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THERMAL BEHAVIOUR OF EMULSIONS STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

This article is a review about the ways in which solidification and the melting may occur within emulsions submitted to steady cooling and heating performed in a differential scanning calorimeter. Simple, multiple and mixed emulsions are considered. Due to nucleation phenomena creating supercooled and supersaturated liquids, the DSC curves obtained during cooling and heating are quite different. The influence of a solute in the disperse phase is described in detail. Some implications about the instabilities of emulsions due to mass transfer phenomena are described.

Keywords: DSC, emulsion, emulsion stability, mass transfer, mixed emulsion, multiple emulsion, solid nucleation

Introduction

Thermal methods are not currently used for studying dispersed system, as rheological techniques appear more suitable specially when emulsions are concerned. However, a number of papers have appeared in the literature recently about differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of emulsions, but not necessarily with the actual aim of characterizing the emulsions themselves. Actually in the 1950's, emulsifying a liquid seemed to be the best way to get a great number of droplets free of foreign particles that could promote solidification and therefore a means to reach the greatest supercooling [1–3].

Furthermore, as nucleation and then solidification are stochastic phenomena, studying the solidification of a great number of droplets during a sole experiment permits to save time and to get more reliable results. The solidification of disperse droplets was first detected by dilatometry [2] and later on by hertzian spectroscopy [4, 5] and by simple differential thermal analysis DTA. DTA is very easy to set up in a laboratory and the first experiments in the field were performed with laboratory made apparatus [3]. Solidification of dispersed droplets was detected with the help of simple thermocouples through the temperature difference between the emulsion and the reference, the difference being due to the heat re-

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leased. Very soon, experiments showed that the results were not reproducible and only qualitative data were obtained. A great progress was made when more sophisticated apparatus became available. Thanks to commercialized differential scanning calorimeters with highly sensitive detectors, controlled cooling-heating rates and small samples for which temperature homogeneity was guaranteed, it was then possible to carry out quantitative studies [6–14]. Nevertheless, despite new apparatus, a part of the results obtained were not reproducible. Consequently, more attention was given to the emulsions themselves and the knowledge about their behaviour when submitted to temperature gradient greatly improved. In this article attention will be focused on the study by DSC of partial or total solidification and melting occurring within emulsions. The resulting mass transfer phenomena and their consequences concerning the instability of emulsions will also be examined.

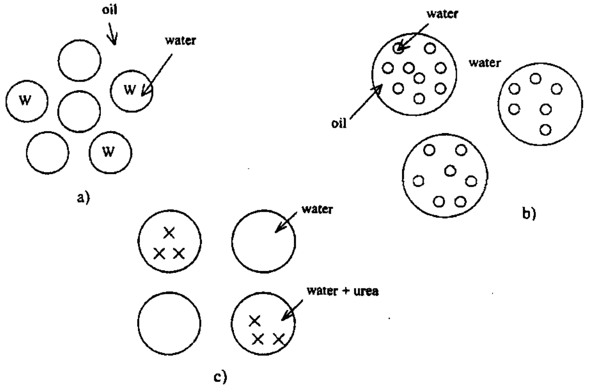

Fig. 1 Sketches of emulsions. a – simple emulsion W/O; b – multiple emulsion W/O/W; c – mixed emulsion

Emulsions

Simple, multiple and what we have named mixed emulsions will be considered in this article. Schematic pictures are given in Fig. 1.

Simple emulsions are very well known. Multiple emulsions are less known although since they are considered as possible membrane liquid systems their importance is increasing [15]. As two kinds of simple emulsions exist, W/O or O/W, two kinds of multiple emulsions exist as well, namely W/O/W or O/W/O. In W/O/W emulsions, oil globules containing water droplets, actually each being a W/O emulsion, are dispersed within an aqueous phase. Finally, mixed emulsions are very close to simple emulsions except that the droplets have different compositions. For example, pure water droplets and water+solute droplets are present in the same emulsion called mixed emulsion as far as it has been obtained by making the mixture of two W/O emulsions, one containing pure water droplets and the other water+solute droplets. Of course, specific surfactants are used for making the named emulsions. Their specificity and characterization will be introduced later in this article when the role they could play in the phenomena examined will be discussed.

