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ON THE STUDY BY D.S.C. OF THE UNEXPECTED ICE MELTING AT 0°C OF EMULSIFIED AQUEOUS SALINE SOLUTIONS

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SUMMARY

Firstly, the behavior of droplets ($\Phi \approx 1\mu m$) of aqueous saline solutions dispersed within an emulsifying medium and subjected to steady cooling and heating is described. Droplets undergo freezing around a temperature $T^*(x)$ and partial ice melting and total salt melting at the eutectic temperature T_E. This melting is followed by progressive melting of the remaining ice which ceases when the equilibrium temperature ($T_e(x)$) ice $\leftrightarrows$ solution is reached. Between T_e and T^* the droplets are undercooled. Secondly, the results obtained when water crystallization occurs versus time at a fixed temperature θ_c, such as $T^*(x) < \theta_c < T_e(x)$ are reported. During heating following crystallization at θ_c, an unusual ice melting at 0° and/or ice melting ending at $T > T_e(x)$ is noticed on the thermogram obtained by differential scanning calorimetry of the emulsion. This shows that pure ice or at all events less concentrated solutions must be present within the emulsion. A possible mechanism of crystallization at θ_c is proposed.

INTRODUCTION

The phases diagram of a binary system such as salt + water differs from the one of a binary system whose components A and B are completely miscible in the liquid state and completely immiscible in the solid state as it is not generally possible to obtain very concentrated salt solutions. A truncated diagram is obtained as represented in Fig. 1. Rather more complex is the case of aqueous solutions dispersed within a suitable medium, undercooling and supersaturation phenomena being observed. Numerous research works have been undertaken to clarify the behaviour of such emulsified systems when subjected to steady cooling or heating (ref. 2-3-4). Ice or salt crystallizes out within the dispersed droplets at temperatures scattered around a most probable temperature T^*, which may be much lower than that given for the composition x of the solution, by the equilibria curves Γ_e (ice + solution) or Σ_e (salt + solution). By plotting on the phases diagram the points whose

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coordinates are (x,T^*), a "hyperfreezing curve" Γ and a "hypersolubility curve" Σ are determinated. These curves are joining at the point ϵ whose coordinates are quite different from the eutectic ones. During a steady cooling, crystallization of the salt (ice having crystallized out first) or the ice (salt having crystallized out first) occurs at around a lower temperature T_α or T_β depending on the composition of the disperse solution. The domains of simple and double metastability of the solutions can be defined (see Fig. 1) from the curves Γ and Σ and the points α and β.

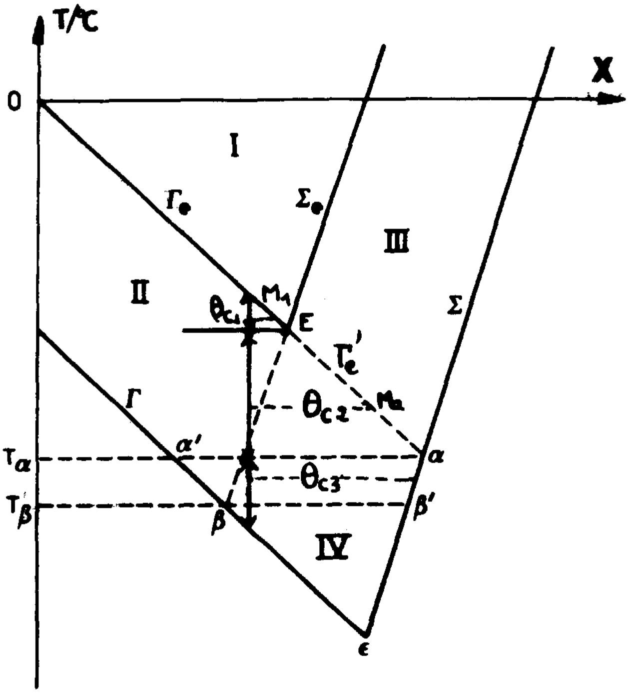

Fig. 1. Schematic phases diagram of disperse aqueous saline solutions within emulsions.

Domain I : stable solutions ; domain II : solutions stable with respect to salt and metastable with respect to ice ; domain III : solutions stable with respect to ice and metastable with respect to salt ; domain IV : solutions metastable with respect to salt and to ice.

$x < x(\alpha')$ The crystallization of water occurs first and the crystallization of salt appears only when the temperature of the system is T_α when there is not salt nucleation by the ice crystals previously formed.

$x(\alpha') < x < x(\epsilon)$ the crystallization of water occurs first and the crystallization of salt just follows as the remaining solution has a concentration which is more than that of point α.

