Ice particles crystallization in the presence of ethanol: investigation by Raman scattering and X-ray diffraction

Bertrand CHAZALLON

Laboratoire de **Ph**ysique des **L**asers **A**tomes et **M**olécules
Université Lille 1
PhLAM

Anatrac Group at PhLAM (Lille1)

C.FOCSA (Pr.)

M. ZISKIND (Ass. Prof)

Y. CARPENTIER (Ass. Prof)

S. GURLUI (Invited Prof., Univ. Iasi)

S. FACQ (Dr.) At present post-doctorant at Lab. Geol. Univ/ENS LYON

O. POMPILIAN (PhD)

P. DELCROIX (PhD)

L. DIOLOGENT (PHD)

http://emlg2013.univ-lille1.fr

EMLG
European Molecular Liquids Group

EMLG - JMLG annual meeting 2013

9 - 13 September 2013, University of Lille 1, France

Global perspectives on the structure and dynamics of liquids and mixtures: Experiment and simulation

http://emlg2013.univ-lille1.fr

It is a pleasure to announce the annual EMLG-JMLG Conference to be held at University of Lille 1 between 9 and 13 September 2013. The theme of the conference is intended to encourage participants to present the most recent experimental methods, theoretical approaches and simulations leading to better understanding of the structure and dynamics in the following areas :

- Liquids and solutions at normal and supercritical fluids
- Clathrate hydrates formation from liquid water or ionic liquid phases
- Ionic liquids and their mixtures
- Supercooled liquids and glassy systems
- Biological systems

The features of the conference

- Leading speakers
- A "young" Scientists contribution
- Sponsorship for two students bursaries (conference fee)
- A poster session with EMLG-JMLG sponsored cash prizes for the three best posters

Invited speakers

- Arieh **BEN NAÏM** (Israel)
- Roland **BÖHMER** (Germany)
- Frédéric **AFFOUARD** (France)
- Steve **MEECH** (UK)
- Kia **NGAI** (Italy)
- Toshiyuki **TAKAMUKU** (Japan)
- Toshio **YAMGUCHI** (Japan)
- Yoshikata **KOGA** (Canada)
- Amadeu K. **SUM** (USA)
- Alessandro **TRIOLO** (Italy)
- Rodolphe **VUILLEUMIER** (France)
- Jean-Marc **ZANOTTI** (France)

Organizers:
Abdenacer IDRISSI (LASIR-Lille)
Maria-Antonietta RICCI (Italy)
Bertrand CHAZALLON (PhLAM-Lille)
Frederic AFFOUARD (UMET-Lille)

http://emlg2013.univ-lille1.fr

Université Lille 1 cnrs Institut Chevreul

Context:

Freezing of aqueous droplets/solutions is also important in cryo-preservation

- ☐ Mechanism and action of protective additives against the freezing damage of living cells is still obscure
- ☐ Protective action of additives against freezing is due to a number of factors:
  - o Ability of the cryoprotector to preserve H-bonds within the solvent upon freezing
  - o the amount of free water molecules within a biological cells reduces during the ice growth → the cryoprotectant should prevent a substantial fraction of water molecules to freeze
  - o It should hamper the formation of large ice crystals which are likely to enlarge during warming, and may damage the cell membrane, and makes the cells leaky
  - o Property of cryo-protector: reduction of the water-cryoprotector eutectic by maintaining a high molecular mobility at low temperature → keep the biological fluids or cellular cytoplasm liquids even at low temperature

Morris & Clarke, Acad. Press, 1981

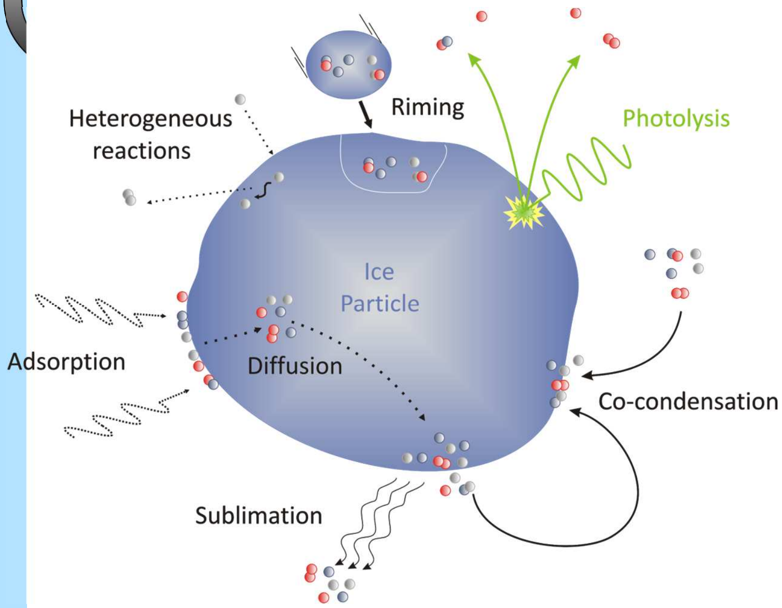
→ alcohol-water system can be regarded as model studies for futur applications of cryoprotection

Context:

→ The atmosphere is a multi-phase medium:

-Common phases of H_2O molecules: water vapor, liquid water, and ice

-Gaseous species can interact with the condensed phases through many incorporation mechanisms



At the surface of ice particle :

- incorporation by ***adsorption***

In the ice particle volume :

- ***Co-condensation***
- ***Riming***
- ***Freezing of aqueous solution droplets***

Effects :

- Affect ice particle structure and reactivity
- Modify the nature and the composition of the incorporated species in ice or in gas phase
- Affect the optical properties (particle sizes, morphologies)

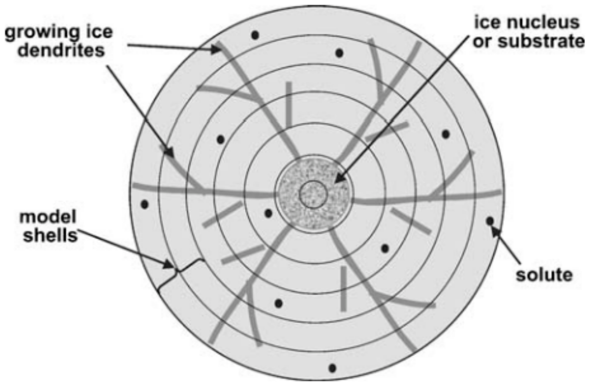
Freezing of droplets: the mechanism

Partitioning of chemical solutes during freezing of an aqueous particle

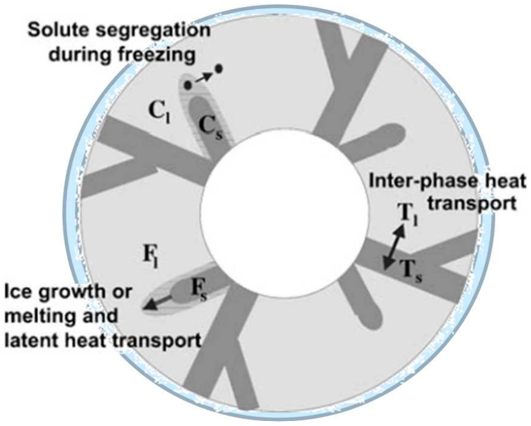
1 mm radius / 100µm ice nucleus radius

Model:

Radial heat transport
Radial solutes transport



Stuart & Jacobson, J. Atm. Chem. 2006



- Dendrites propagates to the particle-air interface and an ice layer is formed at the surface
- Then, freezing propagates inward until the complete freezing of the particle

- Trapping process: solutes is trapped at solubility in ice >> equilibrium (up to ~ 3 O.M.)
  - Fast (ms) : « adiabatic » (~13% of the ice particle freezes)
  - Slower (s): « diabatic »

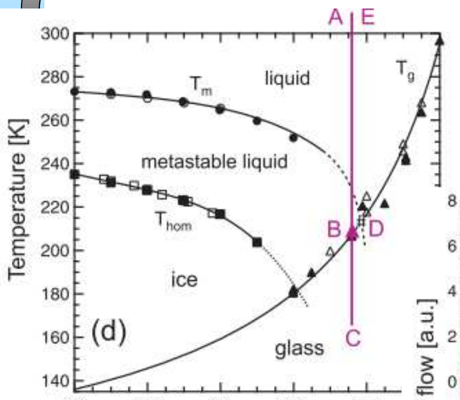
→ Impact on the retention coefficient

The composition of an aqueous aerosol in the atmosphere depends on the ambient relative humidity.

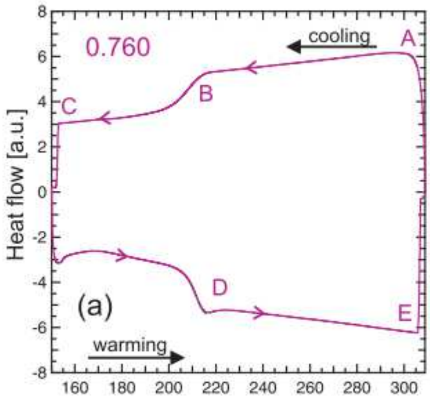
Freezing of bulk and emulsified organic-rich aqueous solutions

(~0.5 – 5 µm aqueous droplet diameters)

Zobrist et al., Atmos. Chem. Phys., 8, 5221, 2008



(DSC-experiments)



Ice is inhibited
→ Glass is formed
on cooling

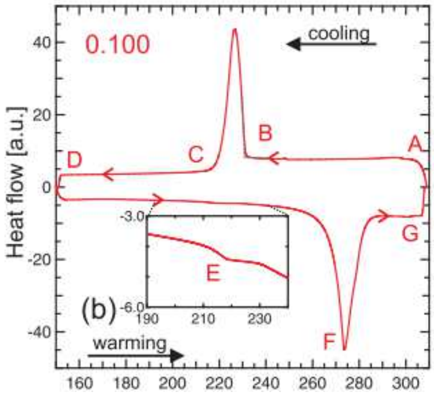
The composition of an aqueous aerosol in the atmosphere depends on the ambient relative humidity.

