Postprint of: Macierzanka A., Szeląg H., Szumała P., Pawłowicz R., Mackie A. R., Ridout M. J., Effect of crystalline emulsifier composition on structural transformations of water-in-oil emulsions: Emulsification and quiescent conditions, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 334, Iss. 1–3, (2009), pp. 40-52, DOI: 10.1016/j.colsurfa.2008.09.053

Effect of crystalline emulsifier composition on structural transformations of water-in-oil emulsions: Emulsification and quiescent conditions

Adam Macierzanka*†§, Halina Szeląg†, Patrycja Szumała†, Roman Pawłowicz‡, Alan R. Mackie§, Michael J. Ridout§

†Department of Fats and Detergents Technology, and ‡Department of Chemistry, Technology and Biotechnology of Food, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland;

§Institute of Food Research, Norwich Research Park, Colney, Norwich, NR4 7UA, United Kingdom.

Abstract

The objective of this study was to investigate the influence of acylglycerol (AG; mono-diglycerides) and acylpropyleneglycol (APG; fatty acid mono-diesters of propylene glycol) lipophilic emulsifiers, as well as their mixtures, on the structural transformations of emulsions, observed during emulsion formation and storage. The investigations aimed to characterize the phenomena that can be encountered during the manufacturing and shelf-life of emulsions prepared with these commonly used emulsifiers. It was found that in the presence of AG or AG-APG mixtures and up to 55–60 wt.% water content (depending on the emulsifiers proportions) continuous emulsification and cooling of the water-in-oil (W/O)

---

* Corresponding author. Tel.: +44 1603-255-242; fax: +44 1603-507-723.
E-mail addresses: adam_macierzanka@yahoo.co.uk,
Adam.Macierzanka@bbsrc.ac.uk (A. Macierzanka)

emulsion initially formed, led to the local phase inversion and finally formation of an oil-in-water-in-oil (O/W/O) double emulsion with unique structure. The inversion was caused by the temperature-dependent formation of the multilamellar liquid-crystalline structures of monoglyceride in the aqueous phase of emulsion. The self-assembled structures encapsulated oil droplets formed under the dynamic emulsification conditions and immobilized them in a liquid-crystalline gel matrix. The resulting oil-in-water (O/W) emulsion gel was then gradually dispersed in the oil phase, which was not involved in the formation of the internal oil droplets. Finally, double O/W/O-type droplets were produced. Their structure can be described as an O/W-emulsion lamellar-gel core surrounded by the interfacial layer of the crystallized surface-active components of the emulsifiers. Such droplets coexisted in the external oil phase with water droplets. When APG emulsifier was used as a sole stabilizer, no phase inversion was observed. The W/O emulsion produced with this emulsifier underwent crystallization- and shear-induced flocculation and subsequent deflocculation during the emulsification. We also report on the time-dependent structural evolutions of the finally-produced emulsions. The outcome of the multiple light scattering experiments and microscopic observations was that emulsions based on the AG emulsifier or the AG-rich AG-APG blends developed with time towards more tightly packed systems due to formation of a fat-crystal network in the continuous oil phase. When the only emulsifier used was APG, the structure of emulsion settled within three weeks, due to formation of crystalline bridges between droplets.

Keywords: Interfacial crystallization, double emulsion, phase inversion, liquid crystals, rheology

1. Introduction

Interfacial crystallization (at oil-water and air-water interfaces) and the ability to form various liquid-crystalline phases with water are two very important features of monoglycerides (monoacylglycerols, MAGs), which have an influence on their wide use in many food applications, cosmetic products and pharmaceutical formulations [1-4]. The phase behavior of saturated MAGs-water systems is relatively well understood [5-10]. Above the Krafft temperature (the melting temperature of the hydrocarbon chains) the liquid-crystalline lamellar phase is formed, which can transform into the cubic phase if the temperature is further raised. Below the Krafft point, the lamellar phase transforms into the so-called α-gel (highly-hydrated structure of the MAG bilayers with ordered hydrocarbon chains), which in turn converts with time to the so-called coagel phase, a network of platelike crystals. Both gel phases can be used in food products [11-13]. Since they differ in functional properties (e.g., hardness, foam stability), strategies for the preferential formation of one of these two phases have been a subject of scientific investigations [13]. The kinetics of the α-gel→coagel transition was studied mainly for binary MAG-water systems [13-19]. The transformation of this type in the MAG-based ternary system, comprised water, oil and acylglycerol emulsifier, was initially shown in our previous work [20,21]. More recently, the transition was studied by Marangoni et al. for ternary gels composed of vegetable oil, water and monoglyceride/co-surfactants [22,23]. The authors proposed that material as “a heart-friendly, low-saturate, trans fatty acid-free” alternative to conventional spreadable fats and shortenings.

In many food and cosmetic applications, mono-diglycerides (a mixture of MAGs and diacylglycerols, DAGs) are used. Both components are main products of either glycerolysis of triacylglycerols (TAGs) or esterification of glycerol (G) with fatty acids (FAs), two main industrial processes used for the production of acylglycerol emulsifiers [24]. The commercial mono-diglycerides always contain some residues of TAGs, FAs and G. In some food products (i.e., non-fat cake systems), MAGs are used in combination with another lipophilic crystalline emulsifier, propylene glycol monostearate (PGMS), in order to make stable α-crystalline blends of emulsifiers [1]. PGMS is an α-tending emulsifier [9,25]. It crystallizes in the α-crystal form at about 39 ºC [10]. PGMS is used in food industry as an effective emulsifier in toppings, bakery shortenings and cake mixes [1]. In cosmetic formulations, it can be used as an auxiliary emulsifier and viscosity modifier [26]. Like mono-diglycerides, fatty acid mono-diesters of propylene glycol (PG) can be obtained by means of direct esterification of PG with FAs or by transesterification of TAGs with PG. The latter process yields a complex mixture of PG mono- and diesters and up to 10–15 % MAG, DAG and TAG as well as G and FAs, and also some unreacted PG [9,24,27].

In oil-continuous emulsions, the emulsifying effectiveness of long-chain saturated fatty acid monoesters of G and PG (e.g., monostearins, monopalmitins) is mainly due to their ability to form mechanically strong crystalline films at the water-oil interface that prevent a coalescence of dispersed water droplets [21,28,29]. The best protection of droplets (i.e., the most effective coverage of the interface) can be obtained when the adsorbed fatty material crystallizes directly at the interface [30], or in other words, when the crystallization follows the adsorption step. Such a sequence can take place if the emulsification process is begun at the temperature higher than the crystallization range of the surface-active substances and followed by their solidification at quiescent conditions, or carried out under progressive decrease of temperature throughout the entire crystallization range [21,29].

In this study, we found that the combination of in situ formation of liquid crystalline phase and interfacial fat crystals determined the types of transitions in emulsion microstructure during the emulsification. The primary goal of our work was to investigate the effect of counterparts of the commercial acylglycerol and acylpropyleneglycol emulsifiers, used separately and together in various proportions, on the character of structural transitions of emulsions. We have reported the results of two sets of experiments, the first on the temperature/shear-dependent transformations of emulsions during emulsification processes, and the second on the post-crystallization changes in emulsion structure under quiescent conditions.