$x(\epsilon) < x < x(\beta')$ the crystallization of the salt occurs first, followed by that of the ice.

$x > x(\beta')$ the crystallization of salt occurs first and the crystallization of water appears only when the temperature of the system is T_β.

The degrees of metastibility corresponding to the curves Γ or Σ are defined as :

curve Γ : $\Delta T_\Gamma(x) = T_e(x) - T^*_\Gamma(x)$, $T_e(x)$ is given by Γ_e as long as $x < x\ (E)$, for $x > x\ (E)$, $T_e(x)$ is given by Γ'_e, the metastable extension of Γ_e

curve Σ : $\Delta T_\Sigma(x) = T_e(x) - T^*_\Sigma(x)$, $T_e(x)$ is given by Σ_e

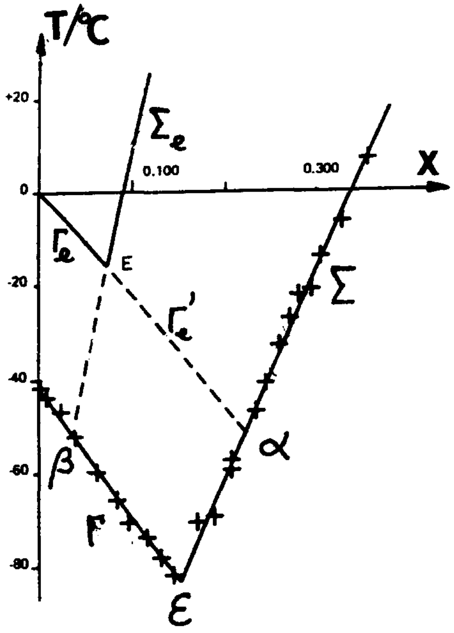

Fig. 2 : Phases diagram of disperse aqueous solutions of ammonium chloride

For emulsified aqueous solutions of ammonium chloride, it has been found that $\Delta T_{\Gamma}(x)$ varys between 40°C (x—>0) and 49°C (x = 0.15) and $\Delta T_{\Sigma}(x)$ varying between 145°C (x = 0,16) and 211°C (x = 0,35), x being the molar fraction of the salt (see Fig. 2) (ref. 4). Owing to the high dregrees of metastability reached, certain solutions fail to crystallize, as is the case for emulsified aqueous solutions of sodium chloride (see Fig. 3).

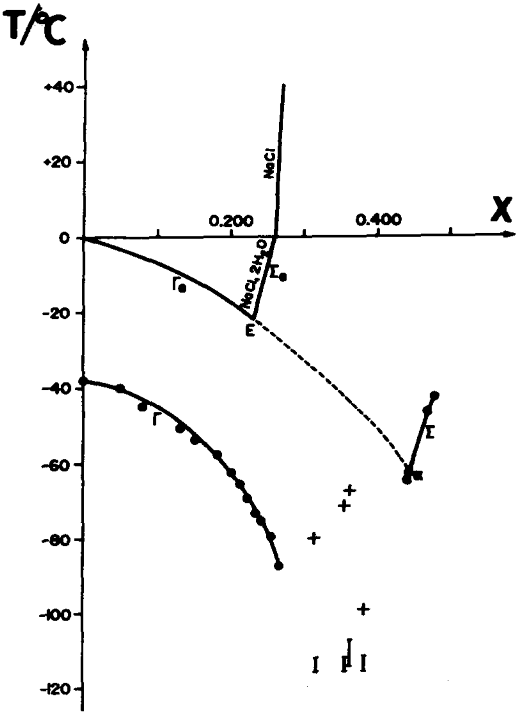

Fig. 3. Phases diagram of disperse aqueous solutions of sodium chloride.

According to the classical nucleation theory, no crystallization of the undercooled phase should be observed when the emulsion is maintained at a fixed temperature θ_c, which is between $T_e(x)$ and a few degrees above T^*.

Experiments performed on pure dispersed liquids such as water or benzene have shown that crystallization in fact occurs. The time required before a finite rate of crystallization is reached is rather long (20 days for emulsified benzene maintained at $\theta_c = -31°C$) ($T_e = +6°C$; $T^* = -68°C$), but nevertheless much less than those predicted by the theory (refs. 5-6). A model of heterogeneous nucleation based on the modification of the interface droplet - continuous medium has been proposed by the authors of this article (refs. 6-7). According to this model, nucleation is supposed to occur at the surface of the emulsified droplet with a non-uniform probability. Preferential nucleating patches are created by previous crystallizations of the droplets during steady cooling, or when the emulsion is preserved at a fixed temperature θ_c. Experiments undertaken on water-emulsions made without surfactant have shown that in these conditions the undercooled water does not freeze for at least three months (ref. 8). These results show that the birth of the ice nucleating patches is certainly enhanced by the surfactant spread on the surface droplet. The part of the surfactant on nucleation phenomena within emulsions has also be considered by other research workers (ref. 9).

