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

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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:
  - Ability of the cryoprotector to preserve H-bonds within the solvent upon freezing
  - The amount of free water molecules within a biological cells reduces during the ice growth \(\rightarrow\) the cryoprotectant should prevent a substantial fraction of water molecules to freeze
  - 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
  - Property of cryo-protector: reduction of the water-cryoprotector eutectic by maintaining a high molecular mobility at low temperature \(\rightarrow\) keep the biological fluids or cellular cytoplasm liquids even at low temperature

\[\text{Morris & Clarke, Acad. Press, 1981}\]

\[\rightarrow\] alcohol-water system can be regarded as model studies for future applications of cryoprotection
The atmosphere is a multi-phase medium:
- Common phases of H$_2$O 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

- 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)

Ice is inhibited
→ Glass is formed on cooling

(Zobrist et al., Atmos. Chem. Phys., 8, 5221, 2008)
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(\(\sim 0.5 - 5 \mu m\) aqueous droplet diameters)

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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

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**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, C₂H₅OH, CH₃COOH, 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**
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 sl (*CS-I*) and a modified sII (F4132)

*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

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: CH₄, Xe, CO₂,

Structure cubic type II
S.G. Fd3m,
lattice: a ~17 Å
Mean cavity radius:
SC - 3.91 Å
LC ~ 4.73 Å

Type II: N₂, O₂, Ar...

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

Eth-H₂O mixtures of compositions: 10, 20, 30 mol% - 60°C < T < 25 °C

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Combined NMR & IR study  
Mizuno et al., J.Phys.Chem. 1995

At low $X_{\text{EtOH}}$: $X_{\text{EtOH}} \uparrow$ → strength of H-bonds (Type A) $\uparrow$ 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 $X_{\text{EtOH}}$: as $X_{\text{EtOH}} \uparrow$ --> H-bonds of type D strength $\uparrow$ and H-bonds between water molecules increases

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

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

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

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

H+ (H2O)21

Equivalent structure as that of liquid water but with 1 EtOH

Water cluster structure is destroyed \( \rightarrow \) layered water – ethanol clusters

Water molecules are bridging the alcohol clusters

A: inherent water cluster structure Clathrate-like

B: layer structure Equal number of water/ethanol

C: alcohol self-aggregation structure at \( X_{\text{EtOH}} \sim 17 \text{ mol\%} \)

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

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

C-O vibrational mode spectral region

C-H vibrational mode spectral region

O-H vibrational mode spectral region

2 spectral regions of interest:

CH and OH stretching modes

Ethanol – Water mixtures:

CH stretching modes

Frequency decreases = Strengthening of H bonds

Raman spectroscopic study
II/ Ice particle crystallization: prediction from the phase diagram

\[ h_2 = E \cdot (2 \pm 0.2 \text{ H}_2\text{O}) \text{ stable (T}_{\text{dec}} = 208 \text{ K}) \]

\[ h_3 = E \cdot (3.2 \pm 0.3 \text{ H}_2\text{O}) \text{ metastable (T}_{\text{dec}} = 204 \text{ K}) \]

\[ h_5 = E \cdot (4.9 \pm 0.4 \text{ H}_2\text{O}) \text{ metastable (T}_{\text{dec}} = 198 \text{ K}) \]
Ethanol-Water at 46 wt%:

- First solid formed during cooling is ice I 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 form and a part of the solution crystallizes around 208 K.
- At point 4, another part crystallizes around 149 K.
- At point 5, crystallization of pure solid ethanol should happen.
- The ethanol content of the solution increases upon further cooling.

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.

**Aqueous solution of 8.7 wt%:**

- First solid formed during cooling is ice I at 248 K.
- Phase separation between ice and an aqueous solution of ethanol.
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Results

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

Experimental set-up

Droplets of ethanol aqueous solutions
- \( r \approx 500 - 700 \mu m \)
- 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
- Two concentrations:
  - 8.7 wt%
  - \( \approx 46 \) wt%
Freezing of ethanol aqueous solution: 46 wt% EtOH

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

"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)
Freezing of ethanol aqueous solution: 46 wt% EtOH

Hydrate 1 = modified CS-I
Cubic S.G.: Pm3m
\( a = 12.1 \text{ Å} \) 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): **hydr.1 → hydr.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 + **hydr.1**
- From 143 to 173 K (E to F): **hydr.1 → hydr.2**
- From 173 to 208 K (F to G): H bond softens + **hydr.2**
- From 208 to 268 K (G to H and I): **I_h melting**

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

**Hydrate 2**
- Monoclinic S.G.: P2/m
- \( a = 20.78 \, \text{Å} \), \( b = 7.01 \, \text{Å} \), \( c = 12.78 \, \text{Å} \)
- **Hydr. 2** \( \sim \) E \( \cdot \) 5 H\(_2\)O
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\text{3}n
Lattice: 11.9 Å at 77 K

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

**Boutron & Kaufmann, JCP, 1978**

**Hydrate 1:** modified CS-1, \( E \cdot 7.67\text{H}_2\text{O} \)

- hyd.1 formed on cooling at 211 K
- stable on annealing from 88 K to 143 K
- hyd.1 \( \rightarrow \) hyd.2 between 143 K and 173 K

**Hydrate 2:** monoclinic, \( E \cdot 5 \text{H}_2\text{O} \)

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

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\( T_m = \) melting of ice
\( T_{hx} = \) melting of hydrate x
Freezing of ethanol aqueous solution: 8.7 wt% EtOH

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 $I_h$ + 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
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 $T_{d0} \sim 169$ K
- Unknown phase at $T_{d01} \sim 150$ K

$T_m = \text{melting of ice}$

$T_{hx} = \text{melting of hydrate } x$

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): $l_i$ melting
Annealing of ethanol aqueous solution: 8.7 wt%, 21 wt% EtOH

Hydrate IV
Orthorhombic S.G.: Pmmm

\[ a = 16.37 \text{ Å} \quad b = 3.86 \text{ Å} \quad c = 3.34 \text{ Å} \]

Ice Ih \( \rightarrow \) (Ice Ih + Hyd. IV) at 150 K
(Ice Ih + Hyd. IV) \( \rightarrow \) (Ice Ih + Hyd. 2) at 158 K
(Ice Ih + Hyd. 2) \( \rightarrow \) Ice Ih at \( \sim \) 200 K

Ice Ih first formed on cooling
Hydrate IV formed on annealing 88 K \( \rightarrow \) 145 K
Hydrate 2 formed on annealing 158 K \( \rightarrow \) 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 h5 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