak of the DSC curve.

The SFC (solid fat content) was determined in accordance with ISO 8292:1999 using a Minispec PC 120 analyser (Bruker).

Preparation of emulsions

All dispersed systems were prepared in a glass thermostated emulsor equipped with mechanical stirrer (Heidolph RZR 2021). Distilled water as well as a mixture of the oil phase (paraffin oil, paraffin wax) and PGFE emulsifier (10 wt.% of the emulsifier, with respect to the total amount of oil and water phases) were separately heated to 75°C, and subsequently water was added to the oil phase. Emulsification (at 500 rpm) was obtained by keeping a constant rate of cooling of the system, in the temperature range of 75–25°C. The type of the dispersed system and the phase inversion temperature was determined from continuous measurement of the electrical conductivity and the temperature of the system. The conductivity was examined using a conductivity cell[15].

Evaluation of the stability of emulsions

Changes in the dispersity of emulsions were monitored by multiple light scattering (MLS) method using a Turbiscan LabExpert (Formulaction). Details of the evaluation have been presented in a recent report[16].

Rheological measurements

The rheological properties of emulsions were measured using a rotational viscometer with coaxial cylinders (Rheotest2). Samples were placed in the temperature–controlled measurement vessel and equilibrated to required temperature for 5 minutes prior to making the measurements. The rheological behaviour of the emulsions was measured 24 h after preparation. The measurements were only accepted when the emulsion had not shown any coalescence before and after shearing. The shear rate $\bar{y}$ (s^{-1}) was changed from 3 to 1312 (s^{-1}).

RESULTS AND DISCUSSION

The synthesis of polyglycerol emulsifier under the specified conditions consisted of two steps: the polymerization of glycerol (G) and the esterification of the obtained polyols (PG) with fatty acid (FA) (Fig. 1). The trivial names glycerol, di-, tri-, tetraglycerol etc. are used internationally and will also be used throughout this article.

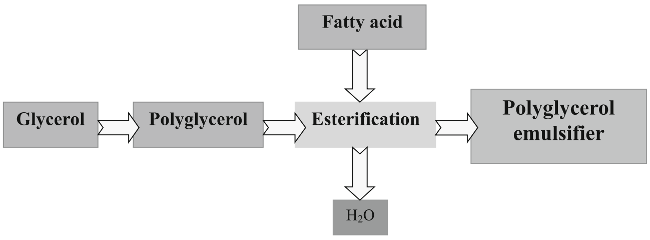

Figure 1. The synthesis of polyglycerol emulsifier

Polyglycerols synthesis

It was observed recently[12] that during polymerization the temperature has a significant effect on the glycerol conversion. Kinetic studies proved that polymerization of glycerol under the condition used is a first order reaction and may be described by the following equation: $[G]/[G]_o = \exp(k \cdot t)$. The rate constant of the reaction was $6.3 \cdot 10^{-5}\ s^{-1}$ (correlation coefficient = 0.9844). The reaction product (PG) was a mixture of glycerol (57.2%), diglycerols (27.5%) and triglycerols (15.3%).

Esterification of fatty acids

It was stated in our earlier work that fatty acids salts of sodium or potassium may be used to effectively emulsify the substrates[17]. Those carboxylates have an ability to adsorb at the polyol – fatty acid interface under the conditions of the esterification process and convert the reaction mixture into a microemulsion. As a result of the creation of huge contact area between the substrates, their conversion to mono- and diesters was much faster than in uncatalyzed reactions.

The direct esterification of polyglycerols with fatty acids leads to a mixture of different compounds owing to the large number of hydroxyl group. It is obvious that if a reaction mixture after polymerization of glycerol contains some part of the unreacted substrate, the product of esterification may contain mono, di- and triacylglycerols. As it can be seen from Table 1, the product of esterification of stearic acid with polyols contains mainly mono- (36.8%) and diesters (31.5%) of polyols.

