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Physicochemical properties of concentrated triglyceride-in-water emulsions stabilized with decaglycerol monolaurate and sucrose

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Abstract

Various experimental techniques, namely rheometry, laser light diffraction and multiple light scattering, are used to study the physical stability of highly viscous O/W emulsions (models of cosmetic creams) containing 80 wt.% oil and formulated with vegetable, biodegradable ingredients: caprylic/capric triglyceride (organic phase), decaglycerol monolaurate (surfactant, DGML) and sucrose (viscosifier, Suc). Formulating such dispersion relies on its end-use properties, so that the main issue lies in finding a compromise between stability, increasing with additive contents, and fluid consistency, which should allow spreading. Among the formulas considered, the emulsion-gel containing 7%DGML-4.5%Suc shows the best performances as regards shelf-stability, easy use and handling.

1. Introduction

The formulation and the desired stability of an emulsion are strongly dependent on the end-use of the product. High-internal-phase-ratio emulsions (HIPRE, or highly concentrated O/W emulsions) have been studied over decades, due to their important technological and daily applications [1-4]. A lot of pharmaceutical semi-solid dosage forms [5-7], cosmetic creams and ointments [8] belong to the HIPRE or to the emulsion gel type. HIPRE possess viscoelastic properties [2-4, 7] and, in the cosmetic field, rheological behavior is of utmost importance since the easiness of spreading is their fundamental physical property. High viscosity formulas are obtained thanks to the addition of a thickener agent [5-7]. The use of polyglycerol fatty acid esters (PGFA) in food and pharmaceutical emulsions is common practice [9-13]. Concentrated triglyceride-in-water emulsions gels, to which sufficient physical stability is brought by the addition of PGFA or sorbitan esters, as surfactants, and sucrose or other sugars as viscosifiers [14, 15], are also possibly useful, simple examples of cosmetic products. The hydrophilic carbohydrate confers the state of a particular fluid (emulsion gel) to the final product. Rheological and stability studies of such or similar model systems appear relevant before assessing their usefulness in cosmetics formulation. It is then necessary to find a compromise between the stability (better for higher viscosifier contents) and the consistency of the complex fluid, which should not exceed a certain value beyond which its final use, namely spreading, becomes difficult.

In the present work, concentrated oil/water emulsions are formulated with highly biodegradable ingredients of vegetable origin. Caprylic/capric acid triglycerides and decaglycerol monolaurate (DGML) were chosen for their moisturizing properties. The effects of DGML and sucrose (viscosifier) on the physicochemical properties and the stability of 80 wt. % caprylic/capric acid triglyceride-in-water emulsions are studied by means of various techniques: rheometry, particle size measurements with laser-light diffraction and optical microscopy, and multiple light scattering analysis with the Turbiscan ags.

2. Materials and methods

Emulsification was carried out at 25 °C in a stirred tank equipped with a Rushton turbine and four baffles: this device was operated in a mixed flow regime (between axial and radial types). The decaglycerol monolaurate (S-

Face L-1001, Rossow Cosmétiques, Paris, abbreviated as DGML) and the sucrose (Suc) aqueous solutions were mixed, then caprylic/capric acid triglyceride (Myritol 318, BASF, abbreviated as O for oil) was added very slowly while stirring with a mechanical stirrer (1000 rpm) to give viscous emulsions with 80 wt. % oil content (10 min were necessary to add 400 g oil, then 10 min to produce fine emulsions). To evaluate emulsion physical stability, a few characteristics, among those susceptible to change during storage, were measured at regular time intervals:

- rheological characterization was performed using an AR2000 rheometer (TA Instruments), equipped with cone-plane geometry of 4° angle, 40 mm diameter and 119 µm troncature,
- droplet size distribution was measured with a laser particle sizer (Mastersizer 2000, Malvern, UK) and the optical microscope Morpho G3 (Malvern,UK),
- backscattered intensity profiles were obtained from measurements with the Turbiscan ags (Formulaction, France) [16-20].

Further experimental details are available [21].

3. Results and discussion

3.1. Viscoelastic properties

Ten samples of concentrated O/W emulsions (80 wt.% O) were prepared; the aqueous continuous phase consisted of 2.75 to 11.25 wt.% DGML, 0 to 8 wt.% Suc and a water content complementary to 20 wt.% (Table 1).

The viscoelastic properties (dynamic moduli: elastic/or storage modulus (G') and viscous/or loss modulus (G")) are indirect measurements of particle-particle interactions (they measure structural characteristics of the formulas) [7].