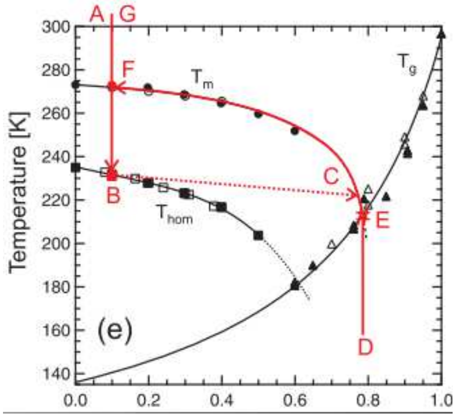
Freezing of bulk and emulsified organic-rich aqueous solutions

(~0.5 – 5 μm aqueous droplet diameters)

Zobrist et al., Atmos. Chem. Phys., 8, 5221, 2008

(DSC-experiments)





Ice first formed then a glass

→ Large or moderate hydrophobic organic molecules are most likely forming glasses at temperature and relative humidity relevant to the atmosphere

---

Implications:

- **Water uptake** by aerosols is diminished or even **fully inhibited** for glassy aerosols
- **Ice nucleation** is **inhibited** at the homogeneous nucleation threshold → higher ice super-saturations than expected for liquid aerosols *Jensen et al., Atmos.Chem.Phys., 2005* *Peter et al., Science, 2006*
- Vitrification leads to cirrus clouds with smaller ice particles number densities relative to the inorganic enriched aerosols → impact the radiative effect of cirrus

→ Potential impact on the direct aerosol effect (light scattering)
→ Indirect aerosol effects (acting as CCN or IN)

Objectives of our study:

How freezing impact the structure and partitioning of the chemical solutes?

→ Non-volatil solutes are known to be retained efficiently upon freezing

(e.g. Mitchell & Lamb, 1989)

→ More volatil species are not well characterized: e.g. VOCs (HCOH, C_2H_5OH, CH_3COOH, etc)

→ Investigation of the phase diagram and structure of the ethanol-water system for potential application in cryoprotection

---

Outline

Background

I. Ethanol and Water: review of the system
II. Freezing of aqueous particle of ethanol: prediction from the phase diagram

Results

III. Incorporation of ethanol by droplets freezing: structure of the ice particles
IV. Incorporation of ethanol by co-condensation: solubility/hydrate formation

Conclusion

Background

I/ Review of the ethanol-water system at low temperature

D. I. Mendeleev (1859) (ρ, X) : 3 compounds in the liquid phase : $E \cdot 12H_2O$, $E \cdot 3H_2O$, $3E \cdot H_2O$

Vuillard & Satragno (1960) DTA & Dielectric: First phase diag. + Hydrate of composition $E \cdot 5H_2O$

Glew (1962) (ρ, X) data: Anomalous partial molar volume + Hydrate of composition $E \cdot 17H_2O$

Potts & Davidson (1965) DTA & Dielectric : $E \cdot 17H_2O$ (existence of H bonds between the ethanol OH group and the water network (modified clathrate of structure II)

Jeffrey & McMullan (1967) : Proposed the term of ***semi-clathrate*** (or modified clathrate)

Sargent & Calvert (1966) XRD : Failed to observed the cubic structure II (***CS-II***)

Calvert & Srivastova (1969) XRD: Hydrate of cubic sI (CS-I) and a modified sII ($F4_132$)

Ott et al, (1979) : Metastable phases occur more often than stable phases + hydrate of composition $E \cdot 2H_2O$

Boutron & Kaufmann (1978) DSC & XRD ***CSI (5.75)+ CS-II present*** but do not fit with *Fd-3m* space group

Takaizumi (1997, 2005) DTA: Many (meta)stable hydrates classified in two groups : ***CS-I et CS-II***

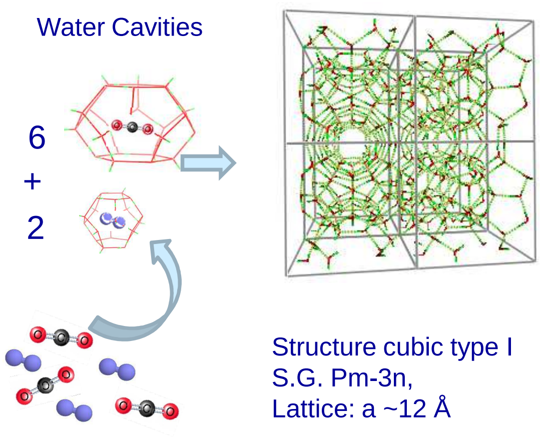
Takamuku et al., (2005) XRD : $E \cdot 4H_2O$ confirmed

Zelenin (2003) DTA: Only three hydrates: $E \cdot 2H_2O$ ***(stable)***, $E \cdot 3H_2O$, $E \cdot 4.75H_2O$ (***CS-I***), BUT ***no CS-II***

Main clathrate structures

Water Cavities

$46\ H_2O$



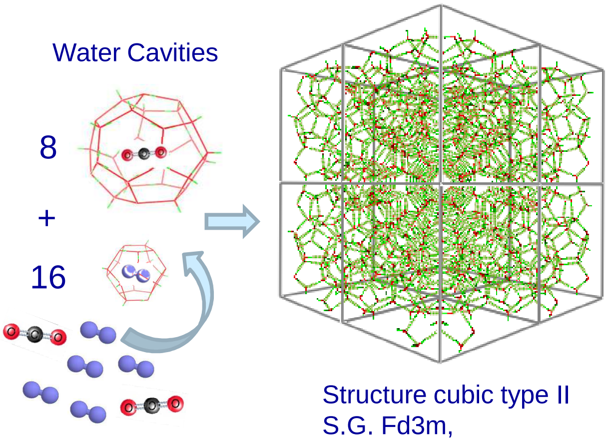
Structure cubic type I
S.G. Pm-3n,
Lattice: a ~12 Å

Mean cavity radius:
SC - 3.95 Å
LC ~ 4.33 Å

Type I: CH_4, Xe, CO_2,…

Water Cavities

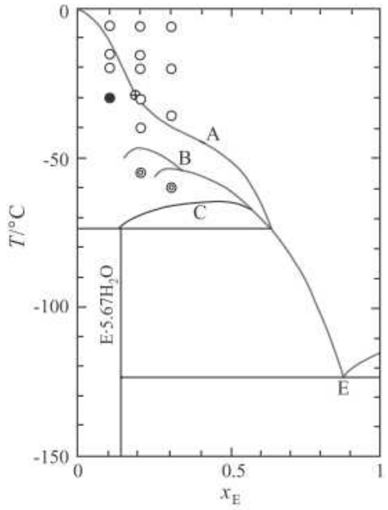
$136\ H_2O$



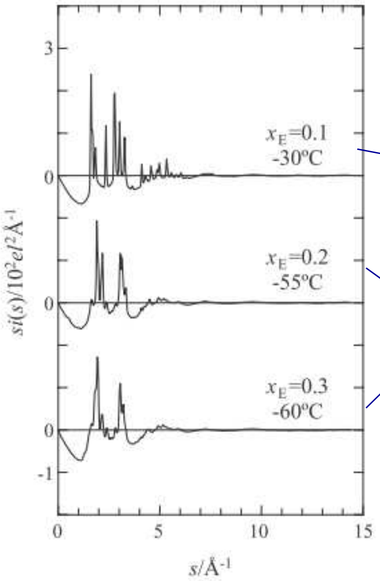
Structure cubic type II
S.G. Fd3m,
lattice: a ~17 Å

Mean cavity radius:
SC - 3.91 Å
LC ~ 4.73 Å

Type II: N_2, O_2, Ar…



Takamuku et al., J.Mol.Liq, 2005



Ice Ih

Ethanol hydrates
E $4H_2O$

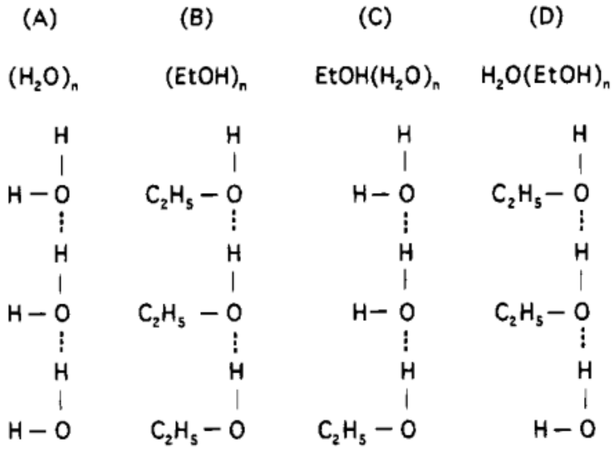
Eth-H_2O mixtures of compositions: 10, 20, 30 mol%

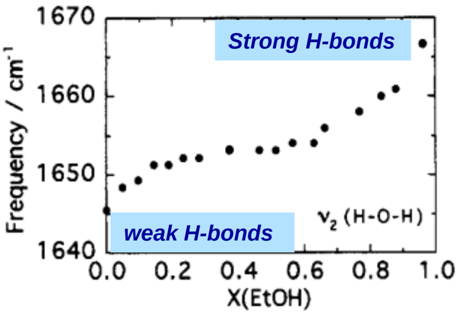
- 60°C < T < 25 °C

Takaizumi et al., *J. Sol. Chem.*, 1997, proposed that ***the structure of dominant clusters change near ~ 17 mol% at the inflexion point. The clusters formed in the mixtures at the ambient temperature is reflected into that of frozen alcohol–water mixtures***”

Combined NMR & IR study

Mizuno et al., J.Phys.Chem. 1995





At low X_{EtOH}: X_{EtOH} ↗ → strength of H-bonds (Type A) ↗ between water molecules surrounding Ethanol alkyl groups (but no type C)

→ Clathrate-like structure of water in the water-rich region

Soper & Finney, PRL, 1993

At high X_{EtOH}: as X_{EtOH} ↗ --> H-bonds of type D strength ↗ and H-bonds between water molecules increases