Table 1. The composition of the synthesized PGFE-C18 emulsifiers

Compound	Concentration [%]
Monoacylglycerol (MAG)	32.7
Monoacyldiglycerol (MADG)	2.5
Monoacyltriglycerol (MATG)	1.6
Diacylglycerol + Diacyldiglycerol (DAG + DADG)	19.1
Diacyltriglycerol (DATG)	12.4
Triacylglycerols + Triacyldiglycerol (TAG + TADG)	12.1
Triacyltriglycerol (TATG)	1.6
Fatty acid (FA)	3.8
Glycerol (G)	3.5
Diglycerol (DG)	4.2
Triglycerol (TG)	0.8
Sodium carboxylate (NaC)	4.4

The reaction progress can be described by means of the changes of the substrate concentration, e.g. fatty acids as a function of reaction time. In order to investigate the influence of the chain length of the fatty acids on the esterification rate of the product of polymerization reaction, the syntheses were performed at 150°C with 0.05 mole fatty acid sodium soap formed in situ at the first step of reaction. The molar ratios $[FA]/[FA]_o = f(t)$ were calculated on the basis of the analytical data and the corresponding mass balances. Rate constants were calculated by a numerical method (Table 2).

Table 2. Influence of the fatty acid chain length on the rate constants of the esterification

Esterification	Fatty acid	The reaction kinetic constant x 10^4 [s^{-1}]
1	C12	18.9
2	C14	10.1
3	C16	9.8
4	C18	9.0

The difference of six CH_2 groups in the hydrocarbon chain length of $C_{12:0}$ – $C_{18:0}$ fatty acids increases the rate with constant ratio $C_{12:0}/C_{18:0} = 2.1$. This means that the shorter chain fatty acids are more reactive.

The obtained results indicate that fatty acids carboxylates are very important components of the reaction mixture because they do increase the interfacial area between polyol and fatty acid just at the first step of the esterification. The formation of a mixed interfacial film of ionic surfactant (carboxylate) and the synthesized nonionic esters of polyols lowers the interfacial tension between phases to produce transparent microdispersion.

Interfacial activity of emulsifiers

Our method of polyols direct esterification with fatty acids in the presence of sodium soaps obtained in situ, creates a possibility to synthesize emulsifiers with programmed hydrophilic properties and surface activity. The higher surface activity means that less surfactant may be needed to perform a function, such as detergency or emulsification, for which surfactants are used. This means less raw materials needed for the synthesis, less manufacturing of the by–product to be handled and less environmental impact of the smaller surfactant quantity used to perform the particular function.

There is only limited information on the interfacial and micellar properties of polyglycerol emulsifiers and no previous studies have been found on interaction and synergism of the mixture of MAG, PGFE and carboxylates. In this study the influence of the composition of synthesized emulsifiers on their interfacial properties in the paraffin oil/water system was investigated. In order to investigate these properties of the synthesized emulsifiers the isotherms of the interfacial tension of the paraffin oil solutions at the O/W interface were determined.

A typical curve showing the interfacial tension γ versus concentration dependencies for synthesized PGFE-C_{18} emulsifiers and DGFE-C_{18} emulsifier are presented in Figure 2. As it can be seen from the figure there is a clear reduction of interfacial tension with increasing