2. Experimental

2.1. Materials

Acylglycerol (AG) and acylpropyleneglycol (APG) emulsifiers were synthesized by means of uncatalyzed esterifications of respectively, glycerol (G; 99.5+% purity; Chempur Company, Poland) or propylene glycol (PG; 99.5+% purity; POCH Company, Poland), with stearic acid (SA; Sigma-Aldrich Chemie Gesellschaft GmbH & Co. KG, Germany). The SA substrate consisted of 92.2 wt.% stearic (C18:0), 4.0 wt.% palmitic (C16:0), 1.8 wt.% shorter and longer saturated and 2.0 wt.% unsaturated fatty acids. Total esterification procedures were analogical to those described in the previous reports [29,31]. The initial molar ratios of G/SA and GP/SA were 1:1 and 1.25:1, respectively. The compositions of the emulsifiers prepared (determined by GC and HPLC) were as follows; (i) AG emulsifier: 43.0 wt.% glycerol monostearate (GMS), 25.4 wt.% glycerol distearate (GDS), 6.1 wt.% glycerol tristearate (GTS), 15.3 wt.% SA, and 10.2 wt.% G; (ii) APG emulsifier: 48.7 wt.% propylene glycol monostearate (PGMS), 14.3 wt.% propylene glycol distearate (PGDS), 25.1 wt.% SA, and 11.9 wt.% PG. The hydrophile-lipophile balance (HLB) of the emulsifiers was determined experimentally via the emulsion comparison method, as described in detail previously [21].

The HLB numbers obtained were 4.0 and 3.4 (±0.1), respectively for AG and APG. In this study, AG and APG emulsifiers were used separately or as mixtures at various proportions, from 9:1 to 1:9 w/w. Note, the name "AG/APG emulsifier" used in the text corresponds to the equivalent mixture of both components. The water used for the preparation of emulsions was purified in a ROpureST/NANOpure system (Barnstead, USA). The oil phase was composed of paraffin oil and paraffin wax, 9:1 w/w (both supplied by Sigma-Aldrich).

2.2. Preparation of emulsions

Emulsions were prepared by stirring in a glass, thermostated emulsor, using a mechanical stirrer (Model RZR 2021; Heidolph, Germany) equipped with a steel agitator. Water and the paraffin/emulsifier mixture (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 gradually added (within about 10 s) to the mixture of oil and emulsifier under continuous stirring (500 rpm). The water:oil weight ratios ranging from 20:80 to 80:20 were examined. Emulsification was carried out in a decreasing temperature range of 75–25 °C. Selected stable emulsions were kept at room temperature (23 ±1 °C) for further experiments.

2.3. Phase diagrams

During the emulsification, the electrical conductivity and the temperature of the studied systems were continuously measured to determine the type of the emulsion formed (i.e., water-in-oil, W/O, or oil-in-water, O/W), the phase inversion temperature, and an eventual separation of the dispersed water phase leading to an emulsion breakage. The conductivity was examined using a conductivity cell [32]. Samples of the systems were taken at various stages of emulsification (i.e., at different temperatures) and immediately microscopically studied. Sudden, considerable changes in the macroscopic appearance of the systems (e.g., homogeneity, phase separation) were also investigated by visual inspection. Moreover, changes in the apparent viscosity of emulsion were monitored in situ over the whole temperature range of the emulsification process as described below in detail. Based on the data obtained, two types of phase diagrams were formulated. The first one shows the dependence of emulsion type/structure on the temperature of emulsification and the water:oil phase ratio. In the second-type diagram, the temperature- and shear-dependent structural transformations of emulsions have been displayed as a function of the relative concentration of AG emulsifier versus APG emulsifier (irrespectively of the AG:APG ratio, the total amount of the emulsifiers was equal to 10 wt.% of both oil and water phases). The diagram of this type was prepared for constant water:oil proportion of 40:60 w/w. The temperatures of the corresponding transitions in emulsion structure were determined from three preparations and showed a maximum standard deviation of ±0.5 °C.

2.4. In situ rheological analysis

The emulsification processes were repeated directly in an AR2000 rheometer (TA Instruments, UK), which gave an opportunity to measure in situ the apparent viscosity of the emulsions as they were being formed. The rheometer was equipped with a vaned rotor/cup arrangement (12 mm and 15 mm radii respectively, bottom gap = 5 mm) operated in constant rotation mode. Prior to experiment, the temperature-controlled cup was filled with the appropriate amounts of emulsifier and oil/wax (as specified above) and heated to 80 ºC. To ensure the components were completely melted and mixed, a 3-min pre-shear was applied. The premix was left undisturbed for 2 min before a pre-heated water phase was introduced into the system in the amount required to give a desired water:oil phase ratio. The emulsification was carried out over a decreasing temperature range 75–25 °C (45 min) at a shear rate of 500 s^{-1}. The high shear rate was chosen to mimic the conditions of emulsion preparation where a high stirring rate was required to thoroughly mix the system and produce the emulsion. The apparent viscosity was measured every 20 s and expressed as a function of temperature. The temperatures of the significant changes in viscosity, related to the transitions in emulsion structure, were determined from three measurements of the emulsion systems produced under the same conditions. The maximum standard deviation did not exceed ±0.5 °C. Control analyses were also done for the emulsions without paraffin wax as well as for the pure paraffin oil.

2.5. Microscopy

Morphology of emulsions was investigated by using a BX-60 microscope (Olympus, Japan), equipped with APO oil-immersion objectives and a DP-50 digital camera (Olympus, Japan). The microscope was operated in differential interference contrast (DIC) or cross-polarized light modes. In some cases the hydrophilic Evans Blue (1 % w/v aqueous solution) or the lipophilic Sudan II (1 % w/v paraffin oil solution) dyes were used to expose the water or oil phase, respectively. Samples of emulsions were transferred to a microscope welled slide. A staining Evans Blue or Sudan II solution was added on the top of the sample and a cover slip was carefully placed on top of the well. The staining solutions were used in the minimum amounts required to achieve the desired contrast between the internal phase and the stained continuous phase of an analyzed system.

2.6. Calorimetric measurements

Differential scanning calorimetry (DSC) was applied to determine the crystallization profiles of AG, APG and mixed AG/APG emulsifiers, in their mixtures with paraffin wax (emulsifier:wax weight ratio = 5:3). Appropriate amounts of emulsifiers and paraffin wax were weighted into 20-mL glass tubes, heated to about 100 ºC, thoroughly stirred and cooled to room temperature. Samples of 30 mg were weighted into 40-µL aluminum pans, hermetically sealed and stored 24 h at room temperature prior to measurements. Thermal analyses were conducted on a Mettler TA 3000 calorimeter (Mettler Instrumente, Switzerland) equipped with a TC 10 TA processor and a DSC 30 temperature cell. After heating to 80 ºC and keeping at this temperature for 5 min, samples were cooled to 0 ºC at the rate of 2 ºC min^{-1}. An empty pan was used as a reference.

