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Y Coulier, A Lowe, Jean Yves Coxam, Karine Ballerat-Busserolles. Liquid-liquid equilibriums in aqueous solutions of demixing amines loaded with gas for CO₂ capture processes. ECCE10+ECAB3+EPIC5, Sep 2015, NICE, France. hal-01226161

HAL Id: hal-01226161

<https://hal.science/hal-01226161>

Submitted on 8 Nov 2015

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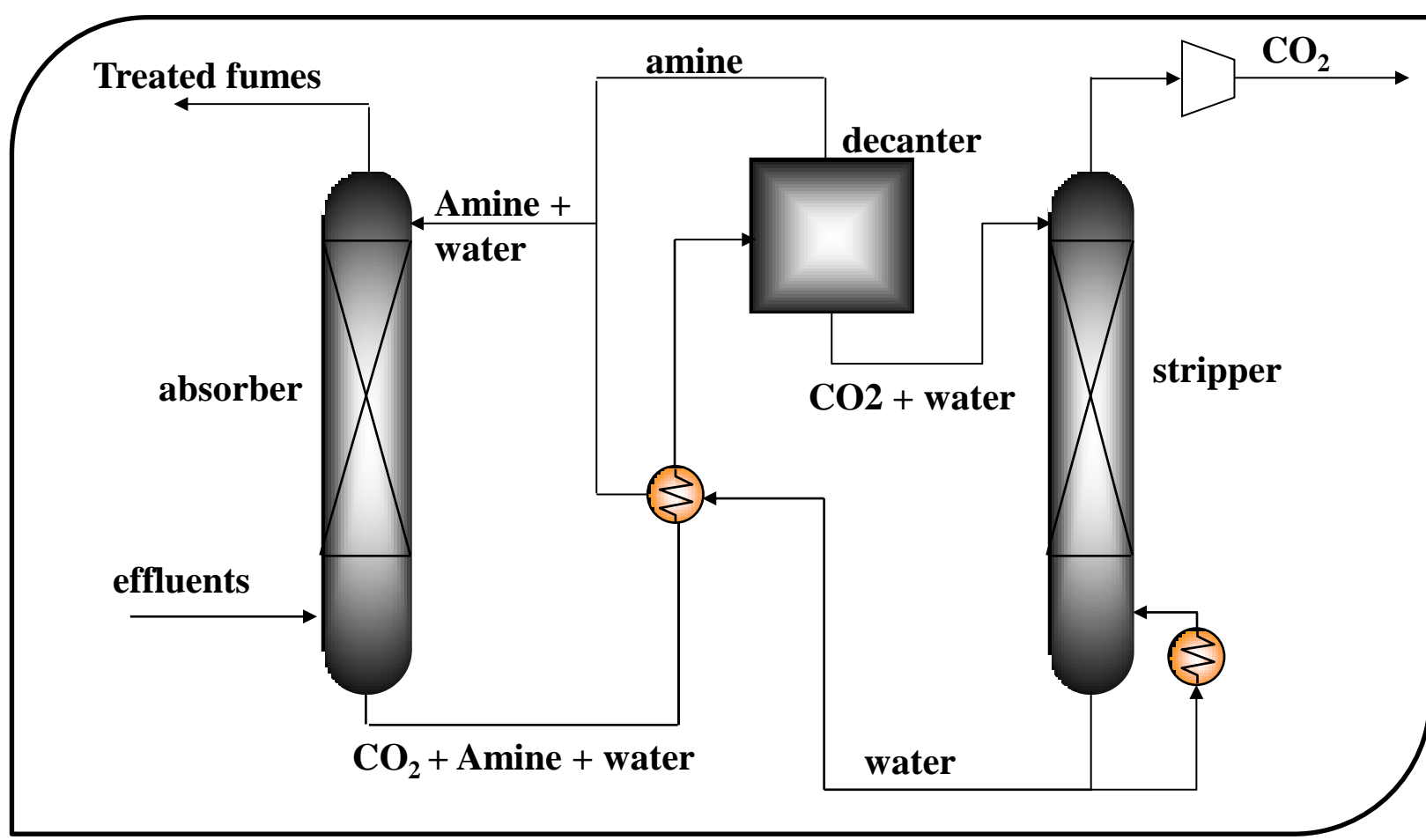
Liquid-liquid equilibria in aqueous solutions of demixing amines loaded with gas for CO₂ capture processes