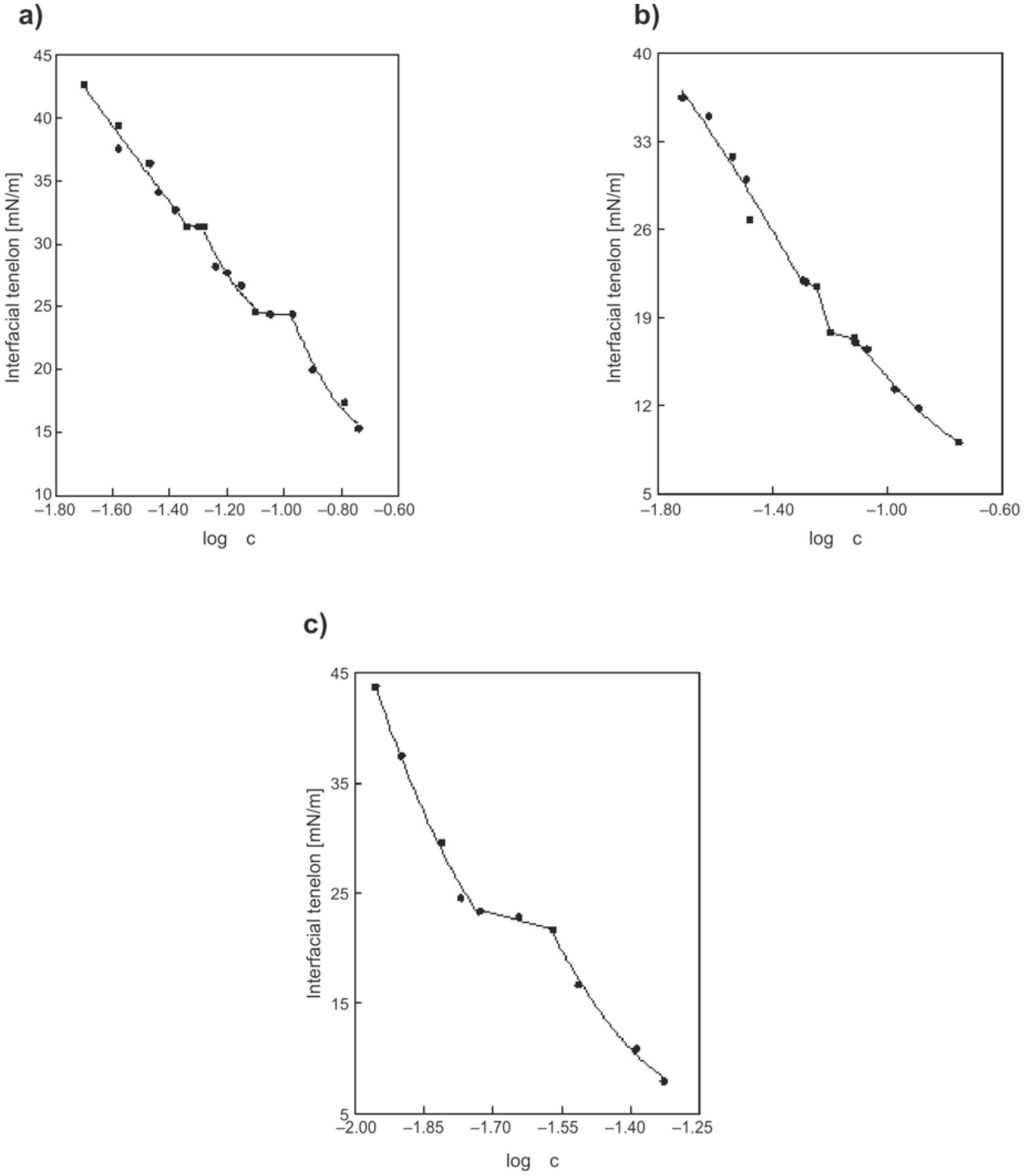

Figure 2. Interfacial tension γ versus log c curves for synthesized PGFE-C18 emulsifiers. Molar ratio of polyglycerol, fatty acid and sodium carboxylate during esterification: a) PG : FA : NaC 1:1:0.05; b) PG : FA : NaC 1:1:0.09; c) DG : FA : NaC 1:1:0.09

the concentration of emulsifier in the oil solution. It was stated that the increase of sodium soap concentration in the emulsifier causes a decrease of interfacial tension at the oil/water interface.

The interfacial tension (γ) of PGFE modified emulsifiers decreased linearly with an increase in log c to a certain point, and beyond that point they maintained the respective plateau values. The transition point in the curve of each of the examined emulsifiers considered its critical micelle concentration (cmc). As it can be seen from Figure 2 two transition points (cmc_1 and cmc_2) are present at the γ = f (log c) curves for PGFE-C18 emulsifiers. It should be noted that for DGFE-C18 emulsifier one transition point (cmc_1) was reached (Table 3). The reason for this may be the very different nature of the interactions involved in the nonionic/nonionic compound, compared to the nonionic/anionic system and different composition of polyols used to the esterification. The interfacial pressure attained by the surfactant at its cmc may be treated as a measure of the effectiveness of the interfacial tension reduction. It is the difference between the interfacial tension of pure solvent (γ_0) and the interfacial tension value at the cmc (γ_{cmc}).

