

OPTIMIZATION OF EXTERNAL OIL PHASE SYSTEMS BY DIFFERENTIAL THERMAL ANALYSIS

C. MILLET, Q.L. NGUYEN, C. ZAFFRAN and C. KOULBANIS

Laboratoires de Recherche de L'Oreal, 94150 Chevilly Larue (France)

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ABSTRACT

The stability of emulsions is, in most cases, linked to the homogeneity and fineness of dispersed particles. For external oil phase systems, surfusion temperature and disperse-phase water-particle crystallization kinetics are particle-size dependent, according to a statistical probability function, $f_1 = 1/N_1 \int_0^D dN$ where N_1 is the number of particles, and D is the diameter.

DTA, investigation of emulsion size distribution by surfusion thermograms, and dispersed phase crystallization kinetics (observed during freeze–thaw cycles with isotherm plateau), can be helpful in the choice of surfactant, coupling agents and raw materials and can provide an approach for estimation of the stability of w/o emulsions. This method has also been applied to technological procedure optimization and quality control of end products.

Retained optimization criteria are, in decreasing order of importance, a very low polydispersity and a particle-size distribution as near Gaussian distribution as possible. Surfusion temperature, which varies from one system to another (–10 to –47°C), must remain stable with time or after the ageing process.

INTRODUCTION

In a w/o emulsion, the hydrophilic site of the emulsifier forms part of the water phase, whereas the uncharged lipophilic end is directed towards the external oil phase. The environment is virtually non-conducting.

Apart from the possibility [1] of interfacial interactions due either to electrostatic forces or to hydrogen bonds, it is generally believed that the stability of the emulsion is related to its viscosity and to the strength of the interfacial film formed by the emulsifiers. The viscosity, arising from the mutual interaction of hydrophobic chains, impedes sedimentation according to Stokes' law. The rigidity of the interfacial film promotes the formation of water droplets with irregular shapes, which in turn prevents coalescence and lowers the interfacial pressure, γ_i : $\gamma_i = \gamma_{o/w} - \Pi$, where $\gamma_{o/w}$ is the original tension between the oil and water before the addition of emulsifying agents, and Π is the pressure of the interphase.

The foregoing conditions lead to the production of the finest possible

emulsions. The most popular methods call for the calculation at the required HLB or the determination of ternary diagrams. The latter method is interesting, however, it is quite tedious and time-consuming. The former method, which in most cases leads to approximate results, can be used easily only with simple emulsifiers (non-ionic, fatty esters, or with typical groupings, etc.). For complex molecules, such as soaps, not mentioned by Griffin [2,3] or Davies [4], one can still refer to the simple HLB scheme by measuring pH. Unfortunately, pH cannot be measured in non-conducting media. In this study, we have used another approach to optimize the formulation of w/o emulsions: the measurement of the droplet size by DTA. In previous studies [5], the relationships between time, volume and supercooling temperature of dispersed droplets were determined by using a probability approach to the phenomenon.

Let us consider the freezing peak of a w/o emulsion (Fig. 1) and the theoretical view of spherical droplets. It has been shown that, at a given time t_i , all droplets with a given diameter have the same crystallization probability, which depends on the droplet volume, the time, t_i , and the supercooling temperature, T_S^i [5-7]:

$$\frac{S_i}{S} = \frac{1}{N_i} \int_0^{t_i} \frac{dN}{dt} dt = f(t_i) = \psi(T_S^i)$$