2.7. Multiple light scattering

The kinetics of emulsion structure being built under quiescent conditions (i.e., storage) was determined at 23 ± 0.5 ºC by the multiple light scattering method, using a Turbiscane LAb Expert analyzer (Formulaction, France). A freshly-prepared emulsion (ca. 25 mL) was placed into a flat-bottomed cylindrical glass cell and stored at 23 ±1 °C. The sample was scanned by using two synchronous optical sensors that detected the intensity of light transmitted through and backscattered by the vertical sample (180º and 45º from the incident laser light, respectively). The reading head acquired backscattering (BS) and transmission data every 40 µm while moving along the entire height of the cell (i.e., 55 mm). The light source was an electro-luminescent diode (λ_{air} = 880 nm). As the emulsions studied were opaque, only the backscattering measurements provided useful data.

The intensity of backscattered light depends on the photon transport length, λ^*, through the dispersed system:

$$\mathrm{BS} \approx [(1-B)/3]\ (h/\lambda^*)^{1/2}$$

where $B \approx 0.2$ is the boundary reflection factor in cylindrical geometry and h is the detector height. The parameter λ^* corresponds to the penetration of photon into a dispersed system (i.e., the distance above which a photon is scattered in the backward direction). λ^* depends on the physical features of dispersed phase (mean particle diameter, d, and particle volume fraction, ϕ):

$$\lambda^* = 2d / [3\phi(1-g)\, Q_s]$$

The optical parameters Q_s and g are given by the Mie theory [33].

Changes in BS values correspond to changes in the structure of an analyzed sample [34,35]. For instance, a decrease in the total BS intensity usually indicates that the particle size has increased due to phenomena such as flocculation/coalescence or Ostwald ripening. In the case of particle migration, the increase in BS levels can be observed at the top or bottom of sample, depending on the type of migration, i.e., creaming or sedimentation, respectively, since the concentration of particles has increased in those regions. It is obvious that creaming (or sedimentation) influences the simultaneous decrease of particle concentration at the bottom (or in the uppermost region) of a vertical sample, and this is recorded by the analyzer as a progressive decrease of BS intensity for that region. As long as BS readings are constant for the entire height of a dispersion vertical sample, mean BS values are acceptable for computation for particular scans recorded at different time points. In our investigations, the monitoring of the microstructural behavior of emulsions was performed as a function of time. The parameters $\Delta BS_{5\text{-}50}$ and $\lambda^*_{5\text{-}50}$ were employed to characterize the kinetics of changes in emulsion structure. $\Delta BS_{5\text{-}50}$ has been defined as a difference in mean BS value (recorded for the emulsion sample in the region from 5 to 50 mm of its height; $BS_{5\text{-}50}$), between the first scan and n scan. Whereas, $\lambda^*_{5\text{-}50}$ corresponds to the mean value of the photon transport length through the emulsion for the same region of the sample height. Results have been reported as the structure change velocities, $d\Delta BS_{5\text{-}50}/dt$ or $d\lambda^{*}_{5\text{-}50}/dt$. Each sample was analyzed three times, and the data are presented as an average.

3. Results and discussion

3.1. Dynamic conditions: Emulsion formation

Fig. 1 shows the phase diagrams formulated for emulsions stabilized by (a) AG emulsifier and (b) the equivalent amounts of AG and APG (AG/APG mixed emulsifier), as well as the evolution of the apparent viscosity of the emulsions as observed during the emulsification. The temperatures of the structural transitions of the emulsion being formed were dependent on the presence of APG, however there were no significant discrepancies in the types of transformations for the two cases. At the beginning of emulsification, W/O emulsions were produced, which is an expected result for the use of strongly hydrophobic emulsifiers. But after cooling to 59–58 ºC (AG-based systems; Fig. 1a) or 56–54.5 ºC (AG/APG- based systems; Fig. 1b), a sudden significant decrease in viscosity was observed, associated with rapid destabilization of the emulsions, i.e. separation of water and oil phases. The transition is thought to be caused by the formation of the GMS-water or GMS/PGMS-water lamellar gel phase. Indeed, gel structures were observed in the samples of the destabilized systems (Fig. 2b). As the stirring was continued, oil droplets were formed and entrapped within the gel matrix, resulting in the formation of the phase-inverted O/W emulsion gel. This process and subsequent changes of emulsion microstructure are schematically depicted in Fig. 2. Formation of the lamellar, MAG-water binary gels has been a subject of many scientific reports, as mentioned in the Introduction. The lamellar liquid-crystalline phase, produced with MAGs and/or different emulsifiers, was also found to be a very effective stabilizer of O/W emulsions [9,22,23,36,37] due to its specific architecture comprising the bimolecular layers of emulsifier separated by layers of water, which penetrates into the planes of the polar headgroups of emulsifier molecules. The resulting lamellar gel is capable of encapsulating oil droplets and, due to imparting steric hindrance between droplets, prevents them from approaching each other and coalescing. With these facts as a basis, it is not surprising that the formation of the gel phase, caused by a gradual cooling of the systems studied here, produces the destabilization of W/O emulsions first and then the phase inversion to O/W emulsions. The MAG-based gels can be produced from the lamellar mesophase when the MAG-water systems are cooled below the Krafft temperature [9].

For low and medium water contents, (up to 55 wt.%) further cooling under continuous emulsification led to another well-defined transformation, namely a sudden increase in the viscosity of the system due to dispersion of the O/W emulsion gel in the external oil phase (Fig. 1). This change corresponded well to the onset of crystallization of both AG and AG/APG emulsifiers in their mixtures with paraffin wax (Fig. 3). It should be noted that the presence of the APG component in the AG/APG emulsifier caused the onset of the crystallization of this mixed emulsifier to be recorded at lower temperature (Fig. 3b) than observed for AG emulsifier (Fig. 3a). Thus, the crystallization of acylglycerols was delayed by acylpropyleneglycols. This in turn influenced the beginning of dispersion of the O/W emulsion gel in the oil phase to be observed at lower temperatures (50.5–49.5 ºC, Fig. 1b) compared to the temperatures obtained for the use of AG emulsifier (56.5–55.5 ºC, Fig. 1a). When cooled separately from AG, the APG emulsifier began to crystallize at about 40 ºC (with the peak temperature at about 38.5 ºC, Fig. 3c). All the exothermic thermograms shown in Fig. 3 were recorded for the blends of the particular emulsifiers with paraffin wax to show the crystallization profiles of all the components of emulsions that crystallize in the course of the emulsification processes. The emulsifier:wax weight ratio applied, 5:3, corresponds to the ratio present in the 40 wt.% water systems.

