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THERMAL BEHAVIOUR OF EMULSIFIER-WATER SYSTEMS STUDIED BY MICRO-DSC

A. Raemy[*]*, C. Appolonia Nouzille, P. Frossard, L. Sagalowicz and M.-E. Leser*

Nestlé Research Centre, Nestec LTD, CH-1000 Lausanne 26, Switzerland

Emulsifiers are often used in the food industry to stabilize interfaces in emulsions and foams, for example. When added to an aqueous phase, emulsifiers form spontaneously self-assembly structures. Such structured fluids can be used for active ingredients encapsulation or as micro-reactors for flavour formation.

In the present paper we describe the potentialities of DSC, mainly micro-DSC, to study phase transitions of emulsifiers alone and with addition of water. The main role of the calorimetric techniques will probably be to precisely determine melting and crystallization zones, to inform about polymorphism and hysteresis due to undercooling, and especially to follow the effects of guest molecules on the weak liquid crystal transitions. Micro-DSC, when compared to other techniques, generally allows measurements over an extended temperature range.

Keywords: *crystallization, DSC, emulsifier, hysteresis, liquid crystal, melting, micro-DSC, monoglyceride, polymorphism, undercooling*

Introduction

Emulsifiers are frequently used in the food industry to stabilize interfaces in emulsions, foams, solid particle dispersions, etc. Common examples are lecithin in chocolate and monoglycerides in spreads (margarines) or in foams (low fat whipped creams).

When added to an aqueous phase, emulsifiers form spontaneously self-assembly structures, such as micelles or liquid crystalline phases. This approach to structure formation is often called bottom-up structuring by opposition to the more common top-down structuring obtained by energy input. Such structured fluids can be used for active ingredients (vitamins, enzymes, etc.) encapsulation or as micro-reactors for flavour formation.

All these arguments to describe the interest in emulsifiers in foods are discussed in more details in [1–5].

These colloidal structures present transitions of practical interest mainly between solid, liquid and liquid crystalline phases. Colloid science aims to understand the mechanisms of these transitions. Traditionally X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and optical methods (polarized light) but also thermal methods are used to detect these transitions and to build phase diagrams [6–13]. In the present paper we describe the potentialities of differential scanning calorimetry (DSC), mainly micro-DSC [14–16], in this context. Even if these phase transitions have been studied for decades, there is still interest for new approaches due to many discrepancies between previous measurements and recent observations. The main emulsifiers used in the food industry are monoglycerides, which are the focus of this paper.

Experimental

Instruments

The instruments used are a standard power compensated DSC Pyris from Perkin Elmer (Norwalk, USA) and a heat flux micro-DSC III from Setaram (Caluire, France) for detecting weak transitions. The first instrument is used at a heating or cooling rate of 2 or 5 K min^{-1} with an empty cell as reference. Sample masses are around 10 mg. Due to the principle of the instrument and to the small sample amounts, the observed peaks are generally narrow and well resolved. The second instrument is used at low heating and cooling rates (0.1 or 0.2 K min^{-1}) in order to add a good resolution to the high sensitivity of the instrument. Cell volumes are 1 cm^3. The reference cell contains Al_2O_3. Sample masses are around 100 mg. With both instruments, tight cells are used.

The measuring strategy consists generally in exploring first the temperature range above 5 (up to 140°C) and below ambient with the standard DSC instrument (quick screening) and then more specifically the temperature range above 5 (up to 120°C, the upper

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[*] Author for correspondence: alois.raemy@rdls.nestle.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

temperature limit of the micro-DSC) presenting the weak liquid crystal transitions with the micro-DSC. Usually two heating and two cooling scans are performed for each sample. The results are then compared with the available phase diagrams obtained from literature or product suppliers.

The standard DSC graphs correspond exactly to the DSC curves given by the Perkin Elmer software (with onset for extrapolated onset temperature, peak and end temperatures). The micro-DSC graphs are adapted from those given by the Setaram software: character sizes are increased. With both types of curves, peak integration limits are defined by the specialist. The base lines are considered as good, even if the references are perhaps not ideal from that point of view; a stable oil with specific heat comparable to the sample ones used as reference material would probably improve this curve characteristic.

Samples

The monoglyceride samples are mainly two types of monoglycerides: Dimodan P or HR as saturated samples and Dimodan U or LS as unsaturated monoglycerides. Both types of samples are from Danisco (Braband, Denmark).

