

# Prediction Versus Composition of the Amount of Ice Formed in Water + Solute Droplets Dispersed in a W/O Emulsion

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## Abstract

This paper deals with investigation of the effect of solute concentration on the amount of ice formation from some materials such as pure water, NaCl and glycerol solutions were dispersed into a W/O emulsion system. The investigations were carried out by inserting sample emulsions into a steady cooling-heating program at constant heating rate,  $\dot{T} = 2.5$  K/min from  $T = (20$  to  $-60)^\circ\text{C}$ , that considered all the water have frozen, then heated back to the initial temperature,  $T = 20^\circ\text{C}$  to bring about the frozen one to the liquid state using differential scanning calorimetry (DSC-131 evoSetaram, France). The proportion of ice formed,  $P$  was then calculated from the recorded thermogram, at which the melting signal is related to the total amount of water frozen. The way the droplets frozen during cooling process is described from the thermodynamics ice/solution phase diagram completed by the curves that give the freezing conditions. The results indicated that the proportion of ice formed calculated from DSC thermogram show very close agreement to thermodynamic theoretical model, at which % error less than 1% of each experiment.

**Keywords:** ice formation, dispersed water, W/O emulsion, thermodynamics, DSC

## 1. Introduction

Freezing is a process of formation of solid, consists of three basic steps; undercooling, nucleation and growth of nuclei. This is a complex process, where every step is essential but do not link one to another, or may occur simultaneously (Mullin & Mullin, 1993). Undercooling is a process of lowering temperature of a fluid below its melting point without becoming a solid. The difference between melting temperature and freezing temperature is called undercooling degree. As nucleation occurs solid molecules rearrange into a nuclei and become large enough to have the ability to grow into a larger size (Kashchiev, 2000). Nucleation can be homogeneous or heterogeneous. Homogeneous nucleation is spontaneously process but requires undercooling medium. While heterogeneous nucleation occurs much more often than homogeneous nucleation, it requires less energy than homogeneous nucleation.

In emulsion system, freezing is occurred by nucleation and growth of nuclei in the droplets. Nucleation is homogeneous when it takes place in the volume of the droplets, provided ideally by pure liquid. It is then heterogeneous and takes place in the droplet volume or at the droplet surface, respectively (Kashchiev et al., 1998, p. 167-177). For theoretical purposes, the emulsion is assumed as the simple ones and focused only on the droplets. The freezing is assumed occurring without interaction between the droplets, and it is seen in two steps; (i) freezing of a single droplet and (ii) freezing of the whole droplets (Clausse, 1985, p. 77). The droplets are known exhibit a high degree of undercooling. The volume is one of the most important parameter that can influence the undercooling phenomenon. The smaller is the volume, the higher is the undercooling degree (Labes-Carrier, 1995, p. 607-631).

In this paper, the effect of solute concentration on the amount of ice formation from some materials such as pure water, NaCl and glycerol solutions were dispersed into a W/O emulsion system to be investigated using

Differential Scanning Calorimetry, DSC. Calorimetry technique has been implemented for many years to characterize the properties of emulsion (Clausse et al., 2005, pp. 694-703). It permits to study various phenomena in emulsion system through detections freezing and melting temperature of the droplets and the continuous phases.

1.1 Determining the amount of ice formed by DSC

DSC is a technique to characterize material by measuring the temperatures and heat flows associated with phase transition of materials. The basic principle underlying of the technique is the measurement of the difference in energy input into a sample and a reference. As a sample undergoes a physical transformation more or less heat will need to flow to the sample than the reference in order to maintain both at the same temperature. The amount of heat flows to the sample depends on whether the process is exothermic or endothermic. As the sample melts to a liquid state, it requires more heat to increase its temperature at the same rate as the reference. Likewise, as the sample undergoes freezing, less heat is required to raise the temperature. Using computer, the temperature and the heating rate will be tracked, recorded the differences between them, and plotted heat flow against time and temperature. The peak area of the recorded signal generally called thermogram, leads to the heat exchange during the thermal phenomena (Figure 1). The curve is represented the relationship between heat flow versus temperature or versus time. The energies involved are measured in exothermic and endothermic flow.