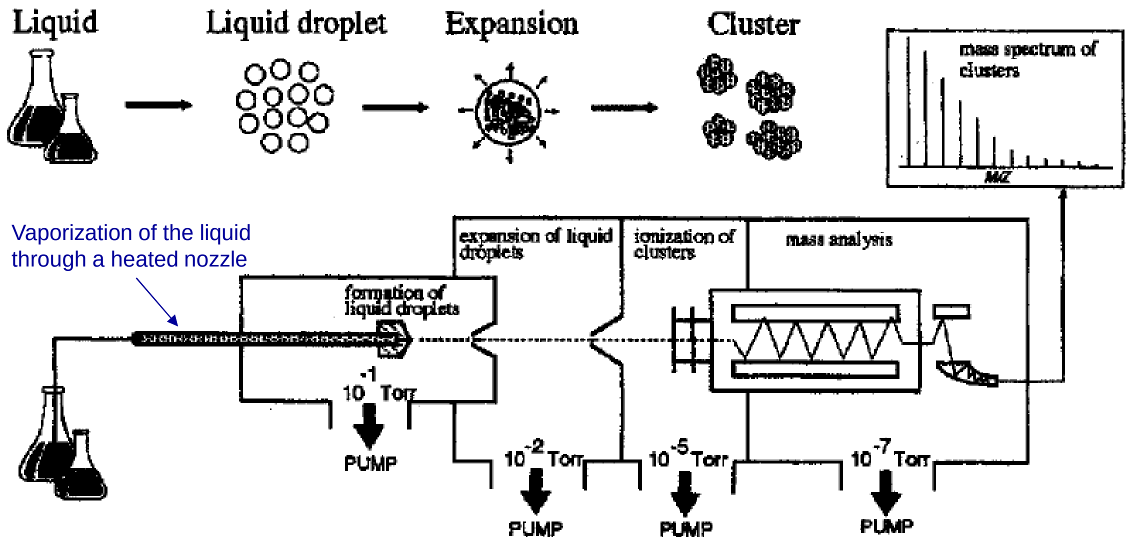
Whole range of X_{EtOH}: Size of the EtOH aggregates ↗ as X_{EtOH} ↗ with H-bonds type B also ↗ (cooperative effects)

---

liquid droplet expansion

- Inhomogeneous clusters are formed
- Clusters structure in solution have been analyzed by mass spectrometry

Experimental set-up build to analyze isolated clusters from alcohol-water-mixtures

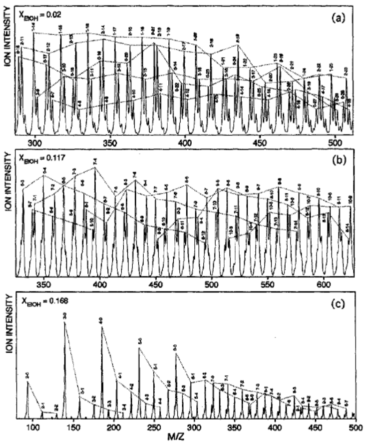


Vaporization of the liquid through a heated nozzle

Wakisaka et al., J. Mol. Liq, 2001

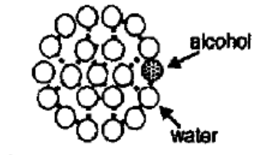
Cluster models derived from mass spectra analysis

Wakisaka et al., J. Mol. Liq, 2001



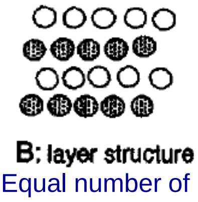
Equivalent structure as that of liquid water but with 1 EtOH

$H^+(H_2O)_{21}$



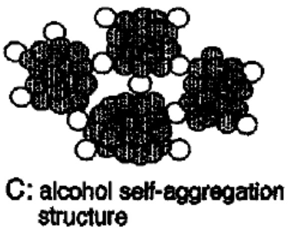
Clathrate-like

Water cluster structure is destroyed → layered water – ethanol clusters

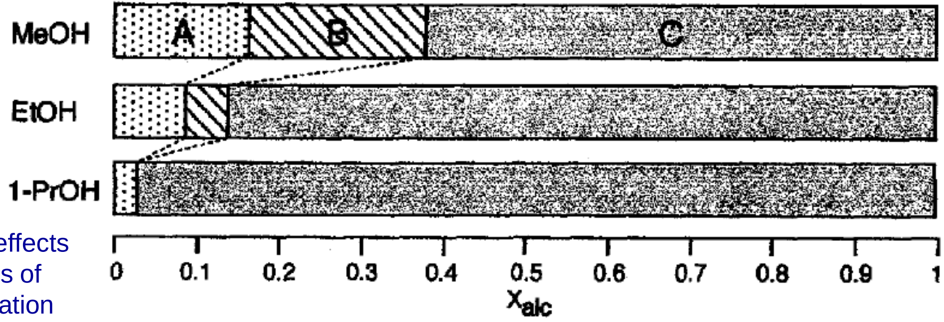


Equal number of water/ethanol

Water molecules are bridging the alcohol clusters



at X_{EtOH} ~17 mol%



Hydrophobic head-groups effects leads to self-aggregations of clusters at lower concentration

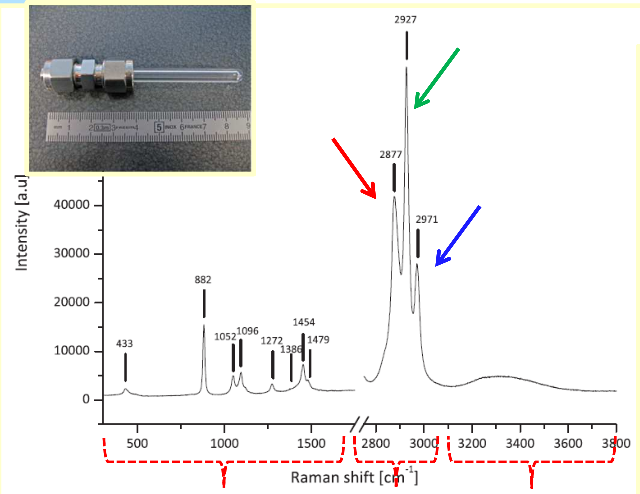
---

Raman spectroscopic study

Facq et al., J.Phys.Chem.A, 2010

2 spectral regions of interest :

CH and OH stretching modes



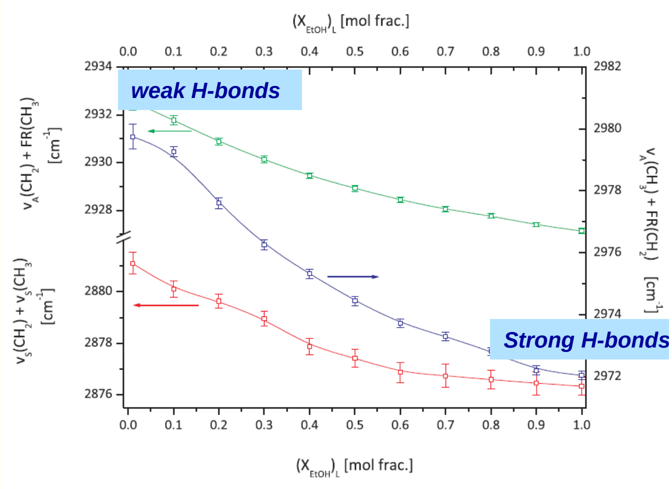
C-O vibrational mode spectral region

C-H vibrational mode spectral region

O-H vibrational mode spectral region

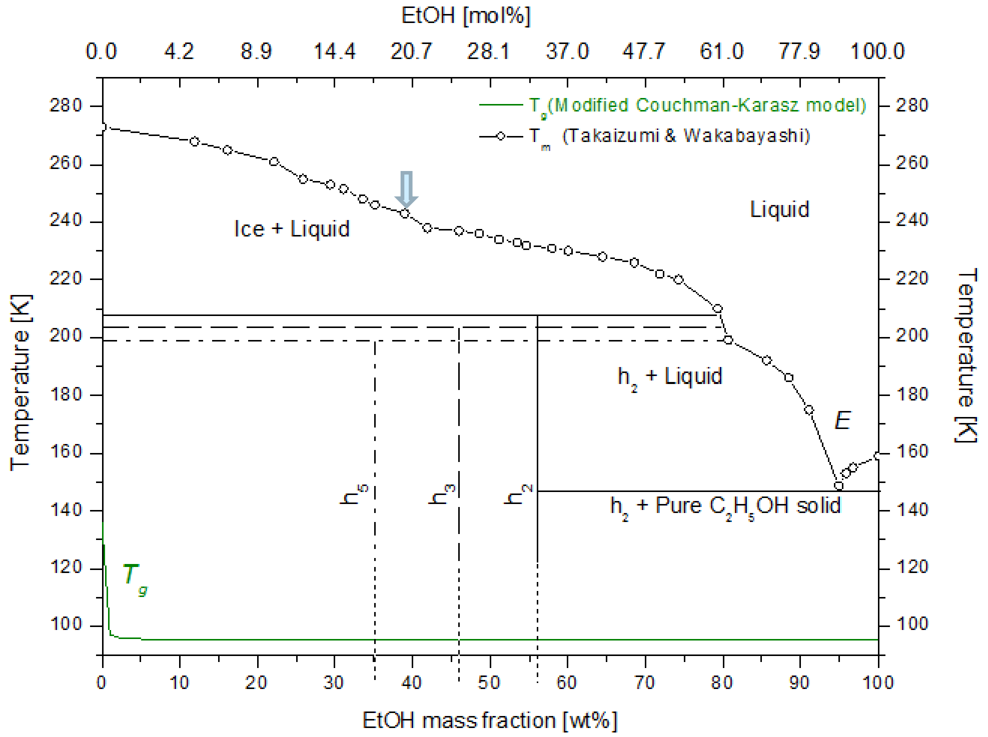
Ethanol – Water mixtures:

CH stretching modes



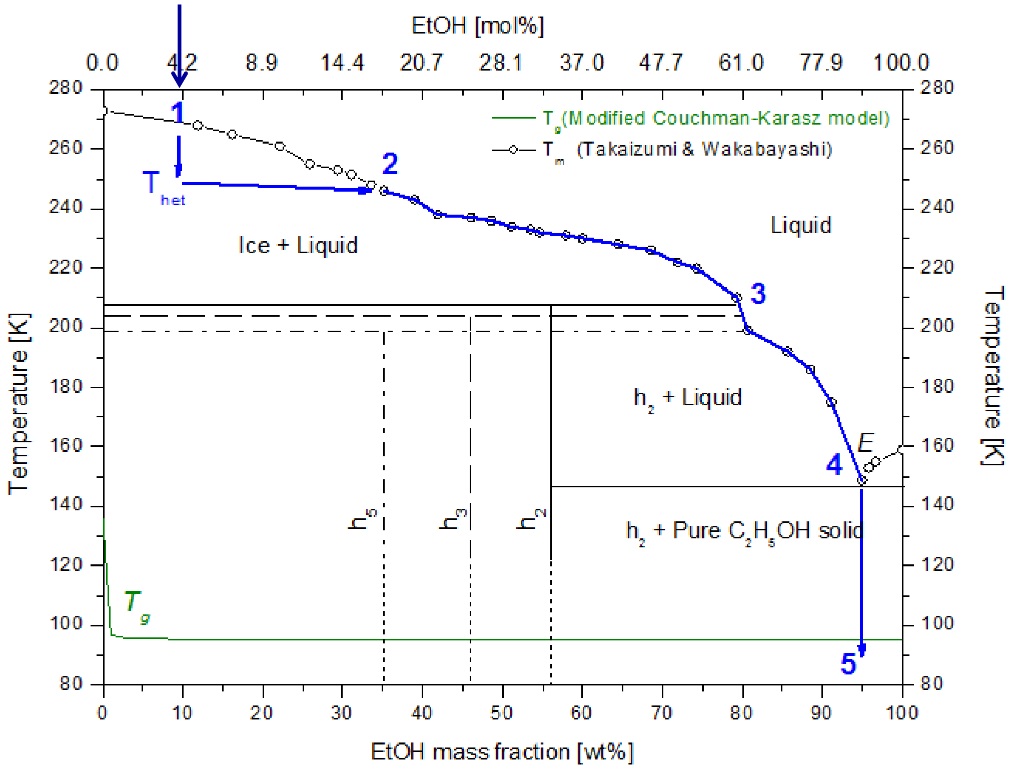
Frequency decreases = Strengthening of H bonds

II/ Ice particle crystallization: prediction from the phase diagram

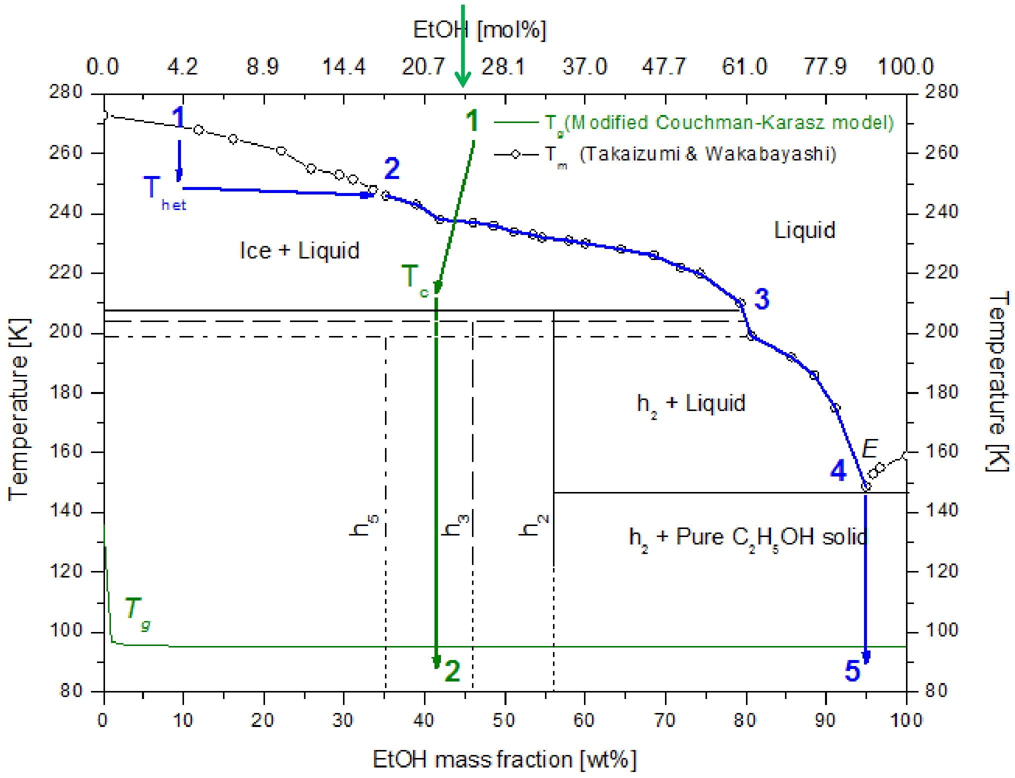


$h_2 = E \cdot (2 \pm 0.2\ H_2O)$ stable ($T_{dec.} = 208$ K)
$h_3 = E \cdot (3.2 \pm 0.3\ H_2O)$ metastable ($T_{dec.} = 204$ K)
$h_5 = E \cdot (4.9 \pm 0.4\ H_2O)$ metastable ($T_{dec} = 198$ K)

Ethanol-Water at 8.7 wt%

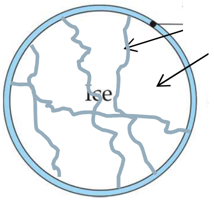


Ethanol-Water at 46 wt%



Aqueous solution of 8.7wt%:

- ➢ First solid formed during cooling is ice I_h at 248 K
- ➢ Phase separation between ice and an aqueous solution of ethanol
- ➢The ethanol content of the solution increases upon further cooling
- ➢ At point 3, an hydrate should formed and a part of the solution crystallizes around 208 K
- ➢The ethanol content of the solution increases upon further cooling
- ➢ At point 4, another part crystallizes around 149 K
- ➢ At point 5, : *Crystallization of pure solid ethanol should happened*



Ice +

2 EtOH hydrates

+

aqueous solution

Aqueous solution of 46 wt% :

- ➢ First solid formed during cooling is ethanol hydrate at ~ 212 K
- ➢ Most of the solution is transformed into an ethanol hydrate
- ➢ The composition of the particle should not vary too much (down to landmark 2)
- ➢ A remaining solution may exist with a composition close to the eutectic at point 2

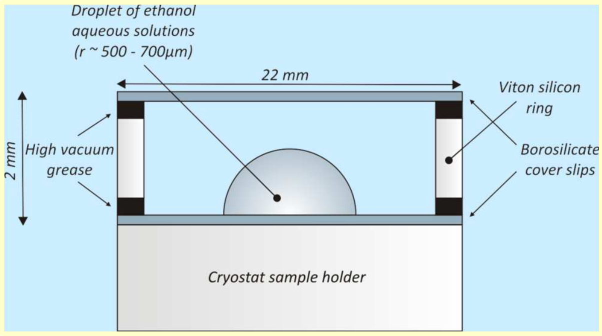
Results

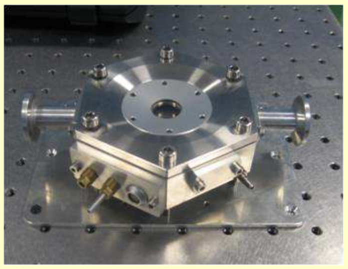
III. . Incorporation of ethanol by droplets freezing: structure of the ice particles

---

III/ Incorporation of ethanol by droplet freezing: structure of particles

Experimental set-up





Droplets of ethanol aqueous solutions :

- r ~ 500 -700µm
- Prepared in **cold room** at 264 K
- Placed in “homemade” cell

“Homemade” cell placed in a cryostat :

- Cooling at 0.7 K.min^{-1}
- Using liquid N_2 circulation
- Annealing at 0.7 K.min^{-1} up to 268 K

Raman spectra :

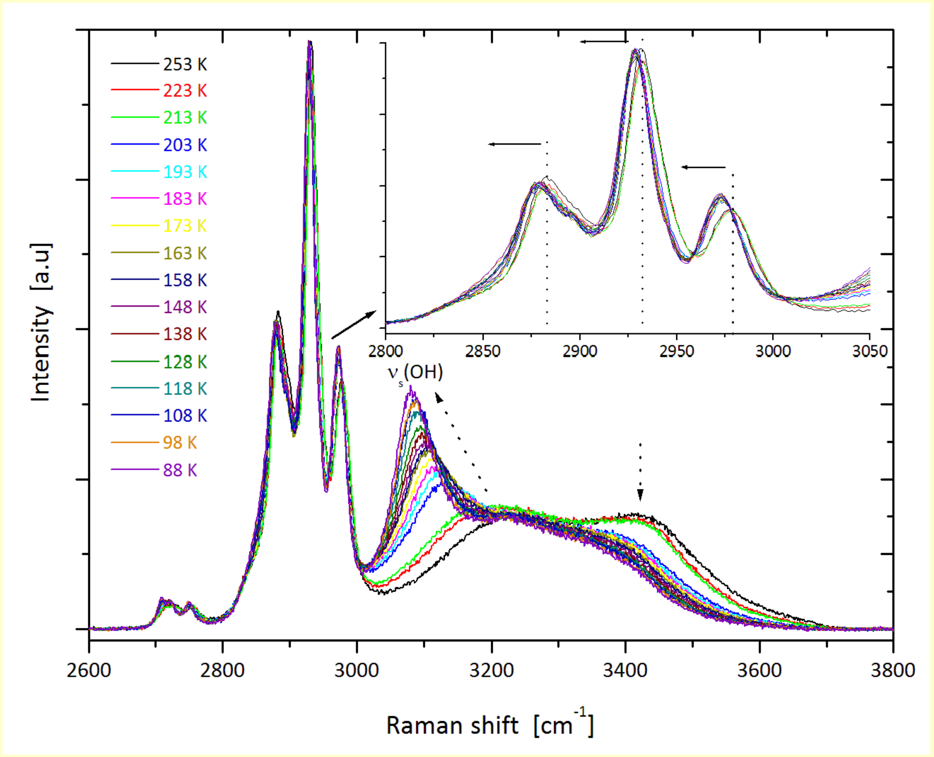
- Recorded during cooling and annealing

First solid formed is ice → *8.7 wt%*

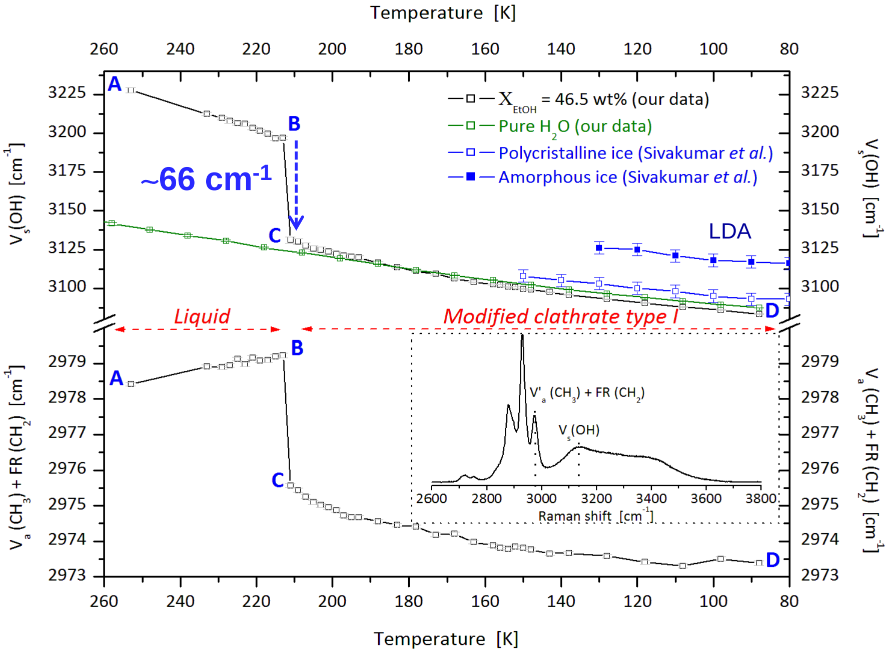
First solid formed is ethanol hydrate → *~ 46 wt%*