where N_i is the number of droplets of a given size, S is the total area of the

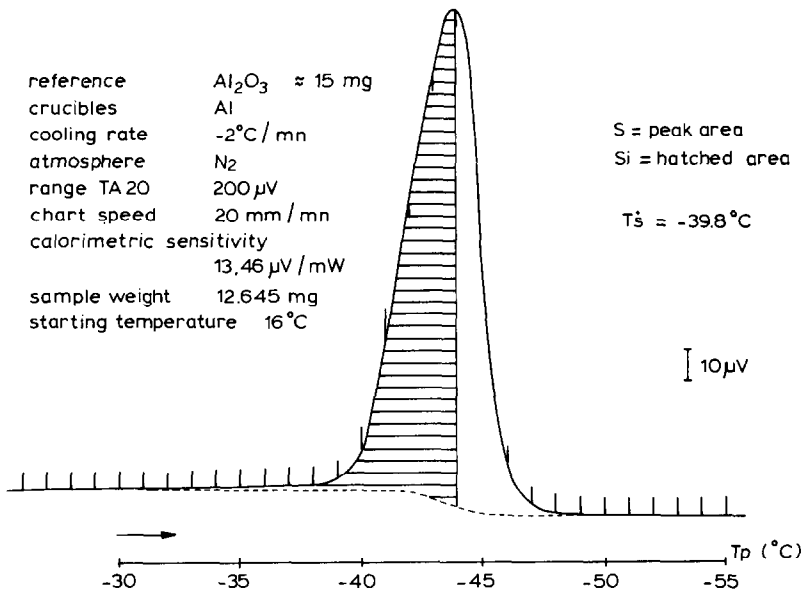


Fig. 1. Freezing peak of a w/o emulsion E2.

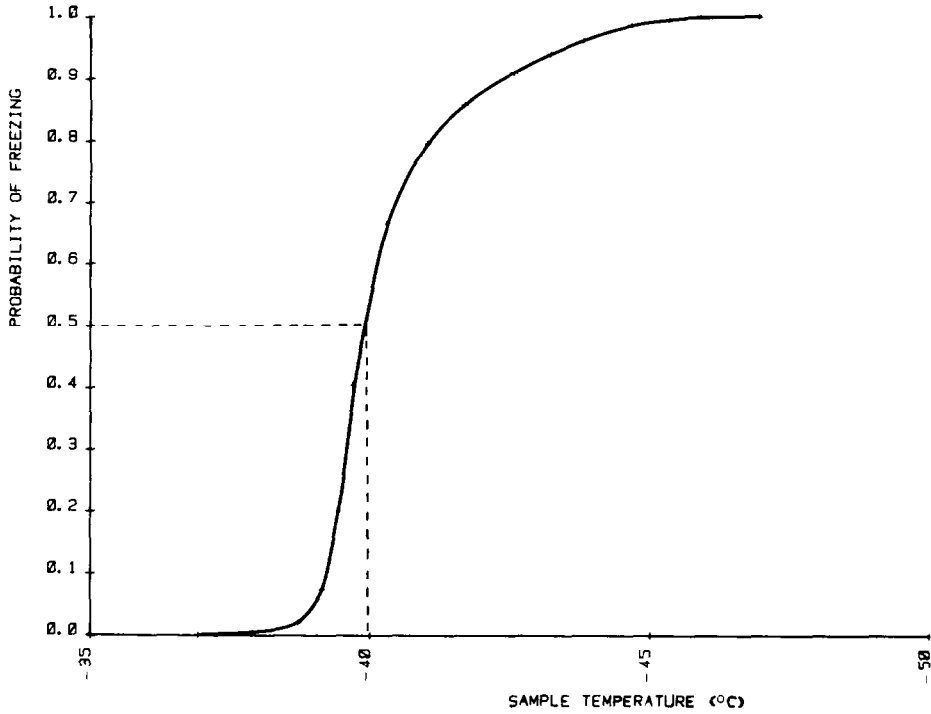


Fig. 2. Crystallization probability as a function of sample temperature, T_s , for each droplet diameter. Emulsion E2.

peak, and S_i is the area of this peak between the crystallization onset temperature and T_s^i .

The integral curve yields the crystallization probability as a function of time (or temperature) for each droplet diameter (Fig. 2)

$$f_i = \frac{1}{N_i} \int_0^{d_i} dN$$

The crystallization probabilities, f_i and f_j , of two droplets of diameters d_i and d_j are related by the equation

$$\frac{\ln(1 - f_j)}{\ln(1 - f_i)} = \left(\frac{d_j}{d_i} \right)^3$$

Rearrangement of the probability equations yields a linear relationship between $\ln(d_i)$ and T_s^i

$$T_0 - T_s^i = -2.956 \ln(d_i) + 16.603 + 0.985 \ln \left(2 \left| \frac{dT_p}{dt} \right| \right)$$

where T_0 is the melting temperature of the internal phase and dT_p/dt the cooling or heating rate.