The dispersion of the O/W emulsion gel in the oil phase might be promoted by the onset of the interfacial crystallization of the glycerol esters, which were not involved in the formation of the lamellar gel. The created systems consisted of large-size agglomerates of the O/W emulsion gel suspended in the oil phase (Fig. 2c). Since they did not form uniform mixtures in terms of appearance (the clear continuous-phase oil was easily observed by a naked eye), the systems have been called ‘O/W + O’ dispersions (Fig. 1, 2c). At the temperature of 48–46 ºC or 40–38 ºC, depending on whether AG or AG/APG emulsifier was used, another significant increase in the viscosity was observed (Fig. 1), which might be connected to the crystallization of the other compounds of the emulsifiers (e.g., GDS, GTS, PG esters). Continuous emulsification under progressive crystallization yielded the gradual break-up of the O/W emulsion gel agglomerates and further gradual increase of the viscosity (Fig. 1). Finally, smooth viscous emulsions were formed containing water droplets and dispersed O/W emulsion gel, both covered by the interfacial layers of crystallized lipids (Fig. 2d). These complex systems have been designated as ‘W/O + O/W/O’ emulsions (Fig. 1, 2) since the O/W emulsion gel dispersed in the external oil phase formed droplets of the oil-in-water-in-oil (O/W/O) type. Existence of some nonadsorbed fat crystals, formed probably mainly of paraffin wax, GTS, GDS and PGDS (the latter in the AG/APG-based systems), and suspended in the continuous oil phase or attached to the crystalline shells of droplets, was also observed (data not shown). To further quantify the investigations, the effect of the paraffin wax on the viscosity profile has been studied in the 40 wt.% water systems. In the presence of the wax the viscosity of the finally-produced ‘W/O + O/W/O’ emulsions was found to be higher than without it (Fig. 1). Since it crystallizes in the continuous oil phase, the wax appears to add to the viscosity of that phase as well as to the effective volume of the dispersed fraction, both effects likely to be responsible for the observed enhancement of an overall final viscosity of the emulsions.

Some representative O/W/O droplets from the ‘W/O + O/W/O’ systems were selected for another microscopic characterization, which gave more insights into their internal organization. The droplets found in the emulsion specimens were gently squeezed by slowly pressing down the cover slip by the microscope lens. This way the crystallized film of emulsifier was destroyed and the core of the droplets leaked out into the oil phase and was easily observed. The interiors of the examined O/W/O droplets comprised small oil droplets surrounded by and suspended in the liquid-crystalline gel matrix. The existence and location of lamellar liquid crystals were revealed in cross-polarized light as a birefringent pattern of the droplets (adsorbed lamellar phase) and the gel matrix between them (Fig. 4). The birefringent pattern is a characteristic feature of lamellar liquid crystal-stabilized emulsions [38]. From the above we can deduct that two types of mechanical stabilizations were present in the structure of the O/W/O droplets. The internal oil droplets were stabilized by the lamellar liquid crystals, forming the layers oriented at the surface of the oil droplets, and immobilized by the gel matrix between them, whereas the external oil/gel matrix interface was stabilized by the surface-active lipid crystals that were formed in situ at the interface. Thus the structure of the O/W/O droplet was the O/W emulsion lamellar gel core encapsulated by the interfacial layer of the solidified lipids.

Both, the W/O- and the O/W/O-type droplets were found to be formed in the final emulsion (‘W/O + O/W/O’ system) if AG emulsifier was used alone or in a mixture with APG emulsifiers. From Fig. 5, the most apparent result of the use of different proportions of AG and APG emulsifiers is a change in the temperature ranges of the particular transitions in emulsion structure. In general, the higher the content of the APG component the lower the temperature of the relevant crystallization-controlled transformations, which might be due to aforementioned shift of the crystallization of mixture of AG and APG emulsifiers towards lower temperatures compared to the crystallization of AG alone. The presence of the AG component was crucial for the formation of the lamellar gel and the subsequent phase inversion, however only 10 wt.% AG content in an AG-APG mixture was required to do that (Fig. 5). When used separately, APG influenced different transformations of emulsion being produced (Fig. 6). For the water contents up to 50 wt.%, they were as follows (with decreasing temperature): (i) the initial formation of W/O emulsion at the temperature range above the level of the crystallization of paraffin wax and APG emulsifier, then (ii) the progressive decrease in the fluidity of emulsion, (iii) the formation of huge flocs of water droplets, due to simultaneous interfacial crystallization of the emulsifier and shear-induced collisions of droplets, leading to the formation of crystalline links between droplets (this phenomenon was observed as a substantial increase in the apparent viscosity at 42-40 ºC; being the more significant the more concentrated the emulsion was), and finally (iv) the shear-induced disruption of the flocs caused by the ongoing emulsification at the temperature below the range of the emulsifier crystallization, which yielded the formation of an ointment-like, smooth W/O emulsion. The water droplets produced were covered by the crumpled crystalline film of APG emulsifier (Fig. 7). Compared to the emulsification processes carried out with AG and AG/APG emulsifiers (Fig. 1), the main difference in the above emulsification pathway was the lack of the phase inversion step. It might be caused by different behaviors of GMS and PGMS in the presence of water. According to Krog [39], in contrast to monoglycerides, propylene glycol esters can not associate with water into mesomorphic phases.

In all final W/O emulsions (stabilized by APG) and ‘W/O + O/W/O’ systems (produced with AG or AG/APG), partially-coalesced (or partially-divided) droplets were observed (Fig. 8). Such a structure of droplets can be produced in two different ways, as proposed in Fig. 9 (note, for AG or AG/APG emulsifiers, the scheme covers only the post-phase inversion part of the emulsification, i.e., the progressive formation of ‘W/O + O/W/O’ emulsions from ‘O/W + O’ systems). During the emulsification, large droplets are deformed, elongated and subsequently broken into smaller ones due to the shear applied (Fig. 9A). Thus, for the successful formation of smaller droplets proper viscoelasticity of the interfacial film of emulsifier is required. Emulsification carried out from high to low temperature can yield the most effective decrease in droplets size if emulsifier is in a liquid or semi-liquid state over some initial temperature range, able to effectively reduce the interfacial tension and supplied in a concentration high enough to cover the new interfacial area being formed during high shearing (adsorption from the oil phase). The emulsifier should finally produce the strong protective barrier against coalescence (end of emulsification at low temperature) to maintain final droplet size (Fig. 9A a→d’). However, on cooling the system under continuous emulsification through the entire range of emulsifier crystallization, various shapes of droplets can be obtained depending of their shape at the endset of the interfacial crystallization, namely spherical and irregular, non-spherical droplets (Fig. 9Ad’ and Ab’, respectively), as well as partially-divided droplets (Fig. 9Ac’), all stabilized by the solidified interfacial layer of emulsifier. Considering the morphology of the partially-divided droplets (Fig. 8), similar structures can be produced as a result of the stirring-induced collision of droplets leading to flocculation and subsequent coalescence (Fig. 9B), but in this case the resulting structures should be called the partially-coalesced droplets due to a different history of their formation. If the interfacial film of emulsifier remains, at a certain temperature, in a liquid or semi-liquid state and is weak enough to rupture after the collision of droplets, the droplets will merge (Fig. 9B a→c). But if in the next step a continuously crystallizing film is not able to regain a spherical shape then two (or more) droplets will finally form a partially-coalesced cluster stabilized by the interfacial membrane of solidified emulsifier (Fig. 9Bc’). On the other hand, the flocculation of droplets can also occur at the temperature at which the interfacial film of emulsifier is sufficiently solidified and strong to prevent a coalescence, and then the crystallized flocs can be produced (Fig. 9Bb'). Such flocs can be disrupted into individual droplets under shear applied during the emulsification (orthokinetic flocculation → deflocculation), as shown above for the use of APG emulsifier (Fig. 6). The kinetics of these dynamic phenomena depends on the temperature at which flocculation took place and, as a consequence, on the physical state of emulsifier, as well as on the energy of collision of droplets, the amount of the crystalline material involved in the formation of links between droplets, and the time-scale for which the flocculated droplets have been exposed to shear.

