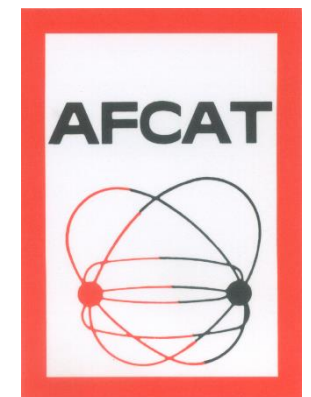


# CARACTÉRISATION D'ÉMULSIONS PAR DSC CHARACTERIZATION OF EMULSIONS BY DSC

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C. DALMAZZONE – IFPEN

**JCAT53 – 22 MAI 2023**



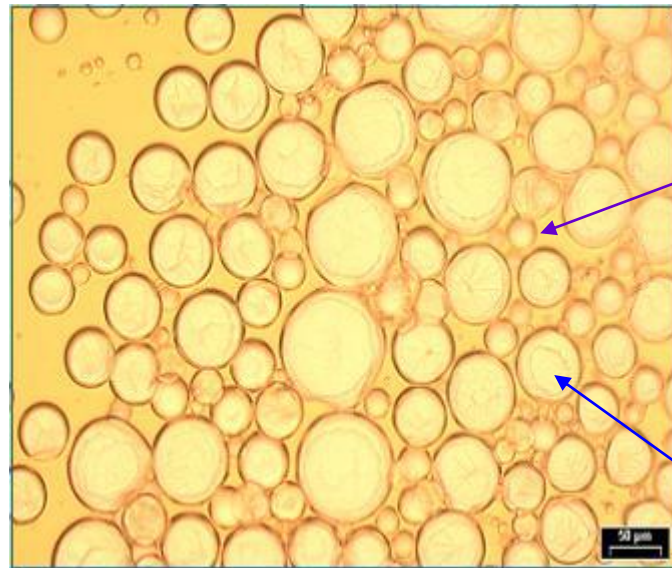
# SUMMARY

- Emulsions
- DSC principle
- Advantages of DSC
- Theoretical aspects
- Typical thermograms
- Information from DSC analysis
- Application to complex emulsions
- Conclusion

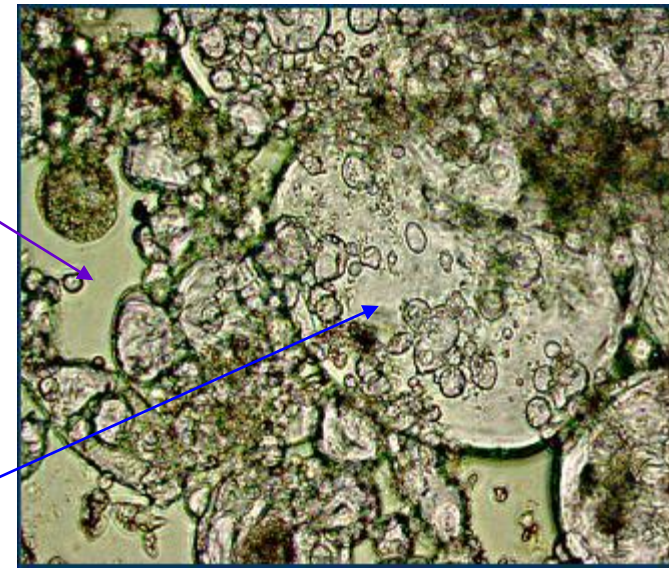
# EMULSIONS

**DISPERSION of one liquid (dispersed phase) in another liquid (continuous phase) : Biphasic System**

- Dispersed phase made of **MICROSCOPIC droplets (0.1 to  $\approx 30\mu$ )**
- An emulsion is theoretically **UNSTABLE** from a thermodynamic point of view but can be kinetically stable over months!

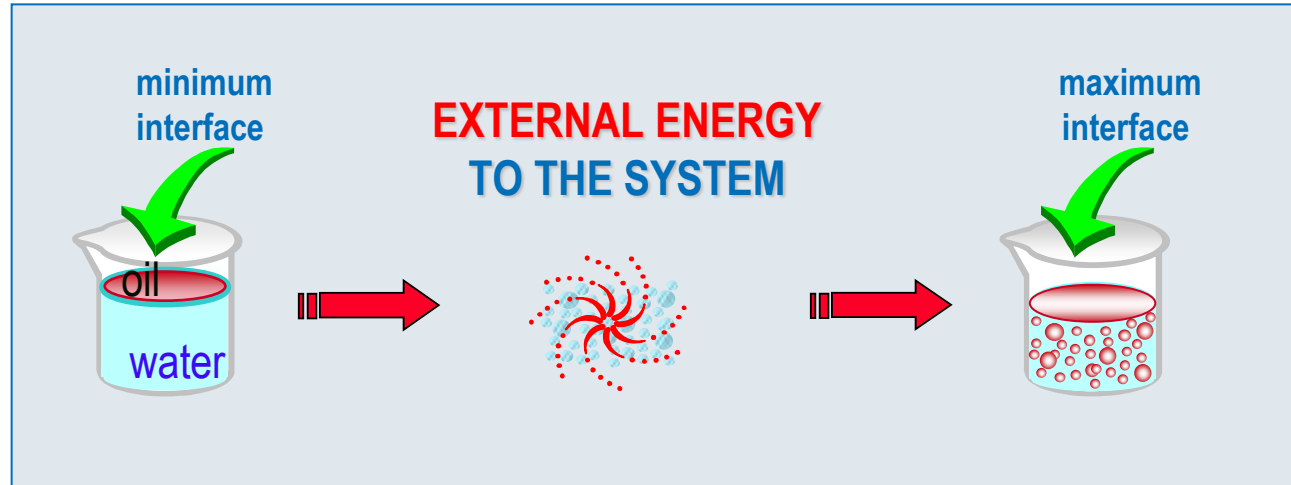


**Water-in-crude oil emulsion**



**Water-in crude oil emulsion stabilized by solids**

## EMULSIFICATION IS A **NON SPONTANEOUS** PROCESS



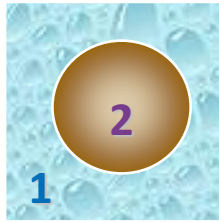
Formation of an emulsion through a calibrated orifice



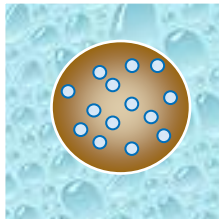
# EMULSIONS TYPES



1 Oil  
2 Water → Simple W/O EMULSION



1 Water  
2 Oil → Simple O/W EMULSION

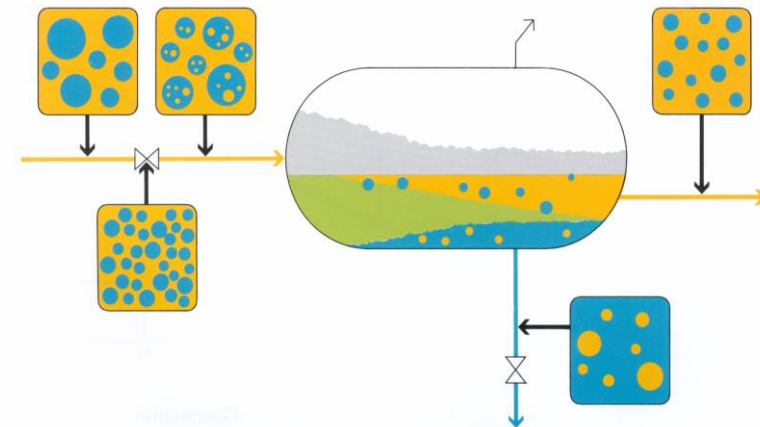


1 Water  
2 Oil → Multiple W/O/W EMULSION  
(or O/W/O if oil is the continuous phase)

W/O/W or O/W/O emulsions are called multiple or double emulsions.

They tend to form at the valves during oil production

*Water droplet break-up in the choke valves is one of the major pre-requisites for the formation of emulsions. After the choke valves, a dual emulsion with very small oil droplets inside the water droplets is often formed.*

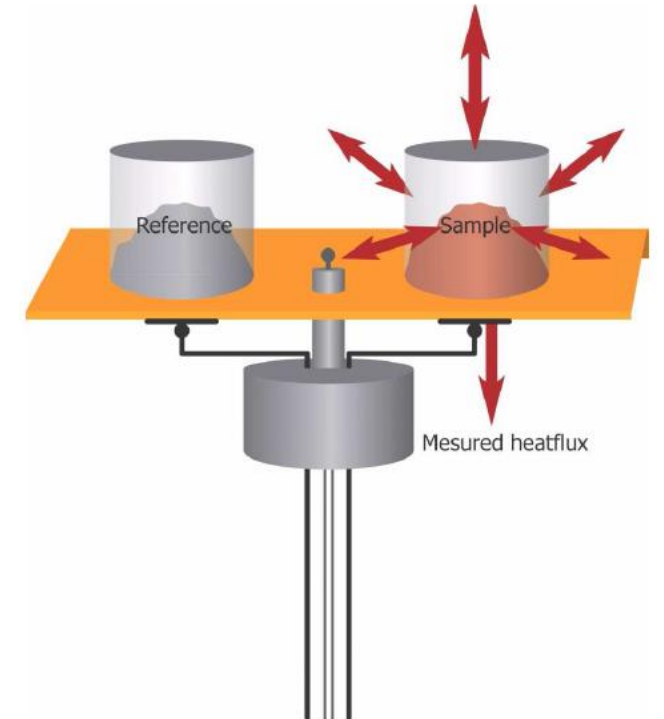


# COMPLEX EMULSIONS

- Emulsions are encountered at all levels in the petroleum industry
  - drilling, production, transport, refining...
- They can be sought (drilling fluids) or suffered (production fluids, etc.)
- These are complex systems:
  - more or less salty aqueous phases, oil phase, presence of solids of different natures and sizes, presence of gas, various chemical additives and surfactants....
- Experimental difficulties with complex water-in-oil emulsions
  - Opaque or black
  - Concentrated (dispersed volume fraction > 10%, up to 90%)
  - Conventional techniques (microscopy, light scattering) difficult to implement: **a dilution of the sample is generally necessary** (possible disturbances)
  - Most used test: “Bottle Test” or stability test in a test tube

# DSC PRINCIPLE

- DSC: Differential Scanning Calorimetry
- Principle: allows heat exchanges to be measured as a function of temperature or time
- Detection of phase changes: l/s, s/l, s/s, l/v, v/l transitions, glass transitions, Cp variations, etc.
- Measuring device: calorimeter working at low temperature (liquid nitrogen cooling)



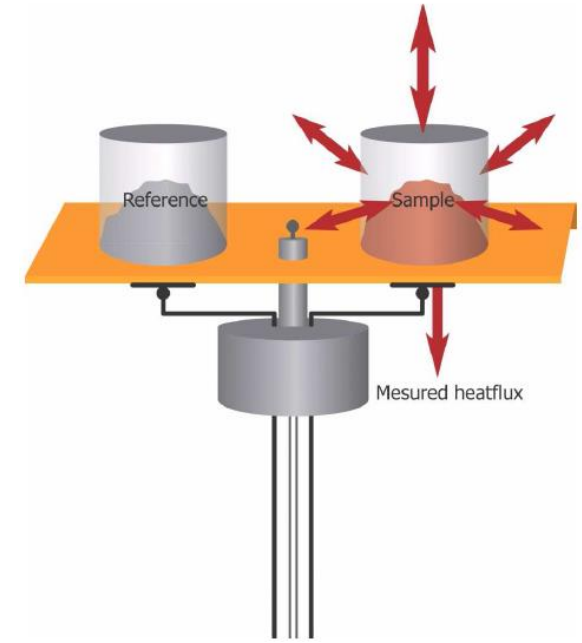
# DSC PRINCIPLE

## ● DSC: Differential Scanning Calorimetry

### ➤ Basic equation

$$\frac{dq}{dt} = \frac{dh}{dt} + (C_e - C_r) \frac{dT_p}{dt} - RC_e \frac{d^2q}{dt^2}$$

### ➤ A simple calibration point allows quantitative use of thermograms over the entire temperature range



### Hypotheses

- ✓ Sample  $T_e$ ,  $C_e$
- ✓ Reference  $T_r$ ,  $C_r$
- ✓ Heat production  $dh/dt$  discharged through the thermostatic temperature block  $T_p$  at a rate  $dq/dt$
- ✓  $T_e$  uniform
- ✓  $C_e$  et  $C_r$  independent from  $T$
- ✓ Same thermal resistance  $R$  for both cells



# DSC PRINCIPLE

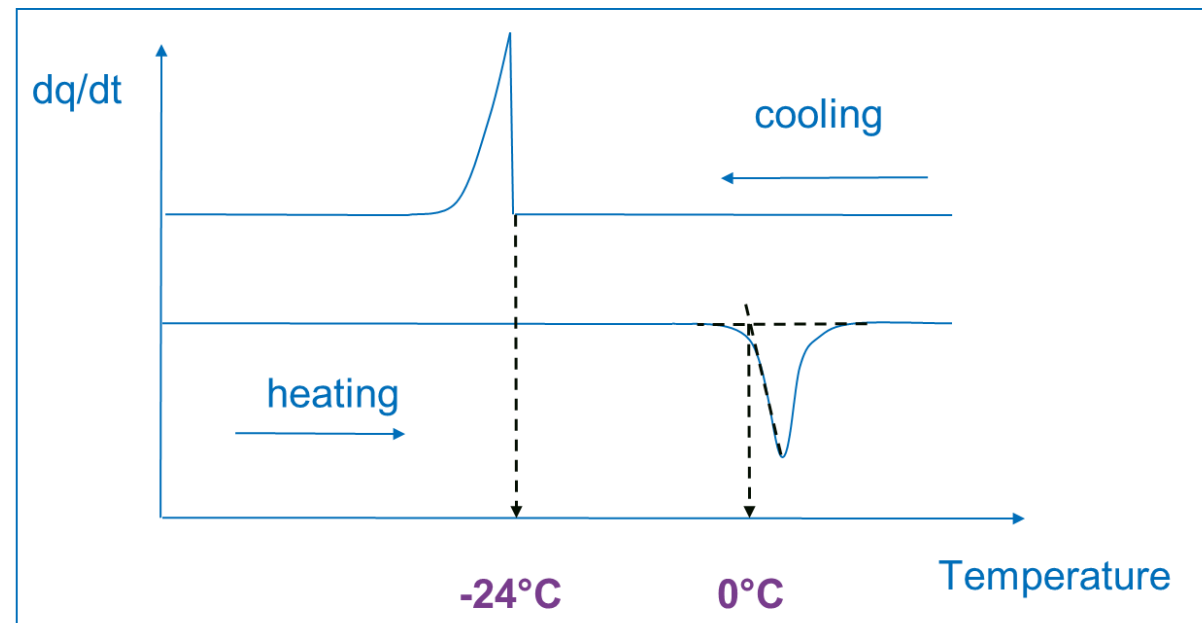
## ● DSC: Exploitation of thermograms

### ➤ Baseline

- $dh/dt = 0$  depends on the evolution of the capacity of the cell containing the sample

### ➤ Area of a signal: direct measurement of the total heat involved: calibration by studying the melting of a pure body

### ➤ temperatures: unlike DTA, no direct identification (calibration by determining the temperatures corresponding to the start of a thermal phenomenon: melting temperature of pure substances)



# ADVANTAGES OF MICROCALORIMETRY (DSC)

## ● Interest of DSC microcalorimetry

- Ease of handling
- Very small samples
- Wide range of thermal phenomena
- Different fields of application
- Thermodynamics
- Kinetics
- Analytics

## ● DSC microcalorimetry can be used to determine

- the nature of the emulsions (w/o, o/w, multiple or mixed emulsion)
- the polydispersity, even the particle size of the emulsions
- water (or oil) content
- the composition of aqueous solutions

## THEORETICAL ASPECTS

- The principle of the method is based on the relationship between the most probable crystallization temperature  $T^*$  of a sample and the volume  $V$  of the sample, whatever its nature (mineral, organic or metallic)
- Example for pure water

Volume of pure water	Most probable temperature of crystallization
1 cm <sup>3</sup>	-14°C
1 mm <sup>3</sup>	-24°C
1 μm <sup>3</sup>	-39°C

## THEORETICAL ASPECTS

- Consider the case of a sample of pure water
  - Regardless of sample size, ice melts at 0°C (except for submicron-sized droplets, for which capillary effects must be taken into account)
  - In contrast, freezing occurs at a temperature that depends on the size of the sample
- Crystallization is a complex process that requires three consecutive steps:
  - Supercooling (cooling below equilibrium temperature)
  - Nucleation (formation of a seed or nucleus of critical size)
  - crystal growth
- During constant rate cooling of a population of droplets, a distribution of crystallization temperatures is observed
  - Only a **most probable crystallization temperature  $T^*$**  can be determined experimentally
  - $T^*$  depends on sample volume
  - From the theory of homogeneous nucleation, it is shown that the smaller the volume, the lower the freezing temperature

# THEORETICAL ASPECTS

The radius of the crystallization seed  $R^*$  is a function of  $T$ :

$$\ln \left( \frac{T}{T_f} \right) = - \frac{2 \cdot \gamma_{ls} \cdot V_i}{R^* \cdot L_f}$$

$\gamma_{ls}$  : surface tension  
 $L_f$  : latent heat of fusion of ice  
 $V_i$  : molar volume of ice

Rate of nucleation  $J$ :

$$J = A \cdot \exp \left( - \frac{\Delta\Phi}{k \cdot T} \right) \quad \text{avec} \quad \Delta\Phi = \frac{4}{3} \cdot \pi \cdot \gamma_{ls} \cdot R^{*2}$$

$\Delta\Phi$  : formation energy of the germ

Probability  $P(V,T)$  of solidification of a droplet between  $T$  and  $T_f$  :

$$\ln [1 - P(V,T)] = \frac{V}{\dot{T}} \int_{T_f}^T J(T) dT \quad \text{avec} \quad \dot{T} = - \frac{dT}{dt}$$