The study of the linear viscoelastic properties of our emulsions (Fig. 1) enables to characterize their structure at rest (the formulas were studied under conditions close to the rest, without rupture of the internal structure). All the formulas present long linear viscoelastic domains (LVED) with predominant elastic properties (G' > G") indicating a strong thickening behavior (associated particles). Once the critical strain (increasing with additive concentrations) is reached, the dependence of the dynamic moduli on the deformation appears, and a transition from the linear to the nonlinear domain is clearly observed: G' starts to decrease (indicating an evolution in the inner structure of the sample, which begins to flow) while G" increases with the deformation, decreasing the G'-G" gap (progressive shift from an elastic to a viscous behavior) [7, 22-24]. At about 30% strain, the G' and G" curves cross each other, *i.e.* an exact balance between elastic and viscous behaviors occurs [23]. This transition (which indicates the onset of spreading of the formula), at low deformations, is an interesting and desirable

Table 1: Composition of the emulsion samples

No.[a]	DGML[b] (wt.%)	Sucrose (wt.%)
1	2.75	4.5
2	4	4.5
3	7	0
4	7	0.95
5	7	2
6	7	4.5
7	7	7
8	7	8
9	10	4.5
10	11.25	4.5

a. All samples contain the same ratio (80 wt.%) of oil (caprylic/capric acid triglyceride);
b. Decaglycerol monolaurate; water amount: complementary to 20 wt.%.

property for topic cutaneous applications, since it simulates the ease of spreading of the cream on the skin, which in turn allows a better absorption of the active product. Consequently, the knowledge of these parameters is a first approach to predict the performances of the products [7].

Over the whole deformation range, the viscoelastic properties (G’, G” and the phase angle (δ)) vary significantly with additive concentrations, *e.g.* G” increases. However, we observe a change of tendency for (11.25% DGML-4.5% Suc). This formula presents the highest critical strains (beginning of the flow) and the highest deformations, corresponding to the exact balance of elastic and viscous behaviors (G’= G”), showing that the flow and the spreading of this formula on the skin will be extremely delicate because of its viscous, sticking texture. This indicates an acceptable limit of additive contents, which should not exceed about 15% of the frequency and time sweeps.

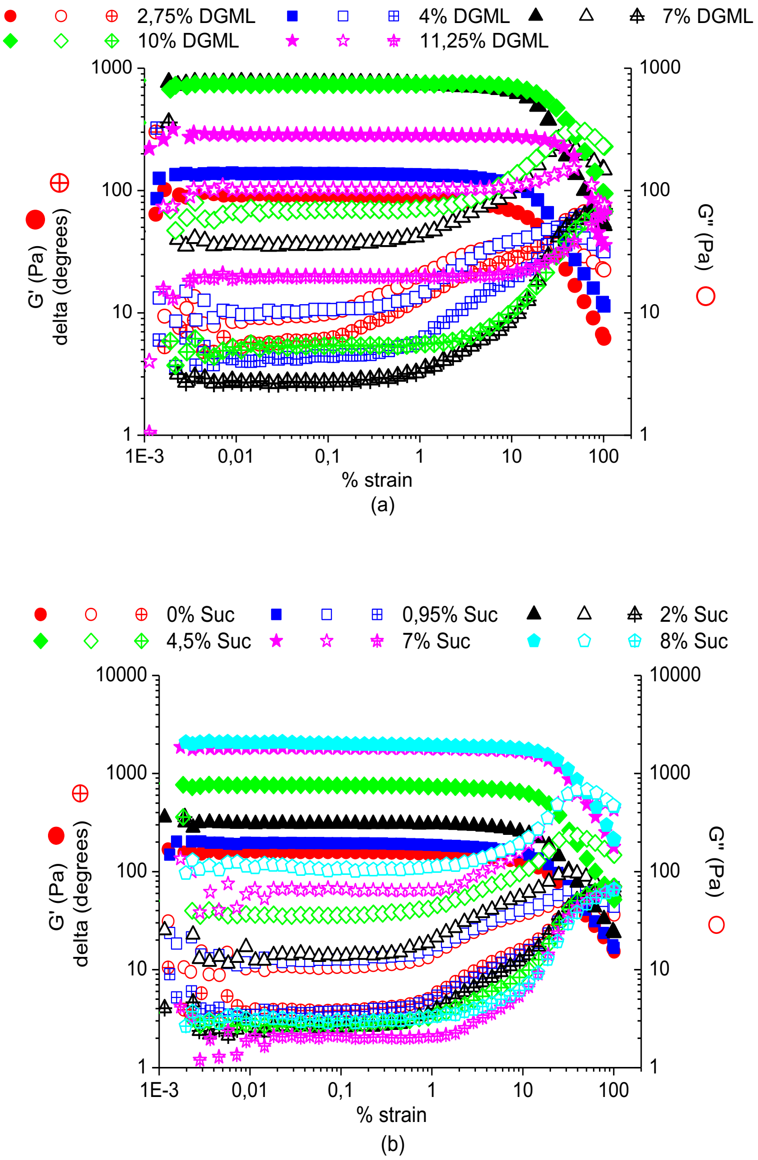

Figure 1: Typical strain sweep profiles: determination of the LVED and study of the viscoelastic properties (G', G" and δ): (a) 4.5 wt % Sucrose emulsions (effect of DGML content), (b) 7 wt % DGML emulsions (effect of sucrose content).