EXPERIMENTAL

DTA measurements were performed on a Mettler TA 2000 instrument, which allows one to record the variation of the temperature difference, ΔT , between the sample cell and the reference cell, as a function of the temperature of the sample holder, T_p . ΔT is then converted into a heat flux.

The actual temperature of the sample, T_s , can be deduced from the temperature of the sample holder, T_p , after taking into account the slight variation due to the change of state and the lag due to the system: $T_s = T_p - \tau_{lag} (dT_p/dt) + \Delta U/S'$, where τ_{lag} is the lag constant for the system, S' is the thermometric sensitivity in $\mu V \text{ } ^\circ\text{C}^{-1}$ and $\Delta U = S' \times \Delta T$.

All these data are treated on line with a HP 9815 calculator coupled to the DTA.

Experimental conditions

Freezing: cooling rate $dT_p/dt = -2^\circ\text{C min}^{-1}$; temperature range = 16 to -55°C .

Freeze-thaw cycles heating or cooling rate = 5°C min^{-1} ; temperature range = 47 to -30°C , with or without an isothermal plateau at high temperature.

RESULTS: OPTIMIZATION OF A NEW FORMULATION

A mixture of emulsifiers is usually more efficient than a single pure emulsifier. Emulsions corresponding to the various emulsifier pairs were prepared by ultrasonic agitation in tubes containing 10 g aliquots (10% emulsifier/coupling agent; 40% oil phase; 50% water phase). The tubes were left to stand for 24 h before the DTA measurement. Samples were taken from the center of the tube.

As can be seen from Fig. 3, the best coupling pair is obtained when the values of S^*/S and T_s are both at a minimum (Fig. 4). In the case of this emulsion, E, the "best" ratio of emulsifier/co-emulsifier is about 30/70, w/w. This result is confirmed by the study of the ternary diagram and the stability after real time conservation.

The efficiency of the co-emulsifier may vary to a very large extent from one batch to another, depending on the supplier and the previous treatment of the compound. The methods that can be used to differentiate between two batches are: monitoring of the freezing peak (and therefore of the droplet

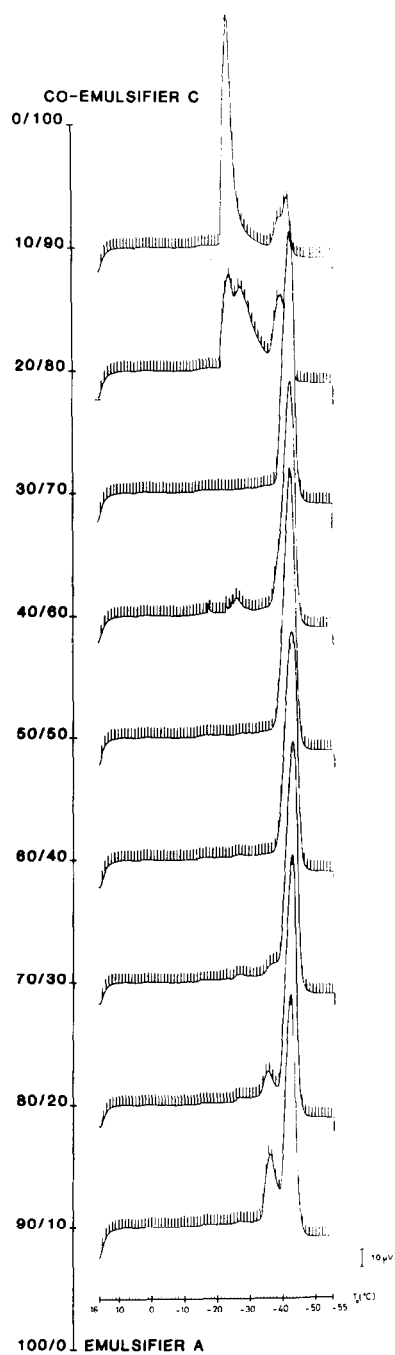


Fig. 3. Freezing peaks of different coupling pairs of the emulsifier A/co-emulsifier C system.