DSC

Differential scanning calorimetry appeared to be a very suitable technique for studying the behaviour of emulsions submitted to a temperature gradient. Should solidification or melting occur within the emulsion, the heats released or adsorbed will be detected and therefore also the solidification or melting. It is also possible to detect glass transitions through the changes in heat capacity. What is less obvious is how it is possible to get information from DSC experiments about mass transfer due to partial solidification or composition gradients. All these points will be examined in this article with the aim of giving general rules permitting to predict the behaviour of any emulsion showing the same characteristics as those described under the same conditions.

DSC of simple emulsions

When DSC is performed on emulsions, the first point to check is that the temperature homogeneity within the sample is guaranteed. Two parameters are of importance in this respect: the sample volume and the scanning rate. The smaller they are, the better.

These two conditions are easily satisfied, although too small a sample may be a problem when a heterogeneous system is under study and too low temperature may be the cause of a not well defined signal when the thermal event gives rise to a small amount of energy. A compromise has to be found and generally this needs practice and preliminary experiments.

The second point is to get a correlation between the direct data given by the calorimeter and the actual thermal data required. For that it is necessary to know the characteristics of the thermal events occurring within the emulsions.

The way in which solidification and melting occur within an emulsion has already been described [7, 16]. Only the main conclusions will be given in this article.

Roughly speaking two phases have to be considered: the disperse and the bulk phase. The volume of the bulk phase is limited by the dimensions of the cell. For current calorimeters it varies from 30 to 300 mm^3. This volume may be greatly reduced if the amount of the disperse phase is important. Nevertheless the important point to notice is that this phase is continuous and that its volume is around a few mm^3. The disperse phase is generally not monodisperse and to characterize it, it might be necessary to have an analytical function describing its polydispersity.

Solidification requires the formation of a nucleus, the critical size of which is so small that capillary phenomena have to be taken into account. Under these conditions, it has been shown that its probability of birth may be almost null when the temperature is near the solid–liquid equilibrium one and at each temperature only a probability P of solidification can be given. P increases as the temperature is lowered and it is volume dependent; the smaller the volume, the lower P.

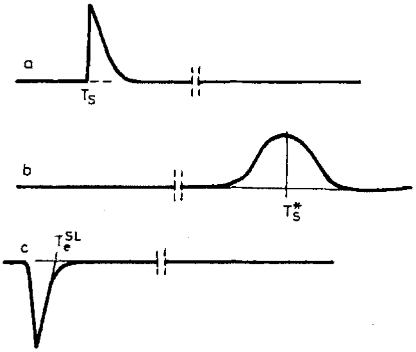

Fig. 2 DSC traces of pure material. a – cooling-bulk material; b – cooling -dispersed material; c – melting-bulk or dispersed material

Therefore the emulsion has to be cooled down below the solid–liquid equilibrium temperature T_e^{SL} of both phases for having a chance to have it solidified. The solidification of the bulk phase is expected to occur abruptly if a significant amount of matter may solidify. The precise quantity can be deduced from the formulation of the emulsion. If pure material were present, all would solidify when the temperature is lower than T_e^{SL} and the corresponding curve obtained would have the shape given schematically in Fig. 2a. The solidification temperature T_s will be taken as indicated in this figure.

For the disperse phase, the solidification is also expected at $T<T_e^{SL}$ but as many droplets are involved the corresponding curve (Fig. 2b) exhibits a different shape compared to the one obtained for the bulk phase (Fig. 2a). The curve shows a nearly perfect Gaussian shape when a low cooling rate is used (<2°C min^{-1}) and when the amount of the disperse phase is not too high, e.g. less than 30 percent. Should these conditions not be satisfied, the created heat is released in a different way and the solidification characteristics are also different [17]. The Gaussian shape is a picture of the scattering of the individual solidification temperatures of the droplets. If a temperature T_s^* is needed to characterize the solidification, the one corresponding to the apex of the exothermic signal may be chosen (Fig. 2b). A few words will be said about the melting of the solidified emulsion as far as no special behaviour is expected. No delay is observed and the shape of the corresponding endothermic signal is very similar to the one observed for the pure material. Nevertheless some differences may be observed due to a relatively bad heat transfer through the emulsion and due to partial solubility of additives such as surfactants. The melting temperatures T_m or T_e^{SL} will be determined as indicated in Fig. 2c.