The samples are a kind of viscous paste obtained by heating under vigorous agitation of the monoglyceride-water (mainly 80/20%) mixture in a pyrex tube. Sometimes a buffer is added instead of water and a small amount of a guest molecule such as limonene or a sugar-amino acid mixture.

They are analysed under air atmosphere or under inert gas if we want to avoid oxidation at elevated temperatures.

Thermal behaviour of saturated monoglyceride-water systems

Results are presented in form of figures with calorimetric curves, transition temperatures and transition enthalpies.

Figure 1 shows melting in one step, around 75°C (peak temperature) of the pure Dimodan HR obtained with the standard DSC instrument. Enthalpy is about 185 J g^{-1}. This information corresponds well to the one of the phase diagram of Dimodan P from hydrogenated lard furnished by the supplier, which shows melting around 70°C and no other transition above (Fig 2). Figure 3 presents the second heating curve which shows a double step melting, around 37 and 70°C, indicating polymorphism. Enthalpies are about 30 and 110 J g^{-1}. These 140 J g^{-1} correspond exactly to the total enthalpy of both crystallization peaks observed before, when cooling down from 140 to 5°C. At 5°C crystallization is thus not complete. There are no other phenomena observed above 70°C.

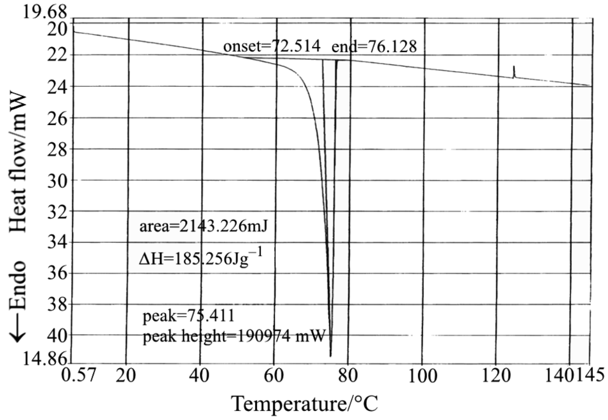

Fig. 1 Melting in one step, around 75°C of the pure Dimodan HR obtained with the standard DSC instrument. First heating curve at 2 K min^{-1}

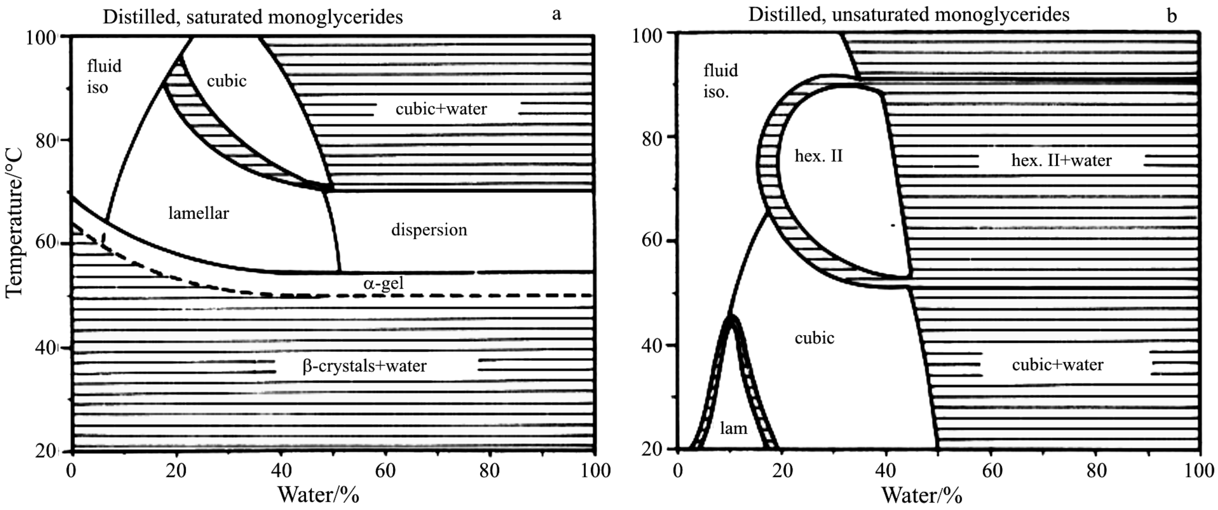

Fig. 2 The Phase diagrams of a – Dimodan P from hydrogenated lard and of b – Dimodan LS from sunflower oil, furnished by the supplier