The flow curves (rheograms) for the various formulas are shown in Figure 2. These curves were obtained using a “steady state flow’’ procedure.

The flow curves (rheograms) show a Casson type shear-thinning behavior for all the formulas [25]:

$$\tau^{\frac{1}{2}} = {\tau_0}^{\frac{1}{2}} + \left(\eta_P\, \dot{\gamma}\right)^{\frac{1}{2}} \qquad (1)$$

where τ is the shear stress (τ_0 for the threshold value), η_p the plastic viscosity and $\dot{\gamma}$ the shear rate.

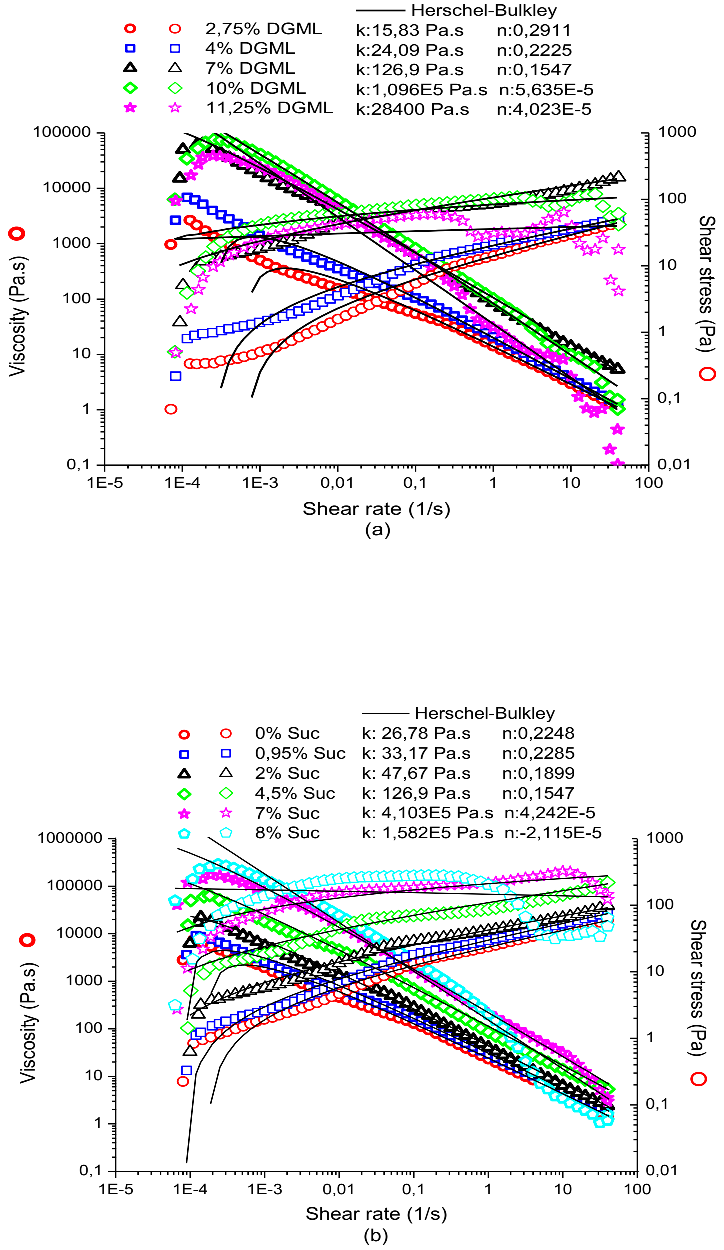

Figure 2: Effects of additive concentrations on the flow curves (rheograms): (a) 4.5 wt % Sucrose emulsions (effect of DGML), (b) 7 wt % DGML emulsions (effect of sucrose). Solid lines: Herschel-Bulkley model (k: consistency, n: flow index).

Except for the formula (11.25% DGML-4.5% Suc), emulsion viscosity increases with sucrose or surfactant concentration. The Herschel-Bulkley model describes emulsion behavior rather well and gives physical information, such as the consistency and the flow index:

$$\tau = \tau_0 + k\,\dot{\gamma}^{\,n} \qquad (2)$$

where k is the consistency (fluid viscosity for $\dot{\gamma} = 1\ s^{-1}$) and n the flow index. The values of n, always lower than 0.3 and decreasing with increasing additive concentrations, come with the shear-thinning properties of the emulsions. Besides, flow curves versus time show a rheopectic behavior, already found in highly concentrated emulsions [24].