In this article, the results obtained by studying ice nucleation in aqueous saline solutions dispersed within emulsions maintained at a fixed temperature θ_c such as $T^* < \theta_c < T_e$ are reported. As we shall see, determination of the amount of ice formed during the preservation of the emulsion at θ_c,requires information concerning the ice melting of the emulsion during heating from θ_c to a temperature higher than $T_e(x)$. It is during this heating that an unexpected behavior has been observed. Emphasis is laid on this phenomenon in this paper. To point out the part of the surfactant on the observed phenomena and concidentally check the nucleation model within emulsion proposed by the authors, the results for two different surfactants are reported.

EXPERIMENTAL SECTION

Detection of the amount of solid M(t) formed versus time, during the preservation of a pure component emulsion has been made through calorimetric measurements. As droplets do not crystallise at the same time, very low heat powers are released and M(t) cannot be determined through direct calorimetric measurements. On the other hand, melting of the pure solid occurs at the same time for the whole dispersed droplets and the study of the heat involved allows the determination of M(t). For this purpose, the emulsion is divided out into n calorimeter pans, each being placed in brass supports, which are afterwards introduced into a thermostat whose temperature is the chosen temperature θ_c. After a preservation time, t, at θ_c, one pan is taken off the thermostat and placed in a calorimeter, Perkin-Elmer DSC 2 or DSC 4, previously stabilized at the temperature θ_c. The emulsion is steadily heated at the rate of 2.5 $K.mn^{-1}$ and the area of the melting signal S(t), is measured. As the amount of the dispersed phase cannot be determined with accuracy, the proportion of solid formed at θ_c is obtained by subjecting the melted emulsion to a steady cooling-heating cycle during which all the droplets have frozen and melted. The area of the total melting signal, S_T, is determined and M(t) is given by

$$M(t) = \frac{S(t)}{S_T} \qquad (1)$$

When the disperse phase is an aqueous saline solution instead of a pure component, determination of M(t) is much more complex, as the disperse phase may be partially liquid at the end of the evolution of the emulsion. It happens when $\theta_c = \theta_{c1}$ is between $T_e(x)$ and T_E (eutectic temperature) (see Fig. 1). The system at equilibrium is made of ice and solution whose composition is given by the abscissa of the point M_1.The amount of water which can transform into ice is determined by analysis of the phases diagram. Another problem arises when one wants to determine the area of the melting signal, S(t), as the ice melts from the start of heating and delimitation of the signal is rendered difficult.

When $\theta_c = \theta_{c_2}$ is between T_E et T_α (see Fig. 1), first the system tends to a metastable state characterized by the point M_2. The droplets are then made of ice and a supersaturated solution, the composition of which is given by the abscissa of the point M_2 belonging to the metastable extension of the equilibrum ice + solution curve, $\Gamma'e$. The remaining water present in the droplet will transform into ice when by breakdown of supersaturation the salt crystallizes. In the case of the sole ice crystallization, melting occurs from the beginning of the heating from θ_c. When both ice and salt have crystallized, the melting begins only at the eutectic temperature, T_E, and ends at the temperature $T_e(x)$.

These experiments were performed on aqueous solutions of NH_4Cl or NaCl dispersed within emulsions maintained at a fixed temperature θ_c such as $T_\alpha < \theta_c < T_E$.

As an example, the results obtained for aqueous solutions of NaCl the molar fraction x being 0.023 ($T_e = -4.4$°C ; $T_E = -21.6$°C ; $T^* = -49.0$°C ; $T_\alpha = -68$°C ; $\theta_c = -32$°C) and dispersed within a mixture composed of methylcyclohexane (MCH) and methylcyclopentane (MCP) and span 65 (MCH/MCP : 50/50 ; Span 65 : 4%) will now be described.

The melting thermogram obtained during the heating from θ_c = -32°C of the emulsion maintained during t = 55 hours at θ_c, is represented in Figure 4.a. After reaching 10°C the emulsion is cooled steadily to $T < T_\alpha$ (see Fig. 5.a) and heated to $T > T_e$ (see Fig. 4b). In order to compare the behaviour of the emulsion before and after the preservation at θ_c, the thermograms obtained during the cooling (see Fig. 5b) and the heating (see Fig. 4c) on an emulsion having not been preserved at θ_c before, are reported. They show the ice crystallizations of the droplets around $T^* = -49°C$ followed by the total solidification around $T_\alpha = -68°C$, the eutectic melting at - 21.6°C followed by the progressive ice melting that ends at $T_e = -4.4°C$.