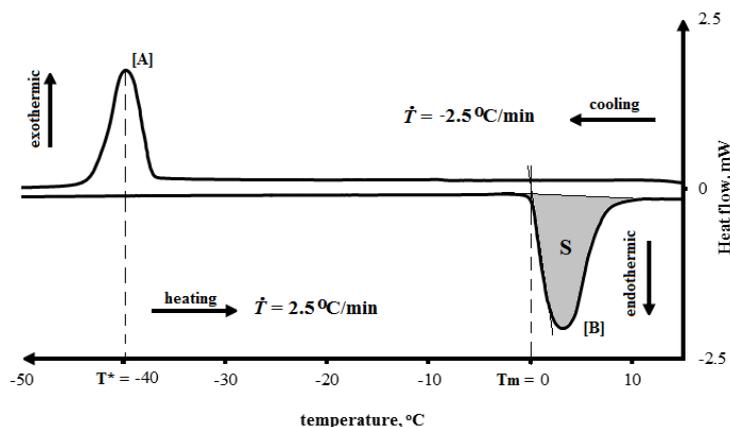


Figure 1. Freezing peak [A] and melting peak [B] of dispersed ice obtained from DSC thermogram

Freezing peaks obtained by cooling the sample below its ice-liquid water equilibrium temperature.  $T^*$  refers to the most probable freezing temperature, can be defined that the temperature at which 50% of the droplets are frozen (Clausse, 2010, pp. 1071-1077). According to Dalmazzone (Dalmazzone, et al., 2009, p. 543-555), the apex temperature may be correlated to the mean droplet size, the lower freezing temperature the smaller droplet size is. The melting peak is generated by heating the heat above its melting temperature  $T_m$ . The droplets melt at  $0^\circ\text{C}$ , which is the thermodynamic equilibrium temperature between ice and pure water at atmospheric pressure.

The proportion of frozen liquid versus time is determined by;

$$P = \frac{M_f(t)}{M} \tag{1}$$

$M_f(t)$  is the amount of the crystallized droplets at time  $t$  and  $M$  is the total amount of droplets dispersed within the sample emulsion. According to Guttman (Guttman & Joseph, 1973, pp. 408-410) the area,  $S$ , in Figure 1 represents the total melting heat  $\Delta H_m$ . Thus it can be written:

$$S = \Delta H_m = L_m M \tag{2}$$

When the cooling is stopped at  $T$  before getting the whole freezing, the area of the melting signal is less and equation (2) can be written:

$$S(t) = \Delta H_m(t) = L_m M_f(t) \tag{3}$$

If the latent heat of melting the dispersed water is known (80 cal/gr for pure water) and the value of  $S(t)$  can be found from the energy involved for the melting,  $Q$  corresponding peak of the endothermic signal in the DSC

thermogram, then the amount of frozen droplet can be determined.

### 1.2 Thermodynamics Diagram

The amount of ice formed in the emulsion system depends on the temperature and the composition of the droplets. The way of liquid freeze during cooling process is described from the thermodynamics ice/solution phase diagram completed by the curves that give the freezing conditions. A schematic diagram of the ice-solution equilibrium is given in Figure 2.  $x$  (molar fraction) is the droplet composition, at which ( $x = 0$ ) is for pure ice and ( $x = 1$ ) is for pure solute.  $\Gamma_e$  represents ice in equilibrium with a solution.  $\Sigma_e$  is salt in equilibrium with a solution and  $E$  is ice + solute + eutectic solution. The eutectic temperature corresponds to the lowest freezing temperature of the system, the only point at which both components (solute and solvent) freeze at the same time

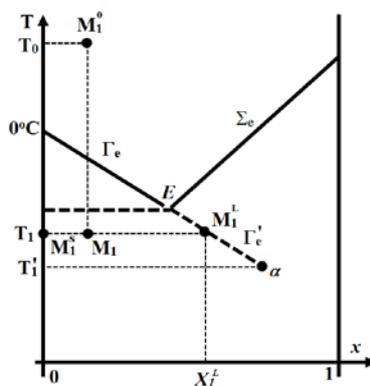


Figure 2. Schematic phases for solution droplets dispersed within an emulsion

$M_1^0$  in Figure 2 refers to the composition of the dispersed aqueous phase under study. When the dispersed solution is regularly cooled (from point  $M_1^0$  to point  $M_1$ ) ice does not appear at the temperature that given by curve  $\Gamma_e$ , due to nucleation phenomena (Clausse, 1998, pp. 191-201). As far the conditions of freezing are not reached, the solution is still liquid state or undercooled state. As the cooling is stop at the point  $M_1$ , and the sample is then maintained at this temperature, the freezing will occur versus time. That gives the state of the solution at time,  $t = 0$ . Time to time some liquid will freeze and for those the amount of ice formed in such of the composition. The remaining solution is given by point  $M_1^1$  that belongs to the extension of the equilibrium curve  $\Gamma_e^1$  (dashed line). As far the temperature is higher than the one that gives the condition of precipitation of the solute (point  $\alpha$ ) the system will stay in this state. In these conditions the amount of ice formed is given by:

$$P = \left[ \frac{M_1^1 - M_1}{M_1^1 - M_1^S} \right] \quad (4)$$

The determination of  $P$  needs the knowledge of the extension curve of the equilibrium one. To do it is written that at point  $M_1$ , the activity of water  $a_{w, \text{ice}}(T)$  in the pure ice equals the activity of water,  $a_{w, \text{solution}}$  in the solution in equilibrium with ice. Assuming that at atmospheric pressure, the water fugacity can be taken to be equal to the vapor pressure,  $a_{w, \text{solution}}$  is given by the relative humidity  $h(x, T)$  of the solution. Assuming that  $h$  shows a weak dependence with  $T$ , its value can be taken at another temperature, namely  $0^\circ\text{C}$  (Breton, 1967). Recent developments (Koop & Zobrist, 2009, p. 10839-10850) permit to estimate the activity of water  $a_{w, \text{ice}}(T)$ .

## 2. Method

Amount of ice formed some materials (pure water, solution NaCl and solution glycerol) when they are submitted to temperature variations between ambient temperatures and sub ambient ones to be calculated. Experiments were carried out on W/O emulsions by submitting into a steady cooling-heating program using differential scanning calorimetry (DSC-131 evoSetaram). Freezing conditions of ice and solute are described from the ice-solution phase diagram completed by the curves that give the conditions of freezing for ice and solute in the dispersed solution and the amount of freezing ice is determined from thermodynamics calculations and calorimetric measurements.

### 2.1 Materials

- Water phase: demineralized water was produced by a purification chain provided by Veolia Water STI (Wissous, France), liquid glycerol from Thermo Fischer Scientific, France and crystal NaCl from Sigma Aldrich, France.
- Oil phase: rapeseed oil methyl ester was supplied by Mosselman, Belgium.
- Surfactant: PolyGlycerolPolyRicinoleate (PGPR) was supplied by Palsgaard, Denmark. PGPR has a HLB number of 4.

## 2.2 Sample Preparations

Composition of water and oil phases is given in Table 1.

Table 1. Composition of water and oil phases

Aqueous phase (50% V/V)		Oil phase (50% V/V)	
Content	% (w/w)	Content	% (w/w)
NaCl	0, 3, 6.6, 10	PGPR	5
Glycerol	0, 2.5, 5, 10	Rapeseed oil methyl ester	95
Water	90 – 100		

Water-in-oil, W/O emulsion was prepared at room temperature. 10 mL of oil phase were filled previously into a 50 mL of bottle formulation using a volumetric pipette. The bottle was then installed in the rotor stator system and set up shearing rate initially at 3000 rpm. 10 mL of aqueous phase were introduced drop by drop into the oil phase using a 10 mL of syringe pipette in 2 minutes. The shearing rate was then increased gradually (1000 rpm per 15 seconds) until the speed reached to 14.000 rpm. Agitation was kept at this speed for 5 minutes. 30 seconds prior to the homogenizing completed, the shearing rate was decreased gradually until the rotor system stops perfectly. The total homogenizing time is 10 minutes.

## 2.3 Differential Scanning Calorimetry, DSC

Differential Scanning Calorimeter type DSC131-evo (Setaram, France) was used in this work. Fresh emulsion sample (30 mg) was placed in a 100  $\mu$ L of aluminium crucible using pipette plastic droppers. Sample was weighted using analytical balance and sealed with piercing lid then inserted into the sample pan holder. An empty aluminium crucible (SETARAM, Alu-D: 6.7 S08/HBB37409) was used as the reference crucible. DSC temperature program was adjusted for measuring conditions, started with equilibrated isotherm temperature at 20°C for 600 seconds, followed by cooling program from 20°C to -60°C, the second isotherm temperature at -60°C for 300 seconds, and heating back until the end of the melting at 20°C. The regularly scanning rate for cooling and heating is  $\pm 2.5^\circ\text{C}/\text{min}$ .