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Introduction

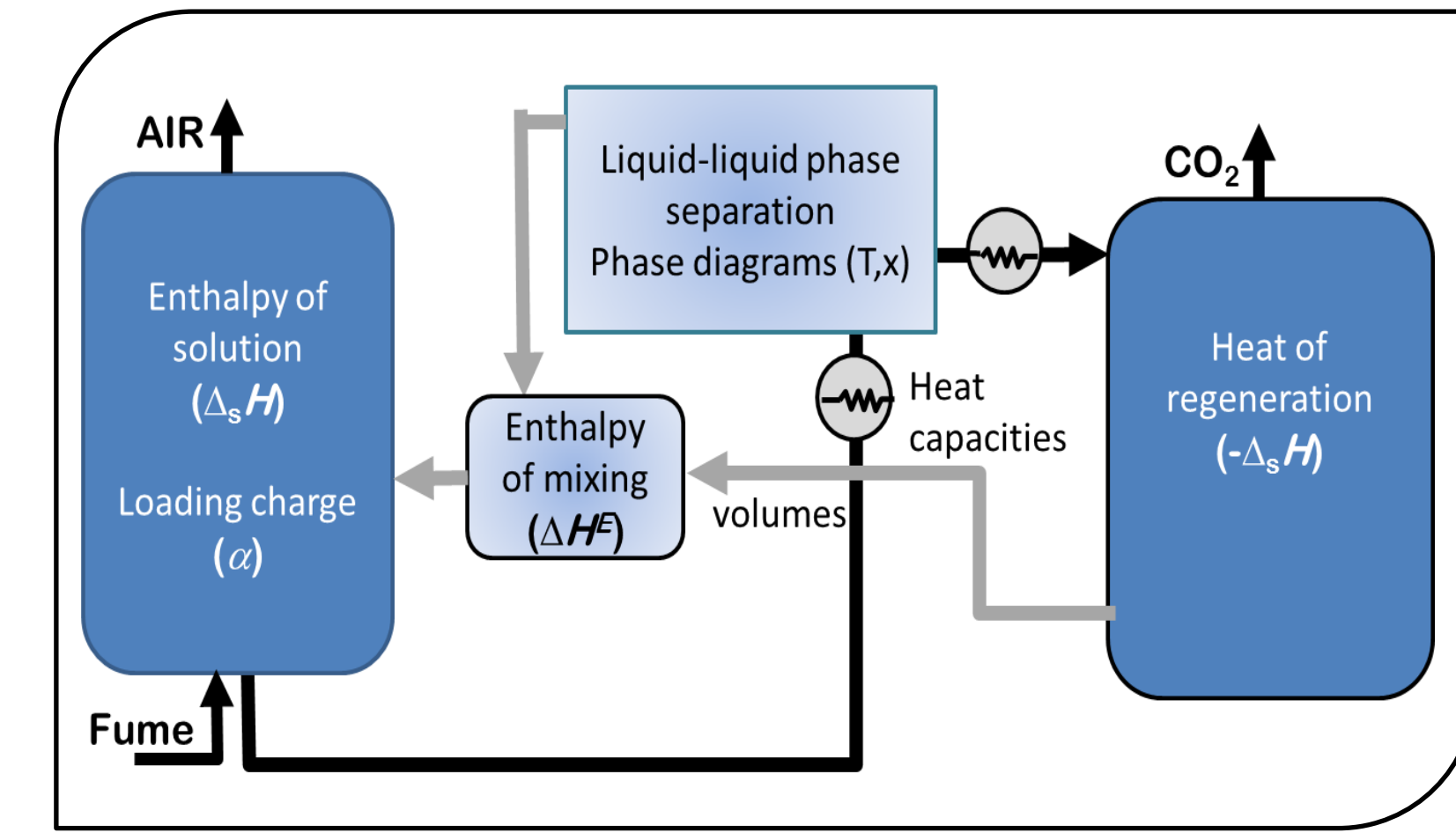
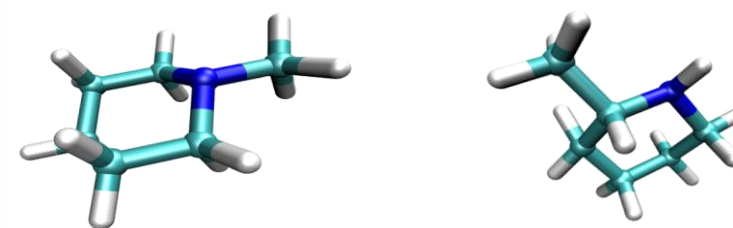


Aqueous solutions of amines are selective carbon dioxide (CO₂) absorbents [1,2]. They are used in CO₂ capture processes working on absorption/desorption cycles.

Demixing amines may be valuable for new capture processes [3]. These amines demonstrate a liquid-liquid phase separation [4] which can be used to reduce energy costs of desorption (absorbent regeneration).

Aim of this paper : presentation of a method developed in the laboratory to study precisely the LLE in the binary solutions water + amines and the ternary mixtures water+amine+CO₂, as a function of the pressure and the CO₂ loading charge.