# THEORETICAL ASPECTS

Most probable crystallization temperature obtained for  $P(V,T) = 0.5$  :

$$-\frac{V}{T} \int_{T_f}^T J \cdot dT = \ln(0,5)$$

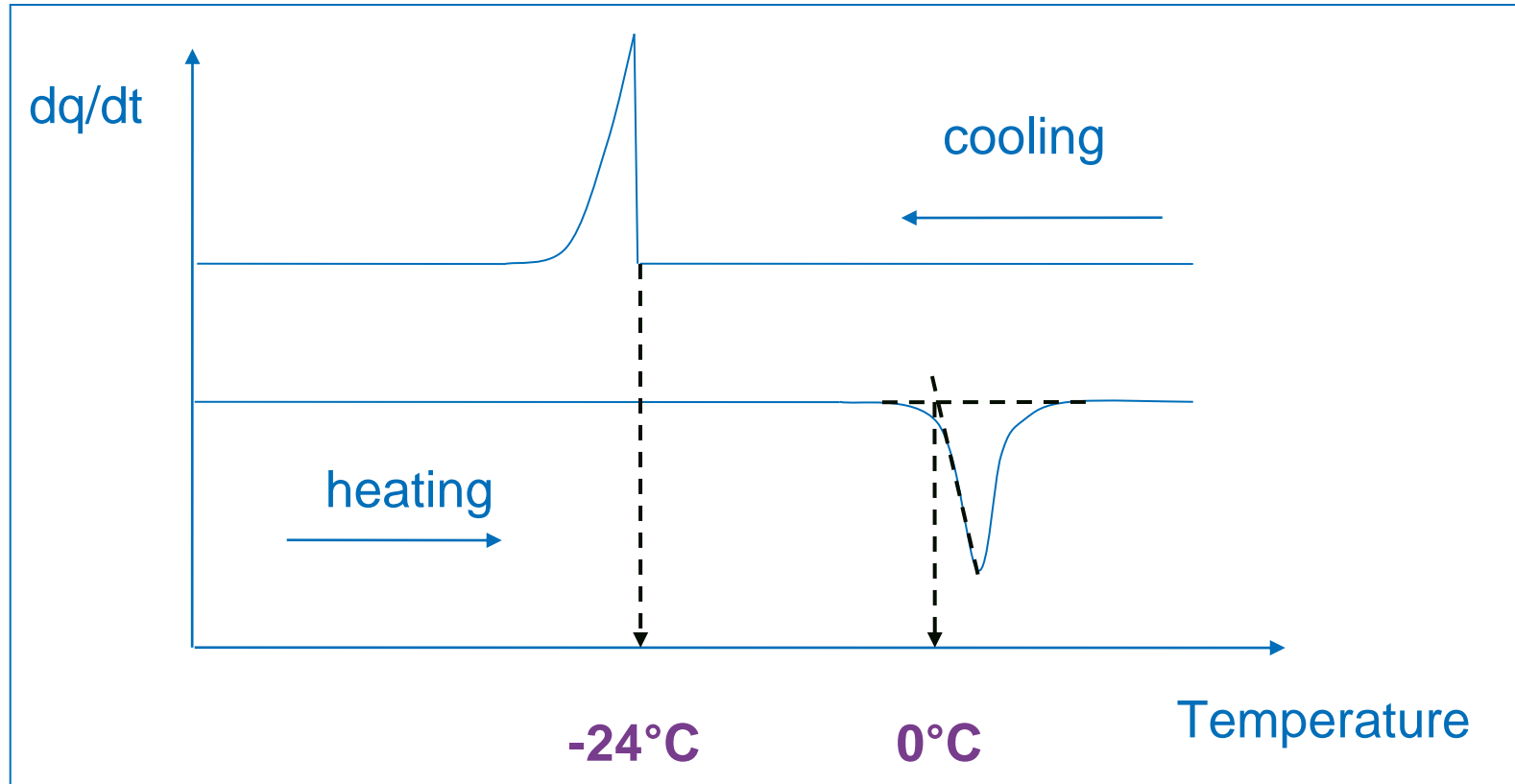


$$R^3 = -\frac{3 \cdot \dot{T}}{4 \cdot \pi} \cdot \frac{\ln(0,5)}{\int_{T_f}^T J \cdot dT}$$

**R : radius of the droplet**

$$J = A \cdot \exp \left\{ -\frac{16 \cdot \pi}{3} \cdot \frac{\gamma_{ls}^3 \cdot V_i^2}{k \cdot L_f^2} \cdot \frac{1}{T \cdot \left( \ln \frac{T}{T_f} \right)^2} \right\}$$

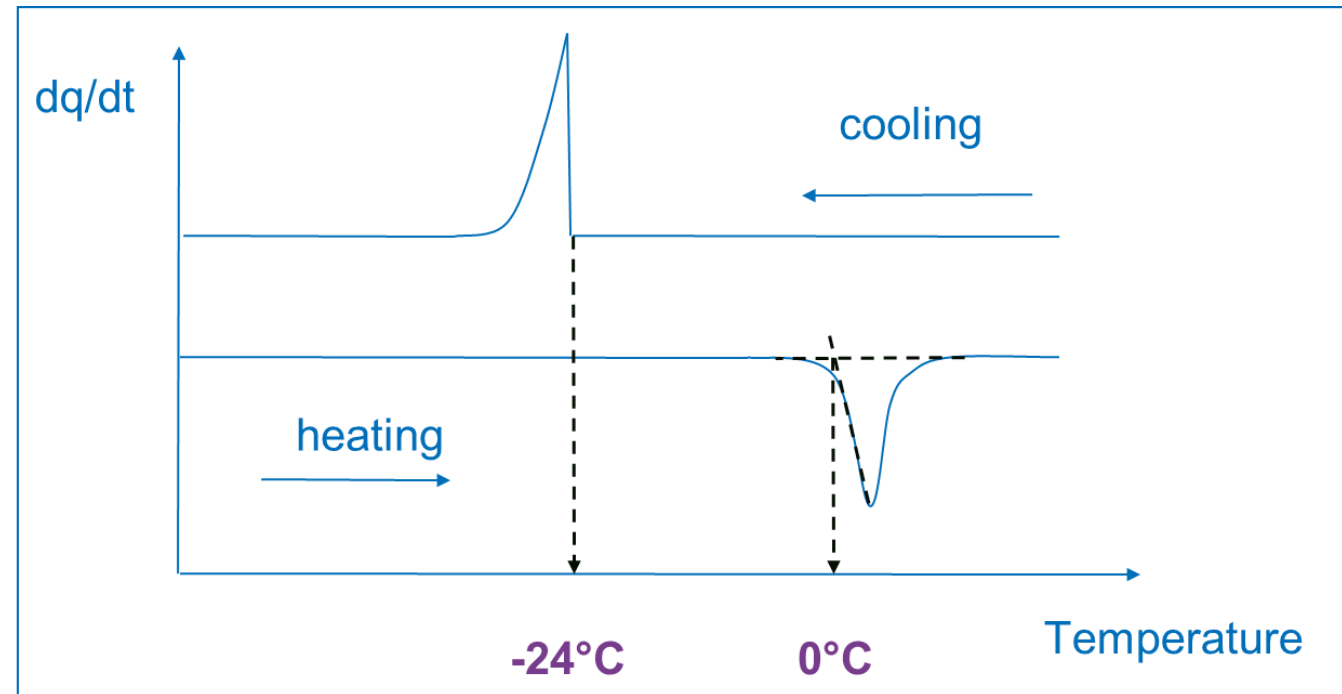
# TYPICAL THERMOGRAMS / PURE WATER



**Sample of pure water**

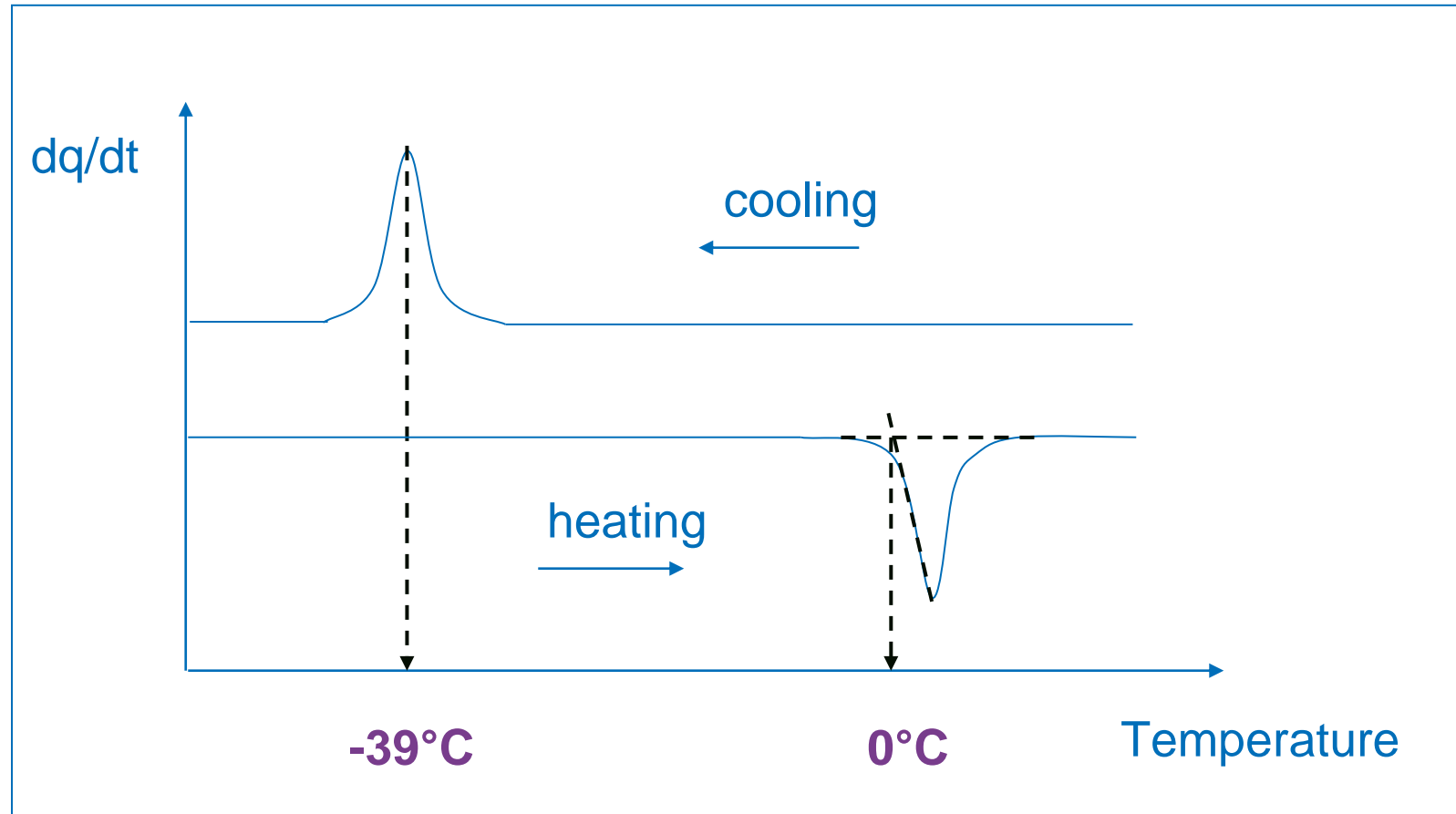
## TYPICAL THERMOGRAMS / PURE WATER

- The figure represents a typical thermogram obtained during the freezing of a sample of water of a **few milligrams**.
- If we consider that the formation of a single seed of ice is sufficient to initiate freezing, **the crystallization process is very rapid**.
- Consequently, a significant amount of energy is released in a very short time: this is why the first part of the exothermic freezing peak is so abrupt.
- It should be noted that the freezing temperature may vary from one sample to another around the value of  $-24^{\circ}\text{C}$  (most probable freezing temperature for this volume).
- On the other hand, melting is always observed at  $0^{\circ}\text{C}$ , regardless of the pure water sample.





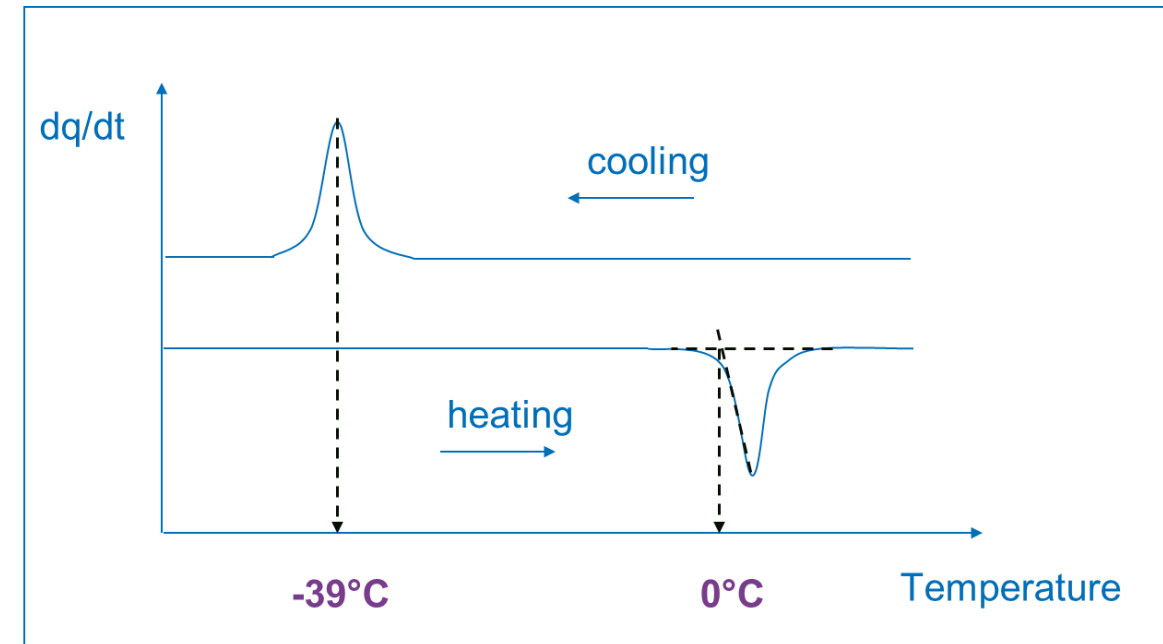
# TYPICAL THERMOGRAMS / PURE WATER



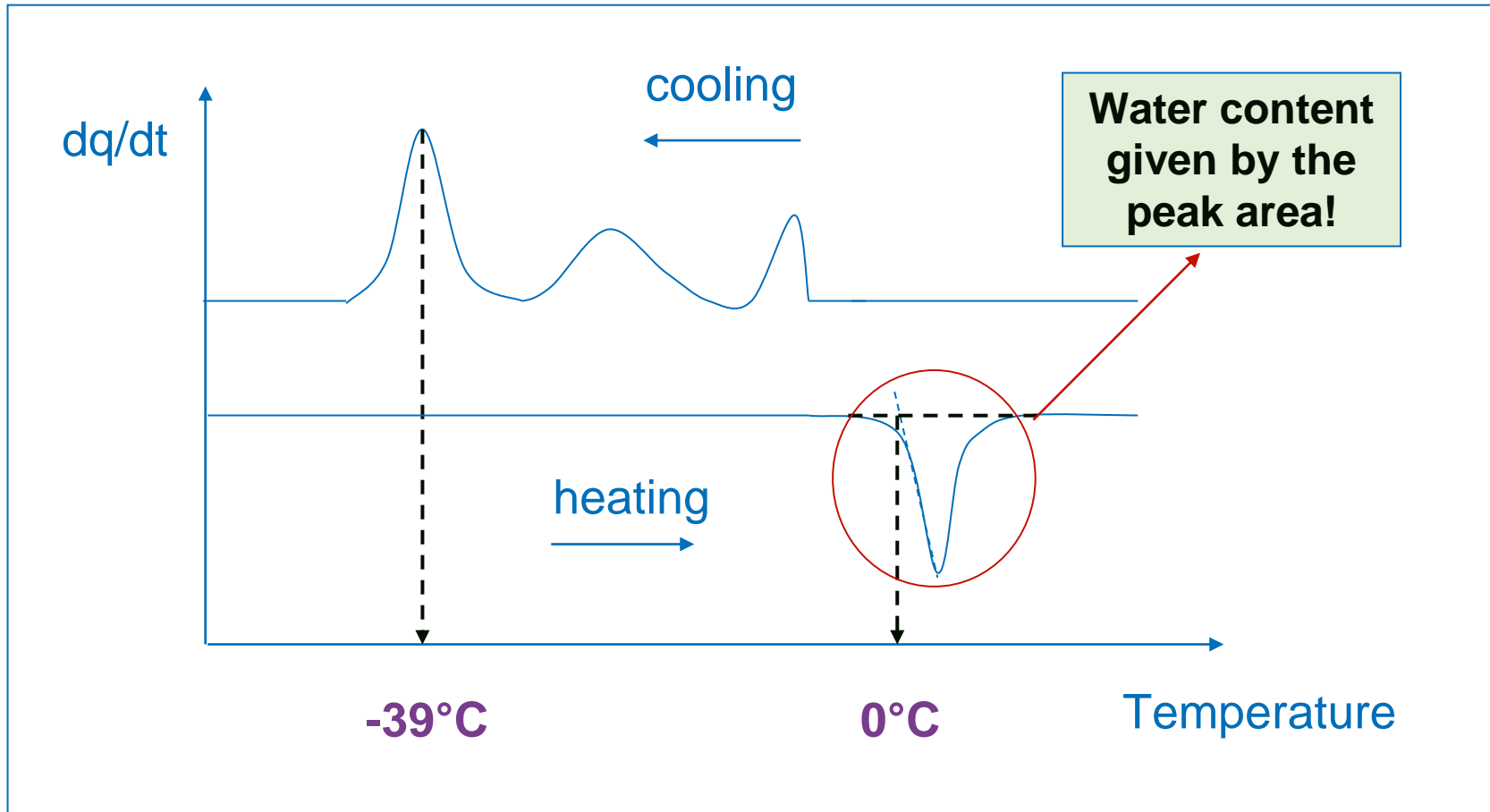
**Monodisperse W/O emulsion ( $1\ \mu\text{m}^3$ )**

## TYPICAL THERMOGRAMS / PURE WATER

- The figure represents a typical thermogram obtained during the freezing of a sample of water in emulsion (diameter of the drops around 1  $\mu\text{m}$ ).
- The number of droplets dispersed in the emulsion sample of a few milligrams is very high and sufficient to allow **a statistical treatment of the freezing temperatures** of all the droplets.
- The energy released during the freezing of the water droplets is represented on the thermogram by a bell-shaped exothermic peak.
- The peak apex temperature can be correlated with the average droplet size.
- On the other hand, since there is no delay observed during the melting, all the droplets melt at the same temperature ( $0^\circ\text{C}$ ), which is the thermodynamic equilibrium temperature between ice and water.