To summarize, when the two phases of an emulsion, the bulk and the disperse ones are supposed to solidify, the expected DSC curve will be a superposition of the curves shown in Figs 2a and 2b.

As an application of these results a quick test carried out on a non-dilute emulsion could be proposed for finding the type of emulsion considered: W/O or O/W. A sample of the emulsion studied is put in a calorimeter and it is submitted to a cooling-heating cycle at a scanning rate around 1.5°C min^{-1}. The emulsion must be cooled at least to –50°C and even lower if a solute is present in the aqueous phase is present as will be seen in the next section. If the water freezing signal is as the one shown in Fig. 2a, the emulsion is of O/W type, otherwise if the signal is like the one shown in Fig. 2b, the emulsion is of W/O type.

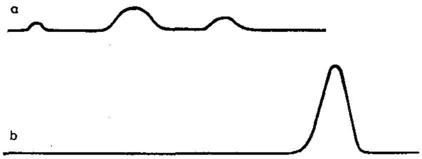

Fig. 3 DSC cooling traces of W/O emulsions. Emulsion 1 (a) more unstable than emulsion 2 (b)

Another application deals with the degree of instability of a W/O emulsion. As it has been found, generally speaking, that the bigger the droplets, the higher the instability and the higher the probable water freezing temperature, a DSC test on the non-dilute emulsion performed under the same conditions as described before appeared to be very convenient. Therefore, by simple observation of the two DSC curves given in Fig. 3 it can be deduced that emulsion 1 is more unstable than emulsion 2.

When a solute is present, the solidification curves are more complicated as will be shown later. Depending on the concentration, one or two exothermic signals are noticed. To find the thermal events they represent it is necessary to know the solid–liquid phase diagram of the binary system (solvent+solute) studied. Figure 4 gives a schematic diagram for a totally miscible binary system showing pure solid phases. The melting temperatures or the solid –liquid equilibrium temperatures of the pure components A and B are indicated by points A_0^e and B_0^e, respectively. The coordinates (x,T) of points A^e and B^e give the composition of the solution in equilibrium with the pure solid A or pure solid B, respectively at temperature T. Point E is the eutectic point the coordinates of which give the composition of the solution in equilibrium with the pure solid A and pure solid B phases.

When an emulsion is introduced into a calorimeter and submitted to a steady cooling, the thermodynamic equilibrium of the disperse phase is not reached at each temperature and it is the discrete solidifications of the droplets that are detected through the exothermic signal. Furthermore, due to nucleation phenomena, the solidification of the disperse solution the composition of which is given by the abscissa of point A^e, will begin at $T<T(A^e)$. For this composition, only the solid phase A appears and, as for a pure material, only a more probable temperature can be defined. Let us suppose that this temperature is given by the ordinate of point A. Should the emulsion maintained at this temperature till the equilibrium is reached, all will solidify (A+B). But when the emulsion is submitted to a steady cooling, the picture is different. The emulsion temperature may rise due to the heat released during partial solidification of A. Nevertheless, it can be expected that during cooling, a partial equilibrium pictured by point A′ will be reached. Then, dispersed droplets are made of solid A+solution whose composition is given by the abscissa of A′. At this point the solution shows still supersaturation against solute B. During further cooling more and more of component A will solidify and consequently, the remaining solution becomes more and more concentrated in component B. When the conditions of solidification of component B are reached, whole droplets solidify as solidification of B lets no chance for component A to remain liquid alone. From the knowledge of conditions of the first solidification of B in the droplets, it is possible to predict this event. For that purpose it is a disperse solution whose concentration is for example given by the abscissa point B^e, that has to be cooled. The more probable solidification temperature of B (Fig. 4a, point B) can then be detected through the exothermic sig-