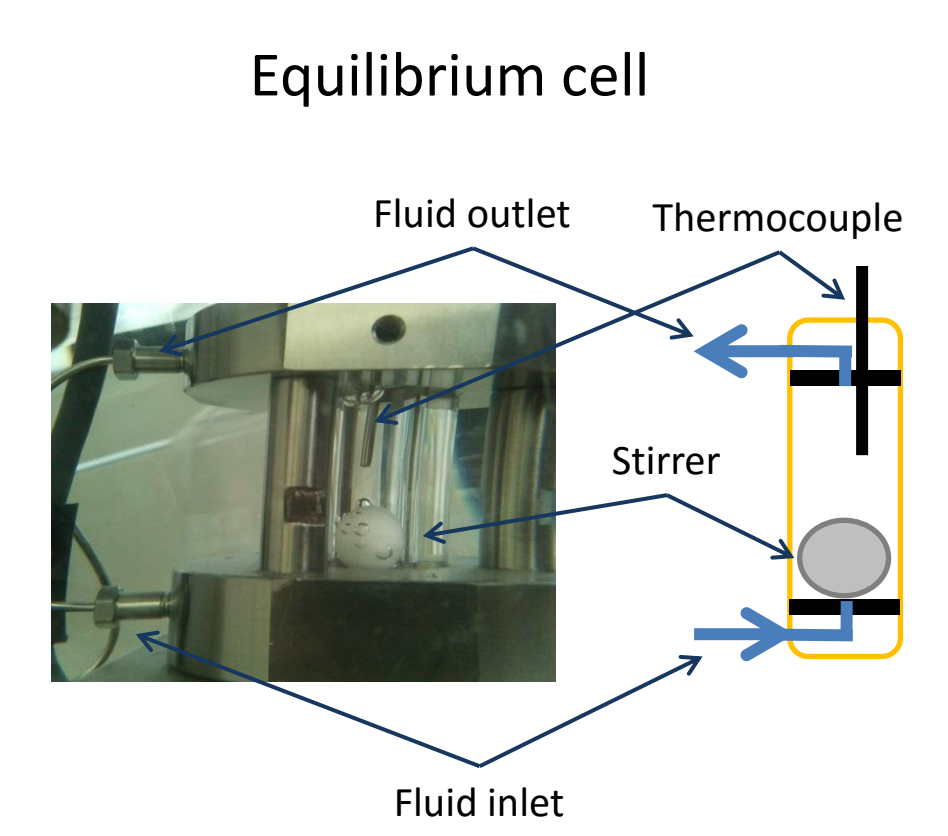
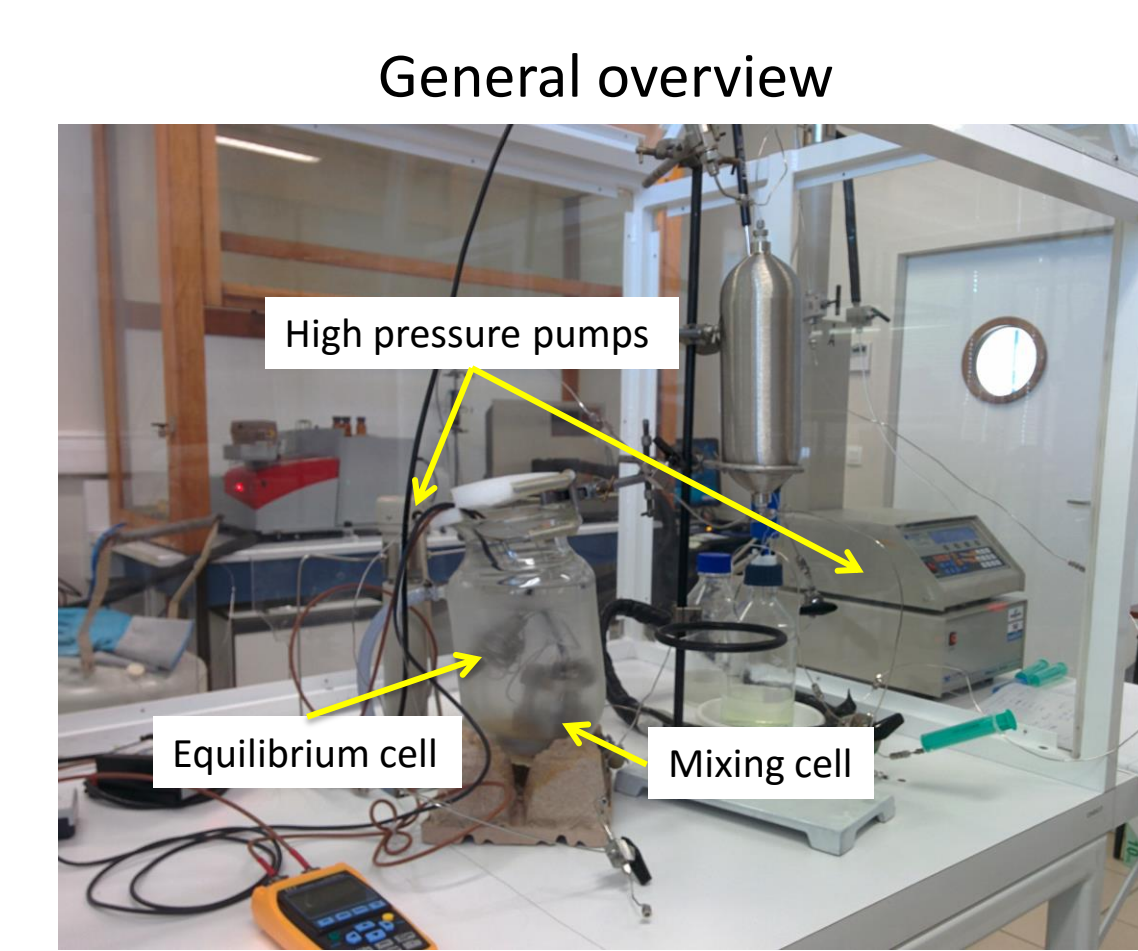