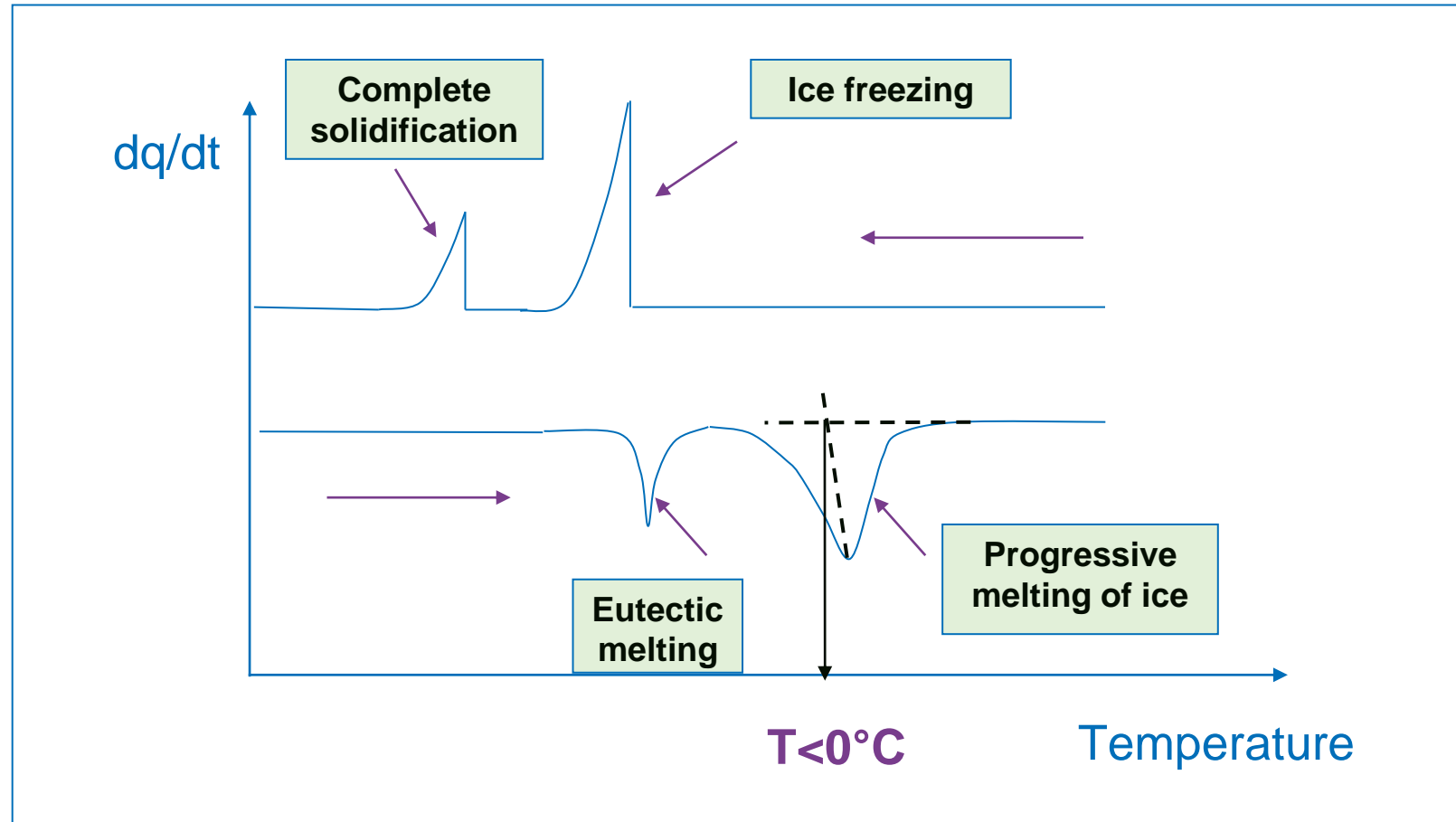


# TYPICAL THERMOGRAMS / PURE WATER



**Polydisperse W/O emulsion**

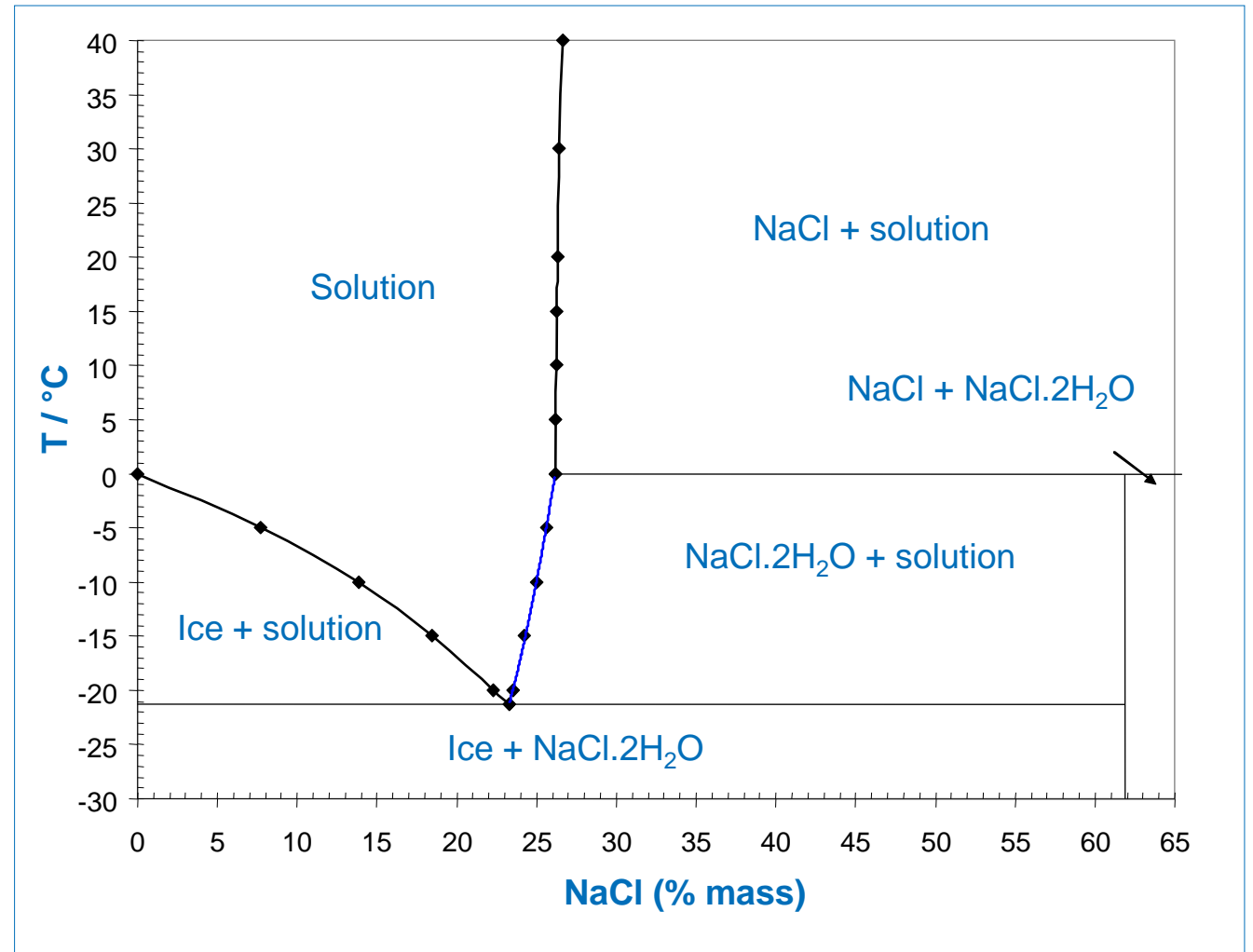
# TYPICAL THERMOGRAMS / AQUEOUS SOLUTION



**Salty water**

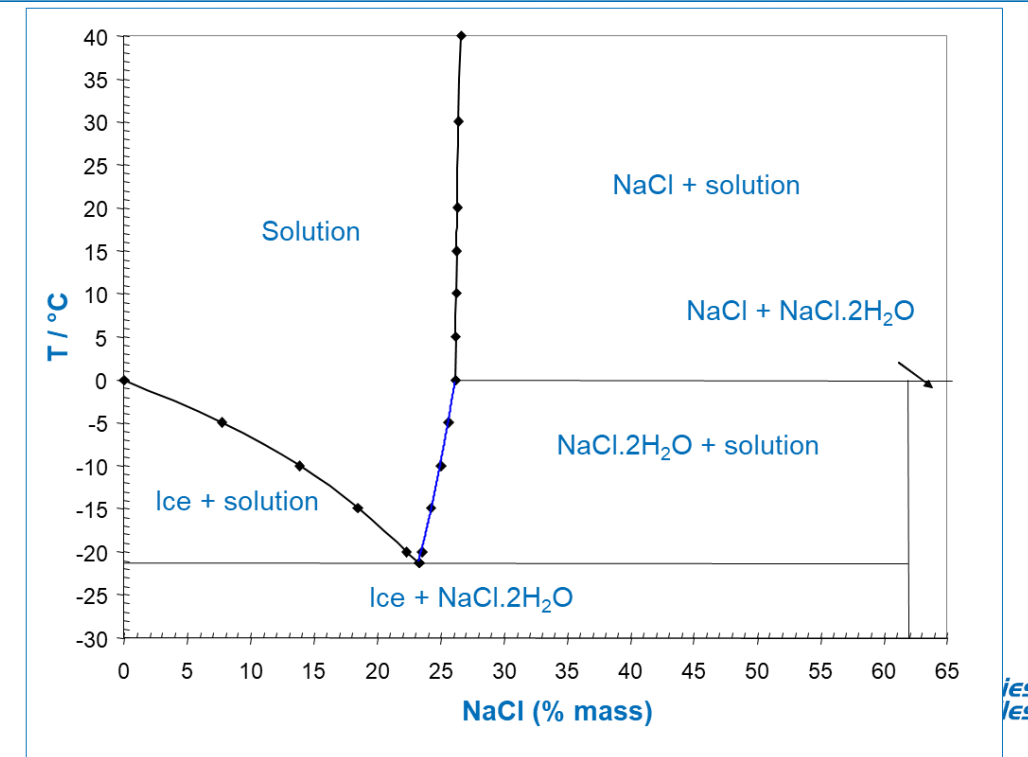
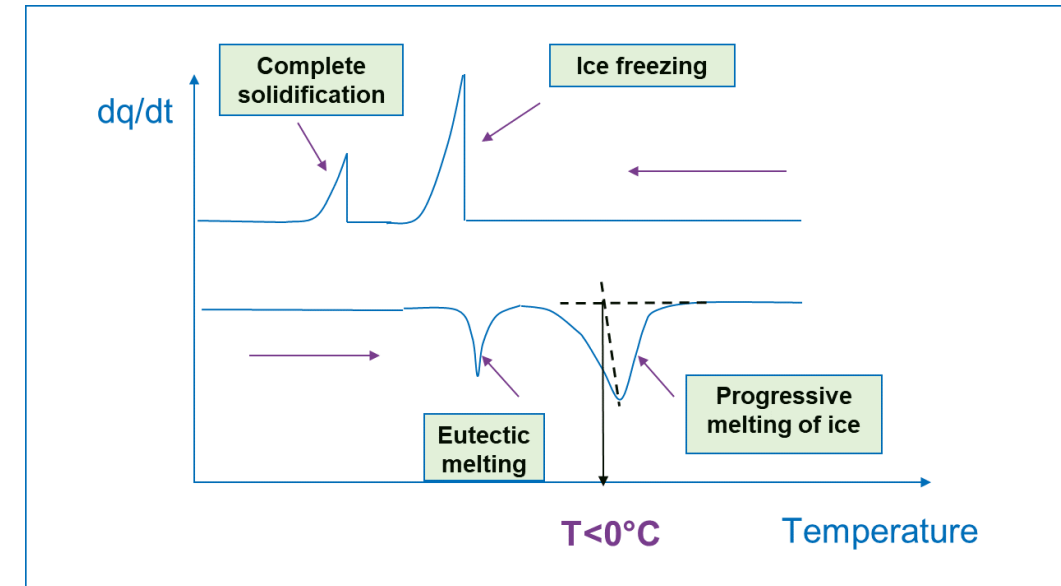
# TYPICAL THERMOGRAMS / AQUEOUS SOLUTION

- The presence of a solute in the water complicates the interpretation of thermograms
- The use of the solid-liquid phase diagram of the water-solute binary system is necessary for the interpretation (example water+NaCl)
- The presence of a solute like NaCl changes the freezing and melting temperatures of ice

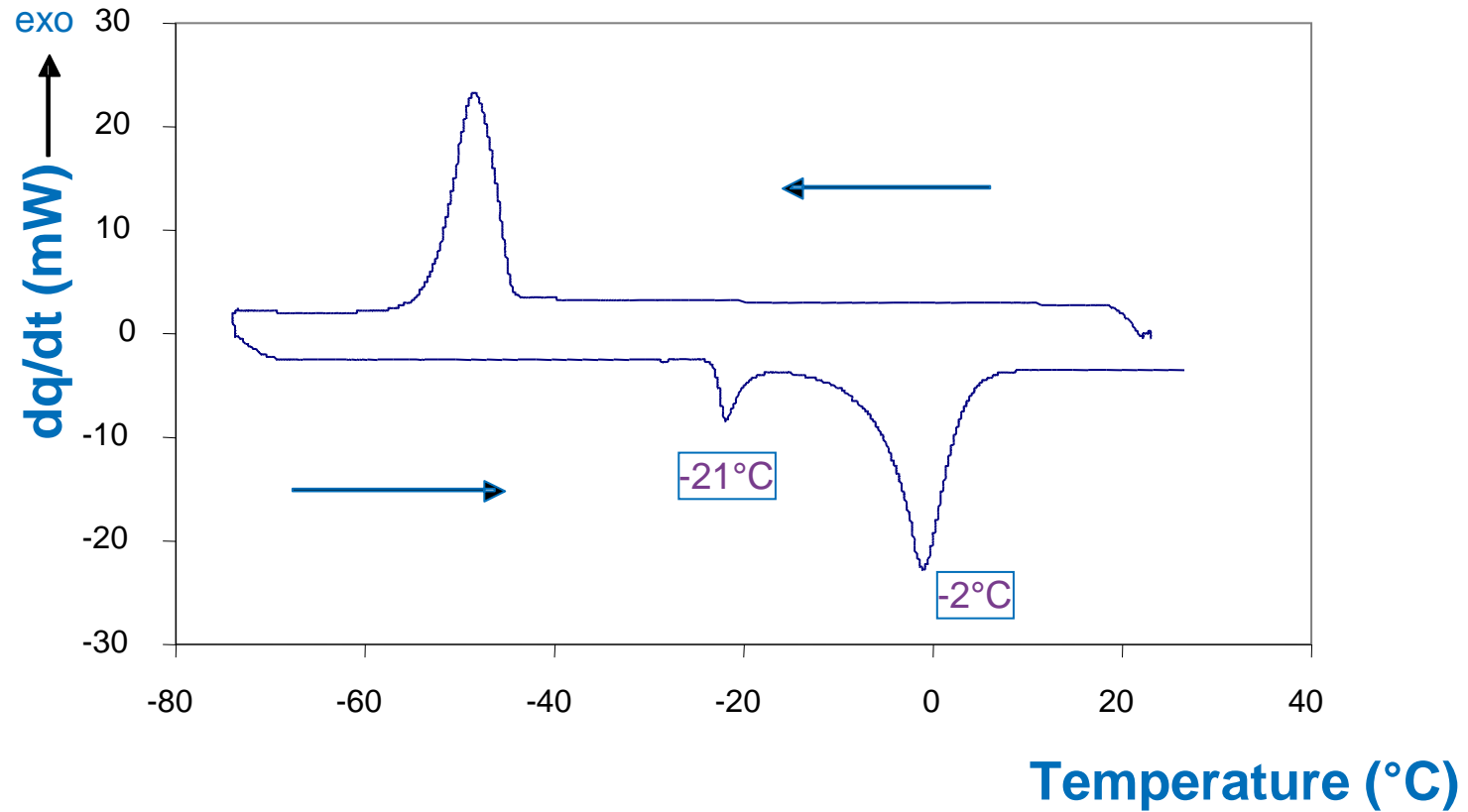


# TYPICAL THERMOGRAMS / AQUEOUS SOLUTION

- During cooling, a first ice freezing peak is observed at a temperature lower than that obtained for pure water (solute effect).
- If the solute concentration is not too high, this peak is generally followed by a second peak which corresponds to the complete solidification of the remaining solution. In the case of high concentrations, a single peak is obtained, corresponding to the total solidification of the system.
- During heating, the first endothermic peak corresponds to the eutectic melting of the binary system ( $-21^{\circ}\text{C}$  for NaCl). This peak is immediately followed by a broad endothermic peak due to the gradual melting of the ice.
- The peak apex temperature, corrected by projecting the peak apex onto the baseline in a direction parallel to that of the linear portion of the eutectic melting peak, gives the equilibrium temperature.
- The value of this equilibrium temperature can be used to determine the concentration of the solution using the phase diagram.