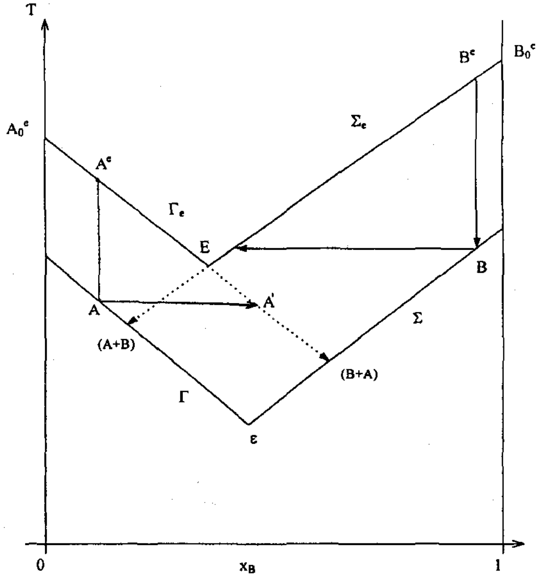

Fig. 4 A hypothetical binary system A+B showing solid–liquid equilibrium curves: solid $x_B=0$, liquidus Γ_e for $x<x(E)$; solid $x_B=1$, liquidus Σ_e for $x>x(E)$
More probable solidification temperatures for dispersed solutions within emulsions.
A solidification : Γ; B solidification: Σ; Complete solidification points (A+B) and (B+A)

nal. Repeating this experiment with various solutions enables to draw on the phases diagram, curve Σ that gives for any composition the more probable temperature of the first solidification of component B (Fig. 4).

Let us go back to the description of the behaviour of the disperse solution whose composition is given by the abscissa of point A^e. The description was stopped at the point where complete solidification is expected.

As far as it is assumed that solid A has no influence on the conditions of solidification of B, the more probable temperature of total solidification will be given by the ordinate of point (B+A) as it belongs to the extension of the curve Γ_e that gives the composition of the solution in equilibrium with solid A and also to the curve Σ that gives the temperature at which component B is supposed to solidify in the remaining solution.

Therefore, during the steady cooling of the emulsion, two exothermic signals will be noticed at temperatures corresponding to point A and point (B+A) (Fig. 4). From what has been said before, it is now possible to predict the behaviour of any emulsion during cooling versus the composition of the disperse phase. The expected signals are drawn in Fig. 5.

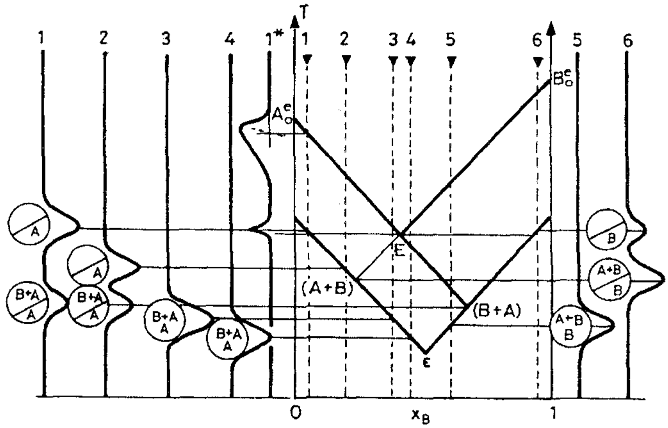

Fig. 5 A hypothetical binary system A+B, with cooling DSC traces and droplet solid contents at six compositions of dispersed solutions within emulsions and with melting DSC traces at composition 1*

No special attention will be given to the melting as far as no peculiar behaviour is expected. The endothermic signals obtained for composition marked by 1^* are given as an example (Fig. 5).

DSC of multiple emulsions

From what has been said before it is possible to predict the behaviour of a multiple emulsion W/O/W submitted to steady cooling.