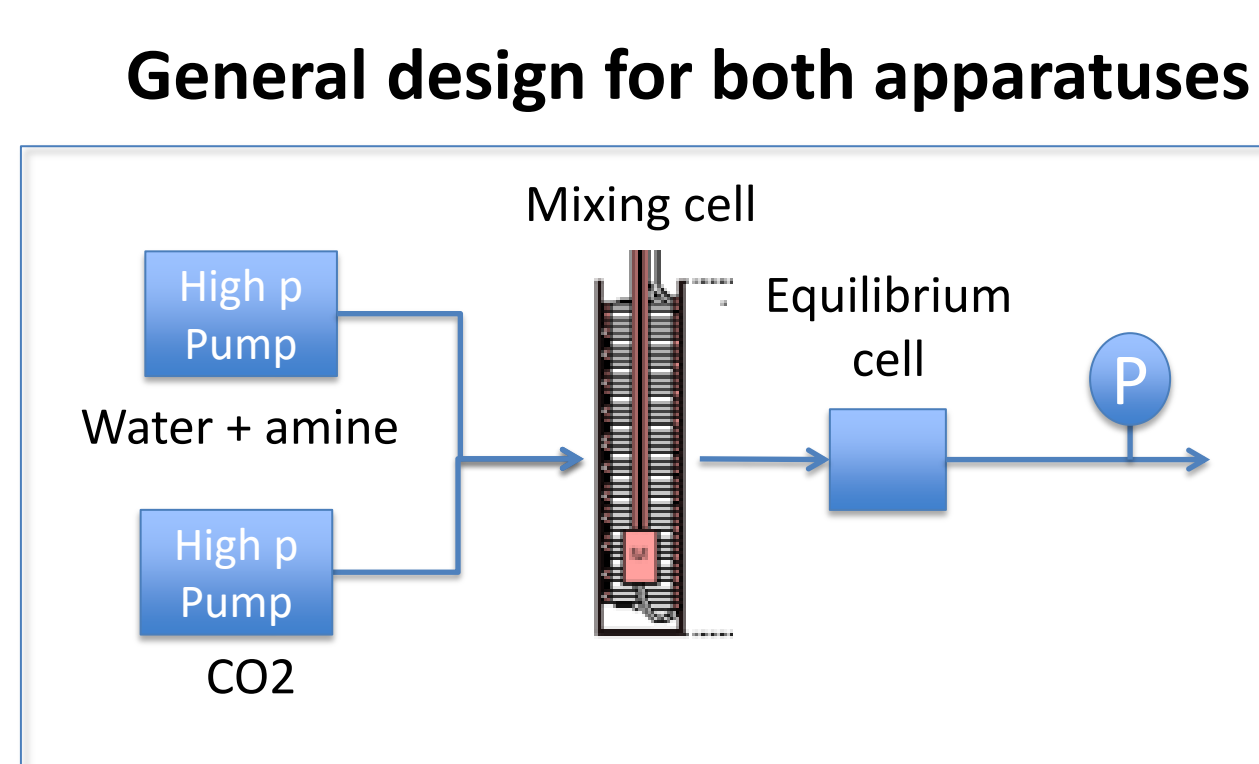
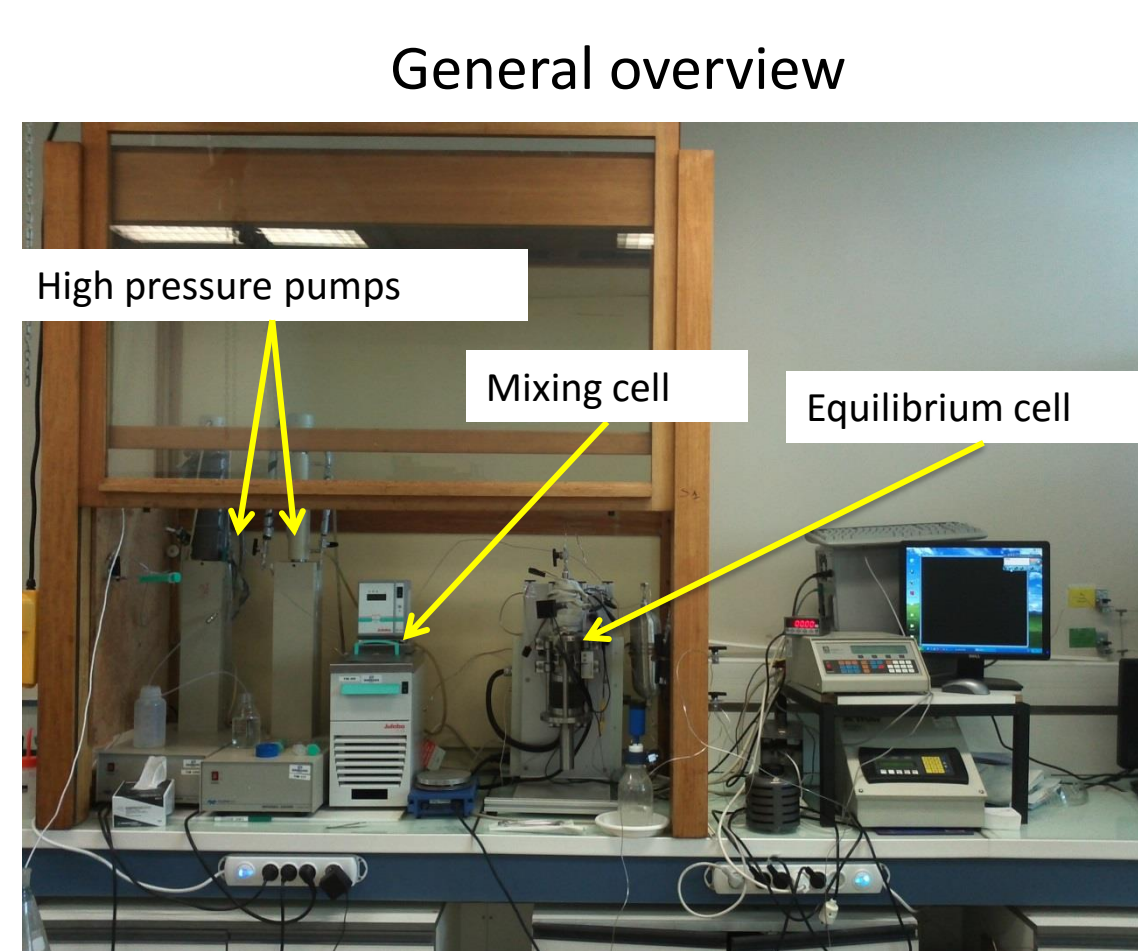