## 3. Results and Discussion

### 3.1 Pure Water

DSC freezing and melting curves of a sample W/O emulsion and bulk pure water is presented in Figure 3A and 3B respectively. The crosshatched area, S represents the total melting heat of dispersed water. In Figure 3A shows that before temperature around -22°C any droplets are found to be frozen. But it does not mean that there is no frozen droplet. As soon as the temperature is lower than 0°C, droplets can freeze but the number is rather small and the energy released is too small to be detected. It can be said also that at around -40°C all the droplets are frozen but for the same reason at this temperature depends upon the sensibility of the calorimeter used. The apex temperature indicates the mean radius of the droplets even if its position is depending upon cooling rate, sample mass under study and the proportion of water dispersed within the emulsion. For emulsion containing around 50% amount of water, regularly cooled at 2.5°C/min, the radius of the droplets is around 10  $\mu\text{m}$ , the temperature referred as the mean freezing temperature is around -32°C.

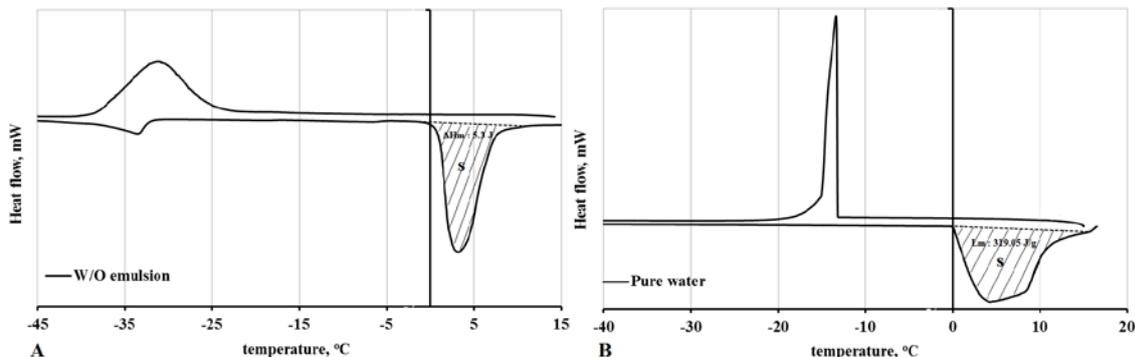


Figure 3. DSC freezing and melting curves, the crosshatched areas, S are; (A) the amount of melting heat dispersed ice of emulsion contains 50% v/v of pure water in dispersed phase and 5% w/w of PGPR in oils phase; (B) melting heat of bulk pure water.

The proportion of ice formed is calculated using the data provided from DSC thermogram. The endothermic peak of the emulsion in Fig 3A relates to the total melting dispersed ice (Dumas et al., 1975, p. 261-275), namely  $\Delta H_m = 5.3$  J. Total ice formed,  $M_f$  is determined by equation (3)

$$S(t) = \Delta H_m(t) = L_m M_f(t)$$

The melting latent heat,  $L_m$  of the dispersed material considered is obtained by performing separate experiment in such a way that is sure that all the droplets have frozen. The crosshatched area, S in Figure 3B represents the melting peak of bulk pure water, that gives latent heat of fusion,  $L_m = 319.05$  J/g. This value is not too far from the theoretical of pure water 330 J/g (Perry, 2008).

So that, total mass of freezing ice;

$$M_f = \Delta H_m / L_m = 16.63 \text{ mg}$$

If total mass sample, ( $\rho_{s,20^\circ\text{C}} = 0.919$  g/cc) is  $M_s = 31$  mg, the density of pure water is  $\rho_{w,20^\circ\text{C}} = 0.987$  g/cm<sup>3</sup> and dispersion volume fraction of emulsion is DV = 50% v/v.

Total mass of dispersed water,  $M_{DW}$  in emulsified system;

$$M_{DW} = M_s \cdot DV \cdot (\rho_w / \rho_s) = 16.63 \text{ mg}$$

The proportion of pure water droplets that have frozen during the cooling is given by;

$$P = \left[ \frac{M_f}{M_{DW}} \right] \cdot 100\% = 100\%$$

From the calculation appears that the proportion of freezing ice,  $P$  within the emulsion is 100% reached.

### 3.2 Water + solute

The way the droplets solidify in the dispersed droplet containing aqueous solution during a steady cooling is described from the ice-solution phase diagram. Both systems studied are totally miscible and are assumed that the solute has no influence on the conditions of solidification of the solvent. Freezing condition can occur at a temperature less than the eutectic temperature. If the freezing temperature is lower than its eutectic point, calculation needs to extension line of the solid-liquid equilibrium curve.