If the oil phase is supposed to remain liquid during the whole time of cooling, only two exothermic signals marking the solidifications of the bulk outer aqueous phase (I) and the disperse inner aqueous phase (II) will be noticed. Therefore the corresponding DSC curve will be like the one drawn in Fig. 6a. During heating, only one endothermic signal will be obtained if the two aqueous phases are pure water both. Actually it is never the case as at least a hydrophilic surfactant is surely present in the outer aqueous phase and a solute such as $MgSO_4$ is dissolved in the inner aqueous phase for stability purposes [18]. Nevertheless, the amounts of these additives are relatively low and the DSC curves are not modified substantially.

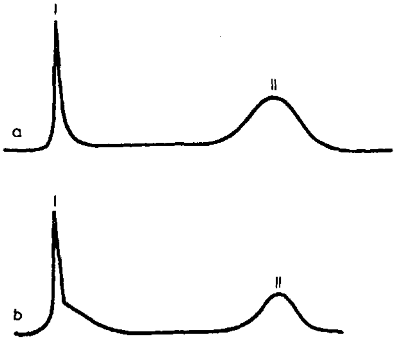

Fig. 6 DSC cooling traces of a multiple emulsion. a) without water transfer; b) with water transfer

The point to be noticed in this behaviour during cooling is that the bulk phase solidifies first around –20°C and the disperse phase around –40°C [19]. Therefore this appeared to be an additional reason for increasing the instability of the emulsion as water transfer from the still supercooled disperse water towards the frozen outer phase may occur due to a difference between the chemical potentials of water in the two phases [19, 20]. Even during a steady cooling, this transfer has been noticed through the deformation of the freezing signal at around –20°C (Fig. 6b). Furthermore, when cooling is stopped at –30°C long enough, no signal is detected at around –40°C. This observation shows that all the disperse water available inside the oil droplets has migrated towards the outer phase and has frozen as soon as it has been in contact with it.

DSC of multiple emulsions has also been proposed for following water transfer at ambient temperature. In this case the water transfer was the result of a difference in composition between the two aqueous phases [18]. From time to time, a sample was taken from the emulsion and sumbitted to a steady cooling in the calorimeter. The idea of getting information through the exothermic signals is to establish a correlation between the energies released due to the solidification of the two aqueous phases and their weights. Following the changes of these quantities *vs.* time it is therefore possible to get information about the water transfer. In fact this was possible because the solidifications of the two phases occur at quite different temperatures due to nucleation phenomena as it was described before. Nevertheless, should water transfer also occur due to partial solidification during cooling, this analysis fails to provide precise information about the two transfers and it is therefore not so convenient to use. Applied to mixed emulsions this analysis was much more easy to do as can be seen in the next section.

DSC of mixed emulsions

The mixed emulsions studied were obtained by manual mixing of two W/O emulsions with different compositions of the dispersed phases: one was made with pure water and the other one with water plus urea as solute [21].

The mixing was realized in such a way that coalescence was reduced to minimum. Therefore two kinds of droplets, water and water+urea, coexist within the final emulsion. From a thermodynamic point of view, this situation is expected to enhance the instability of the emulsion if water transfer can be achieved through the oil medium. Should this transfer occur, the composition of the droplets con-

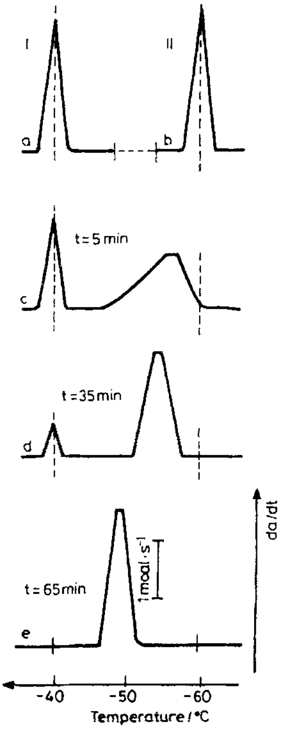

Fig. 7 DSC cooling traces of a mixed emulsion (water+urea) taken at four different times

taining urea will change and the amount of pure dispersed water will decrease. As the areas of the solidification signals are mass dependent and as the solidification temperature is composition dependent, water transfers must be noticed on the DSC curves. Figure 7 gives an example of what has been observed for samples taken from the mixed emulsions at different times.