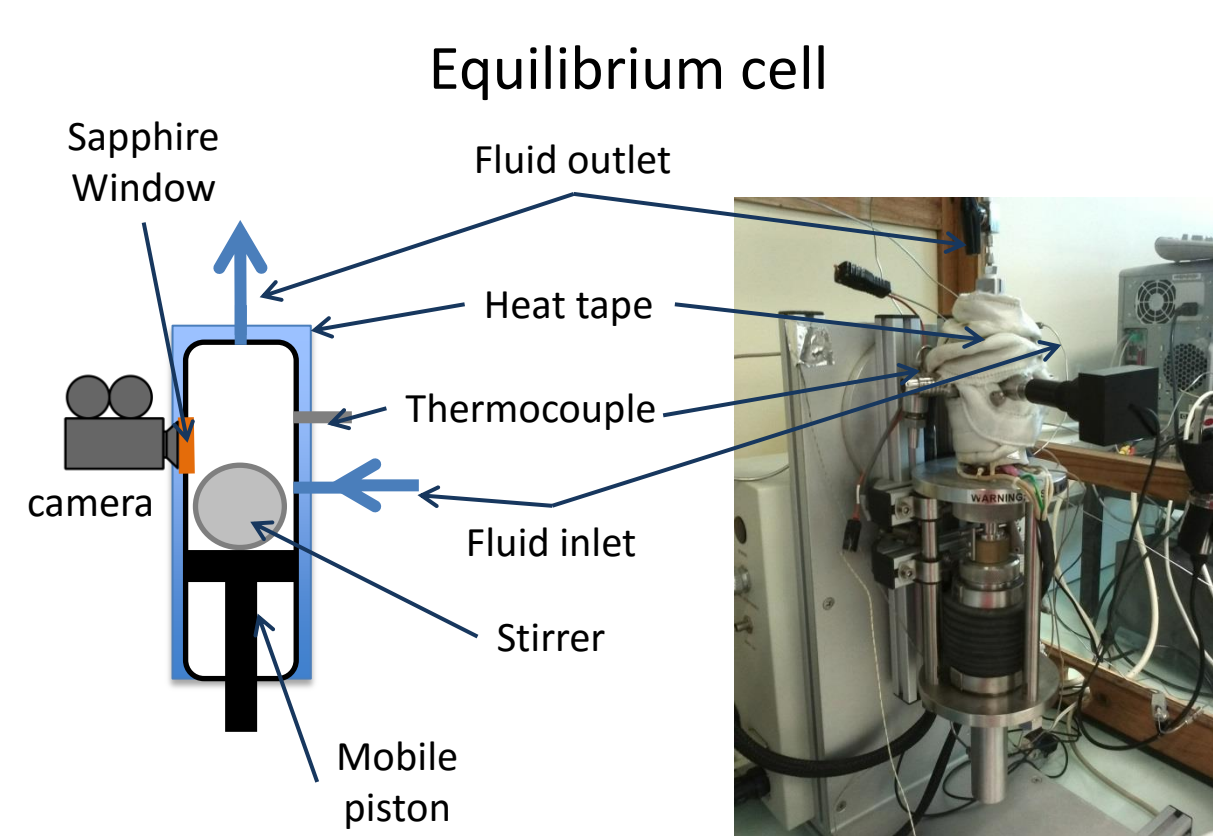
Amines : N-methylpiperidine
2-methylpiperidine