Comparison of the thermograms after and before preservation at θ_c, allows the following remarks to be expressed.

An unexpected melting signal at 0°C characteristic of the melting of pure ice is observed. It has been found that its area is the larger, the longer the preservation at θ_c. This signal is preceded by a weakly marked melting signal characteristic of the progressive melting of ice in equilibrium with a solution. The lack of eutectic melting shows that the salt has not crystallized during the preservation at θ_c. The signal I observed at $T^* = -39°C$ during the cooling of the emulsion after the preservation at θ_c (see Fig. 5a) is characteristic of the ice crystallization of pure water dispersed within an emulsion. This ice crystallization has to be correlated with the pure ice melting at 0°C. In the same figure, the signal II characteristic of the ice crystallization of dispersed solution can be seen. Its molar fraction is slightly higher than that of the solution dispersed within the emulsion. Total solidification of the droplets is observed at $T_\alpha = -68°C$ (signal III), this temperature being independent of the initial composition (see section I).

During the next heating (see Fig. 4b) the area melting signal at 0°C, decreases. Fewer droplets are involved in this phenomenon.

This decrease goes on when cooling-heating cycles between +7°C and -80° C are performed. If the emulsion is stabilised long enough at a positive temperature, it is even possible to "erase" the melting signal at 0°C, the cooling-heating thermograms obtained being identical to those obtained before a thermal treatment (see Fig. 4-5).

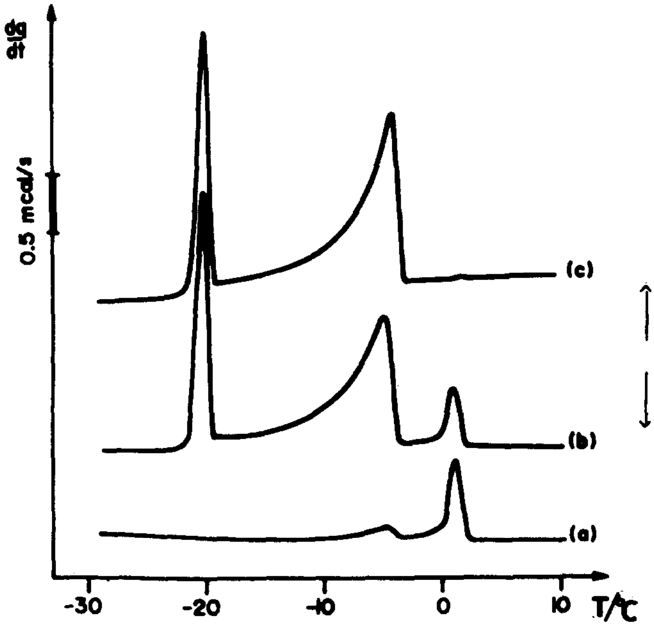

Fig. 4. Melting thermograms of aqueous solutions of NaCl dispersed within MCP + MCH + SPAN 65 medium. x = 0.023, dT/dt = 2.5°C.mn^{-1}

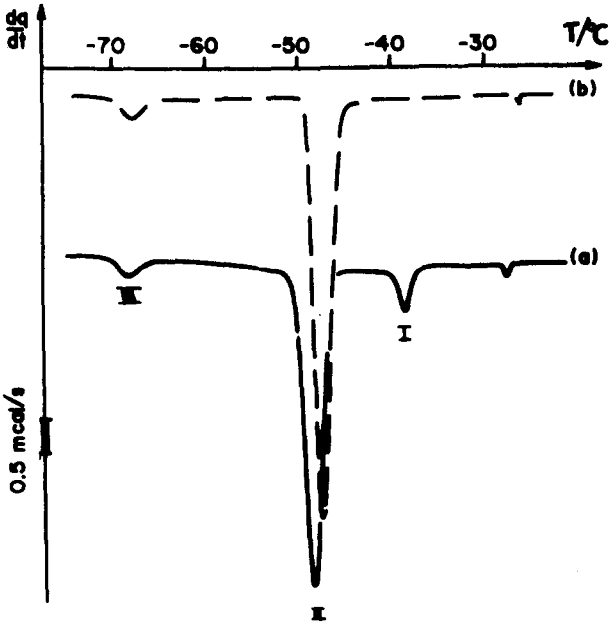

Fig. 5. Cooling thermograms of aqueous solutions of NaCl dispersed within MCP + MCH + SPAN 65 medium. x = 0.023, dT/dt = - 5°C.mn^{-1}

These experiments were undertaken again on the same kind of solutions dispersed within a different oil + surfactant medium, namely vaseline oil plus lanolin (2-3 % wt/wt). The thermograms obtained after maintaining the emulsion 14 days at $\theta_c = -32°C$ (almost all the water which can be crystallized at this temperature -see section I- being crystallized) display a pure ice melting at 0°C, but much less marked than previously and a progressive melting of ice in equilibrium with a solution (see Fig. 6a).