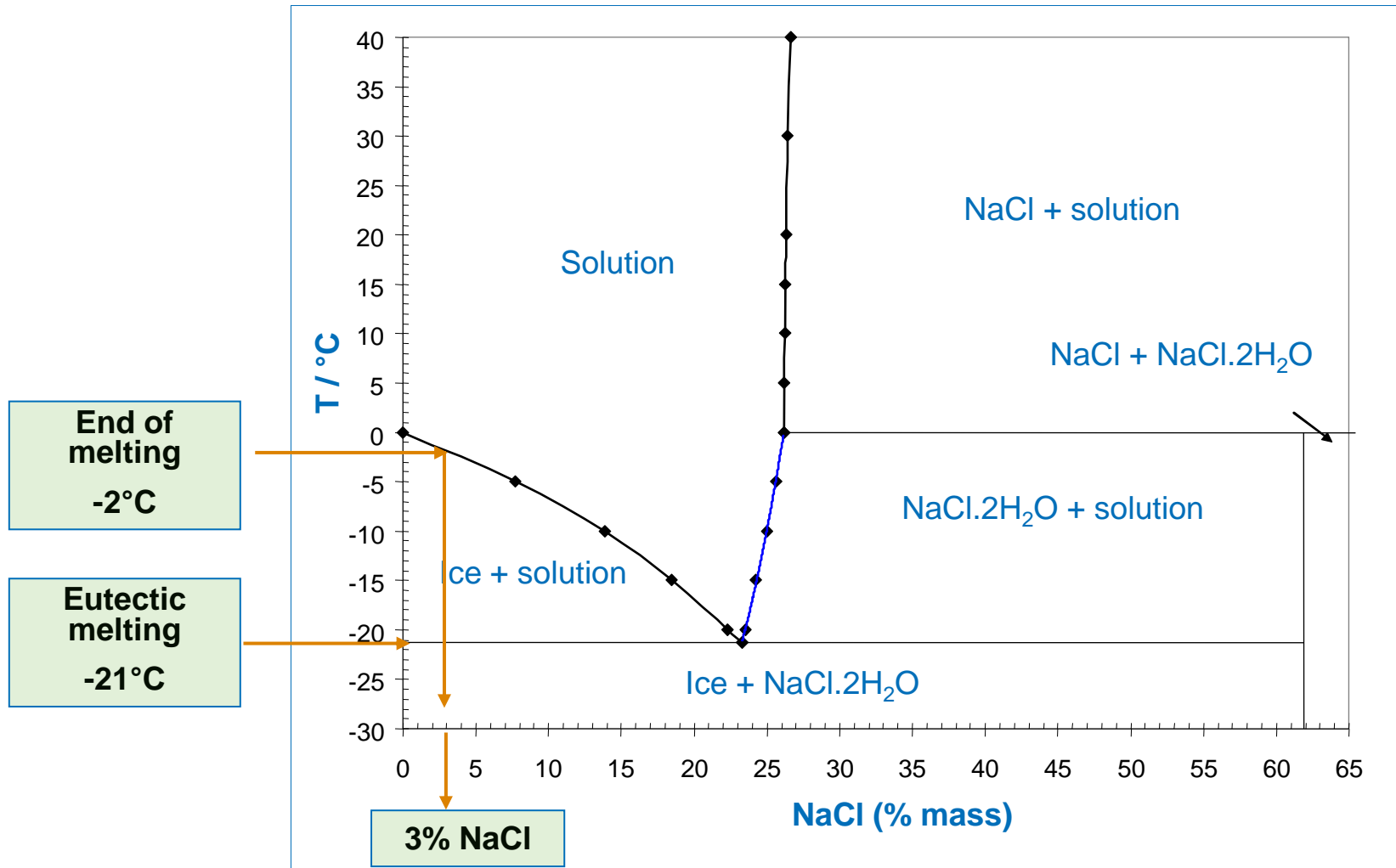


# TYPICAL THERMOGRAMS / AQUEOUS SOLUTION



**W/O emulsion - 30 g/l NaCl**

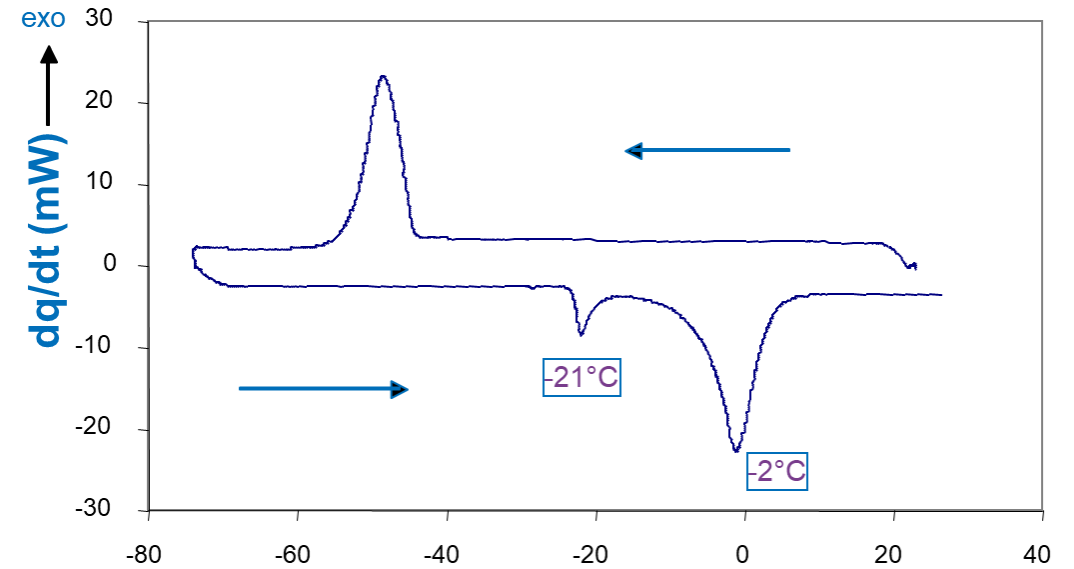
# TYPICAL THERMOGRAMS / AQUEOUS SOLUTION



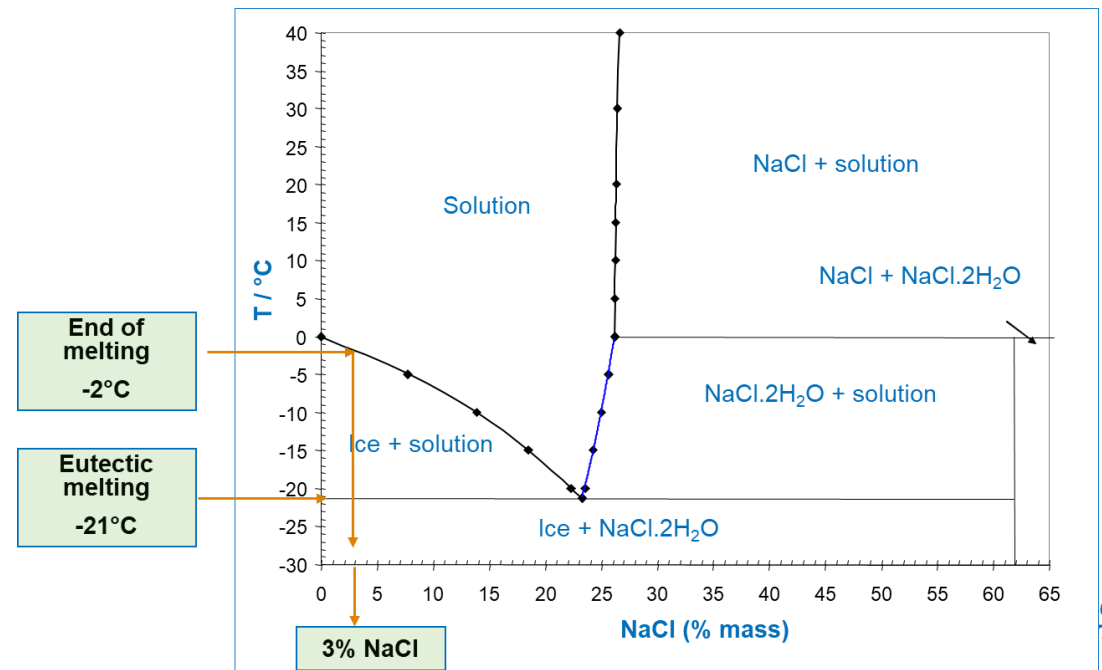


# TYPICAL THERMOGRAMS / AQUEOUS SOLUTION

- In the case of a fine emulsion of salt water in oil, a single exothermic peak is generally observed during the cooling, corresponding to the freezing of the ice.
  - the shape of this peak is similar to that of a pure water emulsion in monodisperse oil, except that the temperature of the top of the peak is shifted towards low temperatures (effect of the solute:  $-45^{\circ}\text{C}$  instead of  $-39^{\circ}\text{C}$  for a 30 g/l NaCl solution).
- We do not observe a second peak corresponding to total solidification, whereas during heating, we find the peak of eutectic melting at  $-21^{\circ}\text{C}$  and the peak of progressive melting of the ice which ends at  $-2^{\circ}\text{C}$ . Several explanations are possible:
  - ice freezing and salt precipitation are simultaneous (unlikely here as salinity is low)
  - the precipitation of the salt takes place during the isothermal phase which precedes the heating
  - the second peak is undetectable because of the low energies involved
  - Note that in some cases, salt precipitation is prevented by the high viscosity of the supersaturated solution during cooling, but is observed as an exothermic peak during heating!!!



Temperature ( $^{\circ}\text{C}$ )

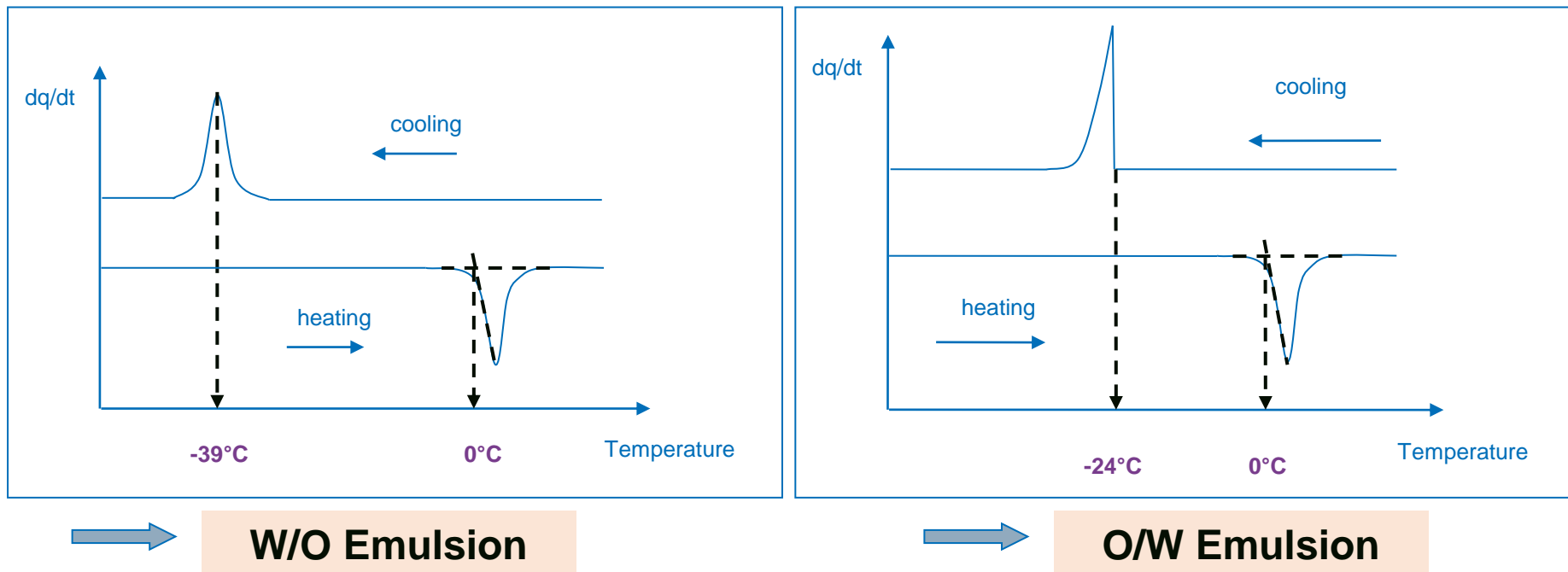


## INFORMATION FROM DSC

- Interpretation of thermograms obtained with emulsions (cooling-heating cycle)
  - ✓ Separate analysis of the different phases (aqueous and oily phase for example): reference thermograms
  - ✓ Use of the standard thermograms seen previously
- Information derived from DSC analyzes
  - Type of emulsion
  - Amount of water (or oil)
  - Presence of a solute
  - Stability
  - Droplet size

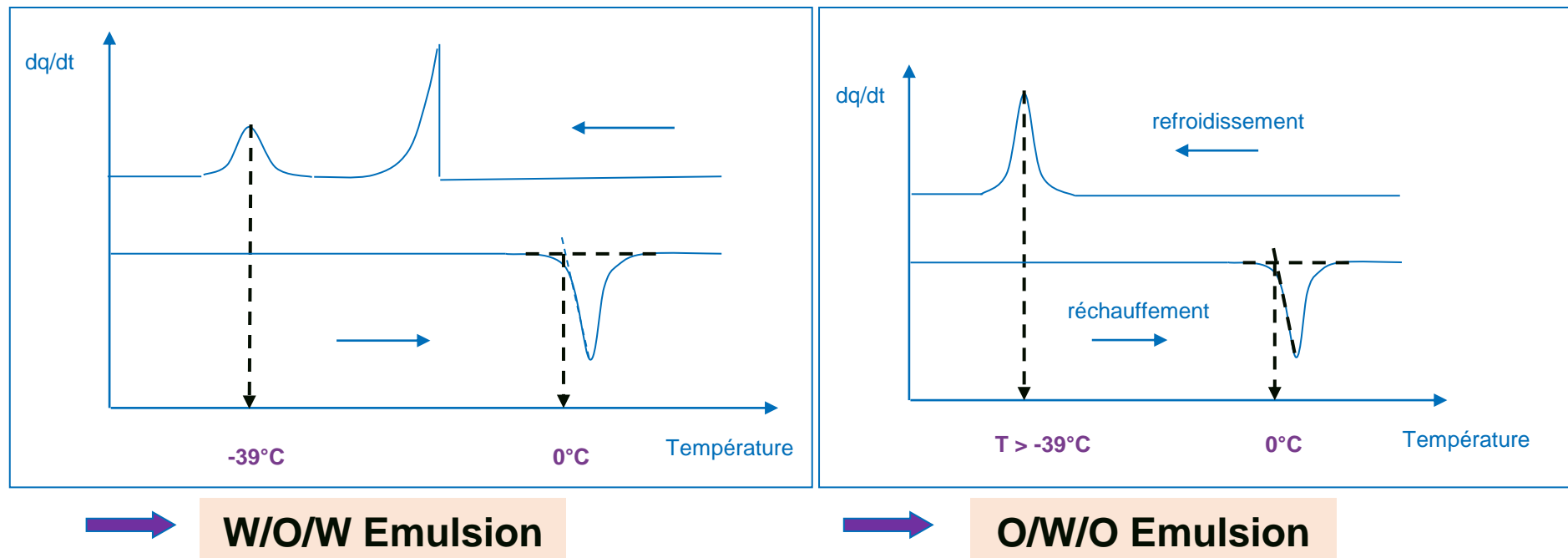
## TYPE OF EMULSION / SIMPLE

- Consider an emulsion of undetermined nature for which a DSC analysis (cooling-heating cycle) is carried out
  - The separate analysis of each phase will make it possible to identify the peaks relating to the aqueous and oily phases
  - In a second step, we will compare the peaks relating to the aqueous phase to the standard thermograms previously presented



## TYPE OF EMULSION / MULTIPLE

- We can also identify a multiple emulsion w/o/w or o/w/o
- If we consider the case of an emulsion identified as multiple by optical microscopy, we will obtain the thermograms below depending on whether it is w/o/w or o/w/o (case of pure water and without the peaks corresponding to the oil):

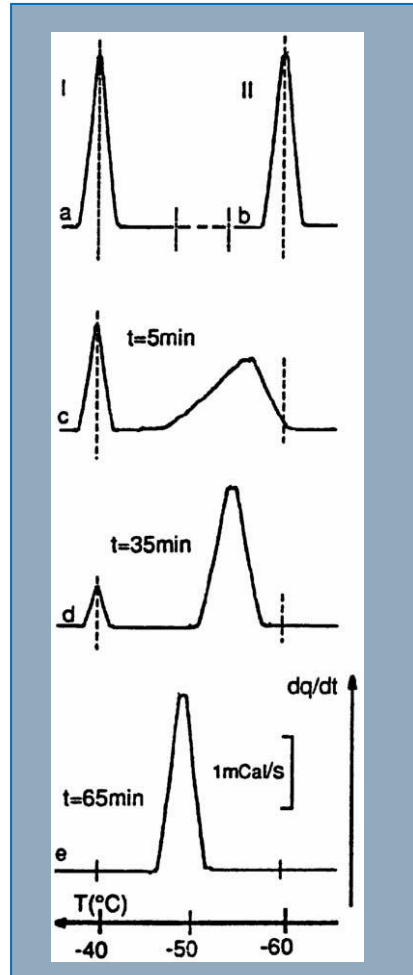


## TYPE OF EMULSION / MIXED

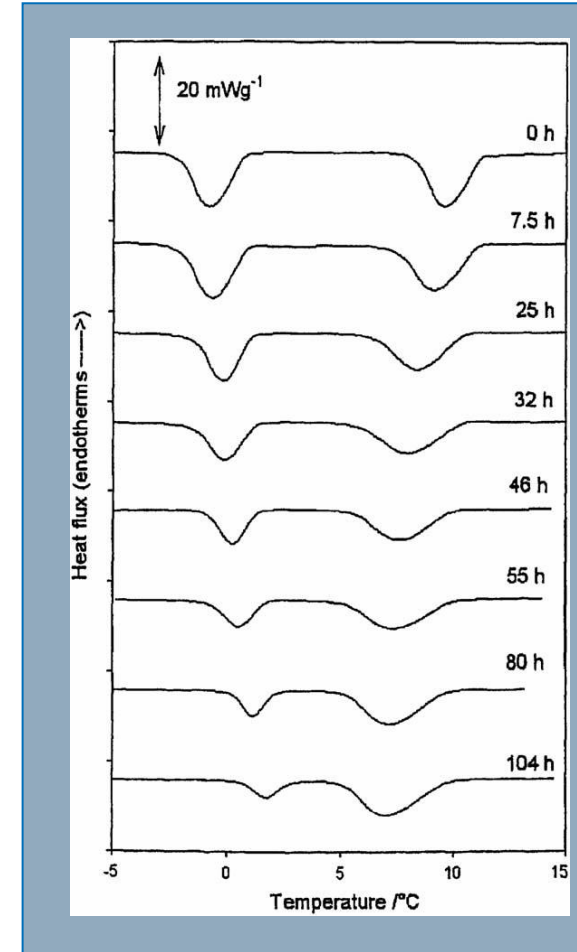
- The last type of emulsion that can be analyzed by DSC is the **mixed emulsion**
- This type of emulsion results from the mixing of two simple emulsions whose composition of the dispersed phase is different
- Generally, we will observe a mass transfer between the droplets linked to the difference in composition (composition ripening)
- The thermogram obtained initially with the mixed emulsion will correspond to the addition of the thermograms obtained for each simple emulsion
- Over time, the thermogram will evolve according to the mass transfer until equilibrium (obtaining a simple emulsion of intermediate composition)
- DSC analysis can therefore make it possible to **follow the kinetics of mass transfer in mixed emulsions**
- This technique applies to both w/o and o/w emulsions (insofar as the oil does not crystallize in the same temperature range as the aqueous phase!)