The amount of freezing ice is depending upon the temperature and the composition of the dispersed droplets. Ice/solution equilibrium curve and its extension for system water-NaCl (Breton, 1967) and water-glycerol (Lane, 1925, p. 924-924) are presented in Fig 4. The extension line referred as in the dashed line, in which the values are modeled by polynomial regression using Microsoft Excel™.

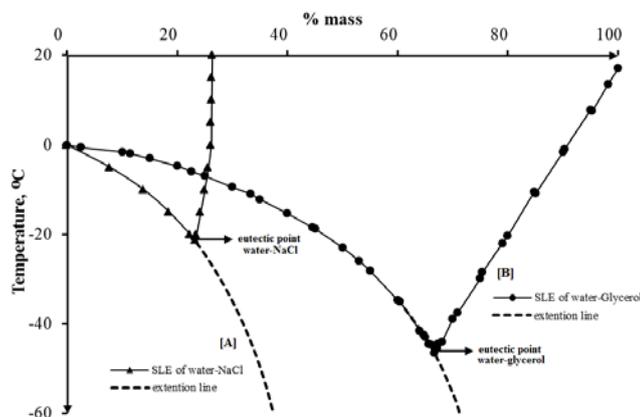


Figure 4. Ice/solution curve system: A. water-NaCl; B. water-glycerol and its extension at P = 1 atm.

### 3.2.1 Thermodynamics Calculation

Figure 5 presents an example to calculate the amount of freezing ice using solid-liquid equilibrium diagram completed by the curves that give the freezing conditions. At 3% w/w of NaCl in aqueous phase has concentration  $x = 0.01$  (mole fraction), the mean freezing temperature of emulsion obtained is  $T_f = -42.4^\circ\text{C}$  (Figure 5A). The proportion freezing ice is given by the ratio of the segments ML and SL (Figure 5B) in which the points L and S respectively are situated on the extension line of melting curve. As  $x = 0$ , it represents the ice of pure water.

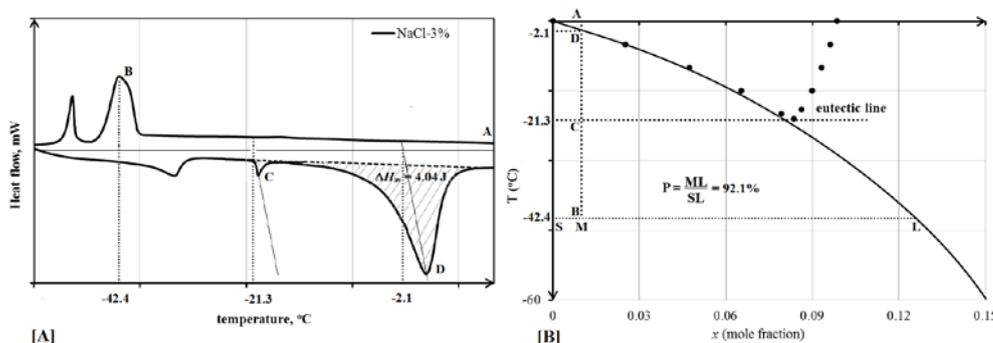


Figure 5. DSC freezing and melting curves (A) Equilibrium curve ice/solution and its extension (B). Emulsion contains 3% w/w NaCl in 50% v/v of dispersed phase

Point M (0.01, -42.4) is the composition of the dispersed aqueous phase under study. SL (dotted line) represents the tie line drawn in the region of liquid-solid equilibrium indicates the compositions of the liquid and solid phases at temperature,  $T = -42.4^\circ\text{C}$ . In this region, the solid phase consists of pure component water (ML line) and the liquid phase is a mixture of NaCl and water (SM line). The proportion of freezing ice is given by;

$$P = \left[ \frac{ML}{SL} \right] \cdot 100\% = 92.1\%$$

Summary of the calculation in the different variable of emulsion is presented in the Table 2.

Table 2. Proportion of water frozen in dispersed droplet of emulsion using thermodynamics calculation

Sample		$M(x, T_f)$		SL	ML	P (%)
Name	% weight	x	$T_f$ (°C)			
NaCl-3%	3%	0.01	-42.4	0.125	0.01	92.1%
NaCl-6.6 %	6.6%	0.02	-45.9	0.132	0.02	83.3%
NaCl-10%	10%	0.03	-48.5	0.138	0.03	76.0%
Glycerol-2.5%	2.5%	0.005	-39.9	0.251	0.005	98.0%

Glycerol-5%	5%	0.01	-41.0	0.256	0.01	96.0%
Glycerol-10%	10%	0.02	-45.1	0.277	0.02	92.8%

$x$  : mole fraction.