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc}$$

It was observed that Π_{cmc2} diminished with increasing the hydrocarbon chain length of a surfactant (Table 3).

In hydrocarbon/aqueous systems pC_{30} is used to measure the efficiency in interfacial tension reduction and was measured by the negative log of the concentration of surfactant required to reduce the interfacial tension by 30 mN/m (C_{30})**[18]**. The reason for this is that the mea-

Table 3. Influence of the fatty acid chain length of the emulsifier on cmc values and some interfacial properties at the paraffin oil/water interface

Fatty acid	cmc_1 [g/dm3]	cmc_1/C_{30}	γ_1 [mN/m]	cmc_2 [g/dm3]	cmc_2/C_{30}	γ_2 [mN/m]	Π_{cmc1} [mN/m]	Π_{cmc2} [mN/m]
C12	0.042	0.78	24.8	0.065	1.20	18.3	26.2	32.7
C14	0.038	0.58	25.8	0.058	0.88	21.4	25.8	29.6
C16	0.036	0.55	29.0	0.054	0.82	24.8	29.0	26.2
C18	0.034	0.38	31.6	0.064	0.70	24.5	19.4	26.5
C18*)	0.018	0.33	22.2	–	–	–	28.7	–

*) Esterification of stearic acid with diglycerol (99.5%, Solvay).

sure of efficiency in this respect is usually taken at a π value where saturation is achieved. This usually occurs at π ~ 30 mN/m in hydrocarbon/aqueous system.

As it can be seen from Table 4, this value was already reached for concentration 0.040 g/dm^3 of PGFE-C12 emulsifier (pC_{30} – 1.40) and for concentration 0.058 g/dm^3 of PGFE-C18 emulsifier (pC_{30} – 1.24).

Table 4. Influence of the fatty acid chain length and molar ratio of the substrates on efficiency of the obtained emulsifiers in interfacial tension reduction at the paraffin oil/water interface

Fatty acid	Molar ratio PG:FA:NaC	C_{30} [g/dm^3]	pC_{30}
$C_{12:0}$	1:1:0.05	0.054	1.27
	1:1:0.09	0.040	1.40
$C_{14:0}$	1:1:0.05	0.066	1.18
	1:1:0.09	0.048	1.32
$C_{16:0}$	1:1:0.05	0.066	1.18
	1:1:0.09	0.044	1.36
$C_{18:0}$	1:1:0.05	0.092	1.04
	1:1:0.09	0.058	1.24
	1:1:0.09*)	0.054	1.27

*) Esterification of stearic acid with diglycerol.

The relation between micellization and adsorption can be measured by the cmc/C_{30} ratio. If the cmc/C_{30} ratio increases upon the introduction of some factor, this indicates that micellization is inhibited more than adsorption, or adsorption is facilitated more than micellization. A decrease in cmc/C_{30} ratio indicates that adsorption is inhibited more than micellization or micellization is facilitated more than adsorption. These observations are valid for the above discussed systems (Table 3).

DSC and SFC profiles of the synthesized emulsifiers

DSC measurements were performed in order to assess phase transition phenomena in all the prepared samples and to obtain the information about mesomorphic behaviour and stabilization mechanisms provided by the investigated PGFE emulsifiers. Among the different ingredients, emulsifiers play a role in controlling the desired properties of a product. To stabilize the emulsion, an emulsifier forms a thin film between the internal and external phases. The nature of the films formed at the interface of the emulsion droplets is controlled by the type of emulsifier and affects the stability of the emulsion interface. The major emulsifiers are used in sufficient amounts to distribute and stabilize droplets of the dispersed phase. Other types of emulsifiers are also used as minor components, often called additives. By controlling crystallization and polymorphic behaviour with emulsifiers additives, it is possible to change the size of fat crystals in the emulsion, which is related to the number of crystals. The addition of a polyglycerol ester with stearic acid moiety was found to accelerate the nucleation of n-hexadecane in O/W emulsion[19]. The effects of adding the PGFE on the crystallization of the palm mid fraction (PMF) in O/W emulsion and influences of fatty acid chains and their esterification were examined using the ultrasonic velocity technique and DSC. Sakamoto et al.[20] confirmed that adding hydrophobic PGFEs remarkably accelerated the crystallization of PMF in emulsion system. The acceleration effects were more enhanced with PGFEs that have long saturated fatty acid chains.