# TYPE OF EMULSION / MIXED

Clausse D, Pezron I, Gautier A. Fluid Phase Equilib 1995; 110: 137



Evolution with time of the freezing thermogram of a mixed w/o emulsion (pure water / water + urea)



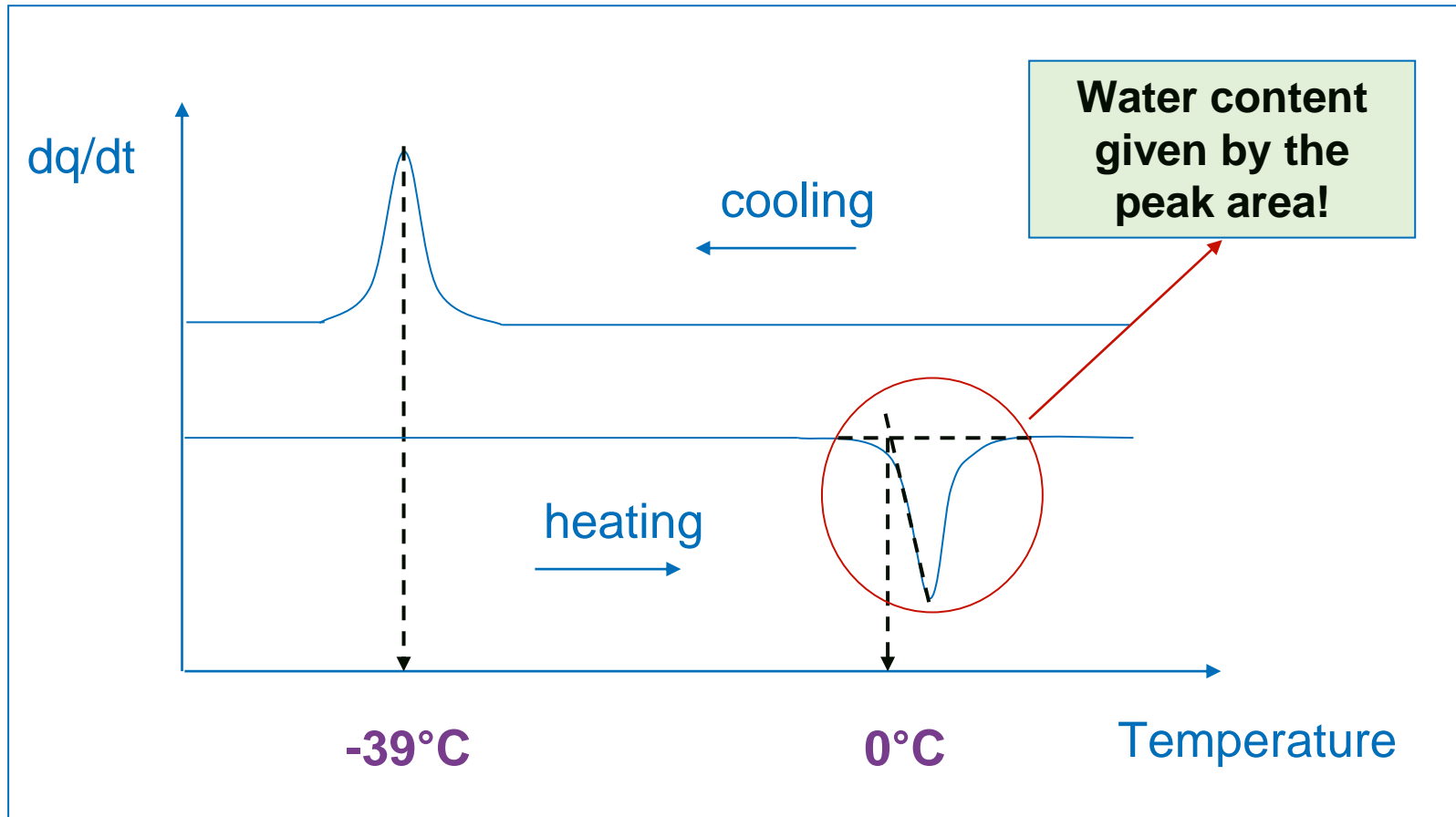
Elwell MW, Robert RF, Coupland JN. Food Hydrocoll 2004; 18(3): 413

Evolution with time of the freezing thermogram of a mixed o/w emulsion (hexadecane / n-octadecane)

## WATER CONTENT

- The amount of energy released or absorbed during a thermal phenomenon can be measured by measuring the area of the corresponding peak by integration.
- In the particular case of water, knowing the value of the latent heat of fusion of water at 0°C (333 kJ/kg) one can easily by a simple rule of 3 determine the water content of an emulsion by integrating the melting peak of the ice.
- **Caution:** the crystallization peak obtained on cooling must not be used. Indeed, the latent heat depends on the temperature. Consequently, if the crystallization takes place at temperatures much lower than 0°C (case of water), a significant error will be made in the water content.
- This method is applicable for any pure substance other than water (oil, metal, organic compound...). For aqueous solutions or complex oily systems in emulsion, it is necessary to determine the fusion energy by carrying out a DSC analysis of the non-emulsified mixture beforehand.

# WATER CONTENT

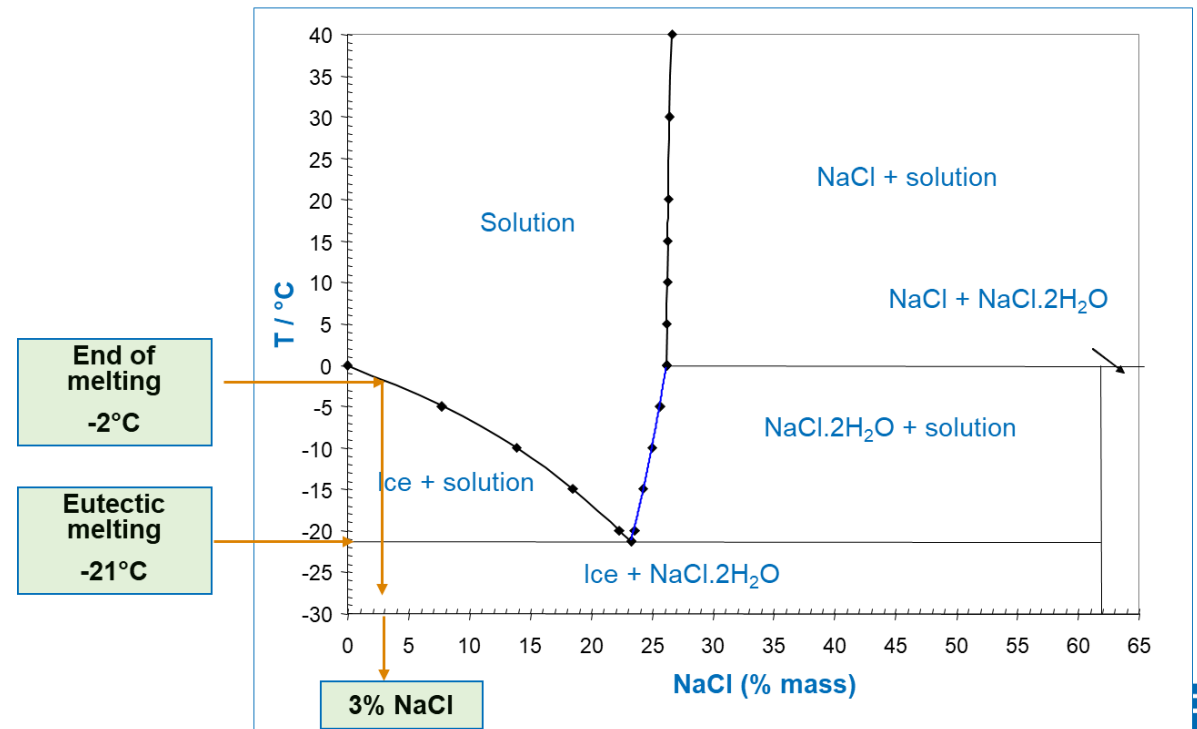
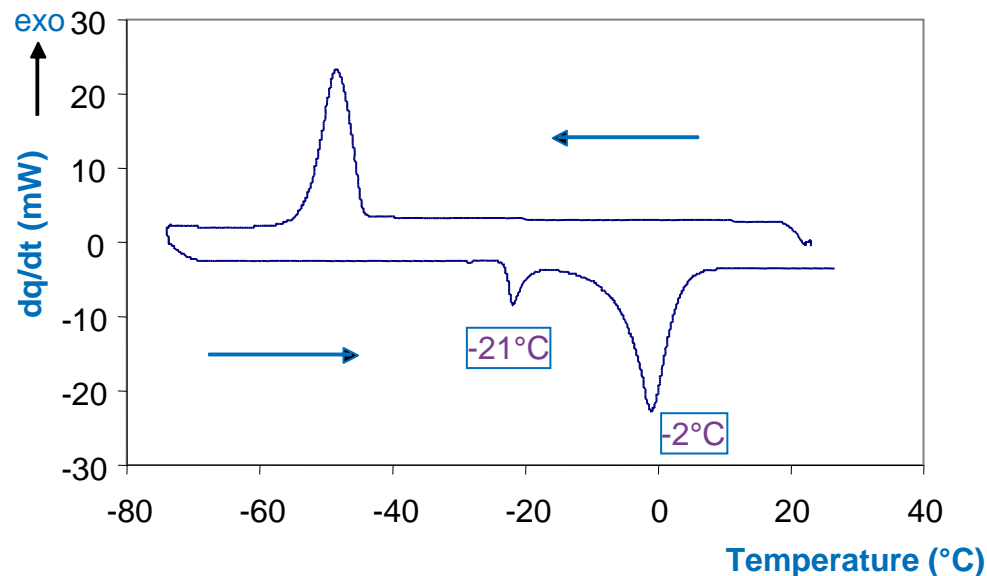


**monodisperse W/O Emulsion ( $1 \mu\text{m}^3$ )**



# EFFECT OF A SOLUTE

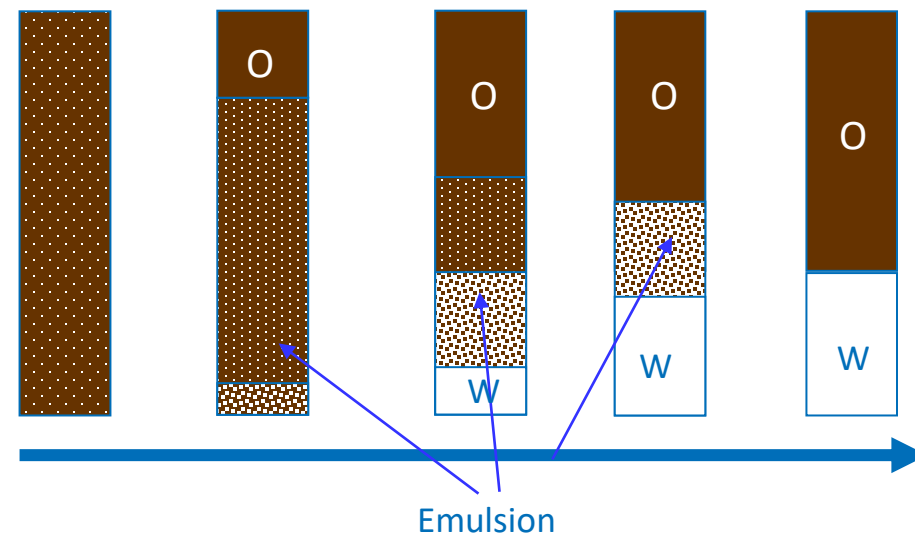
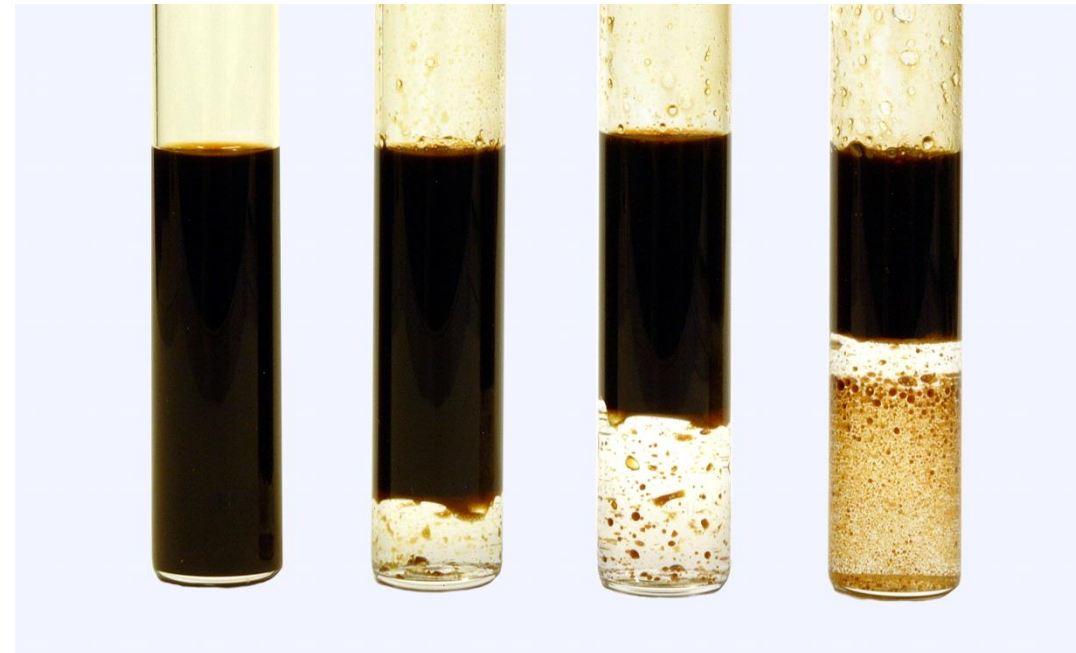
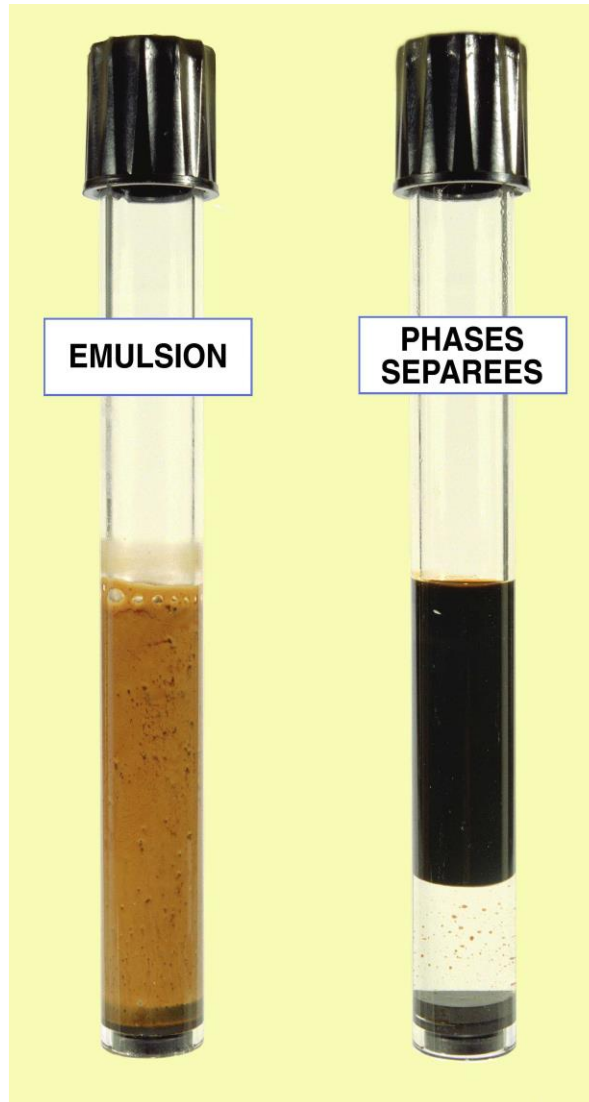
- If a solute is present in the aqueous phase, the melting temperature of the solution will be shifted towards low temperatures ( $< 0^{\circ}\text{C}$ )
- The higher the solute concentration, the lower the melting temperature
- If the "water+solute" binary phase diagram is available, it is possible to determine the concentration of the solute in the aqueous phase