2 concentrations :

Freezing of ethanol aqueous solution : 46 wt% EtOH



Freezing of ethanol aqueous solution : 46 wt% EtOH



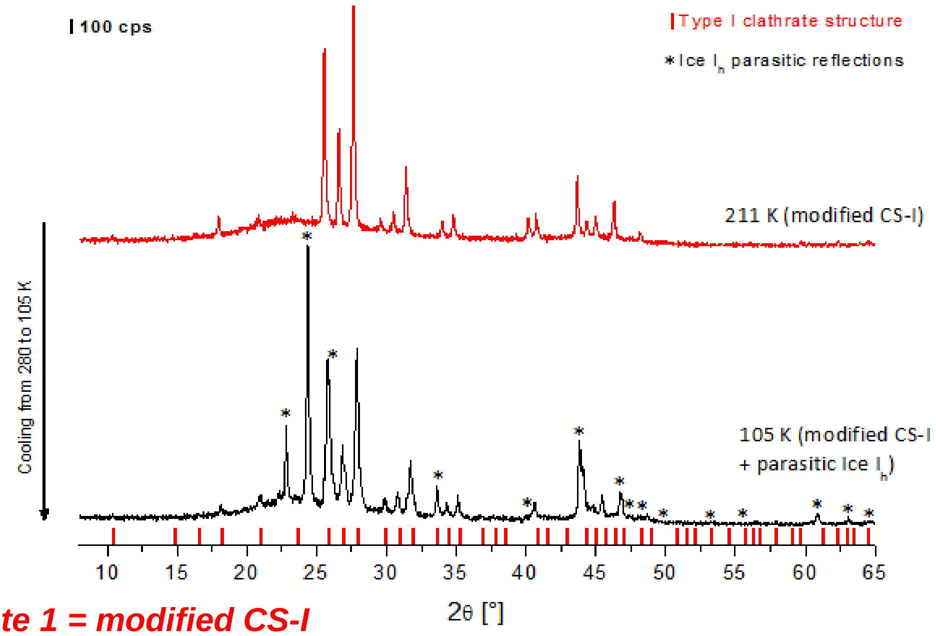
"C-H" Evolution

- From **213 K and 211 K** (B to C): ***hydrate 1***
- Followed by ***H bond strengthening*** from 211 to 88 K (C to D)

O-H Evolution :

- From 253 to 213 K (A to B) : *H-bonds strengthening*
- From **213 to 211 K** (B to C) : ***Hydrate 1***
- From 211 to 88 K (C to D) : *H-bonds strengthening*

Freezing of ethanol aqueous solution : 46 wt% EtOH



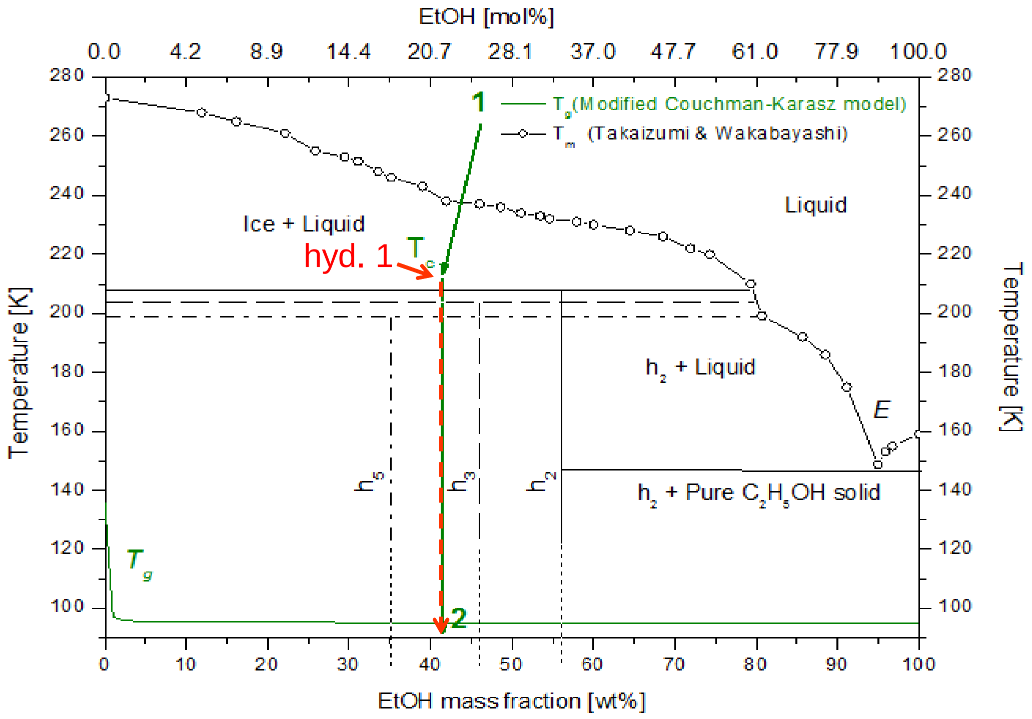
Hydrate 1 = modified CS-I

Cubic S.G.: Pm3m

a = 12.1 Å at 211 K

Hyd. 1 ~ E · (4.75-7.67) H_2O

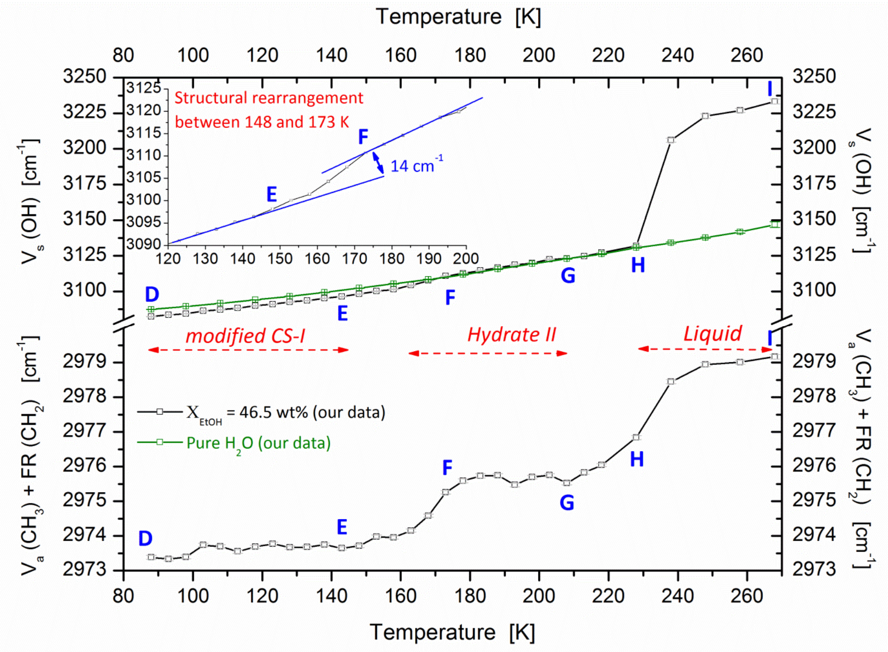
Most likely 7.67 = empty small cages



hydrate 1: modified CS-I

- hyd.1 formed on cooling at 211 K

Annealing of ethanol aqueous solution: 46wt%



"C-H" Evolution

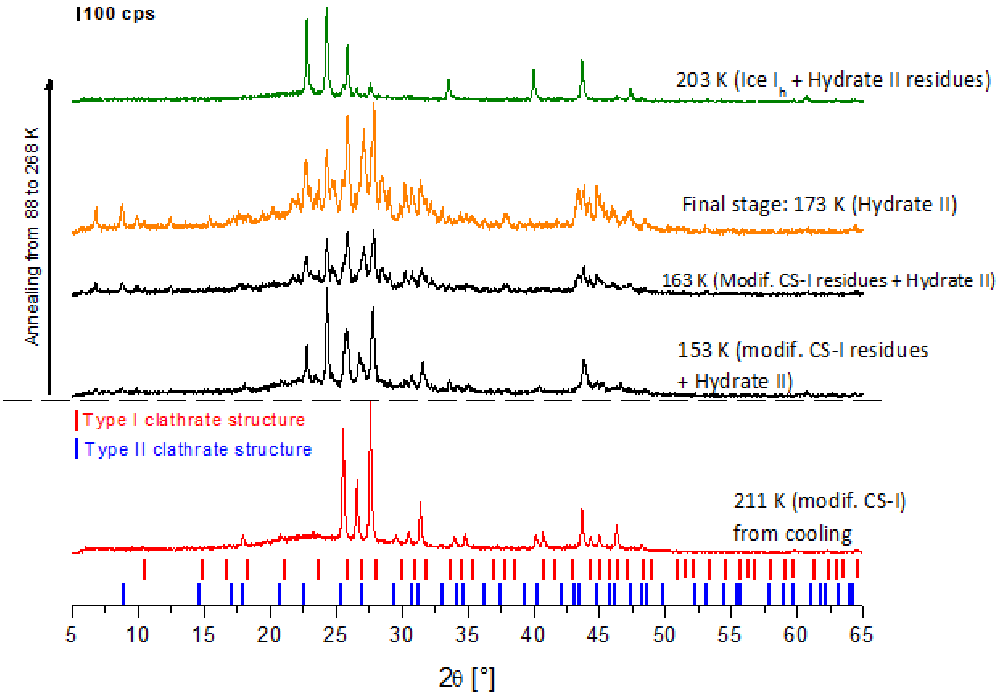
- From 88 to 143 K (D to E) : ***Hydrate 1***
- From **143 to 173 K** (E to F) : ***hyd.1 → hyd 2***
- From 173 to 208 K (F to G) : ***hydrate 2***
- From 208 to 268 K (G to H and I) : *I_h melting*