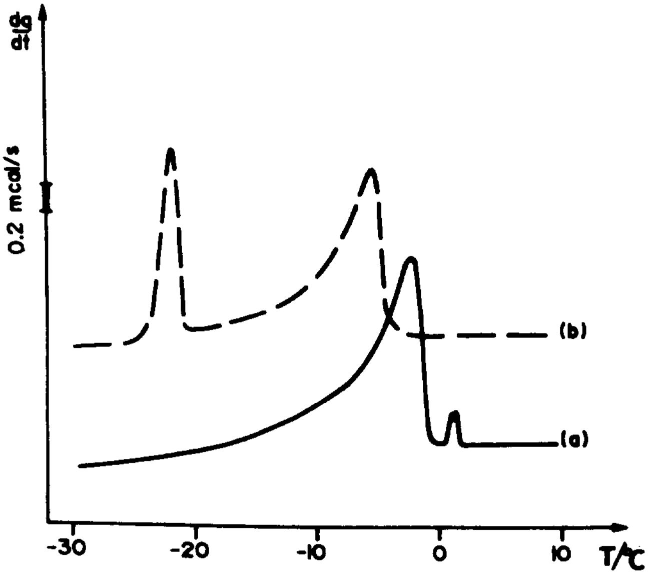

Fig. 6. Melting thermograms of aqueous solutions of NaCl dispersed within lanoline + vaseline oil medium. $x = 0.23$, $dT/dt = 2.5°C.\ mn^{-1}$.

By comparison with the thermogram in Figure 6b obtained during the melting of an emulsion before it was maintained at θ_c, it can be seen that the progressive ice melting after preservation at θ_c, ends at a higher temperature $T_e(x)$. This shows that the solution in equilibrium with ice has a lower composition. In this case, the difference in the behaviours of the emulsions before and after the stabilization of the emulsion at θ_c is less marked than with the mixture MCP + MCH + span 65.

ANALYSIS AND CONCLUDING REMARKS

We have checked that these results are not a consequence of a dammage of the emulsion with time. Part of the mother emulsion was maintained at the ambient temperature and several cooling-heating cycles were performed during the preservation time at θ_c. The thermograms were all identical, showing no modification of the properties of the emulsion. Since the droplets were isolated from each other by the continuous medium, possible distillation of water from the droplets to the sample lid as has been stated for droplets sealed in a sample pan without an enveloping layer has not been considered [10]. This statement is confirmed by the fact that it is possible to "erase" the melting peak at 0°C and then get an emulsion whose properties are the same as those before freezing at θ_c.

Furthermore, it must be stressed that ice melting at 0°C is observed only when the ice crystallization at θ_c has begun.It can thus be regarded as the consequence of ice crystallization versus time at a fixed temperature θ_c. Then it appears that different ice nucleation mechanisms have to be considered, depending on whether the emulsion is steadily cooled or maintained at a fixed temperature θ_c in an undercooled state. These results are in agreement with the nucleation model proposed by the authors, according to which ice nucleation arises on the surface droplet, as has been indicated in section I. Then as the surfactant is spread on the surface droplet, it is not surprising that the extent of the phenomenon observed depends on the surfactant used. As nucleation occurs in the surface droplet, it can be thought that the ice develops itself on the surface giving rise to an ice shell. Then high pressures inside the droplet may exist and produce the burst of the droplet . Similar microscopic experiments performed on droplets with diameters around 1 mm have shown, splinters around the droplets after freezing at a fixed temperature θ_c (ref. 12).

These experiments and the results obtained point out the limit of the use of emulsions as a means for studying the homogeneous nucleation kinetics of undercooled melts. Nevertheless they make possible to specify not only the characteristics of a heterogeneous nucleation of this type but also the evolution of any disperse system analogous to the one studied and placed in similar conditions. Various industrial sectors e.g food processing, pharmaceutical, biological are affected by such systems and the results obtained have their applications in these fields.

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