Duerr-Auster et al.[21] investigated the microstructure and stability of the lyotropic liquid crystalline phases formed by a mixture of a polyglycerol ester of palmitic and stearic acid as a function of temperature in dilute aqueous solution using a combination of DSC, polarized light, and cryo-freeze-fracture electron microscopy as well as different scattering techniques such as XRD and SANS. Using DSC it was stated that the lamellar aggregates can be present in three different physical states, namely, coagel, liquid crystalline or gel, depending on the thermal history of the sample. When PGFE is dispersed in water at room temperature it remains as a biphasic surfactant dispersion (coagel) which, when heated and cooled above the main transition temperature, successively forms a homogeneous lamellar liquid crystalline and a lamellar gel phase. Contrary to monoacylglycerol of similar chain length, this presently investigated gel phase appears to be stable with time.

The thermograms obtained for PGFE-C12 – PGFE-C18 emulsifiers are presented in Figure 3. The heat of melting and crystallization of the studied emulsifiers as a function of the number of carbon atoms of acyl groups is shown in Figure 4. Figure 5 shows the dependence of the melting and solidification temperature as a function

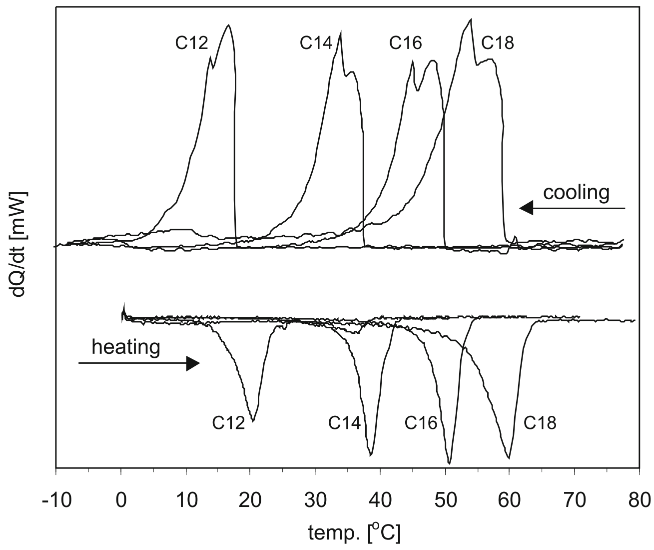

Figure 3. The thermograms obtained for PGFE C12 – PGFE C18 emulsifiers

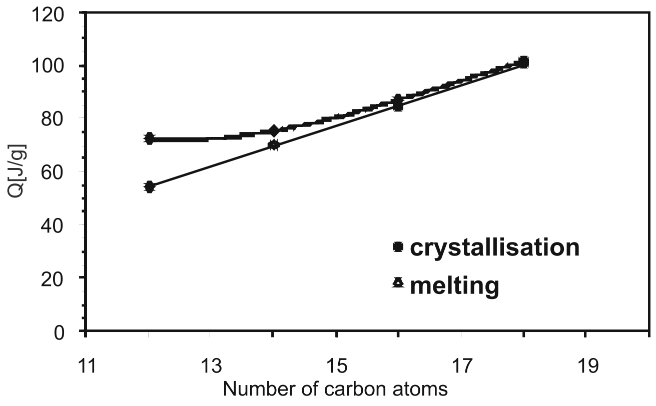

Figure 4. Heat of melting and crystallization as a function of the number of carbon atoms of acyl groups of synthesized emulsifiers