3.2. Drop size distribution

Particle size distribution was measured by a laser diffraction technique with the Mastersizer 2000 in dilute medium for the various formulas. The results are illustrated by Figure 3.

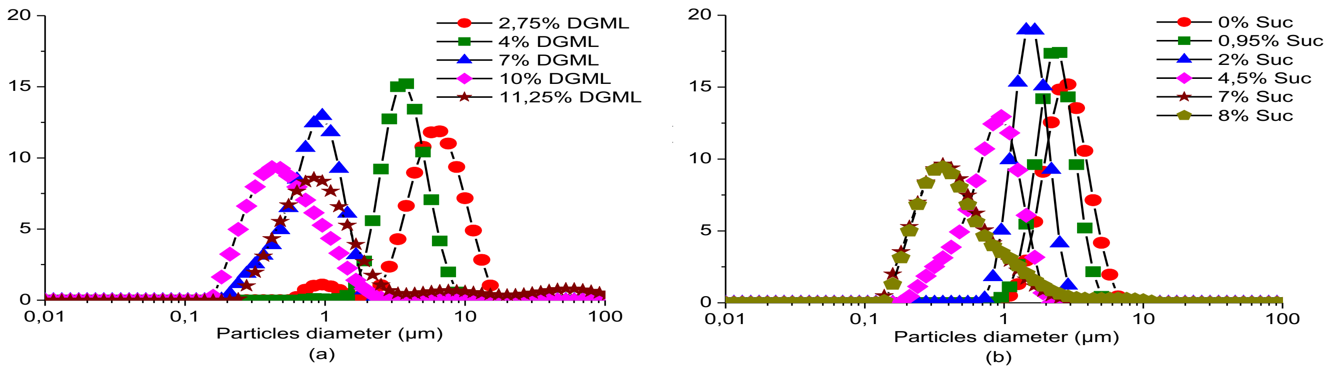

Figure 3: Effects of additive concentrations on droplet size distribution: (a) 4.5 wt % Sucrose emulsions (effect of DGML), (b) 7 wt % DGML emulsions (effect of sucrose).

The average particle size (Sauter diameter) ranges are 0.1 to 2 µm for fine emulsions and 2 to 10 µm for coarse emulsions. Droplets size distributions are very sensitive to additive concentrations: droplet size decreases with the increase of DGML content (Fig. 3(a)), which confers high viscosity to the emulsion (Fig. 2 (a)). Sucrose was used as a viscosifier, however we note that this additive leads to finer emulsions (droplet size is reduced with an increase of the sucrose content) (Fig. 3(b)). We also note that the two formulas (7% DGML-8% Suc) and (7 DGML-7% Suc) are the finest emulsions and their droplet size distributions are practically identical. That confers the highest viscosities and identical viscoelastic properties to these emulsions (beyond 7%, the effect of sucrose is not significant). These conclusions were confirmed by visualizations with the optical microscope Morpho G3 (Fig. 4). An in-depth explanation of this trend should require further investigation.

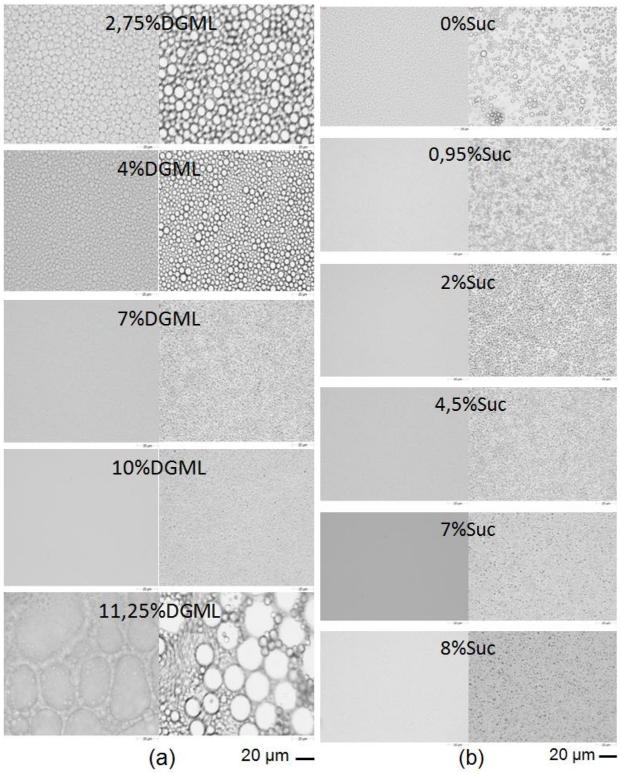

Figure 4: Microscopic image, with « Morpho G3 », showing the effects of additive concentrations on droplet size: (a) 4.5 wt % Sucrose emulsions (effect of DGML), (b) 7 wt % DGML emulsions (effect of sucrose).