O-H Evolution :

- From 88 to 143 K (D to E): *H-bond softens +* ***hyd. 1***
- From **143 to 173 K** (E to F) : ***hyd.1 → hyd 2***
- From 173 to 208 K (F to G) : *H bond softens +* ***hyd 2***
- From 208 to 268 K (G to H and I) : *I_h melting*

Annealing of ethanol aqueous solution: 46wt%

Facq et al., J.Phys.Chem.A, 2013 (in press)



Hyd. 1 → Hyd. 2 at 143-173 K

Hyd. 2 → Ice Ih at ~ 198 K

Hydrate 2

Monoclinic S.G.: P2/m

$a = 20.78$ Å $b = 7.01$ Å $c = 12.78$ Å

Hyd. 2 ~ E · 5 H_2O

T_m = melting of ice

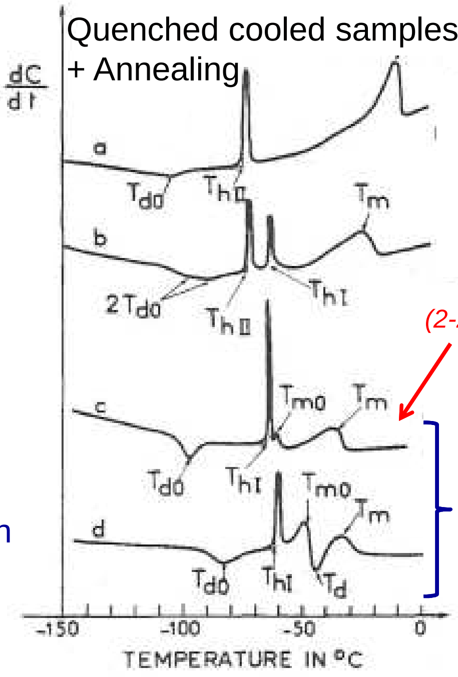
T_{hx} = melting of hydrate x

Combined XRD & DSC

Quench-cooled 45 wt% sample at 77 K

From XRD:
Cubic clathrate CS-I formed at 77 K
clathrate cubic structure I
SG: $Pm\bar{3}n$
Lattice: 11.9 Å at 77 K

From DSC: slow cooling ~ 0.6°C/min
Cubic clathrate CS-I at T_{d0} ~ 172 K
Decomposition at T_{h1} ~ 208 K

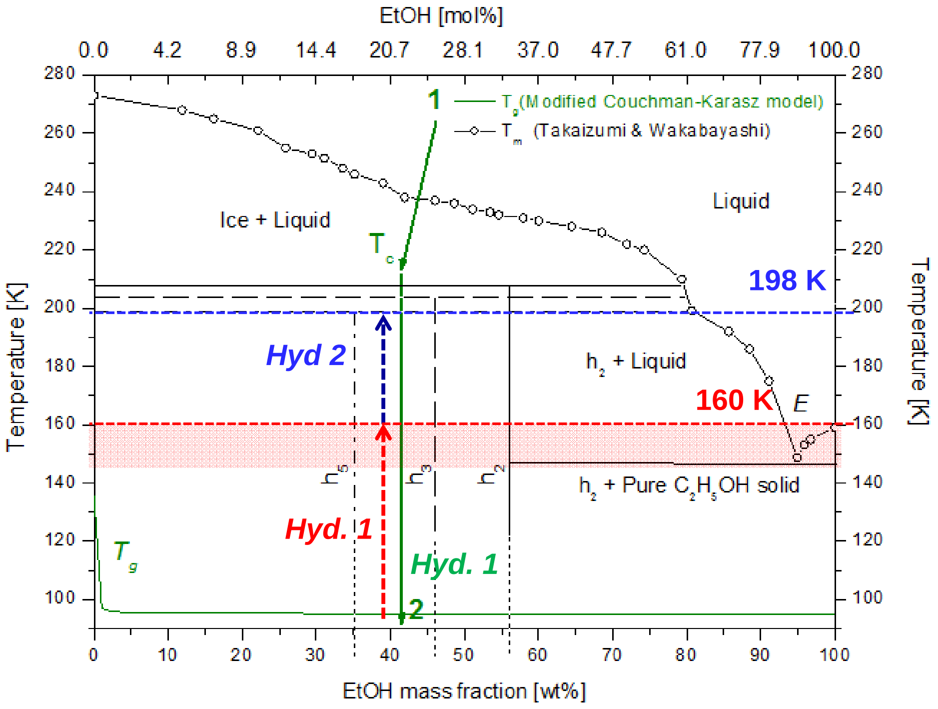


Quenched cooled samples at 120 K
+ Annealing

(2-2.5°/min)

Thermograms in solutions of 35wt% - 70 wt%

Boutron & Kaufmann, JCP, 1978



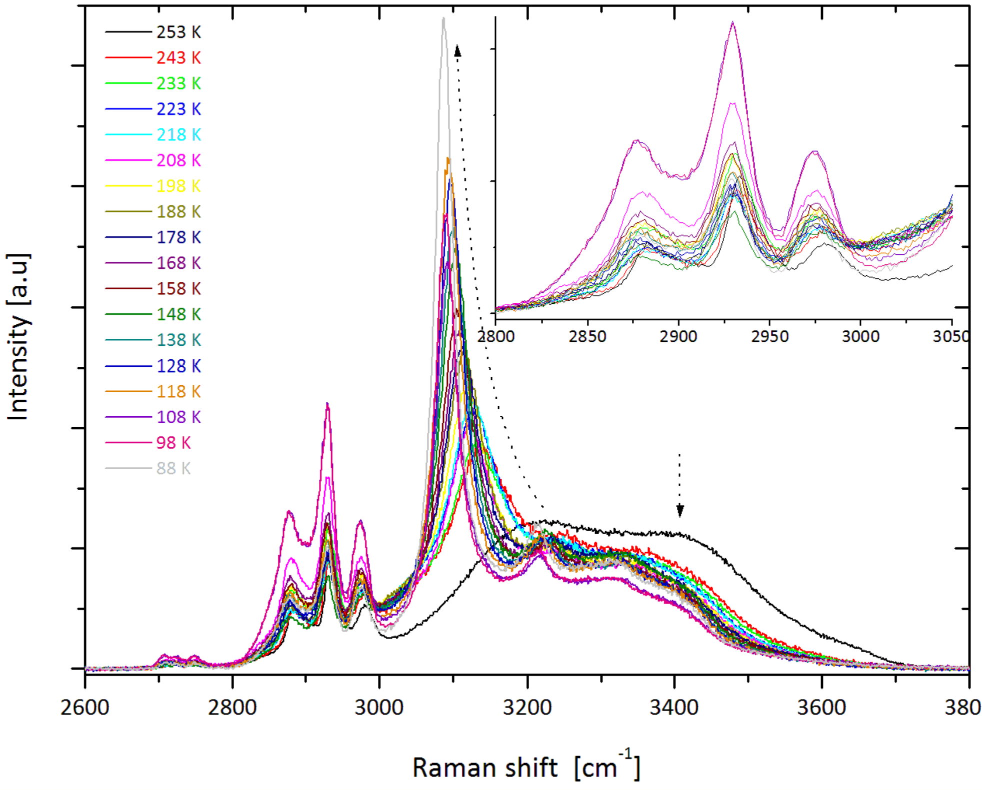
Hydrate 1: modified CS-1, E ·7.67H_2O

- hyd.1 formed on cooling at 211 K
- stable on annealing from 88 K to 143 K
- hyd.1 → hyd.2 between **143 K** and **173 K**