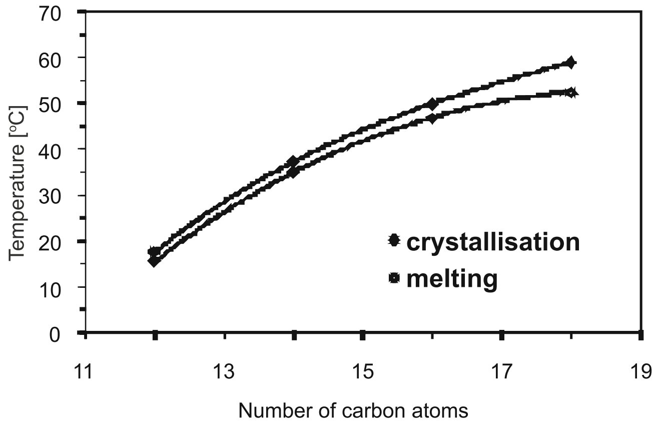

Figure 5. Melting and solidification temperature as a function of the number of carbon atoms of the acyl groups of the synthesized emulsifiers

of the number of carbon atom in the fatty acid chain. These temperatures were determined as previously described. The SFC profiles for the obtained emulsifiers are presented in Figure 6.

Emulsions stability and rheology

The type and the functional properties of dispersions are very much dependent on the amphiphilic properties of the emulsifier. The next stage of the experiments concerned the investigation of the possibility of use the synthesized emulsifiers to stabilize O/W emulsions. For the preparation of the emulsions paraffin oil and mixtures of paraffin oil and paraffin wax in different weight ratios were used as the oil phases.

The stability of the prepared emulsion systems was determined by measurements of the intensity (%) of backscatter light (BS) as a function of time of the storage at room temperature, using the DLS method. It is assumed that good stability is characterized by emulsions with BS values higher than 50% after a definite time of the storage.

The experiments showed that stable O/W emulsions could be prepared with the emulsifiers synthesized in the reaction of PG with $C_{12:0}$ – $C_{18:0}$ fatty acids, realized in the presence of NaC. As it can be seen from Figure 7, the obtained emulsions are characterized by high stability (BS above 60%). High stability of the emulsions may be a result of the presence in the system of synergetic operating emulsifiers: hydrophobic MAG and hydrophilic PGFE and NaC, in spite of the significant differences of hydrophilic–lipophilic properties between these compounds. The lamellar liquid–crystalline phases, produced with MAG and usually an admixture of the other surfactants have been found to be very effective stabilizers of O/W emulsions due to their specific architecture comprising the bimolecular layers of emulsifier separated by layers of water. The lamellar structures are capable of encapsulating oil droplets imparting both the steric hindrance and the ionic barrier (repulsion of charged encapsulated oil droplets) against coagulation.

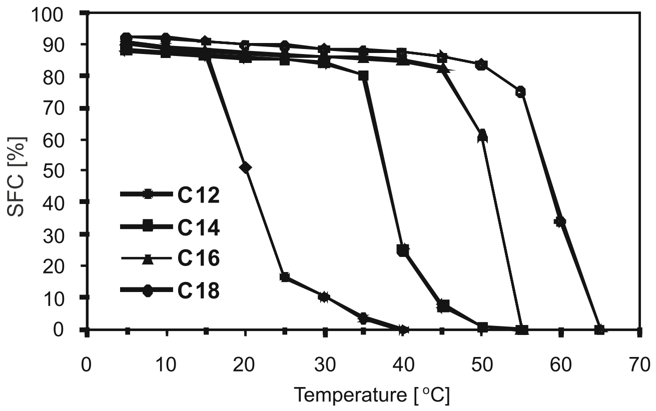

Figure 6. The SFC profiles of the synthesized emulsifiers

The rheology of emulsion is attracting a great interest mainly due to its relationship with emulsion stability, the most important factor to be considered in emulsion technology. It is obvious that in the handling, mixing and storage knowledge of the emulsion viscosity is required.