The shape of droplets also depends on the temperature-dependent changes in the viscosity of the dispersed phase. In general, the higher the viscosity of the dispersed phase the longer it will take to deform and break up droplets of that fluid to form smaller droplets [40]. It can explain why in the 'W/O + O/W/O' emulsions studied, the O/W/O-type droplets were found to be, in general, larger than the coexisting water droplets (Fig. 2d). Namely, the viscosity of water is thought to be much lower than the viscosity of the internal phase of O/W/O droplets, which was an O/W-emulsion gel stabilized by liquid crystalline phase of AG or AG/APG emulsifiers' components. Thus, it could influence a relatively long time-scale that was required to deform and divide such droplets, which along with the progressive interfacial crystallization could yield the considerable number of deformed or even partially-divided large O/W/O droplets. It is obvious that a decrease of temperature can also have an influence on a considerable increase of viscosity of the continuous oil phase itself. As a consequence, it can lead to less effective emulsification and/or enhanced stability of flocs to an orthokinetic deflocculation. The dynamics of changes in the viscosity of continuous phase is expected to depend on the composition of that phase and an emulsifier. In our particular case, the viscosity might be governed by the non-surface active components of the studied mixtures that crystallized in the continuous oil phase, imparting the significant increase of the viscosity of the phase on cooling. In the studied systems such components are thought to be paraffin wax (component of the continuous oil phase), and GTS and PGDS, present in AG and APG emulsifiers, respectively. All these substances can form three-dimensional crystalline networks in oil phases [29,41-45].

In the AG- and AG/APG-based systems containing 55–65 wt.% water, the lamellar phase-induced destabilization and phase inversion yielded a flocculated O/W emulsion or an O/W emulsion with some separated oil and water phases ('O/W + (O + W)'), respectively (Fig. 1). Microscopic examination of these systems gave some insight into possible way of the formation of O/W/O-type droplets for lower water contents. The separation of oil and water, commenced at about 59–58 and 56–54.5 ºC, in respectively AG- and AG/APG-stabilized systems (Fig. 1), resulted in the formation of regions where water was in excess, which in turn might result in closing of the bilayers into spherical aggregates. Such a tendency is a characteristic feature of the lamellar phase in excess of water [46]. The aggregates contained oil droplets bound by the lamellar gel (Fig. 10). Such structures have been thought to be the cores of O/W/O droplets in the 'W/O + O/W/O' systems. Once the core was formed, it was being encapsulated by the polar lipids that were not involved in the formation of the lamellar gel and began to crystallize at the external oil-aqueous gel interface, forming solidified film. The lipids are supposed to be GDS, SA and some amount of GMS, as well as PGMS in AG/APG-stabilized emulsions. The O/W/O-type droplets were further divided into smaller droplets due to the ongoing shearing, as described above for Fig. 9.

As the water content was increased over 65 wt.%, the product of the phase inversion in both AG- and AG/APG-based systems was an O/W dispersion (Fig. 1). The inversion was identified from a rapid increase of the electrical conductivity of the system, from 0-0.1 μS cm^{-1} for the W/O emulsion before the inversion to ca. 10 μS cm^{-1} as the transition to the O/W dispersion took place. The phase inversion was accompanied by a significant decrease of the apparent viscosity (Fig. 1). Once this drop was observed, it was followed by a temporary increase due to formation of the gel phase, and finally the viscosity settled at lower values as the O/W dispersion was formed. In the both systems, the dispersions contained predominantly large (up to 400 μm) oil droplets covered by the crystallized emulsifier, and plenty of fine, submicron-size droplets (data not shown). The lamellar gel phase was located mainly between some fine droplets, and thus could not act as an effective thickening agent for the whole system. Due to such an organization, the large particles formed a cream layer within a relatively short time (up to a few hours) following the emulsification. Over 60 wt.% water systems prepared with APG as a sole emulsifier underwent different transformations (Fig. 6). At temperatures higher than 50 ºC, a coarse W/O emulsion was produced. It contained large water droplets that coalesced under continuous agitation. The water phase released was immediately redispersed and new droplets were generated. When the temperature dropped below 50 ºC a decrease in fluidity of the emulsion was observed, associated presumably with the progressive crystallization of paraffin wax in the continuous oil phase. At about 40 ºC, droplets rapidly flocculated due to the sharp crystallization of the emulsifier (Fig. 3) and emulsion collapsed when emulsification was continued at lower temperatures. For these high water/oil proportions, the crystallized interfacial membrane of emulsifier of many water droplets was destroyed due to the shear applied and the destabilized system appeared, designated in the phase diagram as 'W/O + W' (i.e., remained W/O emulsion + separated water; Fig. 6). The release of water was signalled by a sudden increase of the electrical conductivity, from 0-0.1 to ca. 9 μS cm^{-1}. The above transformations are similar to those described recently for APG emulsifier modified with zinc fatty acid carboxylates [29]. However, as shown previously [47], propylene glycol mono-distearate with admixture of sodium stearate (5-11 %) can yield kinetically stable viscoelastic O/W emulsions for more than 50 wt.% water contents. This is likely because of the formation of the multilamellar gel phase composed of PGMS with strongly hydrophilic anionic surfactant, sodium stearate, and water. Such a phase can encapsulate oil droplets, imparting both the steric hindrance (an onion-like lamellar shell) and the ionic barrier (repulsion of charged encapsulated oil droplets) against coagulation.

3.2. Quiescent conditions: Structure building

After the emulsification, selected stable emulsions were further analyzed under quiescent conditions. Fig. 11 shows a development of the structure of the oil-continuous emulsions, as recorded by the MLS method during the storage at 23 ±1 °C. In the systems based on APG and AG/APG emulsifiers, a progressive decrease in the intensity of backscattered light (BS) was observed during the first 1-3 weeks. Possibly, the decrease was caused by a restoration of the crystalline bonds between droplets destroyed during the emulsification. Under quiescent conditions, relatively rapid sintering between droplets covered by lipid crystals might result in some spatial reorganization of emulsions. In the APG-rich systems, the droplets formed a three-dimensional network stabilized by solid crystalline bridges (Fig. 12). Hence, the emulsions were easier to penetrate by the incident light of the MLS analyzer because the gaps filled with the external oil phase were formed between the sintered droplets. Thus, the intensity of BS was lower than for the freshly-prepared systems. The emulsions stabilized by APG emulsifier obtained their final structure within about 3 weeks and then the settled levels of BS remained constant for at least 2 months (Fig. 11a). In the AG/APG-stabilized emulsions, the initial drop of the intensity of BS, attributed to the sintering between droplets, was followed by an increase after the first week of storage (Fig. 11b). An increase was also observed for the emulsions prepared with AG emulsifier (Fig. 11c), thus it might be connected to the presence of the glycerol esters. It is likely that in these systems the sintering of droplets as well as the existing oil-continuous crystals (i.e., the crystals formed in the oil phase at higher temperatures during the emulsification, likely GTS, GDS and paraffin wax) was accompanied by further crystal growth in the oil phase. In the AG-stabilized emulsions the increase was most pronounced for the low dispersed-water contents (20, 30 wt.%, Fig. 11b). Possibly in these emulsions the emulsifier was in excess and its considerable amount crystallized in the continuous oil phase bringing about a packed structure of the emulsion system. More significant increase in BS was observed for the AG/APG emulsifier (Fig. 11b). It may be assumed that in emulsions stabilized by both AG and APG, sintering of droplets and continuous-oil crystals might be created by acylpropyleneglycols (PGMS and PGDS), since they crystallized at lower temperatures than acylglycerols and paraffin wax (Fig. 3), and are expected to be compatible to both the oil-continuous and the interfacial crystals. The compatibility of adsorbed monoolein and sintering triglycerides (palm kernel fat) was previously shown by Johansonn and Bergenståhl for the dispersion of β’ palm stearin crystals in soybean oil [48]. According to the presented rheological and sedimentation studies, the increased adsorption of the triglycerides might lead to the enhanced bridging of the fat crystals.