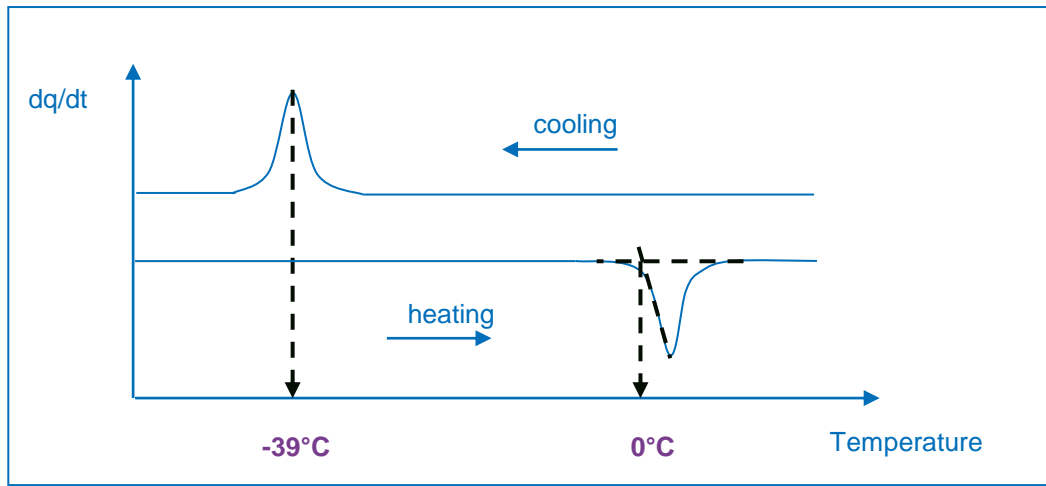


# STABILITY OF EMULSIONS

- DSC analysis of an emulsion gives information on the stability of the system
- For a water-in-oil emulsion for example, the destabilization can be monitored in several ways
  - 1. several samples are prepared from the homogeneous initial emulsion which is left to age in a DSC crucible and the evolution is monitored as a function of time**
    - depending on the destabilization, we will observe thermograms which are between the typical thermogram of a fine and monodisperse emulsion and the typical thermogram corresponding to water in volume (broken emulsion)
  - 2. a sample is taken at different times always at the same place in the bottle (top, middle or bottom)**
    - for a w/o emulsion, the top of the sample will tend to be depleted in water, while the lower part will be enriched in water (sedimentation of water droplets)
    - the water content is monitored by integrating the water melting peak obtained on heating
  - 3. the emulsion sample is subjected to successive cooling-heating cycles**
    - if the emulsion is stable, no modification of the thermograms on cooling

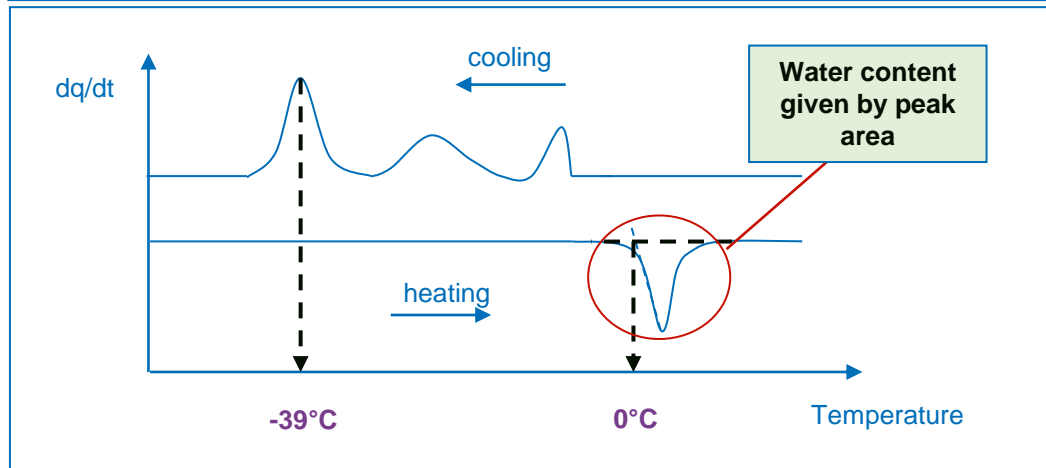
# STABILITY OF EMULSIONS



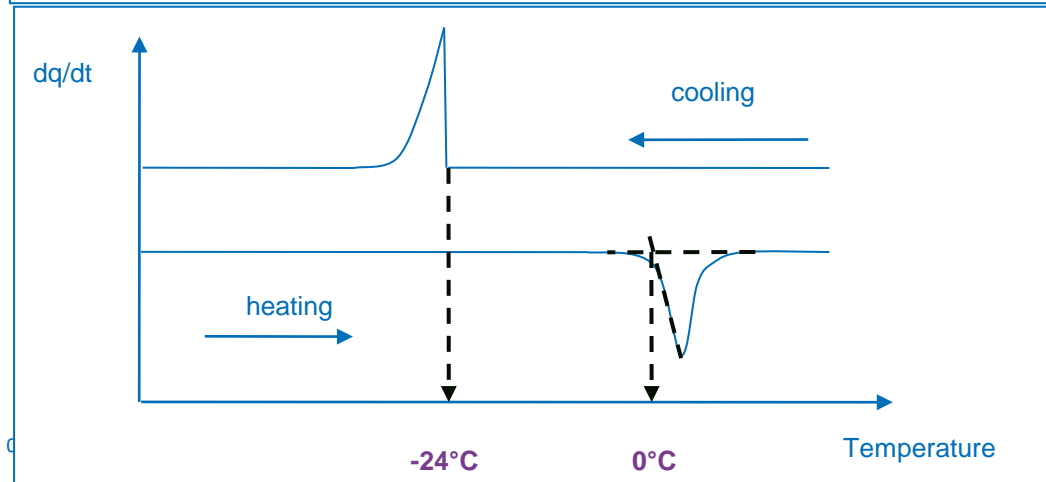


Case of a W/O emulsion

Monodisperse  
W/O Emulsion

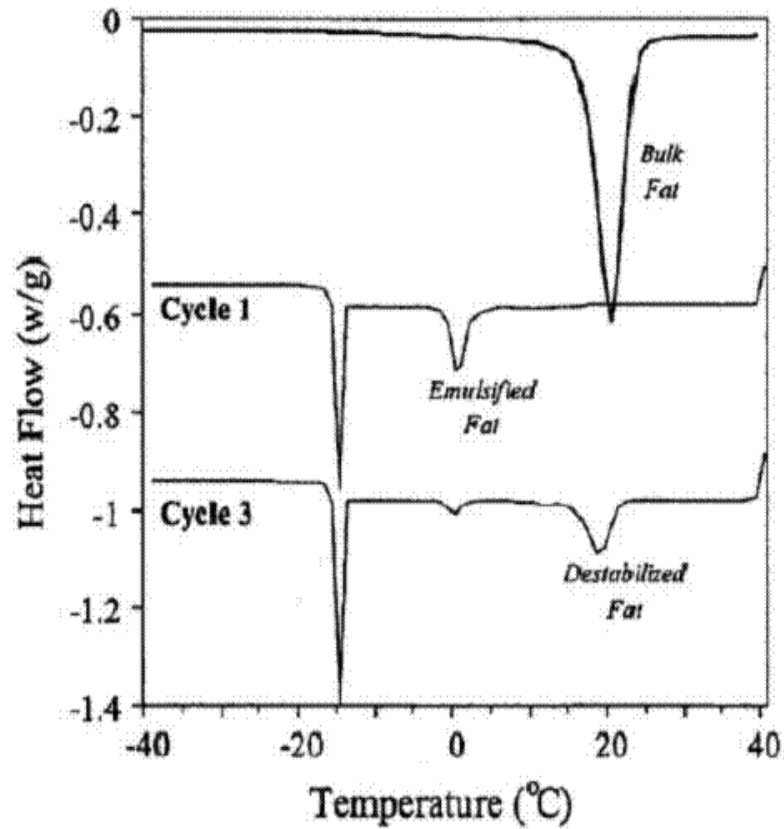


Polydisperse  
W/O Emulsion



Separated  
W/O Emulsion

# STABILITY OF EMULSIONS



Case of an O/W Emulsion

Thanasukarn P et al., 2004,  
Colloids Surf, A Physicochem Eng  
Asp, 246, 49.

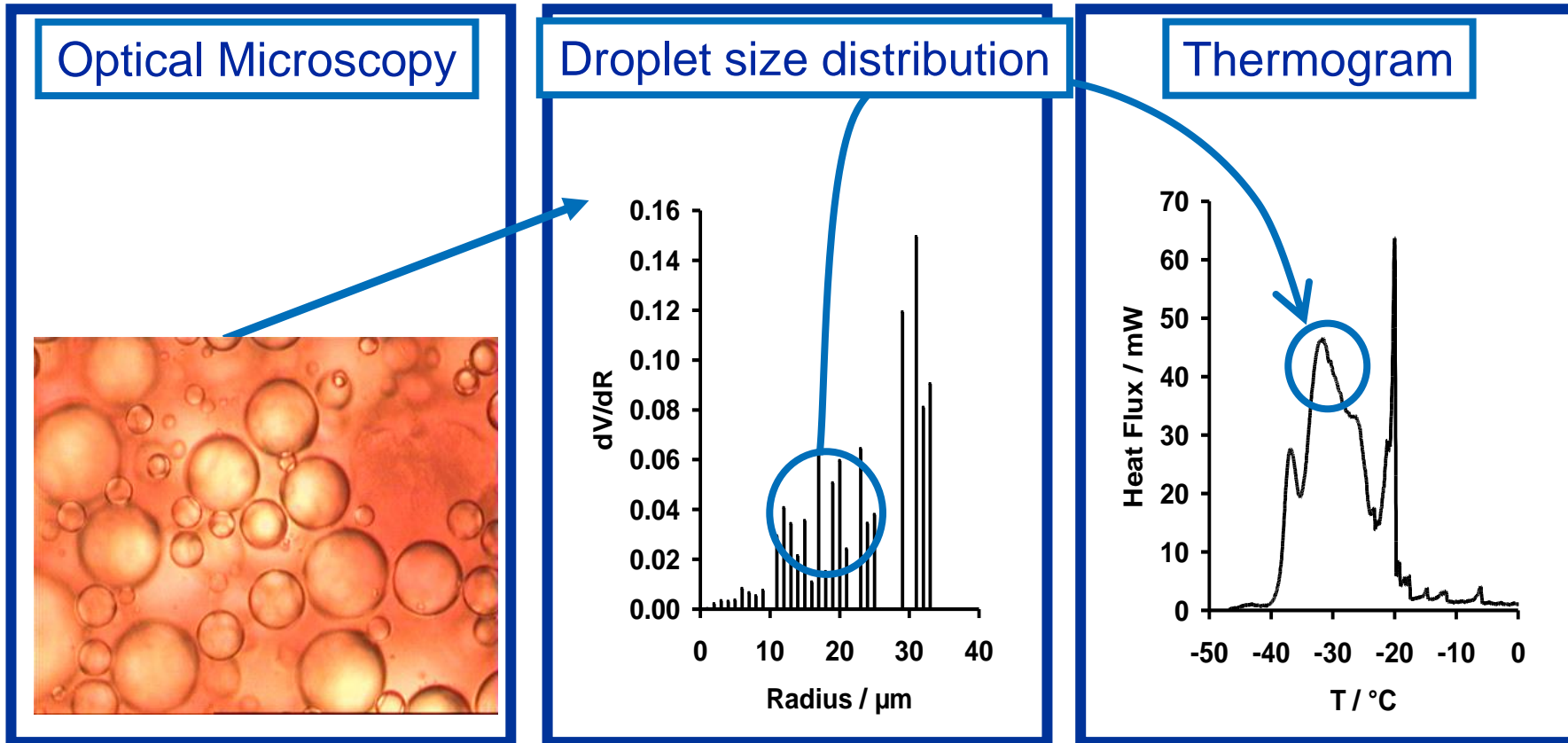
# DROPLET SIZE

- Microcalorimetry makes it possible to obtain qualitative information on the particle size of emulsions by a direct comparison of thermograms
  - one can differentiate a dispersed phase from the same bulk phase
  - the degree of polydispersity of an emulsion can be characterized
- It is also possible to obtain quantitative information on the particle size of the emulsions from the exploitation of the thermograms obtained on cooling.
  - we can use the equation that exists between the crystallization temperature and the size of the droplet (case of homogeneous nucleation)

$$R^3 = 0.69 \frac{3\dot{T}}{4\pi \int_{T_f}^T A \cdot \exp\left[-\frac{16\pi\gamma^3 V_s}{3L_f^2 \ln^2(T/T_f)} \frac{1}{kT}\right] dT}$$

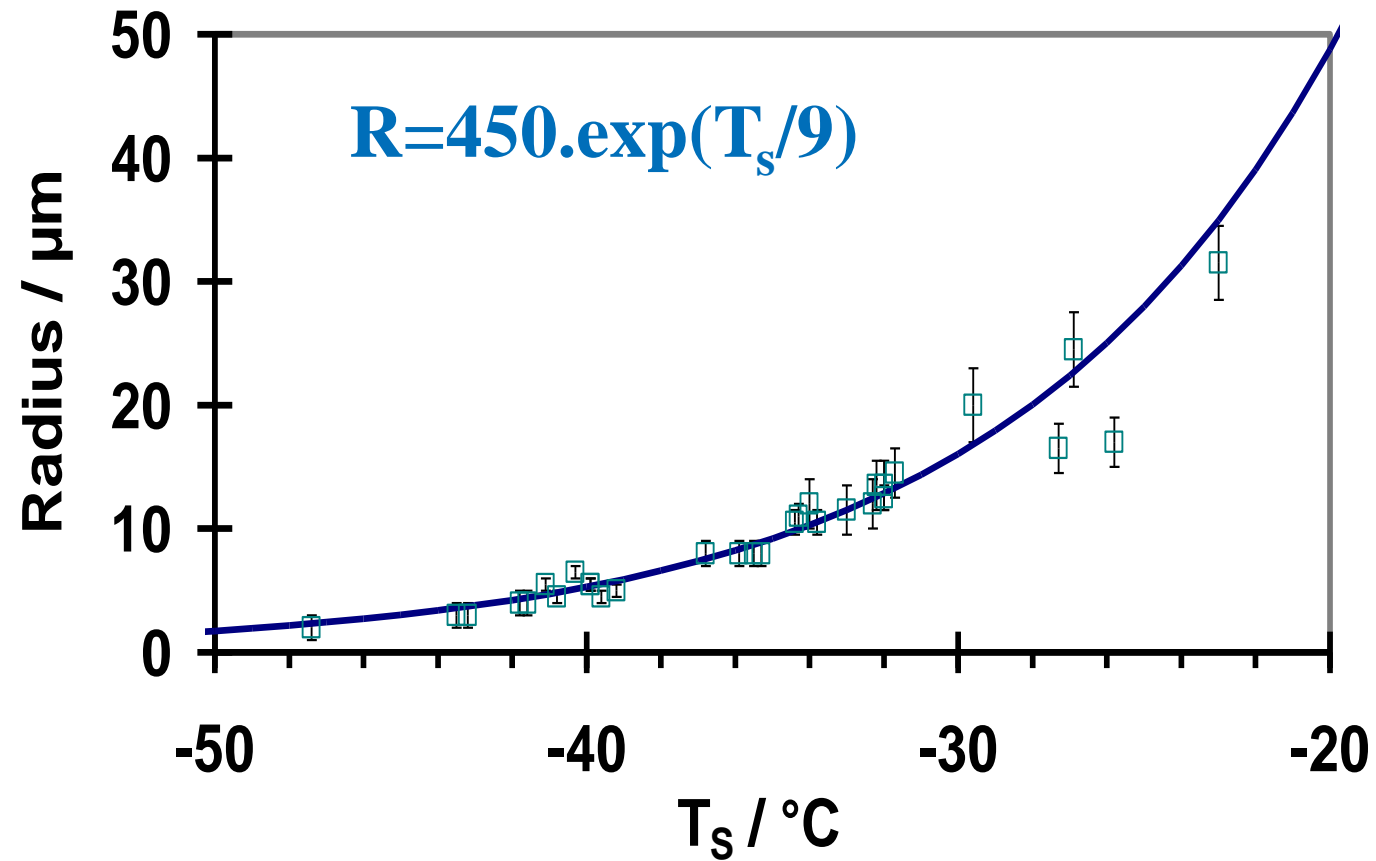
- **but since  $\gamma$  cannot be determined from an experimental point of view**, it is preferable to determine the empirical correlation between R and T by comparing the most probable temperature of crystallization obtained by DSC and that obtained by another technique (optical microscopy for example!)