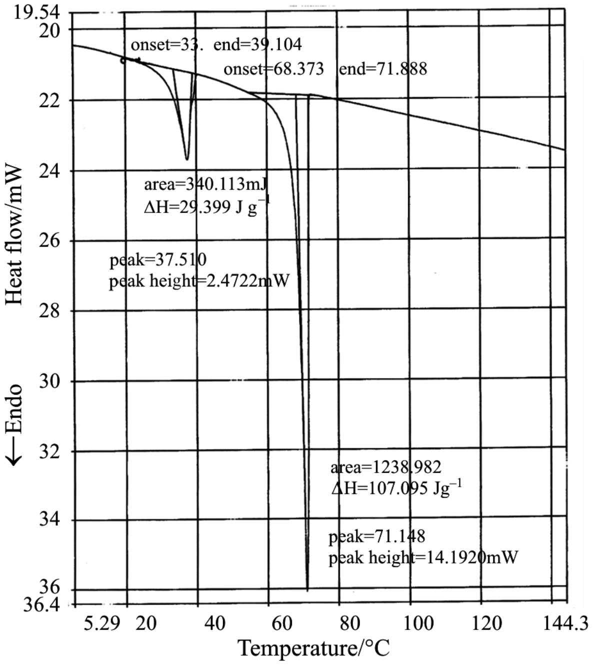

Fig. 3 Second heating curve which shows a double step melting, around 37 and 70°C at 2 K min^{-1} heating rate

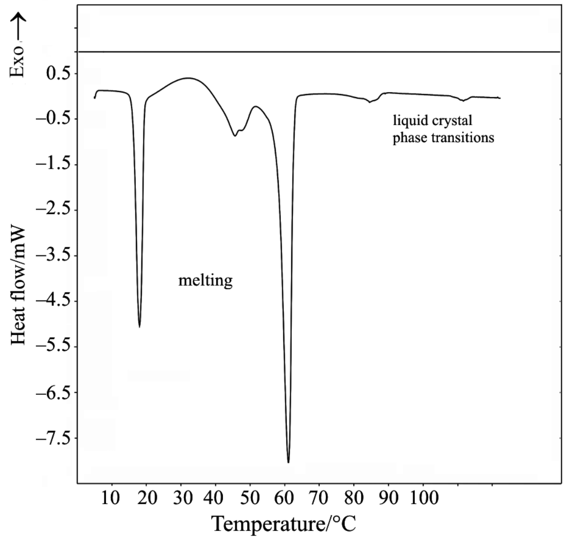

Fig. 4 Behaviour of the Dimodan HR + 20% water mixture, at first heating 0.2 K min^{-1}, with the micro-DSC

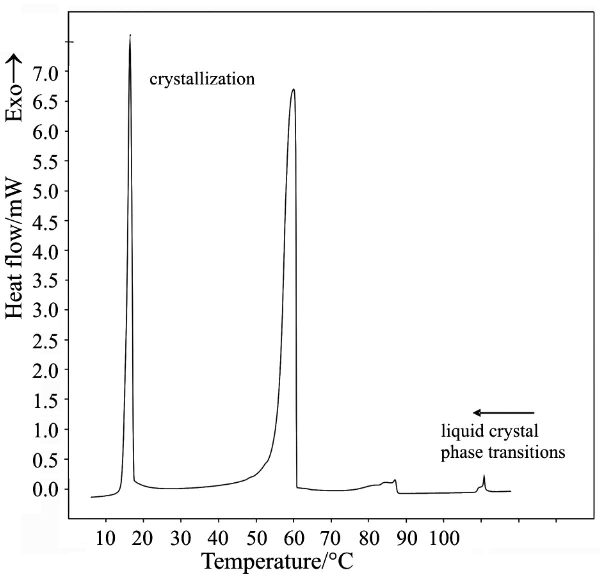

Fig. 5 Behaviour of the Dimodan HR+20% water mixture, at first cooling 0.2 K min^{-1}, with the micro-DSC