methods

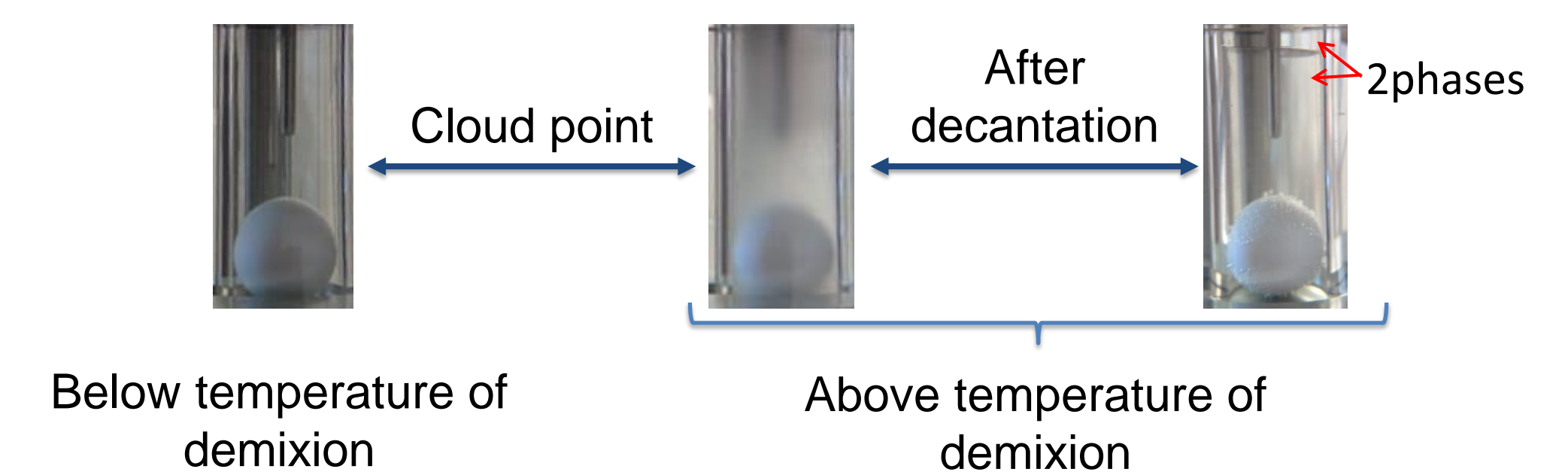
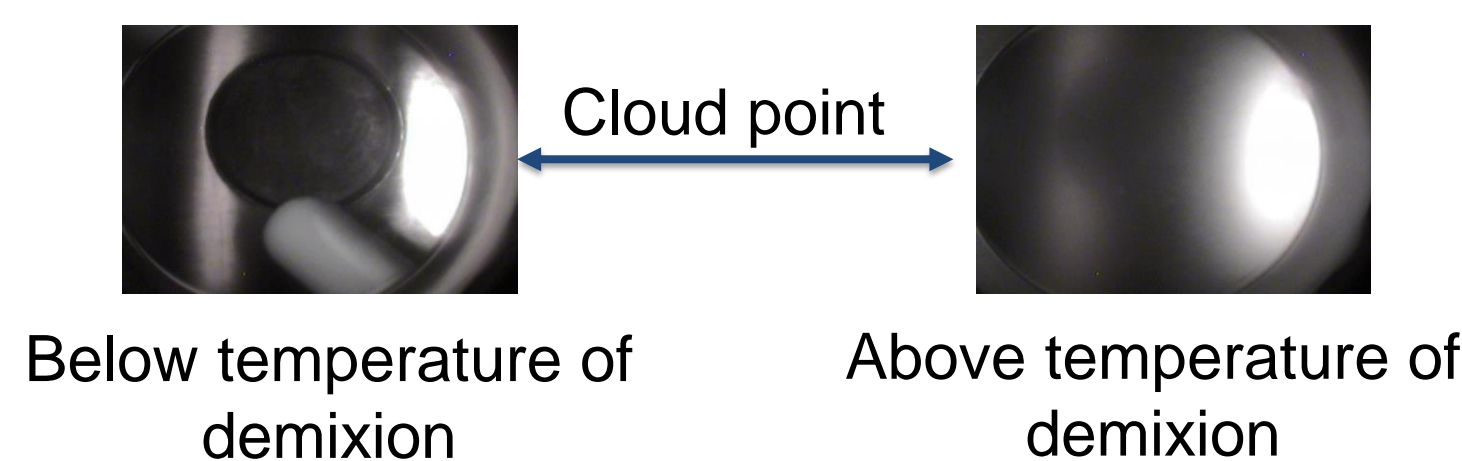
Hastelloy cell : THAR SPM20