It is obvious that there is surely a change *vs.* time of the emulsion maintained at ambient temperature. At the beginning, two signals caracteristic of the freezing of pure water droplets and water+urea droplets are observed. Later on, the signal corresponding to pure water decreases and the one corresponding to water+urea is moving towards higher temperatures. These results point to a dilution of the dispersed solution due to the water transfer from the pure water droplets. At the end, no freezing signal of pure disperse water is noticed and only one well defined signal is observed. From a complete analysis of this signal, it was found that it shows quite well the characteristics of the freezing of a unique disperse solution whose composition was found to agree with the one obtained from the formulation of the emulsion and assuming that all the pure water has transferred towards the water+urea solution droplets.

Considering that the emulsions are relevant to liquid membrane systems, the water fluxes have been expressed *vs.* the chemical potential gradient of water [21].

Conclusions

This analysis of the differential scanning calorimetry of various emulsions points to the high performance of this technique for getting information about the behaviour of emulsions.

First it has been shown how solidification-melting occurs within emulsions whose disperse phase is either a pure material or a binary system. Typical DSC curves were given that could be used for characterizing emulsions for the first time.

Secondly it has been shown how mass transfer can be detected by analysis of the DSC curves obtained during the cooling of the emulsions studied. Information about the relative instabilities of the emulsions has also been deduced.

References

1 B. Vonnegut, J. Colloid Sci., 3 (1948) 563.
2 D. Turnbull and R. L. Cormia, J. Chem. Phys., 34 (1961) 820.
3 L. Babin, C. R. Acad. Sci. Paris, 356 (1963) 3609.
4 J. Lachaise and M. Clausse, J. Phys. D, 8 (1975) 1227.
5 M. Clausse in 'Encyclopedia of Emulsion Technology', Vol. 1 (P. Becher, ed.) Marcel Dekker, New York Chap. 9, 1983, pp. 481–715.
6 C. Lafargue, L. Babin, P. Xans, D. Clausse and M. Lère Porte, C. R. Acad. Sci., Ser. B, 277 (1973) 245.

7 J. P. Dumas, D. Clausse and F. Broto, Thermochim. Acta, 13 (1975) 261.
8 F. Broto and D. Clausse, J. Phys. C, Solid State Phys., 9 (1976) 4251.
9 D. H. Rasmussen and C. R. Loper, Acta Metall., 24 (1976) 117.
10 H. Kanno and C. A. Angell, Science, 193 (1976) 1121.
11 C. A. Angell and J. Donnella, J. Chem. Phys., 64 (1977) 4560.
12 R. W. Michelmore and F. Franks, Cryobiology, 19 (1982) 163.
13 D. Clausse, L. Babin, F. Broto, M. Aguerd and M. Clausse, J. Phys. Chem., 87 (1983) 4030.
14 D. Clausse, J. P. Dumas, P. H. E. Meyer and F. Broto, J. Disp. Sci. and Techn., 8 (1987) 1.
15 N. N. Li, AICHE Journal, 17 (1971) 459.
16 D. Clausse in 'Encyclopedia of Emulsion Technology', Vol. 2: Applications (P. Becher, ed.) Marcel Dekker, New York 1985, p. 77.
17 J. P. Dumas, M. Krichi, M. Strub and Y. Zeraouli. Int. J. Heat Mass Transfer, 37 (1993) 737.
18 S. Raynal, I. Pezron, L. Potier, D. Clausse, J. L. Grossiord and M. Seiller, Colloids Surfaces A, Physicochem. Eng. Aspects, 91 (1994) 191.
19 L. Potier, S. Raynal, M. Seiller, J. L. Grossiord and D. Clausse, Thermochim. Acta, 204 (1992) 145.
20 D. Clausse, I. Pezron and S. Raynal, Cryo-letters, 16 (1995) 219.
21 D. Clausse, I. Pezron and A. Gauthier, Fluid Phase Equilibria, 110 (1995) 137.

Stuctural Studies of Liquid Dispersion material is finished.