# DROPLET SIZE



Clausse D et al. 2005; Journal of Colloid and Interface Science, 287, 694-703

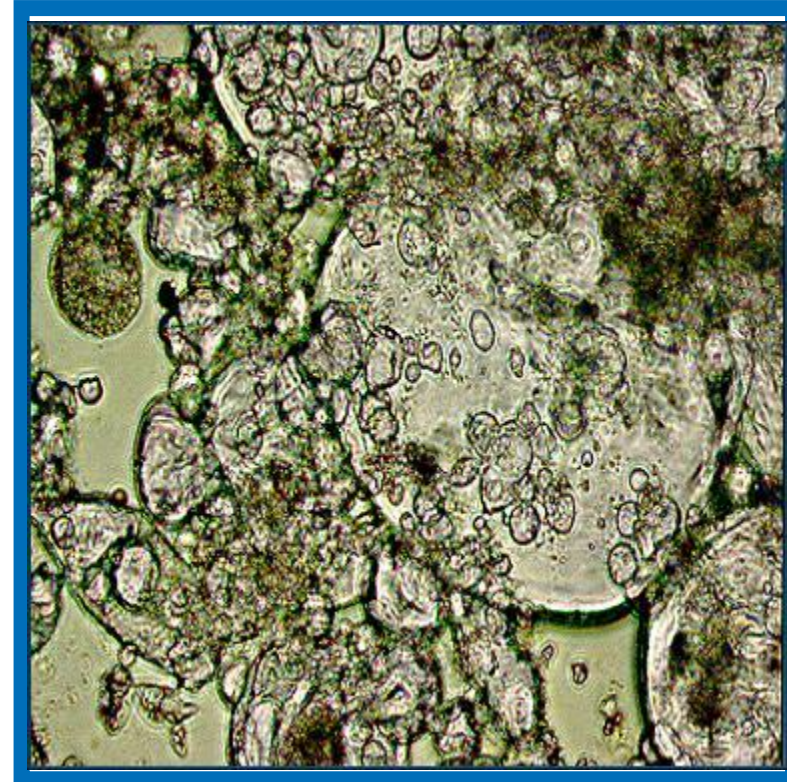
## Case of a water-in-crude oil emulsion





# EXAMPLES OF COMPLEX EMULSIONS

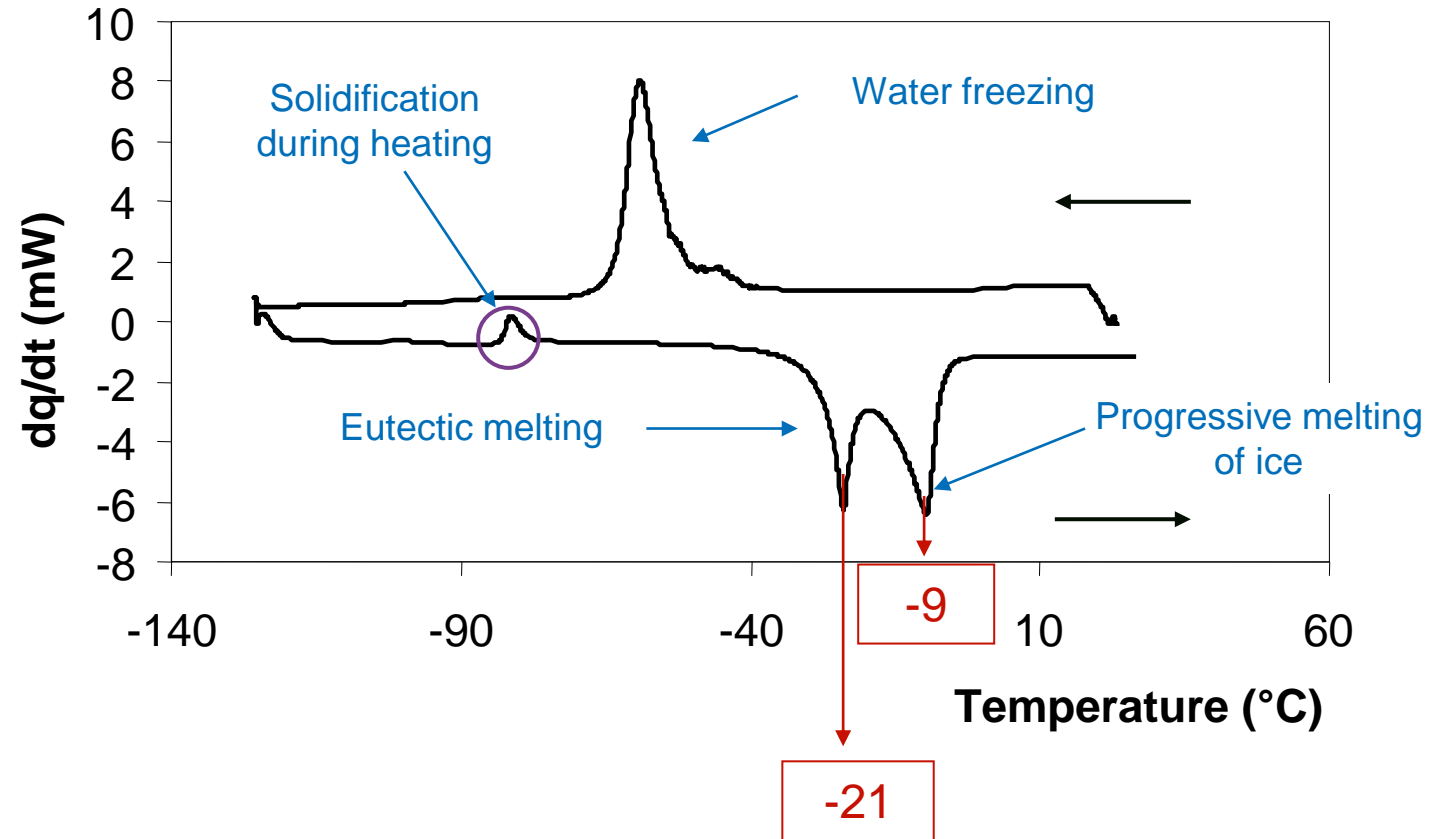
- Emulsions in crude oil production
- Drilling fluids
- Filtercakes during drilling



# CRUDE OIL EMULSIONS

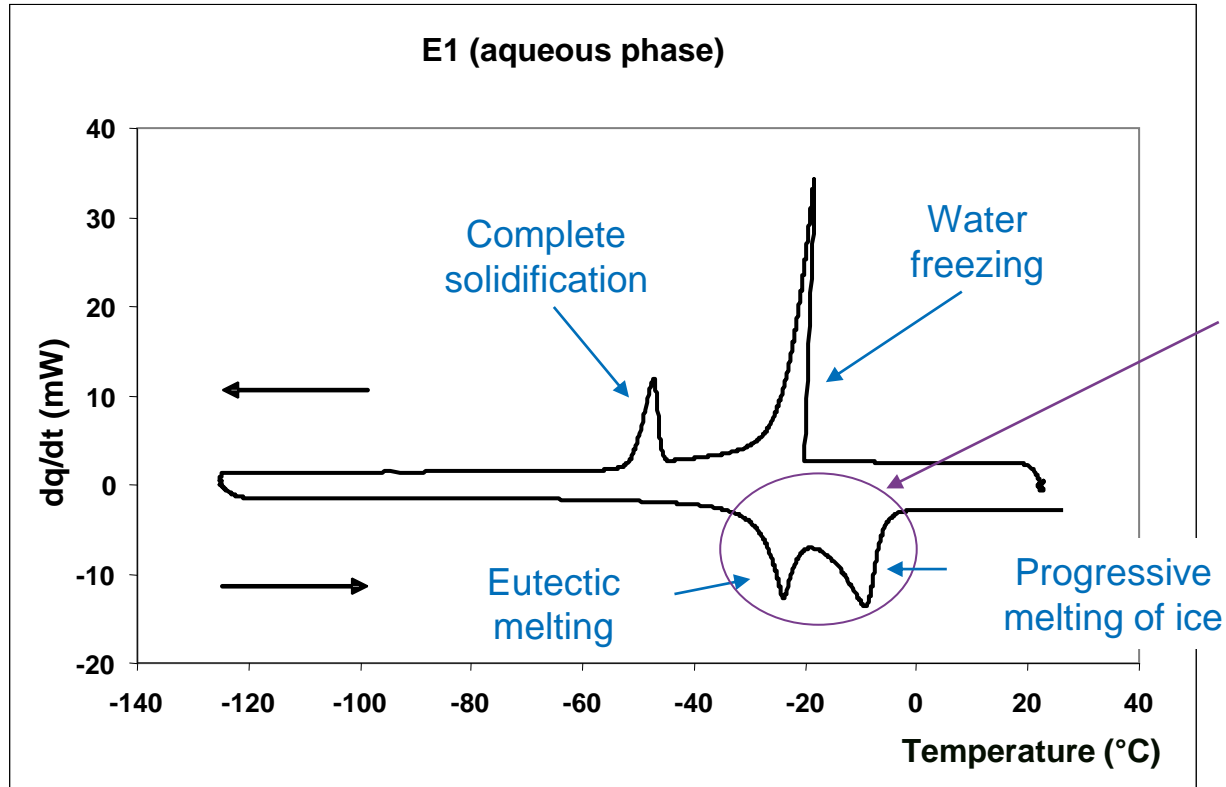
- We note the very frequent formation of water-in-oil emulsions in oil production
  - This emulsification is favored by the presence of strong areas of turbulence and shear (pumps, valves, etc.)
  - These emulsions are generally very stable from a kinetic point of view
- Stability is favored by the presence of natural emulsifying agents in petroleum: asphaltenes, resins, naphthenic acids, etc.
  - colloidal solids will also reinforce the resistance of the interfacial film to coalescence: clays, deposits, paraffin crystals, salts, etc.
- The separation efficiency between water and oil depends on the size of the droplets of the emulsion and its stability
- Demulsifying surfactant formulations are generally used to allow complete separation of emulsions

# CRUDE OIL EMULSIONS



Example of water-in-crude oil emulsion (E1)

# CRUDE OIL EMULSIONS

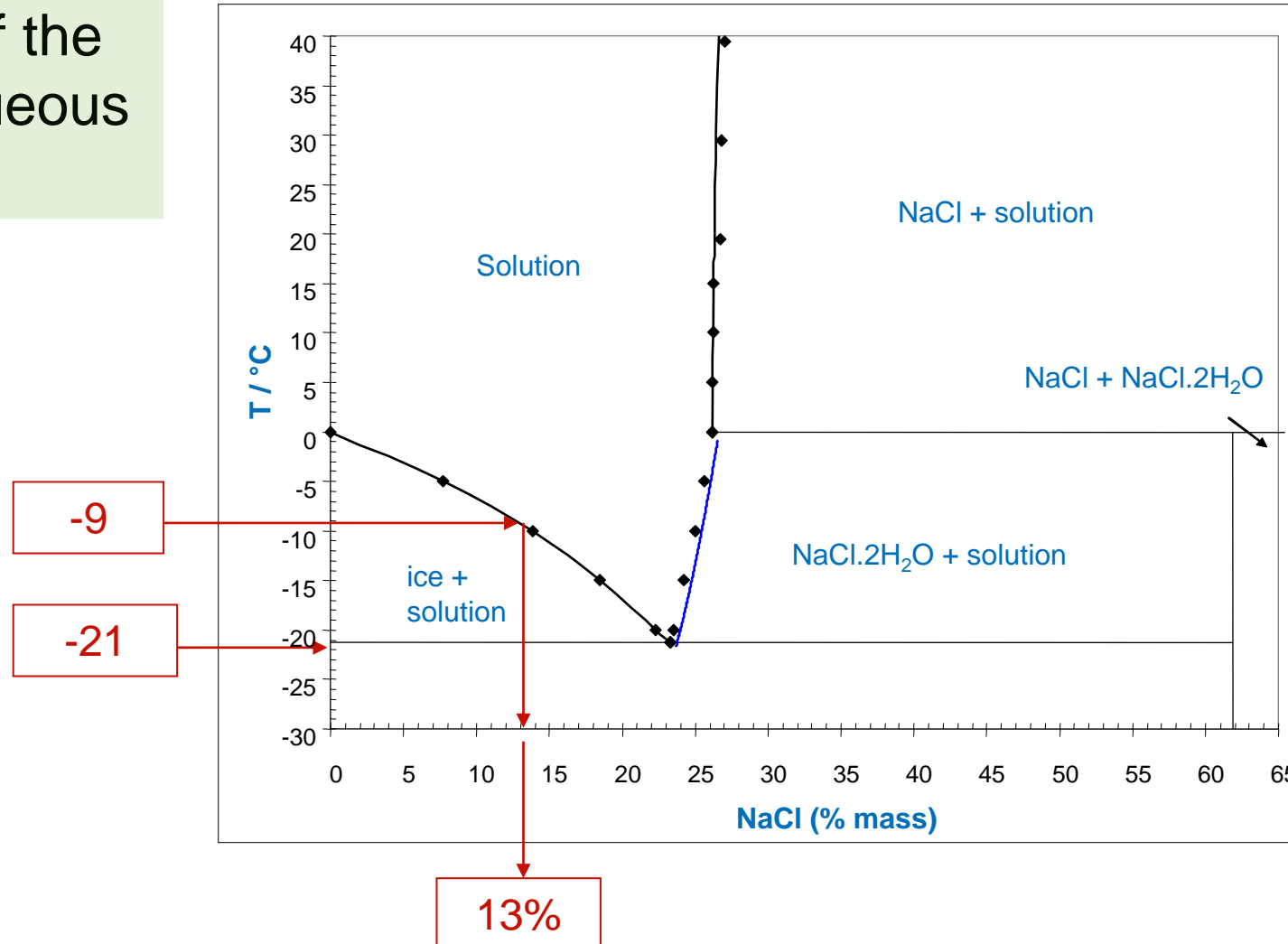


The integration of the peaks corresponding to the melting of the aqueous phase makes it possible to calculate the water content of the emulsion!

DSC analysis of the aqueous phase from emulsion E1

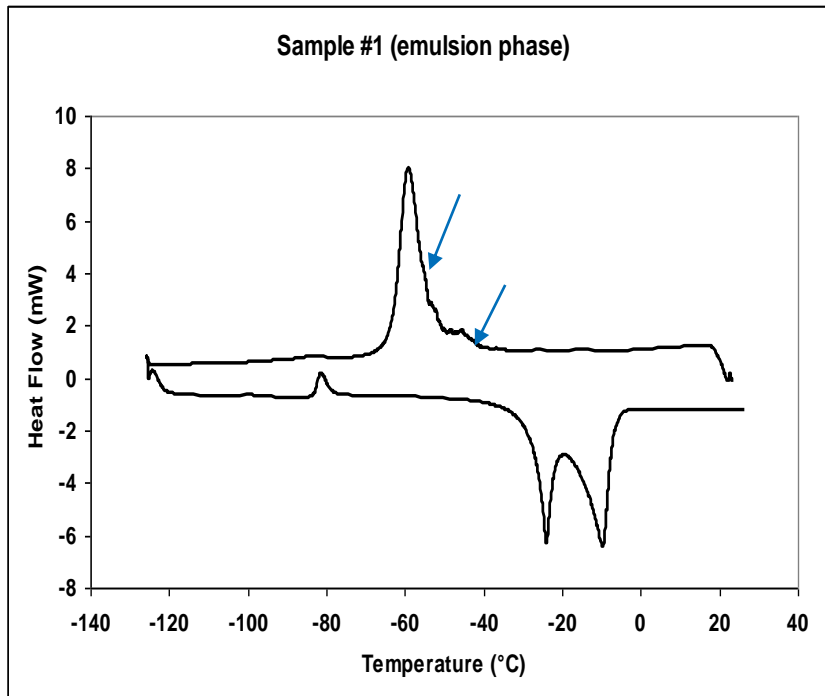
# CRUDE OIL EMULSIONS

Determination of the salinity of the aqueous phase of E1

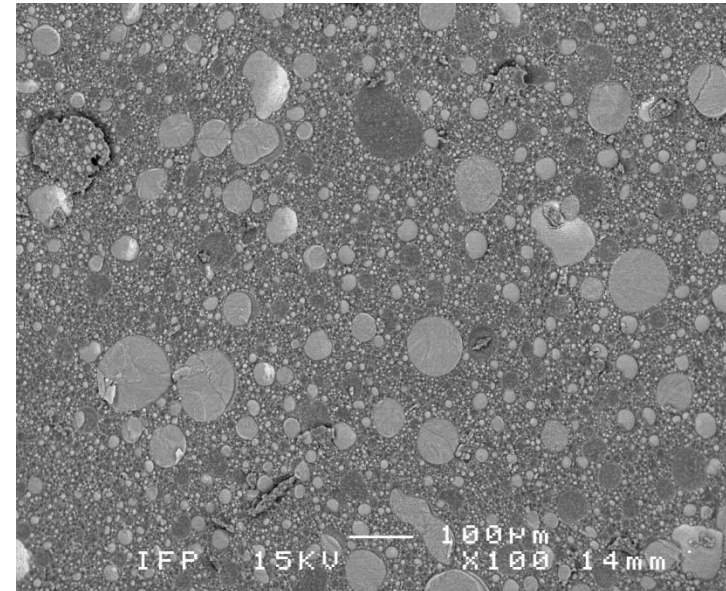


# CRUDE OIL EMULSIONS

DSC: several peaks of solidification



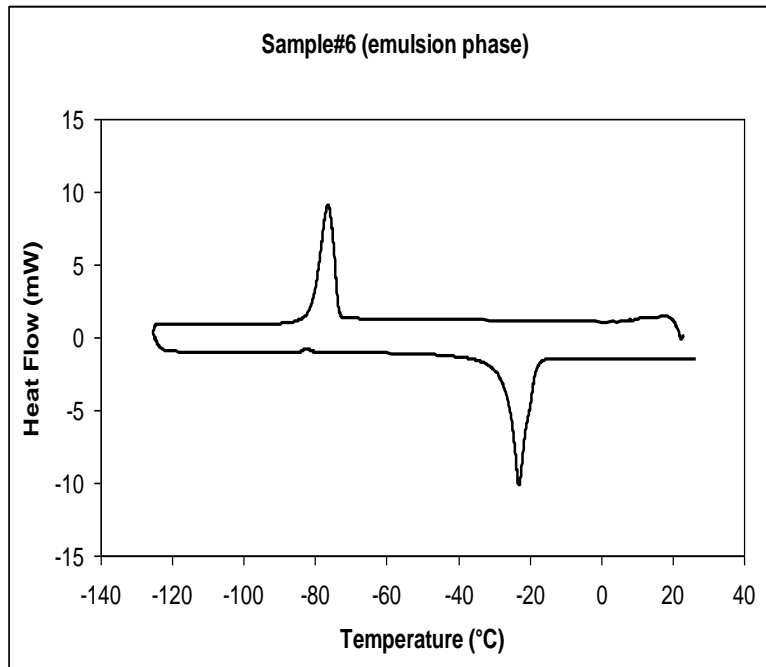
Cryo-SEM: water droplets up to 100  $\mu\text{m}$