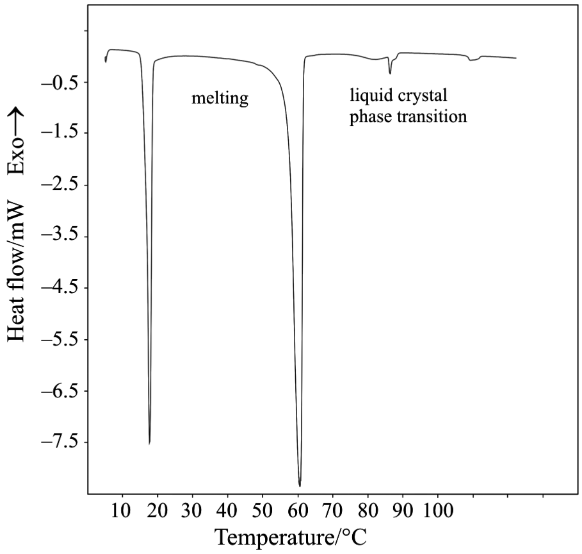

Fig. 6 Behaviour of the Dimodan HR+20% water mixture, at second heating 0.2 K min^{-1}, with the micro-DSC

Figures 4 to 6 show the behaviour of the Dimodan HR+20% water mixture at, respectively first heating, first cooling and second heating with the micro-DSC. Above the melting peaks, respectively crystallization peaks at cooling, showing polymorphism (peak at 45°C disappears at cooling and second heating), there are two small liquid crystalline transitions around 85 and 110°C. These weak transitions (enthalpies are respectively around 3 and 0.8 J g^{-1}) are reversible and show practically no hysteresis. According to the phase diagram, these weak phenomena correspond to (zone) transition from lamellar to cubic at 85°C and from cubic to L_2 (just outside of the available phase diagram), when heating. Second cooling (not shown) corresponds exactly to first cooling.

Thermal behaviour of unsaturated monoglyceride-water systems

We have compared Dimodan U to Dimodan LS, as such, with the micro-DSC to verify if these products are the same or not. Figure 7 with both heating curves and Fig. 8 with both cooling curves show that there is

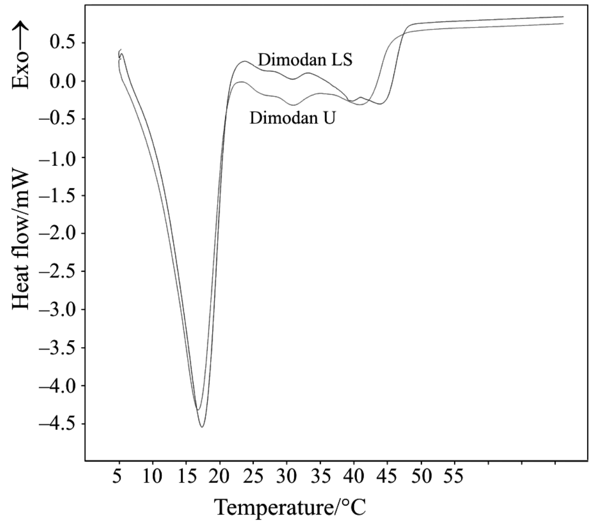

Fig. 7 Heating curves (at 0.2 K min^{-1}) of Dimodan U and Dimodan LS, respectively

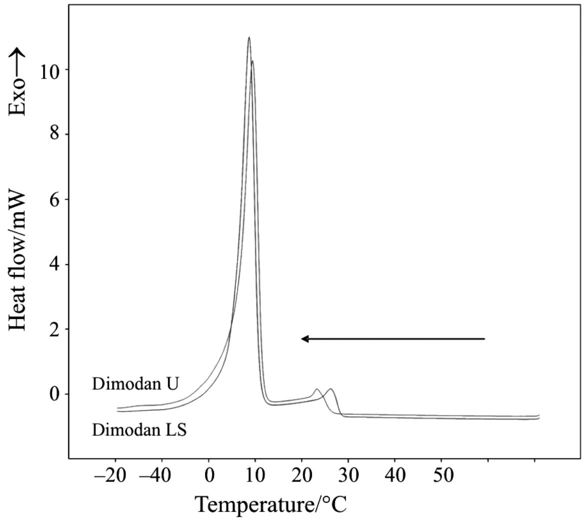

Fig. 8 Cooling curves (at 0.2 K min^{-1}) of Dimodan U and Dimodan LS, respectively

practically no difference. With both samples polymorphism and a strong (more than 5°C) hysteresis between heating and cooling temperatures are observed. Curiously there is no crystalline zone below 50°C indicated in the phase diagram of Dimodan LS from sunflower oil (Fig. 2).