3.3. Evolution of the physicochemical properties as a function of time (evaluation of the physical stability)

As expected, the finest emulsions [(7% DGML-8% Suc), (7% DGML-7% Suc), (10% DGML-4.5% Suc) and (7% DGML-4.5% Suc)] are more viscous and more stable. The evolution of their physical stability versus time was investigated: their droplet size distributions and their flow curves (rheograms), for one month of storage, are given by Figures 5 (a) to (d) and 6 (a) to (d), respectively.

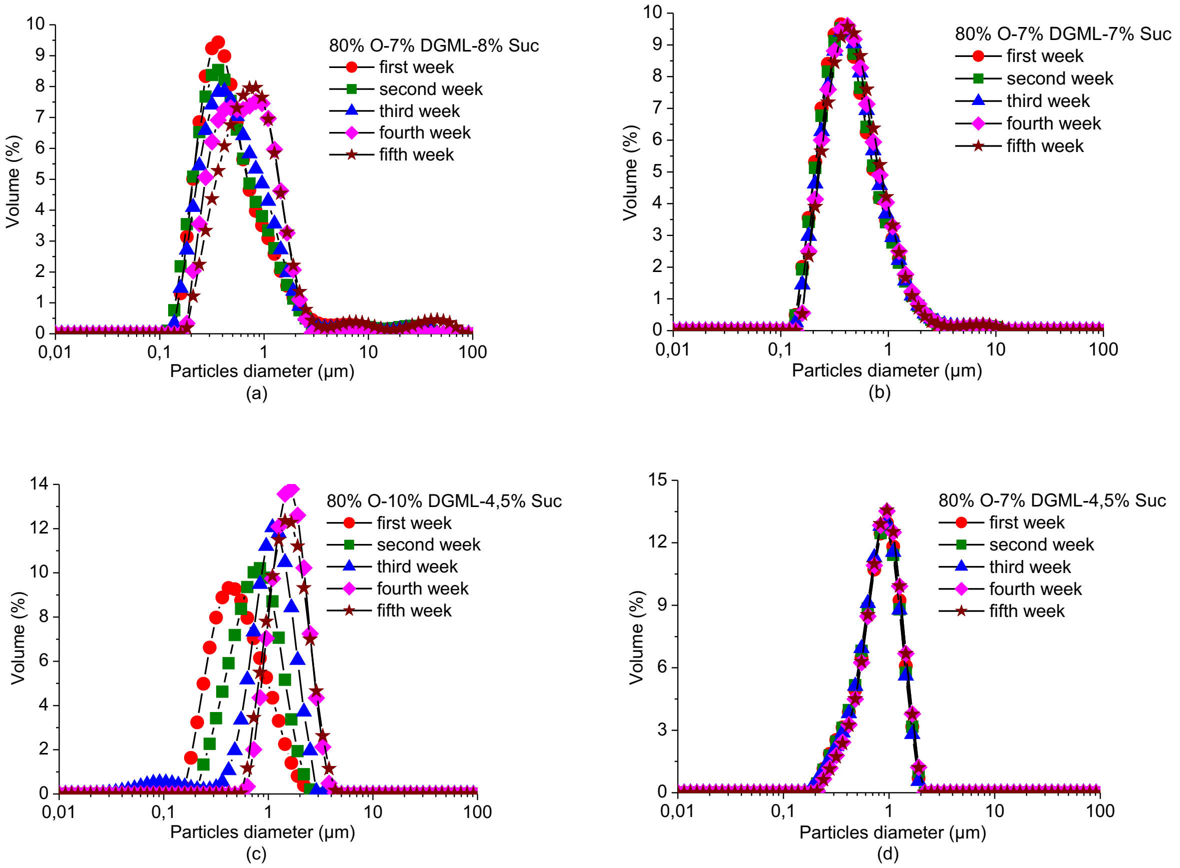

Figure 5: Droplet size distributions *vs*. time, for the finest emulsions.