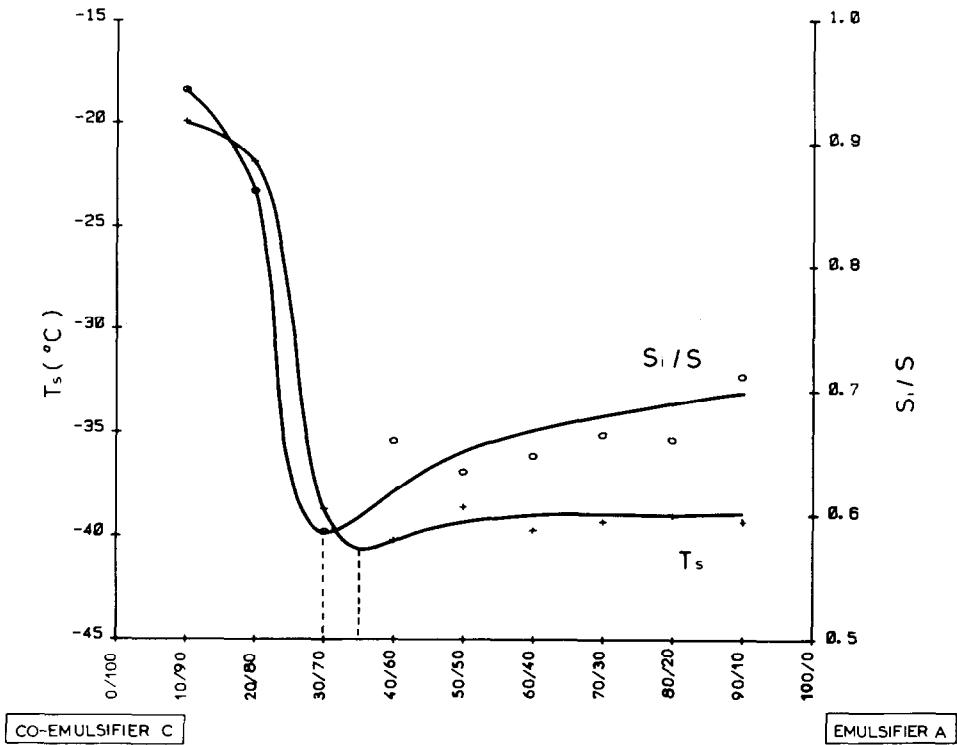


Fig. 4. Sample temperature, T_s , and area ratio, S_i/S , as functions of the different coupling pairs. Emulsifier A/co-emulsifier C.

size); ageing either *in real time or stressed*, and successive freezing (Fig. 5). We have noted that the two ageing processes lead to identical results.

In the case of the E1 emulsion, the shift of the freezing peak towards higher temperatures can be quantified by freeze-thaw cycles (Fig. 6). The size of the emulsion droplets, which are submitted to these cycles can be measured using the melting peak of ice at 0°C (see Fig. 7, the evolution of this peak with the number of cycles for the emulsions E1 and E2). The selected lower temperature corresponds to an average droplet diameter greater than $230\ \mu\text{m}$.

Using these cycles, it is possible to show that, for the E1 emulsion, destabilisation is due to the thaw part of the cycle. The same technique makes it possible to optimize the relative proportions of the constituents.

The E2 emulsion made in the laboratory must be reproduced on an industrial scale. With the two types of instrument at our disposal in the pilot plant, we have tried to optimize the stirring time and the stirring mode. The freezing peaks show that the results are not reproducible if equipment A alone is used, whatever the time, and that it is necessary to complete the stirring with equipment B.