Application of shear (emulsification) broke crystal structures formed at some earlier stages of emulsification, as mentioned in the previous section, and then they started to re-associate under quiescent conditions due to a mutual adhesion. In all probability, the AG- and AG/APG-based emulsions crystallized partly under shear and partly at rest, so the re-built crystals could also act as nuclei for further growth of acylglycerols crystals during the storage. Finally in ‘W/O + O/W/O’ emulsions obtained with the AG emulsifier and the AG-rich AG-APG mixtures, fan-shaped crystals were formed (Fig. 13). They were located in the external oil phase, between water droplets. All the above post-emulsification processes, i.e., re-association of existing crystals, their sintering and the sintering of the crystallized shells of water droplets, and new crystals growth might occur simultaneously. Formation of the new crystals in the continuous oil phase yielded a considerable increase in the effective volume fraction of emulsions, which was recorded as a progressive enhance of BS values with time (Fig. 11b, c). The influence of relative AG-APG proportions on the development of emulsion structure has been shown in Fig. 14. The ratio determined the structure of the freshly-prepared emulsions and the type of the structural changes observed during the storage. The parameter $\lambda^*_{5\text{-}50}$ (the mean photon transport length through emulsion) recorded for the freshly-prepared emulsions was dependent mainly on the degree of dispersity of emulsions, increasing with the increase of droplet size for the APG-rich systems. The formation of network of droplets, observed during the first days of storage allowed photons of incident light to penetrate deeper into the examined samples, so the parameter $\lambda^*_{5\text{-}50}$ increased. When the AG content was more than 10 wt.% in AG-APG mixture, the increase was followed by a step-by-step decrease, which corresponded to the aforementioned post-emulsification formation of the aggregates of crystals and, especially, the new crystals growth in the external oil phase. The emulsions were kinetically stable for at least two months at room temperature. After this time, their structures varied from a meshed network of coherent continuous-oil crystals and water droplets in the AG-rich systems to huge droplets linked by crystal bridges in the APG-stabilized emulsions (Fig. 12). Thus in the latter, the dominant post-crystallization process was the formation of solid crystal bridges between crystalline membranes of droplets, whereas in the presence of acylglycerols, the sintering of the continuous-oil crystals as well as the new crystals growth in the oil phase could also take place. The first sign of destabilization, an oiling-out, was observed after about 80 days in the 20 wt.% water emulsions. More concentrated emulsions were stable against gravitational migration of droplets and oil phase during the time-scale of storage (up to 6 months). Coalescence and separation of water phase were not observed at that time.

4. Conclusions

The above investigations showed how a microstructure of emulsion can be modified by both the relative proportions of two emulsifiers crystallizing during the emulsification process and the water/oil ratio. Among the systems produced, the most complex, and thus interesting, seem to be 'W/O + O/W/O' emulsions. Compared to the early Friberg's study on the phase equilibrium between oil, water and lamellar liquid-crystalline phase of MAG in liquid-crystal stabilized emulsions [36], as well as the ternary systems of aqueous phase, oil and surface-active lipid crystals, reviewed recently by Larsson [46], the 'W/O + O/W/O' emulsions reported in this paper are examples of more complex systems, consisting of oil, water, and both liquid-crystalline lamellar phase and polar lipid crystals located at the water-oil interface. The emulsions are systems where three different types of mechanical stabilization have been found to occur. The internal oil particles in O/W/O-type droplets were encapsulated by the lamellar liquid crystals, whereas the external water-oil interface was stabilized by the solidified layer of the surface-active lipid crystals. Both, the liquid crystals and the lipid crystals were formed in situ during the emulsification. Third stabilizing mechanism derived from the post-emulsification processes observed in the continuous oil phase. These comprised the sintering of continuous-oil crystals, the sintering between the crystallized films covering water droplets, as well as the new crystals growth. They led to the formation of the three-dimensional network of crystals and water droplets, which protected the system from gravitational migration of the dispersed particles for a considerable time.

The 'W/O + O/W/O' emulsions are a good example of how complex colloidal structures can be created by controlled but simple processing. The emulsions may have possible applications as the oil-continuous formulations where a controlled release of water-soluble ingredients is required. Such components could be introduced to the system with water at the beginning of emulsification and then incorporated into the gel matrix of the finally-formed ‘W/O + O/W/O’ emulsions.

Acknowledgements

The work was financially supported by Polish Ministry of Science and Information Society Technologies (Research Project 3 T09B 089 27). Part of the work was funded by the Biotechnology and Biological Sciences Research Council (BBSRC, UK) through the core grant to the Institute of Food Research.

References

[1] N. Krog, Food emulsifiers, in: F.D. Guneston, F.B. Padley (Eds.), Lipid Technologies and Applications, second ed., Wiley-VCH, New York, 1999, pp. 521-534, and references therein.

[2] N. Krog, K. Larsson, Crystallization at interfaces in food emulsions – a general phenomenon, Fat Sci. Technol., 94 (1992) 55-57.

[3] L. Sagalowicz, M.E. Leser, H.J. Watzke, M. Michel, Monoglyceride self-assembly structures as delivery vehicles, Trends Food Sci. Technol., 17 (2006) 204–214, and references therein.

[4] G.M. Eccleston, Functions of mixed emulsifiers and emulsifying waxes in dermatological lotions and creams, Colloids Surf. A: Physicochem. Eng. Aspects, 123-124 (1997) 169-182.

[5] K. Larsson, The structure of mesomorphic phases and micelles in aqueous glyceride systems, Zeit. Phys. Chem. Neue Folge, 56 (1967) 173-198.

[6] N.J. Krog, K. Larsson, Phase behavior and rheological properties of aqueous systems of industrial distilled monoglycerides, Chem. Phys. Lipids 2 (1968) 129-143.

[7] K. Larsson, N. Krog, Structural properties of the lipid-water gel phase, Chem. Phys. Lipids 10 (1972) 177-180.

[8] N. Krog, A.P. Borup, Swelling behavior of lamellar phases of saturated monoglycerides in aqueous systems, J. Sci. Food Agr. 24 (1973) 691-701.

[9] N.J. Krog, Food emulsifiers and their chemical and physical properties, in: S.E. Friberg, K. Larsson (Eds.), Food Emulsions, third ed., Marcel Dekker, New York, 1997, pp. 141-188, and references therein.