The droplet size distributions of the formulas (7% DGML-8% Suc) and (10% DGML-4.5% Suc) show displacements towards the large diameters, indicating the formation of large drops by destabilization (coalescence due to Van der Waals interaction forces between droplets). The formula (10% DGML-4.5% Suc) reveals a second population of droplets, after two weeks of storage, likely to be due to the formation of significant aggregates with a shift of this peak toward larger sizes. Therefore, the suspended particles are of two types: a first population of primary droplets and a second population of large drops (with diameter reaching 100 µm after three weeks of storage). These displacements towards the large diameters are characterized by the decrease of the viscosity of these formulas (Figs. 6 (a) and (c)).

The formula (7% DGML-7% Suc) contains the finest droplets, but a low displacement towards the large sizes appears at the fourth week of storage. This formula presents two populations of particles: a first one, constituted by primary droplets, showing a maximum at 0.4 µm, and a second one at 8 µm, which indicates the beginning of coalescence. However, the droplet size distribution of the formula (7%DGML-4,5%Suc) remains monomodal and invariant versus time, that can predict the stability of this formula.

The rheograms of the two formulas (7% DGML-7% Suc) and (7% DGML-4,5% Suc) are reproducible during all the period of storage and over the whole shear rate range studied, indicating an equilibrated balance of the rheological behavior for these formulas (Figs. 6(b) and (d)). However, we note that the structure of the formula (7% DGML-7% Suc) starts to break for shear rates higher than 10 s^{-1}.

The backscattered intensity profiles given by the Turbiscan ags, and the effect of sucrose on the visual aspect of the formula (7% DGML-4.5% Suc) are illustrated by Figure 7.

Droplet migration was characterized with the Turbiscan ags. The time-dependent behavior of the backscattering intensity is related to the local variations of droplet concentration (migratory phenomena: sedimentation and creaming) and to changes occurring in the inner structure of the emulsions (namely droplet size) due to particle-particle interaction forces like Van der Waals'ones, responsible for the formation of aggregates (flocculation) [16-20]. The backscattered intensity profiles (%), as a function of the height of the sample and of the time of storage in the apparatus, for the formula (7% DGML-4.5% Suc) are given by Figure 7. The backscattered profiles remain uniform and invariant *vs*. time all along the sample (this formula remains stable and homogeneous). For this formula, the backscattered intensity is strongly correlated with the droplet size distributions and the flow curves (rheograms) which showed a remarkable reproducibility *vs*. time (Figs. 5(d) and 6(d)). The formula (7% DGML-4.5% Suc) shows a low backscattered intensity, due to the effect of the sucrose which transforms our white emulsion (sucrose-free emulsion (7% DGML-0% Suc)) into a transparent viscous emulsion (emulsion gel) (Fig. 7 (b)).