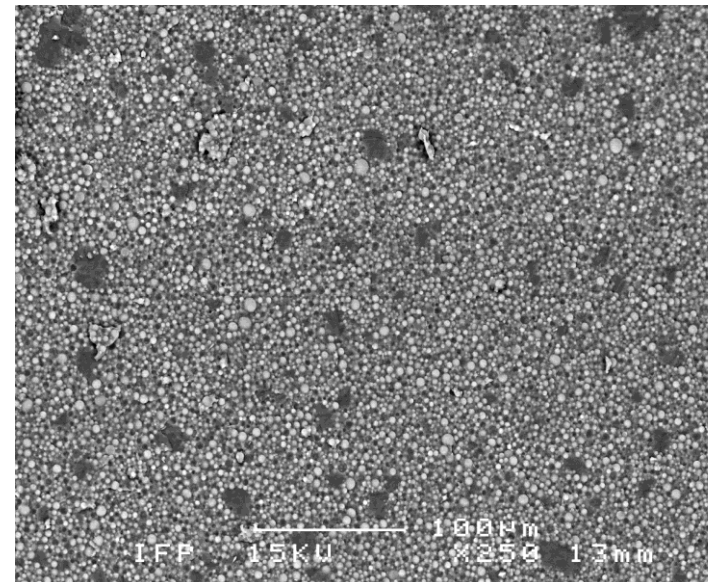
E1: polydisperse W/O emulsion

# CRUDE OIL EMULSIONS

DSC: a unique peak of water freezing at  $-70^{\circ}\text{C}$



Cryo-SEM: water droplets of 1-2  $\mu\text{m}$

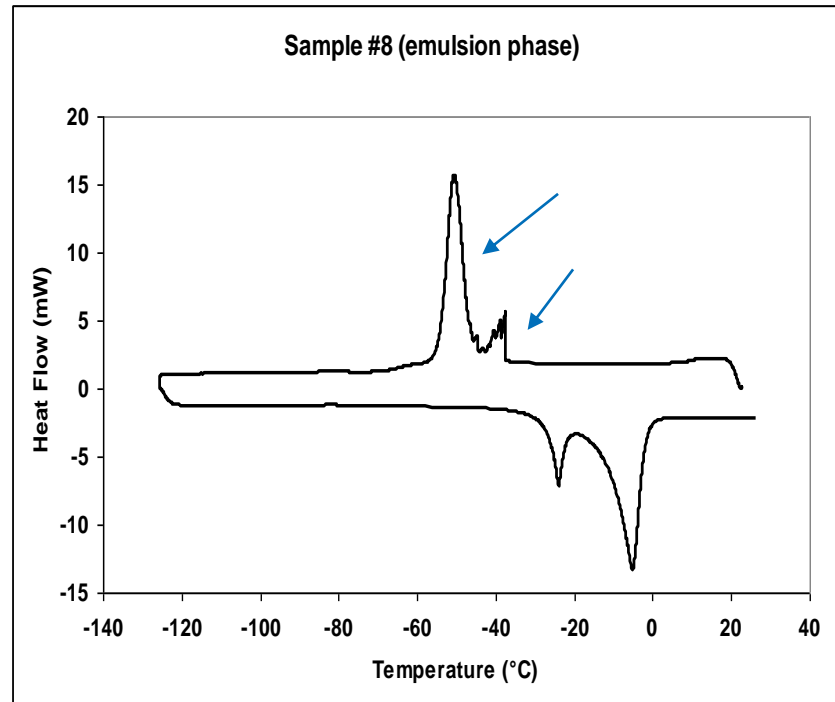


E6: monodisperse W/O Emulsion

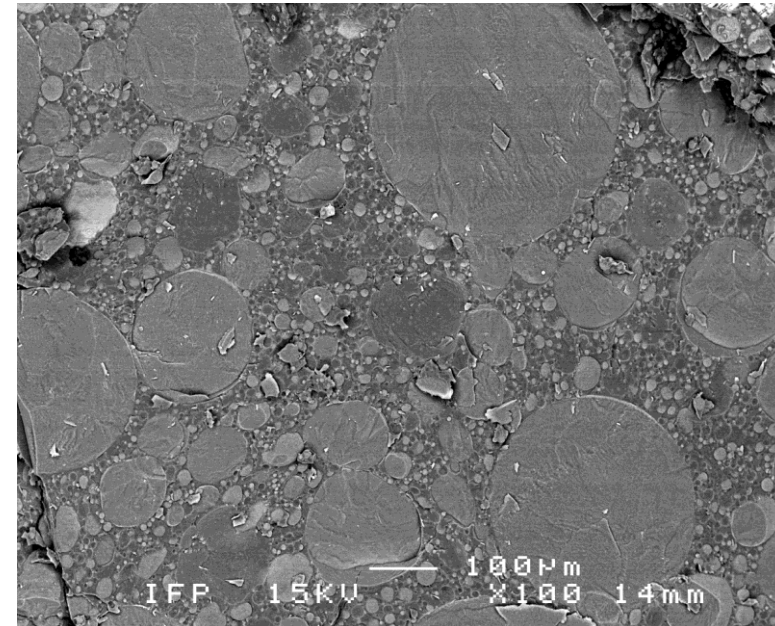


# CRUDE OIL EMULSIONS

DSC: several peaks of water freezing



Cryo-SEM: water droplets up to 600  $\mu\text{m}$



E8: polydisperse W/O Emulsion



# CRUDE OIL EMULSIONS

	Emulsion E1	Emulsion E6	Emulsion E8
Emulsion type (DSC)	W/O polydisperse	W/O monodisperse	W/O polydisperse
Droplets size (cryo-SEM)	2-100 $\mu\text{m}$	2 $\mu\text{m}$	4-600 $\mu\text{m}$
Water content (DSC)	66%	62%	78%
Water content (Karl Fischer)	56%	58%	55%
Salinity NaCl (DSC)	13%	21%	7%
Salinity TDS (field data)	110 g/L	200 g/L	66 g/L

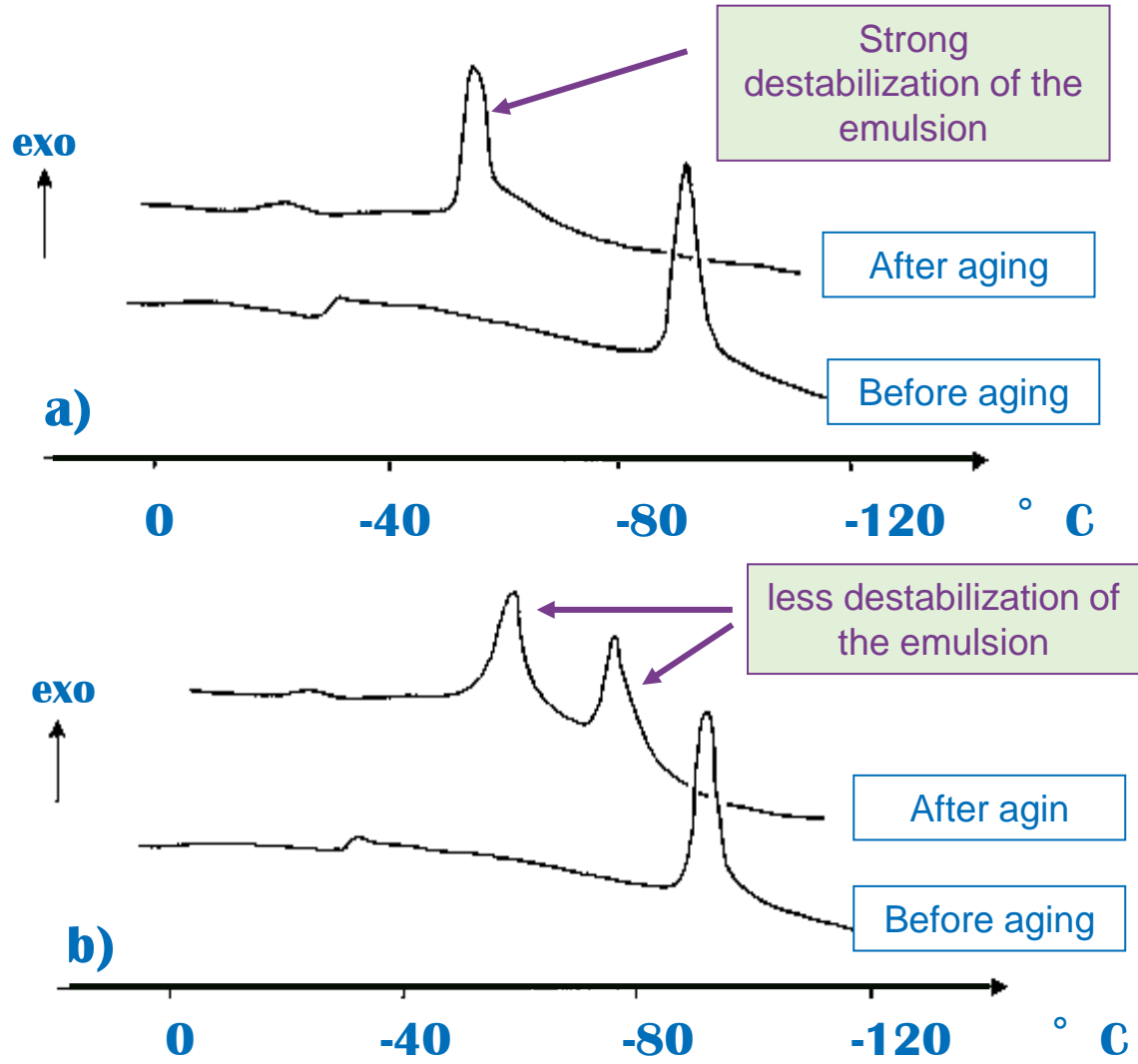
# DRILLING FLUIDS

- The success of a drilling operation depends on many factors, one of the most important being the drilling fluid
- Drilling fluids are generally composed of aqueous or oil-based suspensions of finely divided solids of various natures
  - water based mud
  - oil mud
  - light mud
- Oil-based muds are the most suitable fluids for difficult drilling conditions. These are water/oil emulsions (between 5 and 40% dispersed aqueous phase) which contain:
  - aqueous phase: brine
  - emulsifiers (to ensure stability)
  - organophilic clays (to control rheological properties and in particular thixotropy)
  - weighting agents (calcium carbonate or barium sulfate) to adjust density

# DRILLING FLUIDS

- Drilling fluids are used under extreme temperature and pressure conditions
- The characterization of the temperature stability of these fluids is essential
- Classic characterization techniques
  - bottle testing
  - electrical stability
- DSC is used to characterize the stability of oil-based muds
  - development of new emulsifying systems suitable for high temperatures
  - emulsifying formulation optimization

# DRILLING FLUIDS



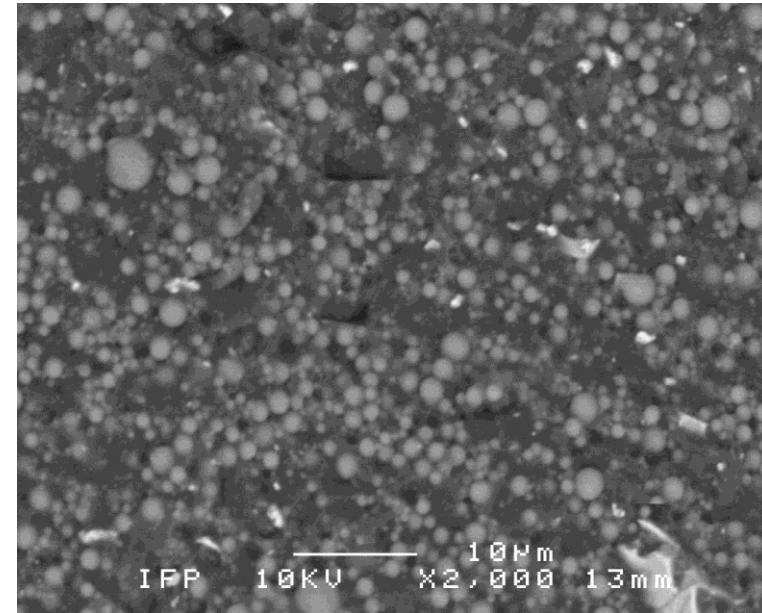
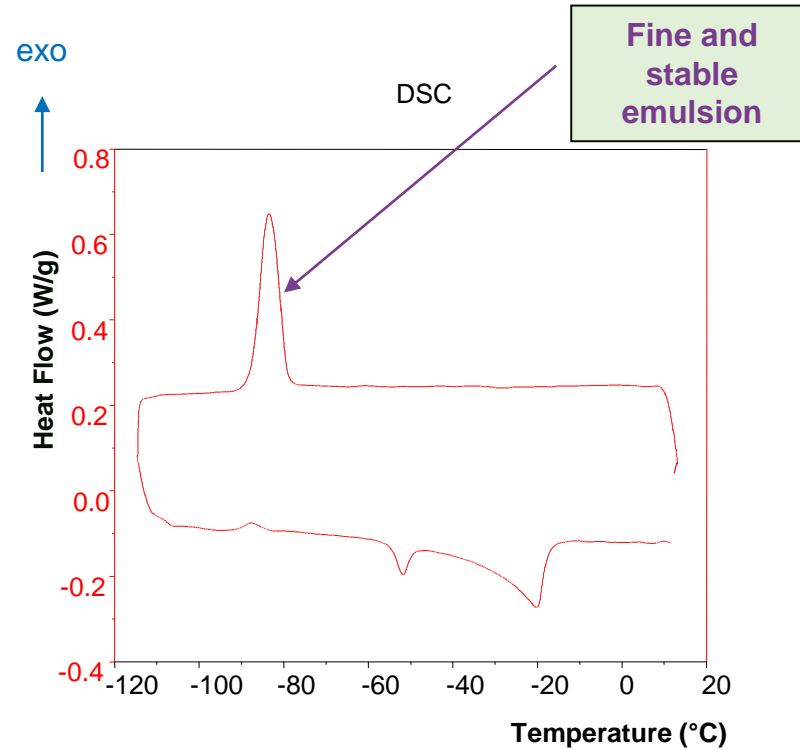
Commercial Formulation

Experimental Formulation

## FILTERCAKES DURING DRILLING

- Oil-based drilling fluids are used to drill complex wells. If these fluids are less damaging for the reservoir than water-based fluids, they can however induce severe damage which will reduce the productivity of the well.
- During drilling, drilling fluid solids and emulsion brine droplets tend to form a filter cake along the walls of the well.
- To restore the productivity of the well, it is necessary to clean this filter cake, most often by chemical treatment.
- The DSC analysis of the filter cake treated makes it possible to select the additives likely to destabilize the emulsion and therefore to break down the structure of the filter cake.

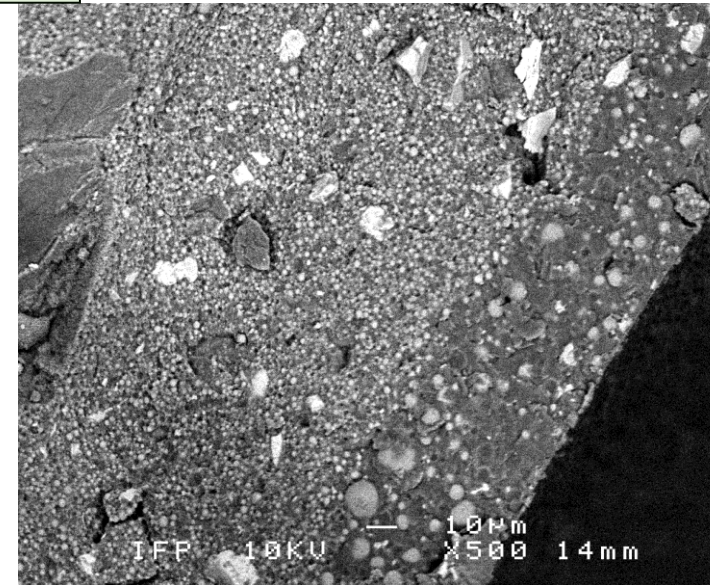
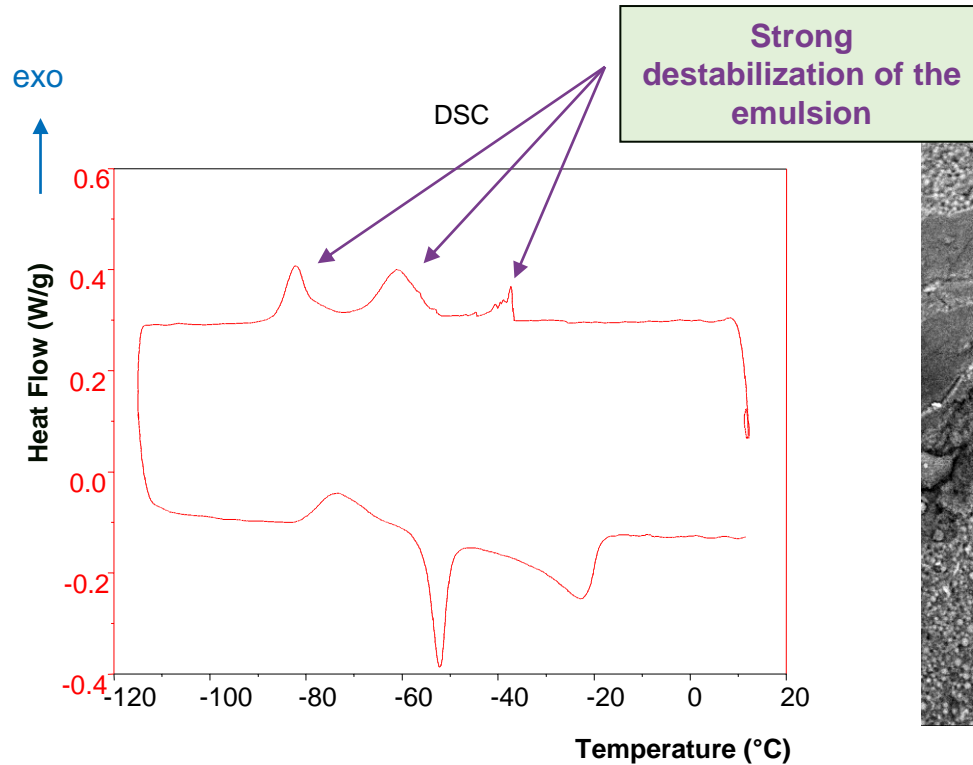
# FILTERCAKES DURING DRILLING



**Filtercake  
(reference)**

**Cryo-SEM analysis  
(reference)**

# FILTERCAKES DURING DRILLING



**Treated filtercake, product B,  
240h**

**Cryo-SEM Analysis  
(treated filtercake)**

## Advantages of DSC

- Study of real and complex fluids
  - without preparation
  - without dilution
- Particularly suitable for opaque and concentrated emulsions and suspensions
- Technique increasingly used in the oil industry (see "hydrates" applications)



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