Sapphire Cell



Comparison of the apparatuses

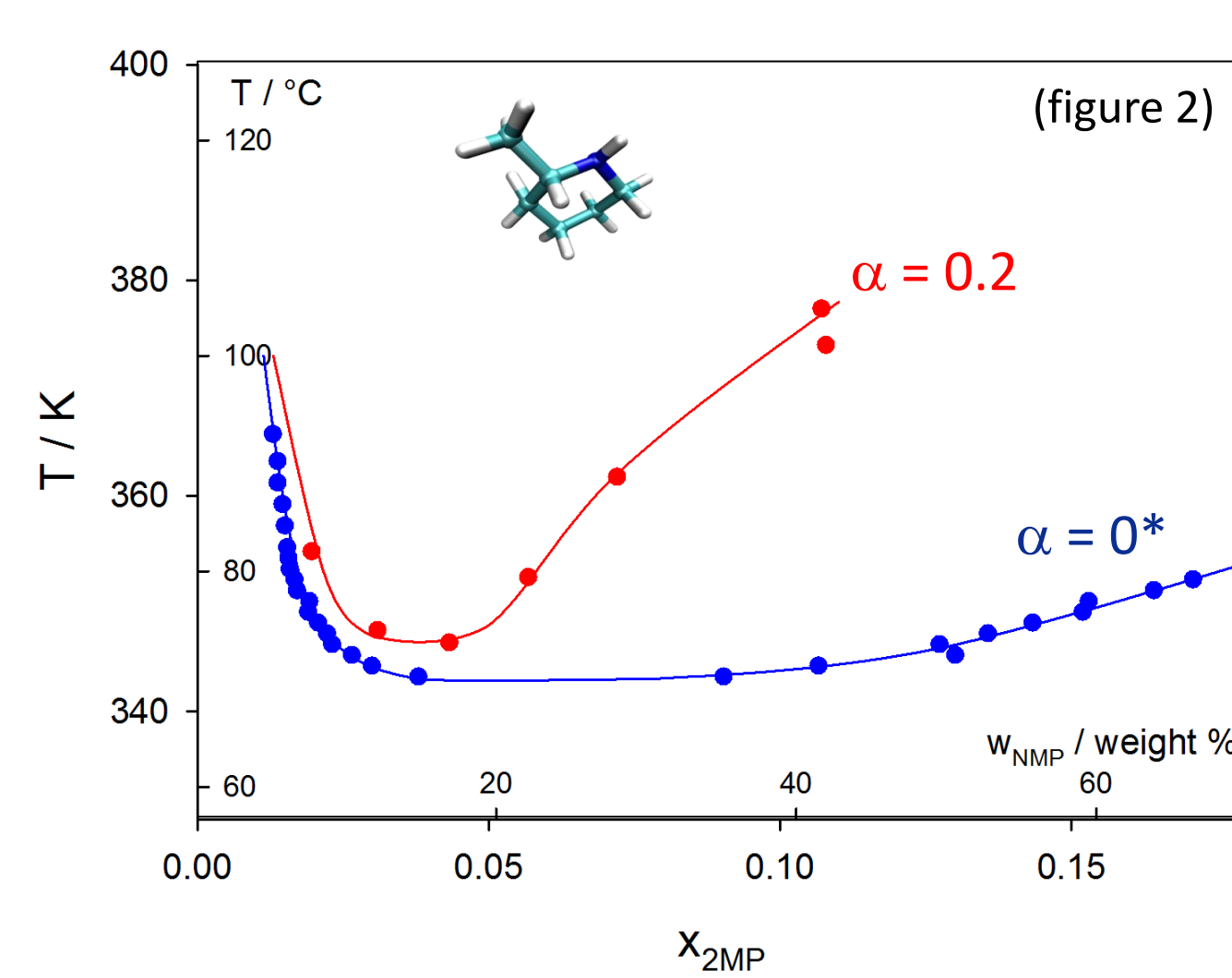
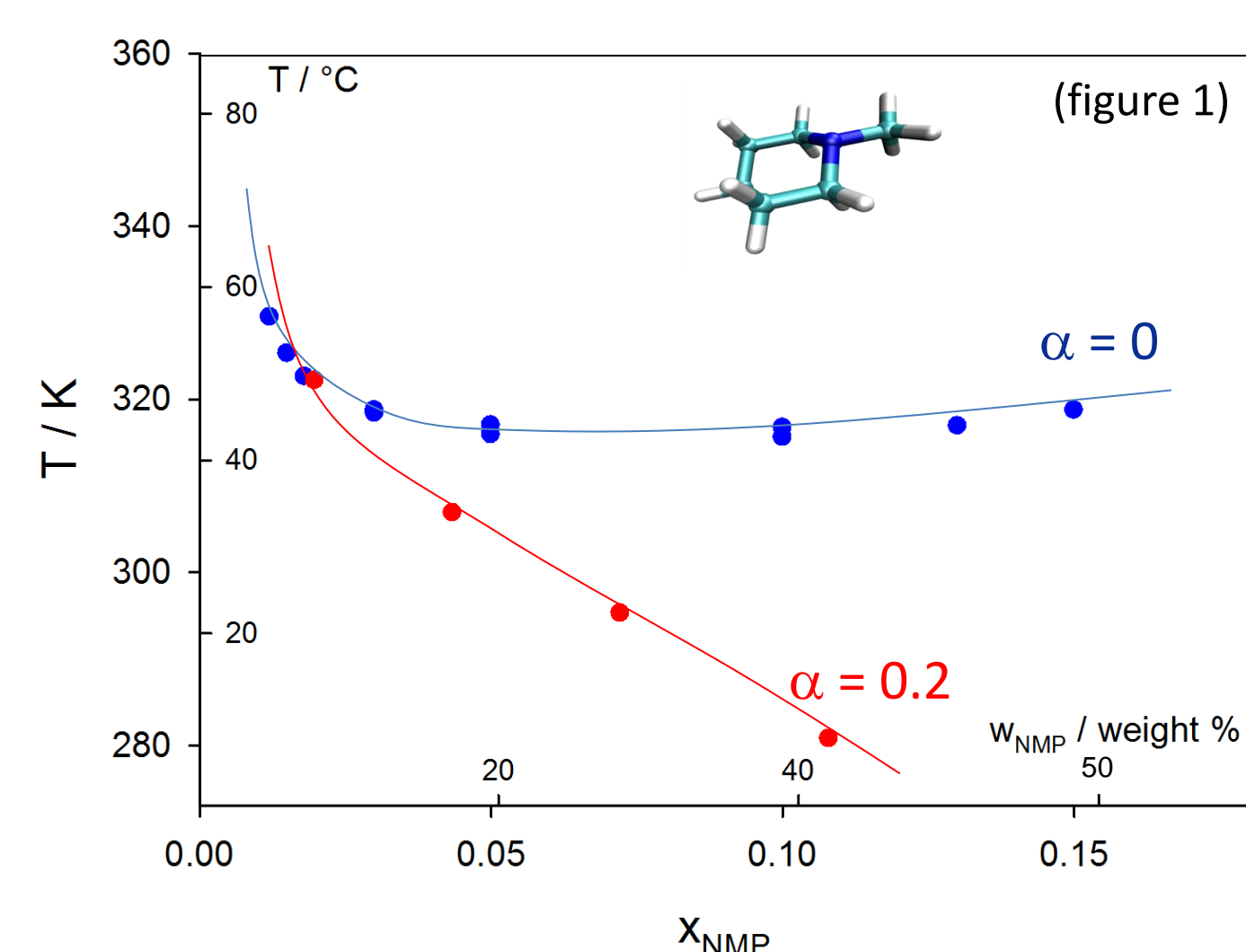
| | Hastelloy cell | Sapphire cell |
|-----------------------------|-----------------------------|-------------------|
| Temperature T | Room T – 428 K | 263 – 423 K |
| Control of T | Heat tape | Thermostatic bath |
| Pressure p | 0.1 – 40 MPa | 0.1 – 8 MPa |
| Control of p | Buffer volume | Buffer volume |
| Volume of the cell | 15 to 20 mL adjustable | 5 mL |
| Visualization of the sample | Through the sapphire window | Full sample |