From the results above appear that during cooling, crystallization of either component solvent or solute is observed depending on the droplets compositions. For the system contains NaCl,  $x = 0.01$ , the solidification occur far below its eutectic composition,  $x > x_e$ . It means that solidification of NaCl will be observed first. Whereas the system contains glycerol,  $x = 0.01$  the solidification occur before its eutectic composition attained,  $x > x_e$ . It means that water solidified first.

### 3.2.1 Calorimetric Measurement

From DSC thermogram, the droplet solidify is described in Fig 5A. Point A is the initial state of the emulsion at  $t = 0$ . All the droplets are in liquid state. As cooling continuous, some droplets will freeze and the amount of ice formed is given in point B with mean freezing temperature,  $T_f = -42.4^\circ\text{C}$ , the composition of the remaining solution is given by point B=M (Figure 5B, thermodynamics diagram). During reheating, the first endothermic peak corresponds to the eutectic melting of the binary NaCl-water system is given in point C, at  $-21.3^\circ\text{C}$ , and is immediately followed by a large endothermic peak due to the progressive melting of ice in point D. Melting temperature is corrected by projecting the top peak to the base line in a direction parallel with the linear portion of the eutectic melting peak (Fig 5A point C and D). It gives the equilibrium temperature at  $T_m = -2.1^\circ\text{C}$ .

The measured heat,  $\Delta H_m$  is represented by the crosshatched area in Figure 5A. It is relating to the total melting of dispersed ice of sample emulsion contains 3% NaCl. Total energy to melt the ice formed is obtained by integration the endothermic peak of the aqueous phase to the baseline. This linear baseline can be assumed approximately for the transitions of the phase solid to liquid. The DSC measured thermogram is  $\Delta H_m = 4.04 \text{ J}$ . The latent heat during phase change of binary system is measured separately from bulk NaCl solution, namely  $L_m = 274.33 \text{ J/gr}$ . The summary of the measurements and the comparison with thermodynamics calculations for both systems are presented in the Table 3.

Table 3. Calculation and comparison of the proportion water frozen in dispersed droplet of emulsion using calorimetric measurement and thermodynamics calculation

Sample		Thermogram		Calculation		P (%)	
Name	$M_{DW}^1$ (mg)	$\Delta H_m^2$ (J)	$L_m^3$ (J/g)	$M_{FW}^4$ (mg)	DSC	Thermo calculati on	$\Delta\%$
NaCl-3%	16.08	4.04	274.33	14.74	91.7%	92.1%	0.41%
NaCl-6.6%	15.26	3.23	255.96	12.64	82.8%	83.3%	0.43%
NaCl-10%	14.98	2.73	242.44	11.28	75.7%	76.0%	0.65%
Glycerol-2.5%	18.38	4.47	249.29	17.94	97.6%	98.0%	0.38%
Glycerol-5%	17.05	3.72	228.00	16.30	95.6%	96.0%	0.59%
Glycerol-10%	16.25	3.05	202.29	15.08	92.8%	92.2%	0.39%

1. Total mass dispersed water; 2. Melting heat; 3. Latent heat; 4. Total mass frozen water.

The results show very close agreement on the two method calculations (i.e., Calorimetric measurements and thermodynamics calculation) with % error less than 1% of each.  $P$  gives the proportion of frozen water within the emulsion containing droplets made of a mixture of NaCl-water. The first point to notice is that 100% is not reached, that means that all the water are not frozen. The presence of solute NaCl and/or glycerol has changed the freezing and melting temperature of ice. These temperatures are lower as the solute concentration is higher. Depending on the concentration, total solidification (ice + solute) may appear at the same or at different temperatures if the remaining solution after ice freezing is still liquid and oversaturated with regards to salt precipitation that occurs at a lower temperature.

## 5. Conclusion

Differential scanning calorimetry (DSC) was used to measure the proportion of ice formed in dispersed droplets. The amount of ice formed in the emulsion was depending upon the temperature and the composition of the droplets. The variation of an unfrozen aqueous phase was determined by measuring the endothermic enthalpy changes,  $\Delta H_m$  and thermodynamic calculations based on the solid-liquid phase diagram of solute material in

water solution. The addition of solute (NaCl or glycerol) into the dispersed phase increased the fraction of unfrozen water present in the emulsions.

There was good agreement between the DSC measured and thermodynamic calculated amount of ice formed. The results indicated very close agreement on the two method calculations (i.e., Calorimetric measurements and thermodynamics calculation) with % error less than 1% of each.

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