REAL TIME AGING

at room temperature

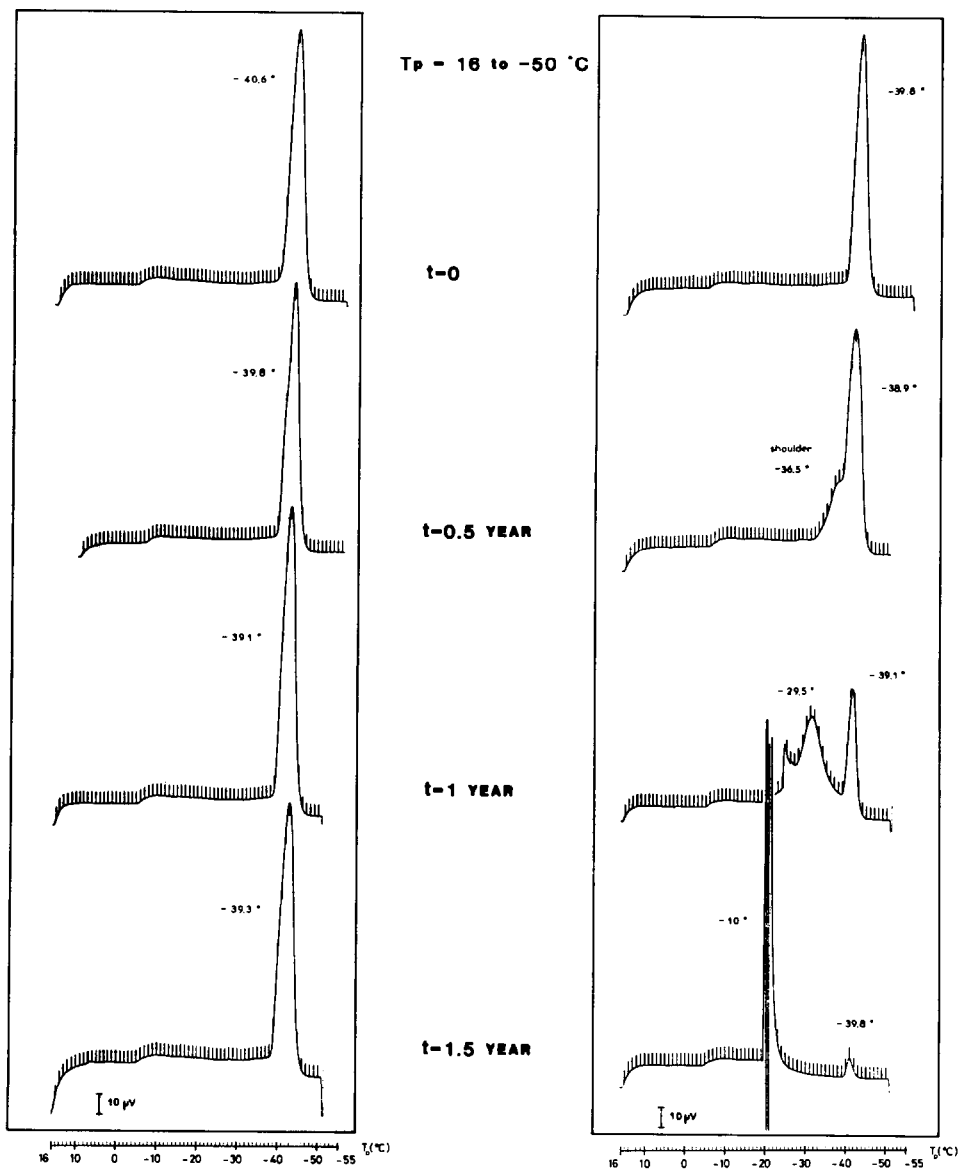
EMULSION E2**EMULSION E1****EVOLUTION OF THE FREEZING PEAK**

Fig. 5. Evolution of the freezing peak as a function of time. Emulsion E2 is more stable than emulsion E1.

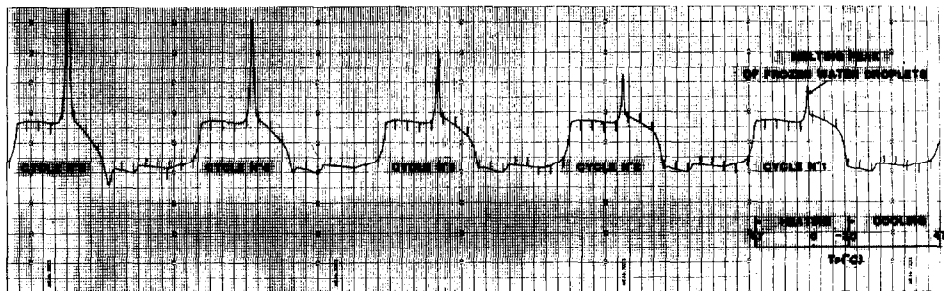


Fig. 6. DTA freeze-thaw cycles of the w/o emulsion E1. Evolution of the melting peak of frozen water droplets as a function of the number of cycles.