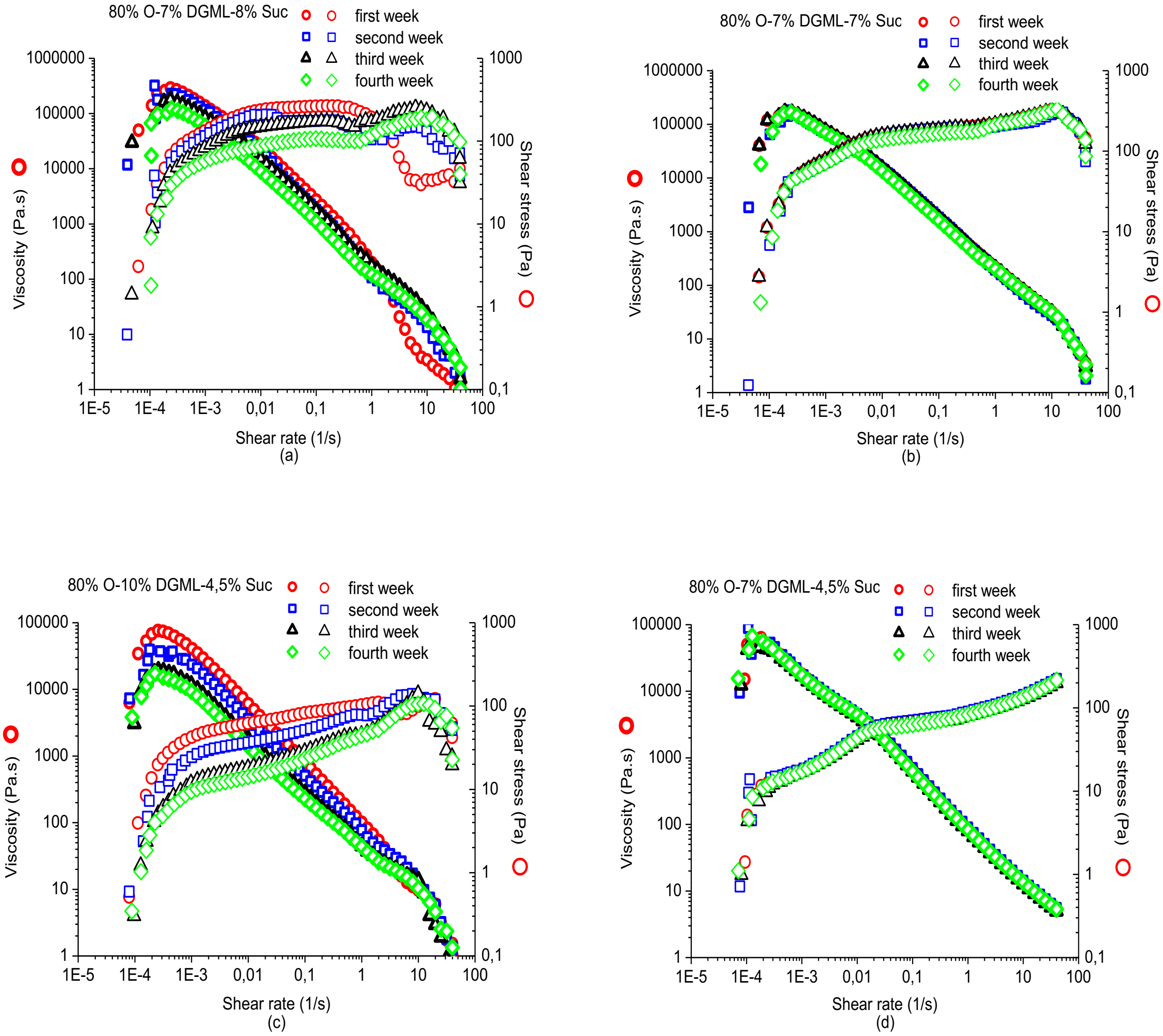

Figure 6: Evolution of the flow curves, as a function of time, for the finest emulsions.

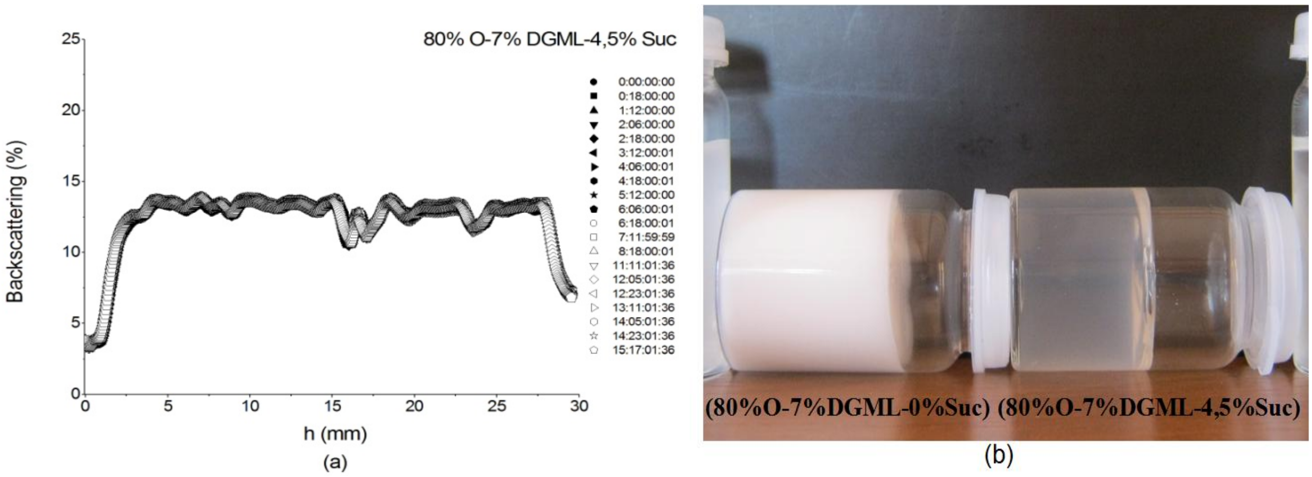

Figure 7: (a) Evolution of backscattered intensity profiles, as function of time, for the formula (80% O-7% DGML-4.5% Suc); (b) Effect of sucrose on the visual aspect of the formulation (transparent emulsion gel).

Conclusion

The physical stability of concentrated oil/water emulsions, containing 80 wt. % oil, formulated with vegetable and highly biodegradable products; caprylic acid triglyceride (organic phase), decaglycerol monolaurate (surfactant), and sucrose (viscosifier) has been monitored by different methods of investigation: rheological characterization, particle size measurements (with laser-light diffraction and optical microscopy) and multiple light scattering analysis with the Turbiscan ags.

The viscosity of the emulsions increases with the decrease of the particle size, which seems well confirmed by our experimental results.