The emulsifiers were compared using the measurements of the flow properties of the model emulsions. Figure 8 shows the rheograms (shear stress vs. shear rate plots) of the emulsion systems at different values of dispersed phase concentration. The shape of the hysteresis loop is characteristic for the viscoelastic fluids e.g. concentrated emulsions. The relationship between the viscosity of the emulsion and the shear rate is presented in Figure 9. On increasing the dispersed phase concentration of emulsion, the viscosity was found to increase in all the emulsion systems studied.

It is obvious that the concentrations of surfactants e.g. non-ionic esters of polyglycerols and monoacylglycerol and anionic sodium carboxylate, are greater than those required to provide a complex condensed film at the interface, and the excess material modifies the physical, specially the rheological properties of emulsions. The process may be described as a self-bodying action, whereby the surfactant which stabilizes the emulsion may also be used to control the viscosity.

CONCLUSIONS

Synthesis of polyglycerol derivatives in the presence of sodium carboxylates makes it possible to obtain emulsifier with controlled chemical and interfacial properties. The modification of the surface activity of emulsifiers may be obtained by programming the fatty acid acyl group in the polyglycerol ester as well as the hydrocarbon chain length in sodium soap and concentration of this compound. It allows the potential use of these products in different dispersion systems. Polyglycerol emulsifiers