The quality control standards for the E2 emulsion can be determined: a single freezing peak at $T_s^* = -40.0 \pm 0.5^\circ\text{C}$; latent heat of crystallization of the emulsion, $\Delta H_c = 260 \pm 4 \text{ J g}^{-1}$.

The foregoing temperature range corresponds to an average droplet size of $5.8 \pm 1 \mu\text{m}$.

The DTA control was run 24 h after fabrication.

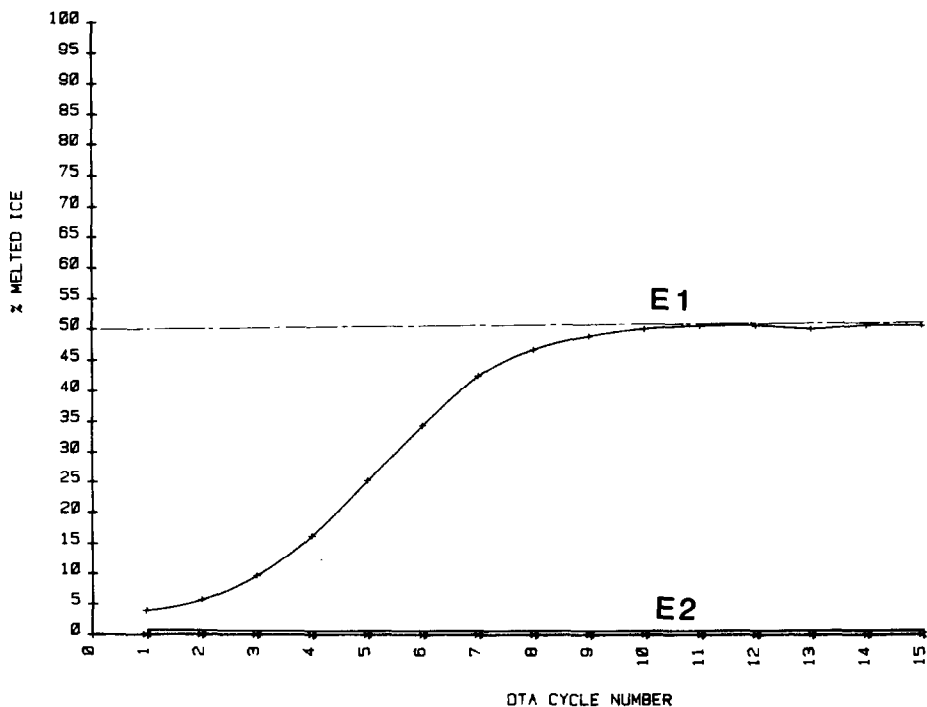


Fig. 7. Evolution of the melting peak of frozen water droplets as a function of the number of DTA cycles for the two emulsions. Emulsion E2 is more stable than emulsion E1. Total aqueous phase 50%.

CONCLUSION

The polydispersity of the freezing peak of water must be small, which implies a minimum for the surface ratio S_i^*/S .

In w/o emulsions, with a cooling rate of 2°C min^{-1} , the average crystallization temperature of the water droplets lies in the range -37 to -40.5°C . As a result, this mean temperature, T_s^* , must be below -38.8°C . In the presence of salt solutions, however, two situations may occur: T_s^* may be either lower than -38.8°C , in which case the difference $T_s^* - (-38.8)$ will be proportional to the salt concentration (Raoult's law), or higher, because of the presence of crystalline seeds which may lower the activation energy of the nucleation process [8,9]. This latter case, however, is very rarely encountered. These side effects do not have any effect on droplet diameter.

Emulsion stability, which is somewhat related to the droplet size, may be evaluated in a comparative way by monitoring the S_i^*/S ratio for an emulsion aged in real time or with thermal stress.

DTA proved to be a useful tool in every step of the elaboration of a new w/o formula.

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