The rheograms, the droplets size distributions and the backscattered intensity profiles given by the Turbiscan ags are reproducible during the whole period of storage, especially for the formula (7% DGML-4.5% Suc).

The different methods of investigation enabled us to assess the interactions between the ingredients and to determine the optimal additive concentrations allowing a physical stability consistent with the considered end-use. In this respect, the formula containing 7% DGML and 4.5% Suc is recommended, since it shows the best performances as regards shelf-stability, easy use and handling.

Nomenclature

		Greek letters	
DGML	decaglycerol monolaurate	$\dot{\gamma}$	Shear rate (s^{-1})
G'	elastic/storage modulus (Pa)	δ	Phase angle (°)
G"	viscous/loss modulus (Pa)	η	Dynamic viscosity (Pa.s)
LVED	linear viscoelasticity domain	τ	Shear stress (Pa)
O	oil		
Suc	sucrose		

References

1. H.A. Bampfield, J. Cooper, Emulsion Explosives, *In:* Encyclopedia of Emulsion Technology, P. Becher, Ed., Marcel Dekker, New York, ISBN 0-8247-1878 Vol. 3 (1988) ch.7, pp. 281-306.
2. R. Pons, P. Erra, C. Solans, J.C. Ravey, M.J. Stébé, *J. Phys. Chem.* 97(1993) 12320-12324.
3. R. Pons, C. Solans, Th. F. Tadros, *Langmuir* 11 (1995) 1966-1971.
4. C. Bengoechea, F. Cordobés, A. Guerrero, *Rheol. Acta* 46 (2006) 13-21.
5. D. Marquardt, H. Sucker, *Eur. J. Pharm. Biopharm.* 46 (1998) 115-24.
6. M. Shahin, S. Abdel Hady, M. Hammad, N. Mortada, *AAPS PharmSciTech* 12(1) (2011) 239-247.
7. M.C. Adeyeye, A.C. Jain, M.K.M. Ghorab, W.J. Reilly, *AAPS PharmSciTech* 3(2) (2002) article 8.
8. Th. F. Tadros, Applied Surfactants, Principles and Applications, Wiley-VCH, Weinheim (2005).
9. W. Hemker, *J. Am. Oil Chem. Soc.* 58(2) (1981) 114-119.
10. F. Nielloud, G. Marti-Mestres, Pharmaceutical Emulsions and Suspensions, 2nd ed., Drugs and the Pharmaceutical Sciences, Marcel Dekker, New York, Vol. 105 (2000).
11. S. Motohiro, Y. Kobayashi, Y. Kimura, S. Adachi, R. Matsuno, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 238 (2004) 83-90.
12. S. Katagi, Y. Kimura, S. Adachi, *LWT-Food Sci. Technol.* 40 (2007) 1376-1380.
13. L.J. Yin, I. Kobayashi, M. Nakajima, *Food Biophys.* 3 (2008) 213-218.
14. A. Murakami, K. Fukada, Y. Yamano, S. Gohtani, *J. Oleo Sci.* 54(6) (2005) 335-340.
15. A. Murakami, K. Fukada, Y. Yamano, S. Gohtani, *J. Oleo Sci.* 54(12) (2005) 633-639.
16. O. Mengual, G. Meunier, I. Cayré, K. Puech, P. Snabre, *Colloid Surf. A: Physicochem. Eng. Aspects* 152 (1999) 111-123.
17. A. Durand, G.V. Franks, R.W. Hosken, *Food Hydrocolloids,* 17 (2003) 671-678.
18. C. Lemarchand, P. Couvreur, C. Vauthier, D. Costantini, R. Gref, *Int. J. Pharm.* 254 (2003) 77-82.
19. H. Buron, O. Mengual, G. Meunier, I. Cayré, P. Snabre, *Polym. Int.,* 53 (2004) 1205-1209.
20. N. Azema, *Powder Technol.* 165 (2006) 133-139.
21. M. Chabni, Etude de la stabilité physique de systèmes dispersés, Ph. D. Thesis, University of Tizi-Ouzou (Algeria) (2012).
22. M. Safouane, Drainage des mousses aqueuses : rôle de la rhéologie du fluide moussant, Ph. D. Thesis, Paris XI (Orsay) University (2003).
23. S.K. Yeong, P.F. Luckham, Th. F., Tadros, *J. Colloid Interface Sci.* 274 (2004) 285-293.
24. **I.** Masalova, M. Taylor, E. Kharatiyan, A. Ya. Malkin, *J. Rheol.* 49(4) (2005) 839-849.
25. G. Couarraze, J.L. Grossiord, Initiation à la Rhéologie, 3rd ed., Tec & Doc Lavoisier, Paris, (2000).