[10] N. Krog, Crystallization properties and lyotropic phase behavior of food emulsifiers: relation to technical applications, in: N. Garti, K. Sato (Eds.), Crystallization Processes in Fats and Lipid Systems, Marcel Dekker, New York, 2001, pp. 505-526.

[11] G.H. Doerfert, Distilled monoglycerides, Food Eng., 34 (1962) 97-100.

[12] I. Heertje, H.A.C.M. Hendrickx, A.J. Knoops, E.C. Roijers, H. Turksma, Use of mesomorphic phases in food products, European Patent 0 558 523 B1 (1991).

[13] I. Heertje, E.C. Roijers, H.A.C.M. Hendrickx, Liquid crystalline phases in the structuring of food products, Lebensm.-Wiss. u.-Technol., 31 (1998) 387-396.

[14] G. Cassin, C. de Costa, J.P.M. van Duynhoven, W.G.M. Agterof, Investigation of the gel to coagel phase transition in monoglyceride-water systems, Langmuir, 14 (1998) 5757-5763.

[15] V. Chupin, J.-W.P. Boots, J.A. Killian, R.A. Demel, B. de Kruijff, Lipid organization and dynamics of the monostearoylglycerol-water system. A ^{2}H NMR study, Chem. Phys. Lipids, 109 (2001) 15-28.

[16] A. Sein, J.A. Verheij, W.G.M. Agterof, Rheological characterization, crystallization, and gelation behavior of monoglyceride gels, J. Colloid Interf. Sci., 249 (2002) 412-422.

[17] J.P.M. van Duynhoven, I. Broekmann, A. Sein, G.M.P. van Kempen, G.-J.W. Goudappel, W.S. Veeman, Microstructural investigation of monoglyceride-water coagel systems by NMR and CryoSEM, J. Colloid Interf. Sci., 285 (2005) 703-710.

[18] C. Alberola, B. Blümich, D. Emeis, K.-P. Wittern, Phase transitions of monoglyceride emulsifier systems and pearlescent effects in cosmetic creams studied by ^{13}C NMR spectroscopy and DSC, Colloids Surf. A: Physicochem. Eng. Aspects, 290 (2006) 247-255.

[19] C. Alberola, T. Dederichs, D. Emeis, M. Möller, T. Sokolowski, K.-P. Wittern, Ultrasonic velocity measurements as a method for investigating phase transitions of monoglyceride emulsifier systems in pearlescent cosmetic creams, J. Colloid Interf. Sci., 307 (2007) 500-508.

[20] A. Macierzanka, H. Szeląg, Phase transition dissimilarities of the emulsion prepared with acylglycerols/zinc stearate and acylpropyleneglycols/zinc stearate emulsifiers, in: Proceedings of the “26th World Congress and Exhibition of the International Society for Fat Research (ISF); Modern Aspects of Fats and Oils”, Prague, Czech Republic, 2005.

[21] A. Macierzanka, H. Szeląg, T. Moschakis, B.S. Murray, Phase transitions and microstructure of emulsion systems prepared with acylglycerols/zinc stearate emulsifier, Langmuir, 22 (2006) 2487-2497.

[22] A.G. Marangoni, S.H.J. Idziak, C. Vega, Heidi Batte, M. Ollivon, P.S. Jantzi, J.W.E. Rush, Encapsulation-stucturing of edible oil attenuates acute elevation of blood lipids and insulin in humans, Soft Matter 3 (2007) 183-188.

[23] H.D. Batte, A. J. Wright, J.W. Rush, S.H.J. Idziak, A.G. Marangoni, Phase behavior, stability, and mesomorphism of monostearin-oil-water gels, Food Biophys., 2 (2007) 29-37.

[24] R.J. Zielinski, Synthesis and composition of food-grade emulsifiers, in: G.L. Hasenhurttl, R.W. Hartel (Eds.), Food Emulsifiers and their Applications, Chapman & Hall, New York, 1997, pp. 11-38.

[25] C.E. Stauffer, Emulsifiers and stabilizers, in: K. Rajah (Ed.), Fats in Food Technology, Sheffield Academic Press, Sheffield, 2002, pp. 228–274.

[26] B. Idson, Surfactants and cosmetic macroemulsions: properties and application, in: M.M. Rieger (Ed.), Surfactants in Cosmetics, Marcel Dekker, New York, 1985, pp. 1-28.

[27] C.E. Stauffer, Emulsifiers, Eagan Press, St. Paul, MN, 1999.

[28] J.C. Wootton, N.B. Howard, J.B. Martin, D.E. McOscar, J. Holme, The role of emulsifiers in the incorporation of air into layer cake batter systems, Cereal Chem., 44 (1967) 333-343.

[29] A. Macierzanka, H. Szeląg, Microstructural behavior of water-in-oil emulsions stabilized by fatty acid esters of propylene glycol and zinc fatty acid salts, Colloids Surf. A: Physicochem. Eng. Aspects, 281 (2006) 125-137.

[30] D. Rousseau, Fat crystals and emulsion stability – a review, Food Res. Int., 33 (2000) 3-14.

[31] A. Macierzanka, H. Szeląg, Esterification kinetics of glycerol with fatty acids in the presence of zinc carboxylates: preparation of modified acylglycerol emulsifiers, Ind. Eng. Chem. Res., 43 (2004) 7744-7753.

[32] D.J. McClements, Food Emulsions: Principles, Practice and Techniques, CRC Press, Boca Raton, 1999.

[33] H.C. van de Hulst, Multiple Light Scattering: Tables, Formulas and Applications, Academic Press, New York, 1980.

[34] O. Mengual, G. Meunier, I. Cayré, K. Puech, P. Snabre, TURBISCAN MA 2000: multiple light scattering measurement for concentrated emulsions and suspensions instability analysis, Talanta, 50 (1999) 445-456.

[35] O. Mengual, G. Meunier, I. Cayre, K. Puech, P. Snabre, Characterisation of instability of concentrated dispersions by a new optical analyser: the TURBISCAN MA 1000, Colloids Surf. A: Physicochem. Eng. Aspects, 152 (1999) 111-123.

[36] S. Friberg, L. Mandell, M. Larsson, Mesomorphous phases, a factor of importance for the properties of emulsions, J. Colloid Interf. Sci., 29 (1969) 155-156.

[37] S. Friberg, L. Mandell, Phase equilibria and their influence on the properties of emulsions, J. Am. Oil Chem. Soc., 47 (1970) 149-152.

[38] S.E. Friberg, Z. Ma, Emulsions: factors and issues for skin care, in: J.J. Wille (Ed.), Skin Delivery Systems: Transdermals, Dermatologicals, and Cosmetic Actives, Blackwell Publishing, Ames, 2006, pp. 187-209.

[39] N. Krog, Functions of emulsifiers in food systems, J. Am. Oil Chem. Soc., 54 (1977) 124-131.

[40] P. Walstra, P.E.A. Smulders, Emulsion formation, in: B.P. Binks (Ed.), Modern Aspects of Emulsion Science, The Royal Society of Chemistry, Cambridge, 1998, pp. 56-99.

[41] S.S. Narine, A.G. Marangoni, Relating structure of fat crystal networks to mechanical properties: A review, Food Res. Int., 32 (1999) 227-248.

[42] A.G. Marangoni, The nature of fractality in fat crystal networks, Trends Food Sci. Technol., 13 (2002) 37-47.