Thermal behaviour of systems with addition of guests

The addition of hydrophilic guest molecules such as xylose and glycine in the solutions does not change dramatically the calorimetric curves as observed in Fig. 9 which shows the superposition of three curves: one obtained with Dimodan U and 19% buffer with addition of 0.33% glycine and 0.66% xylose and the identical curve for Dimodan HR and a Dimodan U/Dimodan HR mixture, both with the additives. The only curiosity is that the Dimodan U curve shows only one weak transition and not two as the other curves obtained the same way. To have an explanation more measurements should be performed with different concentrations.

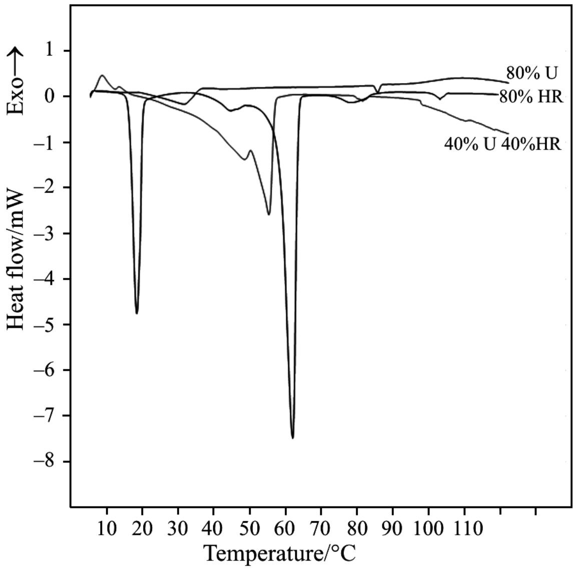

Fig. 9 Superposition of three curves: one obtained with Dimodan U and 19% buffer with addition of 0.33% glycine and 0.66% xylose and the identical curves for Dimodan HR and for a Dimodan U Dimodan HR mixture, both with the additives. First heating at 0.2 K min^{-1}

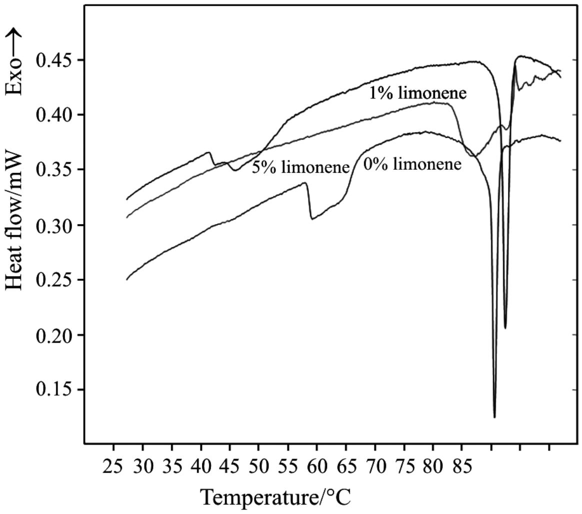

Fig. 10 Effect of the addition of the lipophilic limonene up to 5% on the heating curves of 80% Dimodan U+20% water. Second heating at 0.2 K min^{-1}

Figure 10 shows the effect of the addition of the lipophilic limonene up to 5%; here dramatic changes occur as one weak transition disappears in the melting peak at the highest concentration. So the addition of 5% limonene induces a transformation from cubic to hexagonal phase.

Conclusions

It is clear today that thermal analysis and calorimetry do not replace XRD, NMR and optical methods to obtain phase diagrams of emulsifier self-assembly structures. All these techniques must be considered as complementary methods. The main role of the calorimetric techniques will probably be to precisely determine melting and crystallization zones, to inform about polymorphism (related to the nature of the product and his thermal history) and hysteresis due to undercooling (related to the product structure, the crystallization nuclei and impurities), and especially to follow the effects of guest molecules on the weak liquid crystal transitions. In addition, micro-DSC, when compared to other techniques, generally allows extended temperature range.

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