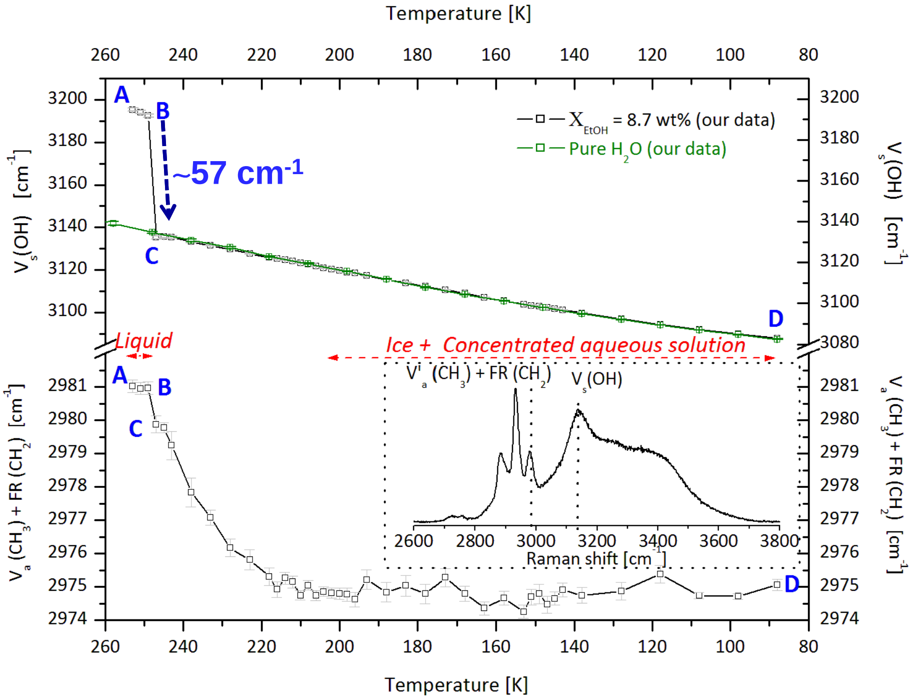
Hydrate 2: monoclinic, E ·5 H_2O

- Stable between 173 K and 198 K
- Decomposition at 198 K

Freezing of ethanol aqueous solution : 8.7 wt% EtOH



Freezing of ethanol aqueous solution : 8.7 wt% EtOH



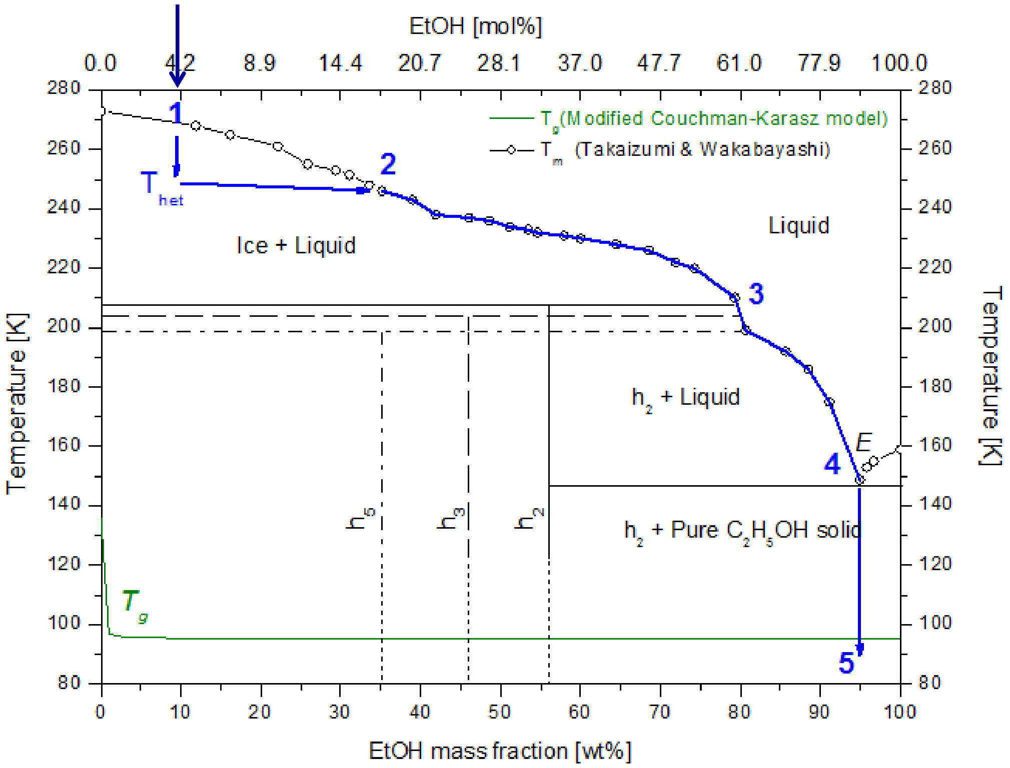
"C-H" Evolution

- From 253 to 249 K (A to B) : *H-bond strengthening*
- From 249 to 247 K (B to C) : *Ice I_h + aq. sol EtOH*
- From 247 to 200 K : *Ice Ih + EtOH ↗ in aq. sol.*

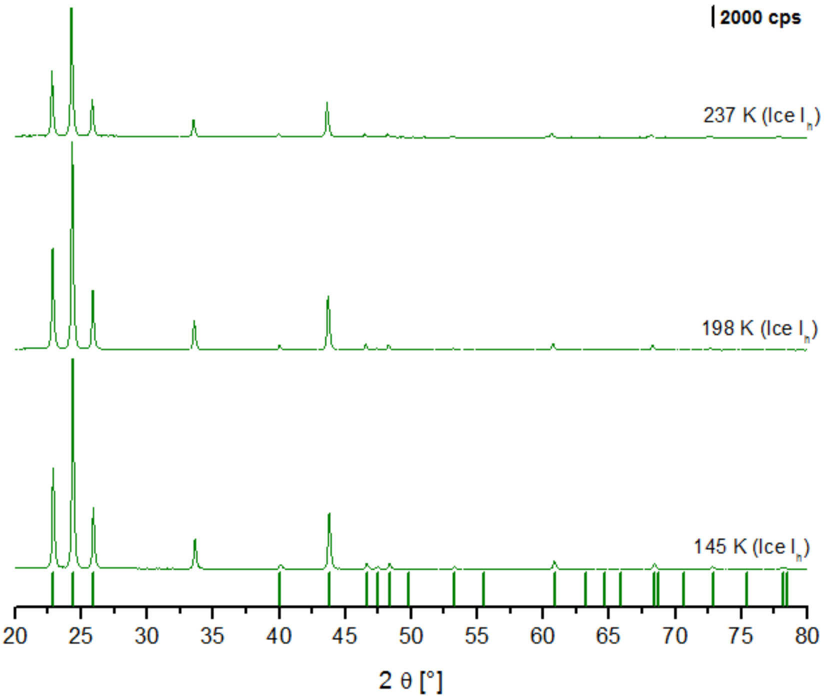
O-H Evolution :

- From 253 to 249 K (A to B) : *H-bond strengthening*
- From 249 to 247 K (B to C) : *Ice I_h + aq. sol. EtOH*
- From 247 to 88 K (C to D) : *H-bond strengthening*

Ethanol-Water at 8.7 wt%



Freezing *of* ethanol aqueous solution : 8.7 wt%, 21 wt% EtOH



Ice Ih formed on cooling at ~ 237 K. No other phases than ice down to 100 K

Combined XRD & DSC

Quench-cooled 25 wt% sample at 77 K

From XRD:

- ice Ih formed on cooling at 77 K
- Modified clathrate CS-II formed on annealing at 180K

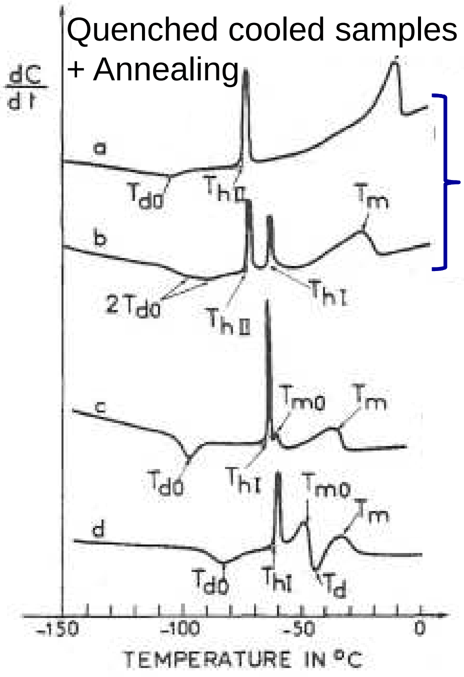
From DSC:

Modified CS-II at T_{d0} ~ 169 K

Unknown phase at T_{d01} ~ 150 K

T_m = melting of ice

T_{hx} = melting of hydrate x

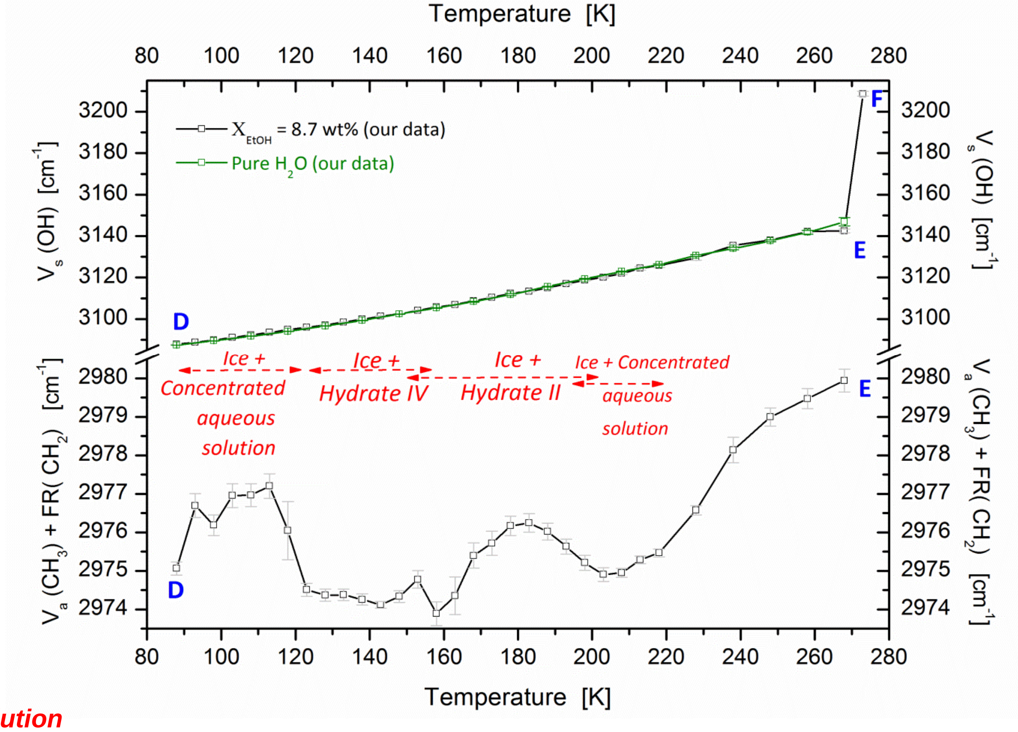


Quenched cooled samples at 120 K + Annealing

Thermograms in solutions of 20wt% - 32 wt%

Boutron & Kaufmann, JCP, 1978

Annealing of ethanol aqueous solution: 8.7 wt% EtOH



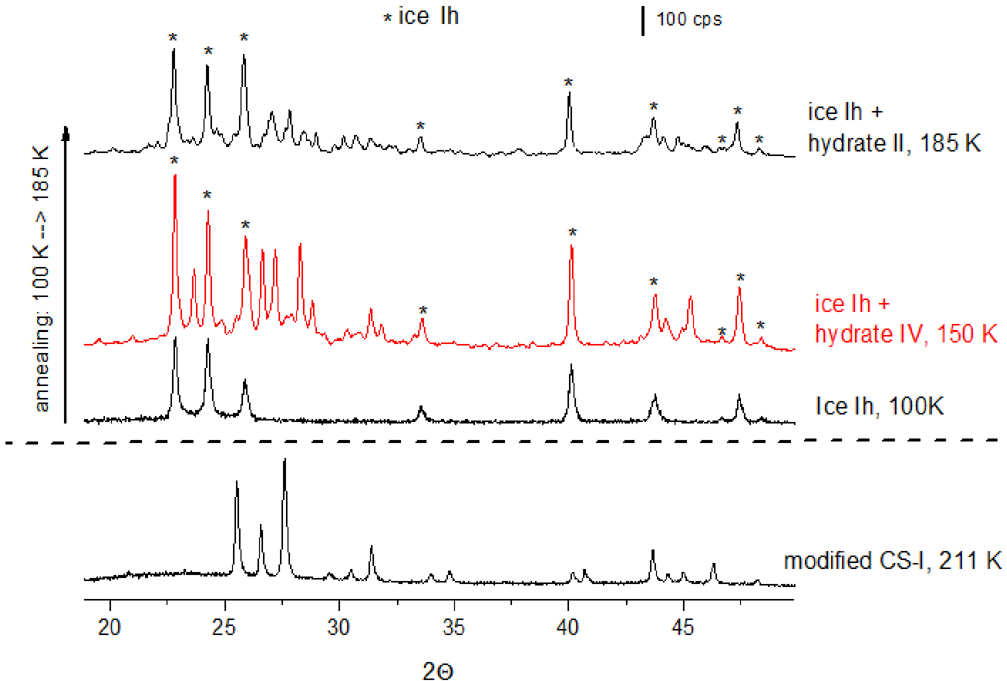
"C-H" Evolution

- From 88 to 113 K (A to B) : ice Ih + *H-bond softens*
- From 113 to 123 K: ice Ih+ Hydrate IV
- From 158 to 183 K: ice Ih + Hydrate II
- From 208 to 258 K : melting of ice Ih & evaporation of EtOH

O-H Evolution :

- From 88 to 268 K (D to E) : *H bond softening*
- From 268 to 273 K (E to F) : *I_h melting*

Annealing of ethanol aqueous solution: 8.7 wt%, 21 wt% EtOH



Ice Ih → (Ice Ih + Hyd. IV) at 150 K

(Ice Ih + Hyd. IV) **→ (Ice Ih + Hyd. 2) at 158 K**

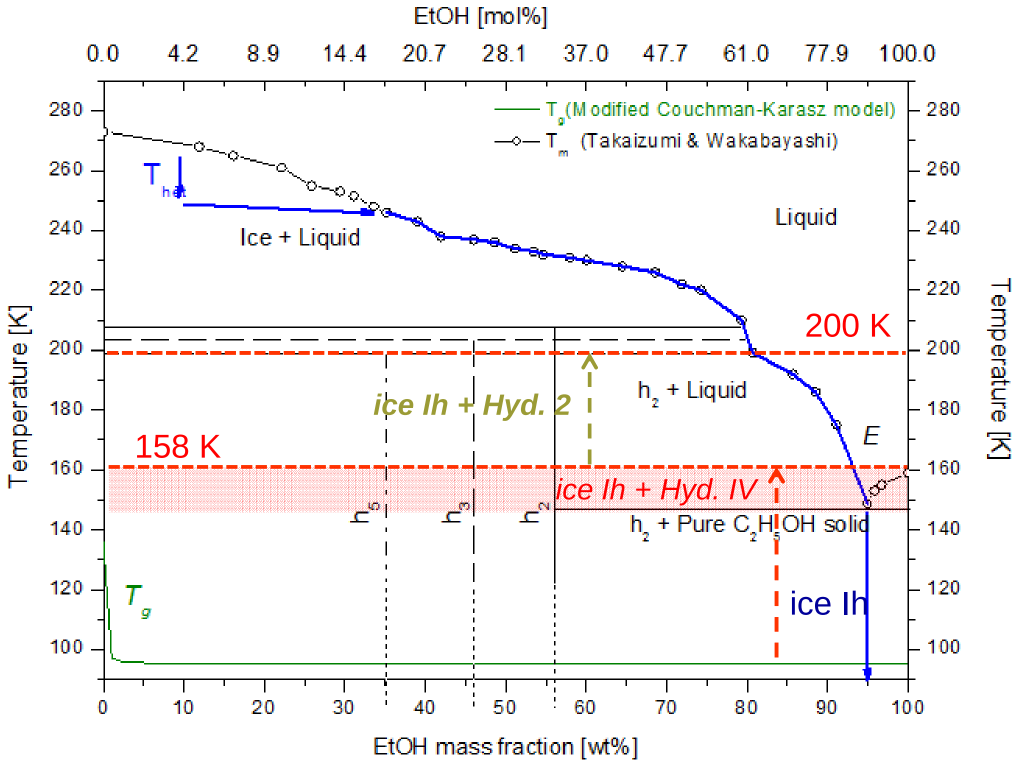
(Ice Ih + Hyd. 2) → Ice Ih at ~ 200 K

Hydrate IV

Orthorhombic S.G.: Pmmm

$a = 16.37$ Å $b = 3.86$ Å $c = 3.34$ Å

Hyd. 2 ~ E · 5 H_2O



Ice Ih first formed on cooling

Hydrate IV formed on annealing 88 K → 145 K

Hydrate 2 formed on annealing 158 K → 200 K

Conclusion

1°) The freezing of liquid droplets containing *volatile chemical solutes* shows a distinct behavior in comparison to that with *high molecular weight solutes (glasses)*:

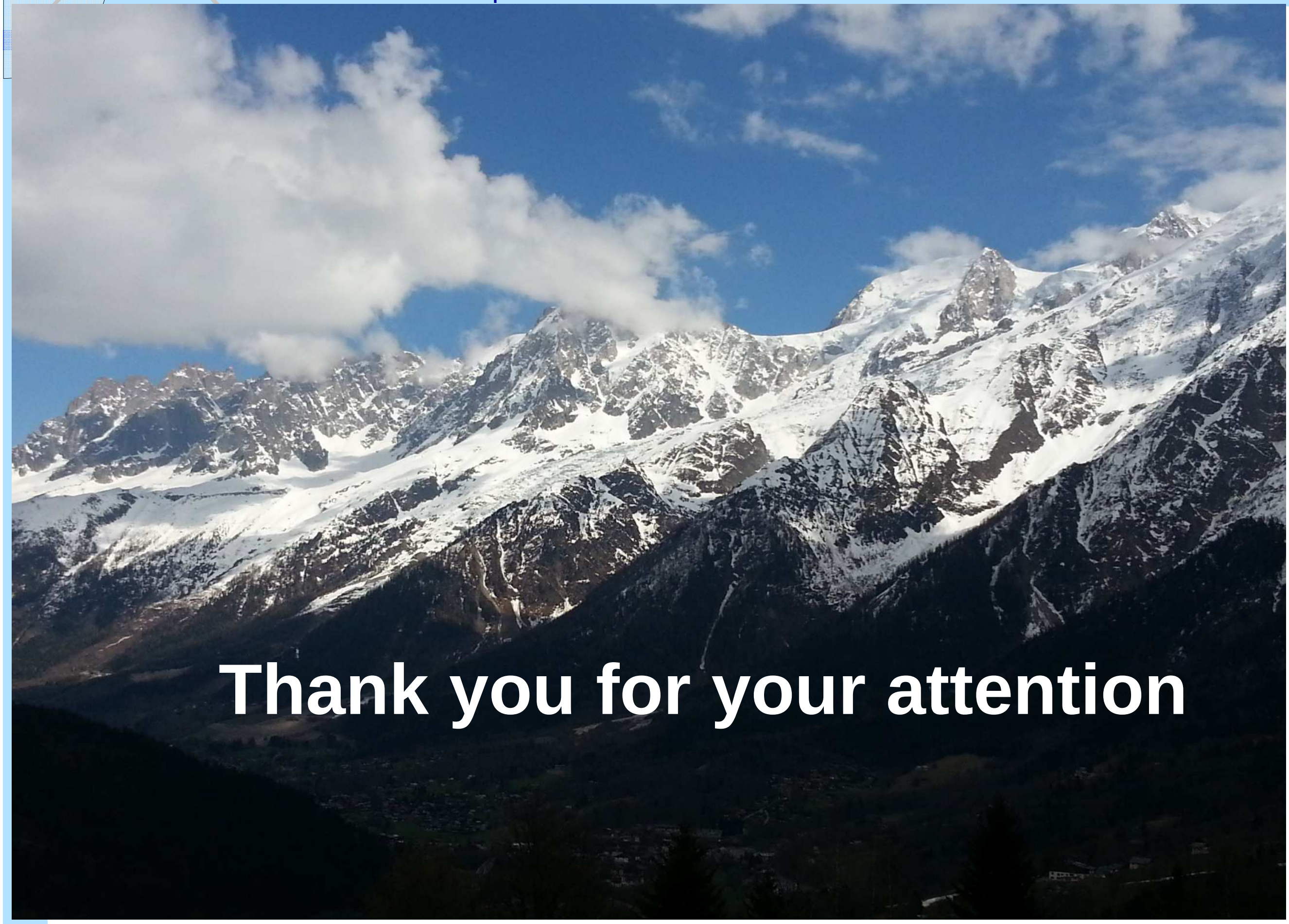
- ☐ At low X: *ice Ih + concentrated liquid pockets* **+** (distinct hydrates) **on annealing**
- ☐ At high X: *1 composition* = "**modified CS-I**" + liquid solution + hydrate II **on annealing**

2°) EtOH-Water phase diagram re-investigated: *H-bonds modification upon hydrate formation*, a modified CS-I (hydrate 1) instead CS-1, the modified CS-II probably does not exist, Zelenin's attribution of h_5 is not CS-1 but hydrate 2 (monoclinic)

3°) *New ethanol hydrates characterized*

- ☐ Hydrate III at 183 K, (Vapor deposition at high X_{EtOH} content)
- ☐ Hydrate IV at 150 K (freezing of droplets of low X_{EtOH})

4°) Same behavior expected for other VOCs: methanol, butanol, propanol, i.e.
→ crystallization and no glass transition expected



Thank you for your attention