[43] S.M. Hodge, D. Rousseau, Flocculation and coalescence in water-in-oil emulsions stabilized by paraffin wax crystals, Food Res. Int., 36 (2003) 695-702.

[44] D. Rousseau, S.M. Hodge, Stabilization of water-in-oil emulsions with continuous phase crystals, Colloids Surf. A: Physicochem. Eng. Aspects, 260 (2005) 229-237.

[45] S.M. Hodge, D. Rousseau, Continuous-phase fat crystals strongly influence water-in-oil emulsion stability, J. Am. Oil Chem. Soc., 82 (2005) 159-164.

[46] K. Larsson, Kinetically stable aqueous dispersions prepared by crystallization processes, J. Dispersion Sci. Technol., 28 (2007) 39-42.

[47] A. Macierzanka, H. Szeląg, Viscoelastic properties of oil-in-water emulsions stabilized by acylpropyleneglycol emulsifiers obtained with sodium soaps, in: Proceedings of the "3rd Conference: Surfactants and Dispersed Systems in Theory and Practice", Polanica Zdrój, Poland, 2005.

[48] D. Johansonn, B. Bergenståhl, Sintering of fat crystal networks in oil during post-crystallization processes, J. Am. Oil Chem. Soc., 72 (1995) 911-920.

Figure captions

Fig. 1.

The phase diagrams (left-hand side) and the apparent viscosity profiles (right-hand side) of the water-oil systems prepared with (a) AG and (b) AG/APG emulsifiers. The black-colored areas show the temperature ranges at which a sudden decrease of the viscosity and a phase separation were observed during the emulsification. The dashed arrows correspond to the temperature ranges of the gradual shear-induced transition of 'O/W + O' system to 'W/O + O/W/O' emulsion (both systems coexisted at that stage).

Fig. 2.

Schematic representation (the left-hand side column) and microscopic visualization of the lamellar gel-induced phase inversion of W/O emulsion, and the formation of the O/W emulsion gel-loaded O/W/O double droplets, in the systems produced with AG (the middle column) and AG/APG (the right-hand side column) emulsifiers, under continuous emulsification at decreasing temperature and for water content ≤55 wt.%. The white arrows in the micrographs of the panel (b) indicate the gel phase formed in the water, whereas the black arrows in the micrographs (c2') and (c3') show the localization of the gel phase in the 'O/W + O' systems produced at lower temperatures ('W' and 'O' correspond to water and oil, respectively). Samples shown in micrographs (b2, b3) and (c2, c3) were stained with Evans Blue and Sudan II, respectively.

Fig. 3.

DSC crystallization profiles of (a) AG, (b) AG/APG and (c) APG emulsifiers in their mixtures with paraffin wax (emulsifier:wax weight ratio = 5:3). The arrows indicate the peak crystallization temperature of paraffin wax.

Fig. 4.

The squeezing visualization of the internal structure of representative O/W/O droplets in the 'W/O + O/W/O' emulsion systems (W:O = 40:60 w/w) obtained with (a) AG and (b) AG/APG emulsifiers; internal oil droplets covered by multilamellar liquid crystal layers and incorporated into liquid-crystalline gel matrix, as observed using DIC (upper images) and cross-polarized light (lower images) microscopies. Birefringent patterns around droplets (lower images) show oriented liquid crystals. 'W' and 'O' correspond to water and external oil phase, respectively. The scale bar = 10 µm.

Fig. 5.

Effect of the relative proportions of AG and APG emulsifiers and the temperature on the structural transformations of emulsions during the emulsification process. The water:oil weight ratio = 40:60. The black-colored area shows the temperature range at which a sudden, temporary decrease of the viscosity and a phase separation were observed. The dashed arrows correspond to the temperature range of the gradual shear-induced transition of 'O/W + O' system to 'W/O + O/W/O' emulsion (both systems coexisted at that stage).

Fig. 6.

The phase diagrams and the apparent viscosity profiles of the water-oil systems prepared with APG emulsifier. The gray-colored area represents the temperature range of the progressive decrease in the fluidity of emulsion before the interfacial crystallization of the emulsifier and the flocculation of droplets took place. The dashed arrows correspond to the temperature range of the gradual shear-induced deflocculation of W/O emulsion.

Fig. 7.

Interfacial crystallization of the APG emulsifier in W/O emulsion (40:60 w/w; (a) the system obtained after cooling to 25 ºC). Image (b) shows the magnified DIC view of the surface of a representative water droplet. The scale bars correspond to (a) 30 µm and (b) 10 µm.

Fig. 8.

DIC micrographs of the partially-coalesced/divided droplets formed in 40 wt.% water systems. Samples were taken at the end of emulsification (25 ºC). Emulsifier used: (a) AG:APG = 70:30 w/w, (b) AG:APG = 20:80 w/w, (c, d) APG. The scale bars correspond to 15 µm.

Fig. 9.

Schematic representation of the influence of the continuous emulsification and the progressive interfacial crystallization of emulsifier in W/O-type emulsions on the possible ways of formation of the partially-divided and partially-coalesced water droplets (Ac' and Bc', respectively); Stirring and shearing leading to an elongation and break-up of droplets (A), and the collision of droplets resulting in flocculation and coalescence (B). For more details see text.

Fig. 10.

Spherical aggregates of the gel phase with incorporated oil droplets observed in the 60 wt.% water systems obtained with the AG emulsifier for the temperature range of 56–33 ºC (see

Fig. 1a). The aggregates are suspended in the continuous water phase. Micrographs (a) and (b) show variations in the size of the aggregates produced. Scale bars correspond to 10 μm.

Fig. 11.

The time-dependent evolution of $\Delta BS_{5\text{-}50}$ values for the W/O emulsions stabilized by (a) APG emulsifier and the 'W/O + O/W/O' emulsions produced with (b) AG/APG and (c) AG emulsifiers. Water:oil weight ratio: (○) 20:80, (●) 30:70, (□) 40:60, (×) 50:50 and (♦) 60:40 (graph c only). Emulsions were stored at 23 ±1 °C.

Fig. 12.

Effect of the relative proportions of AG and APG emulsifiers on the microstructure of emulsions (W:O = 40:60 w/w). After the emulsification from 75 to 25 ºC, the emulsions were stored for 60 days at 23 ±1 °C. The arrow indicates an example of the crystalline bridge formed between droplets in the APG-stabilized emulsion. The scale bar corresponds to 30 μm.

Fig. 13.

An example of the fan-shaped crystal formed in the continuous oil phase of the 'W/O + O/W/O' emulsions. The micrograph was taken for the 40 wt.% water system prepared with AG:APG (70:30 w/w). 'W' indicates the surface of water droplet. The scale bar corresponds to 5 μm.

Fig. 14.

Time-dependent evolution of the emulsion structure (W:O = 40:60 w/w) expressed as changes in the mean photon transport length through emulsion ($\lambda^*_{5\text{-}50}$). Effect of the relative proportions of AG and APG emulsifiers (w/w); (●) 100:0, (○) 70:30, (■) 50:50, (□) 30:70, (▲) 20:80, (◊) 10:90, (♦) 0:100. Emulsions were stored at 23 ±1 °C.