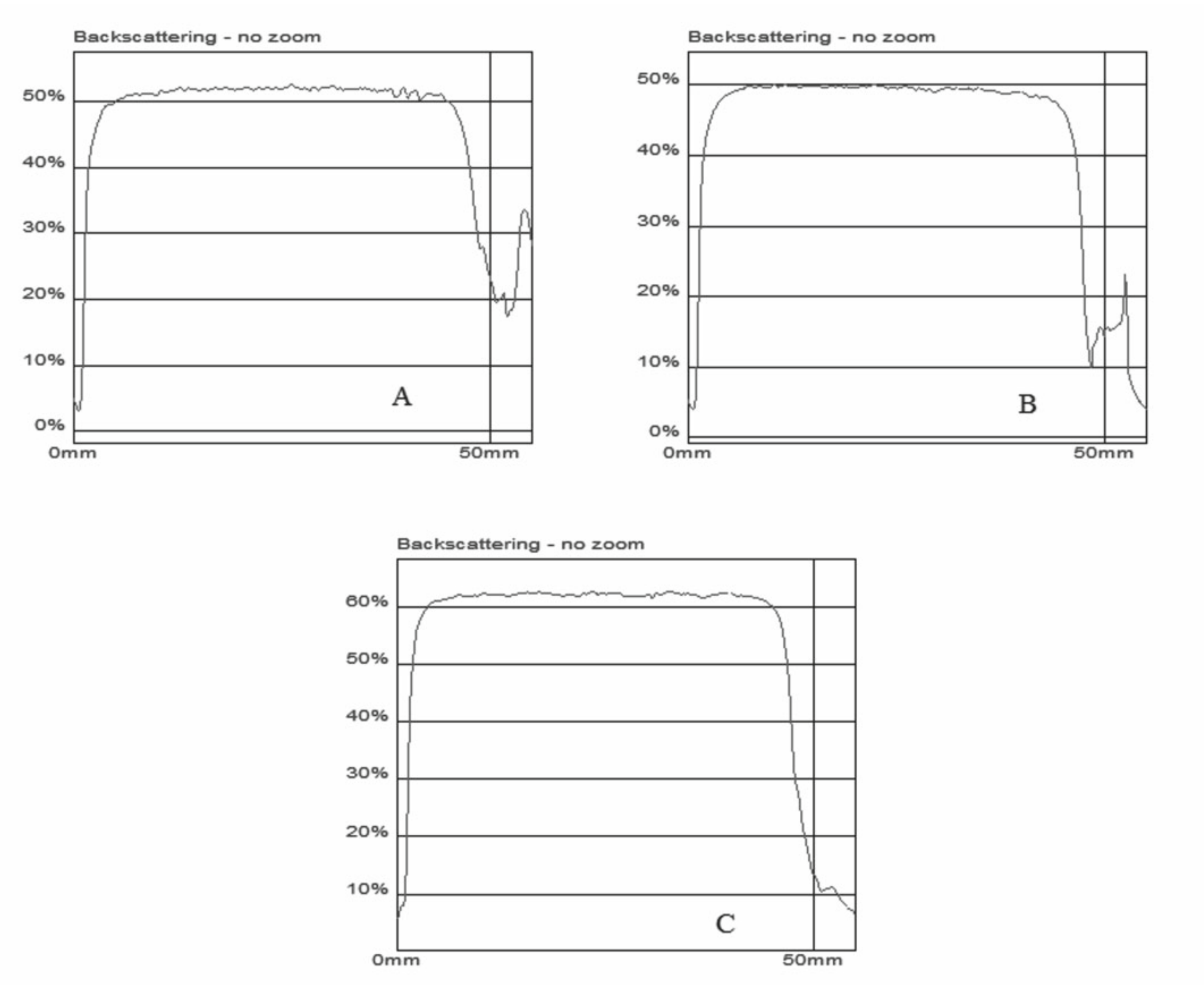

Figure 7. The stability of the emulsion obtained with PGFE-C18 emulsifier
A. The oil phase: paraffin oil. W/O weight ratio: 20/80, emulsifier – 5 wt.%
B. The oil phase: paraffin oil : paraffin wax (9 : 1 w/w). W/O weight ratio: 20/80, emulsifier – 5 wt.%
C. The oil phase: paraffin oil : paraffin wax (9 : 1 w/w). W/O weight ratio: 20/80, emulsifier – 10 wt.%

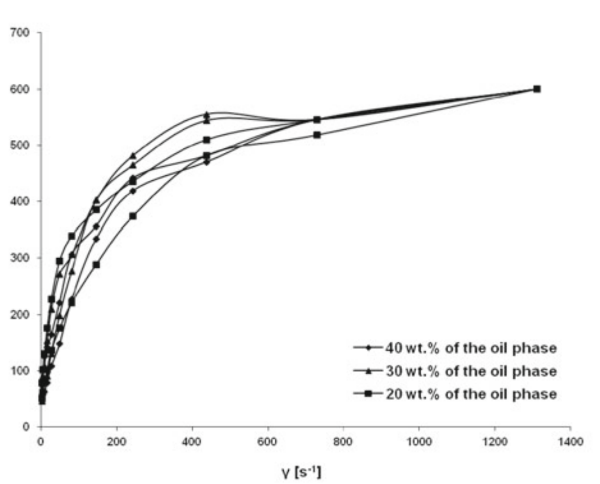

Figure 8. Flow curves of emulsions prepared with PGFE-C18 emulsifier

obtained in proposed conditions can be tailored to stabilize the defined emulsion system. The final product of this one pot synthesis may be used directly as emulsifiers without purification or fractionation. For the preparation of the modified emulsifiers – esters of polyols and fatty acids, renewable fatty raw materials may be used and the process of the synthesis does not lead to ecological hazardous by products.

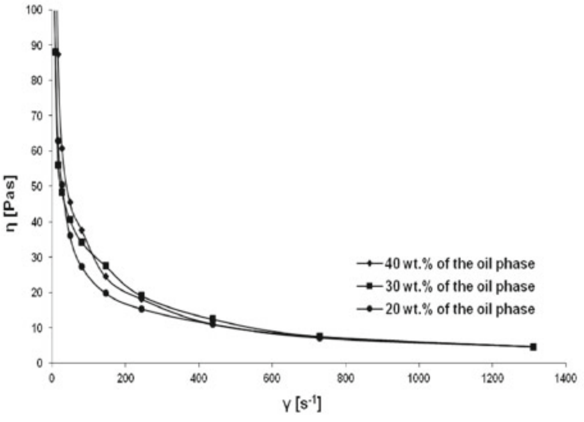

Figure 9. Viscosity – shear rate curve for emulsions obtained with PGFE-C18 emulsifier

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