Results and Conclusions

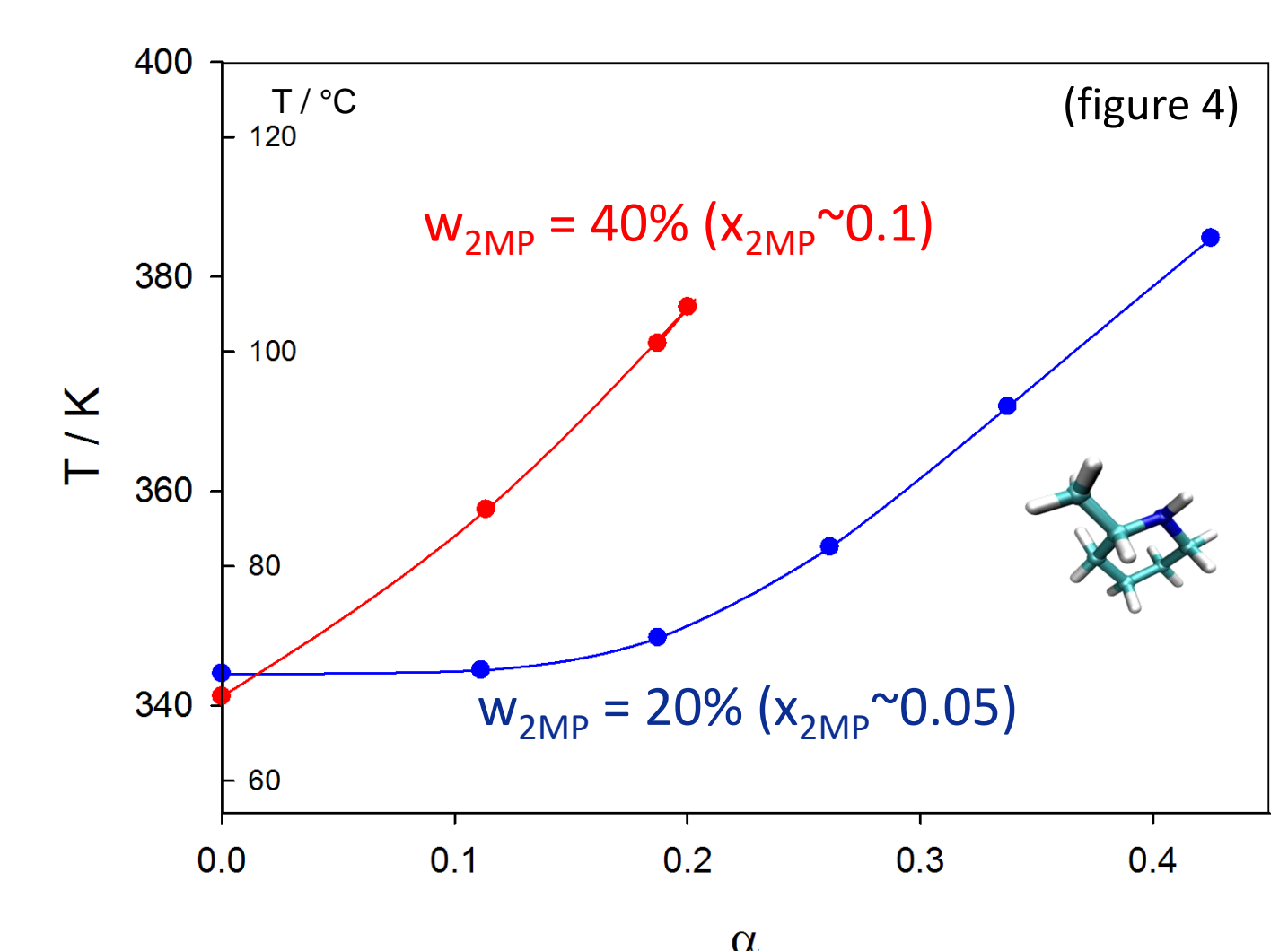
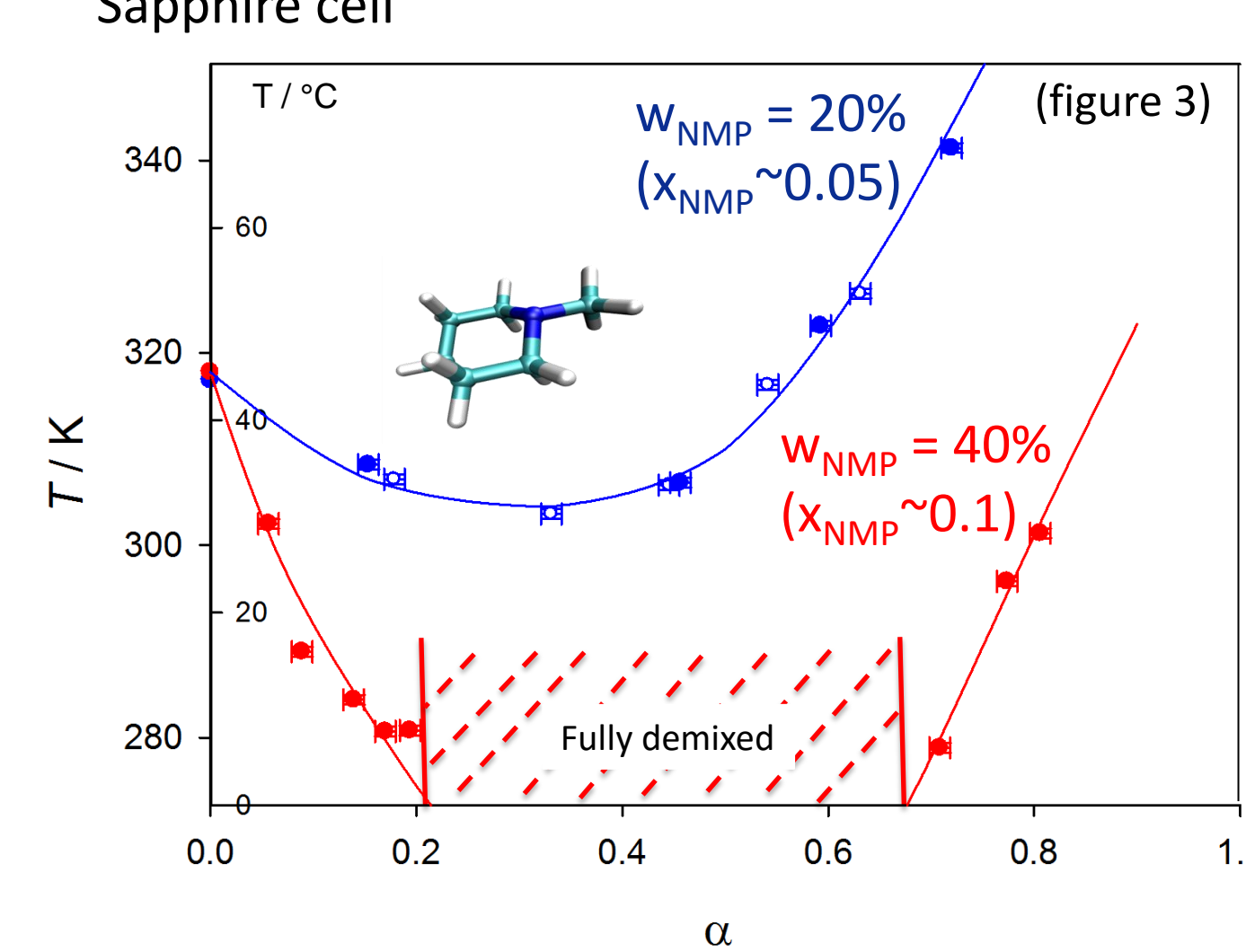
Constant loading charge

Temperatures of liquid-liquid phase separation for solutions of water + N-methylpiperidine (NMP) + CO₂ (figure 1) and for solutions of water + 2-methylpiperidine (2MP) + CO₂ (figure 2) versus composition of the binary mixture water + methylpiperidine at different loading charges α. For 2MP, data at α = 0 are from reference [5]



Constant amine-water composition

Temperatures of liquid-liquid phase separation for solutions of water + N-methylpiperidine (NMP) + CO₂ (figure 3) and for solutions of water + 2-methylpiperidine (2MP) + CO₂ (figure 4) versus loading charge α at different compositions of the binary mixture water + methylpiperidine. Open symbols : Thar Inst. Cell; full symbol : Sapphire cell



- Measurements were realized at 5 bar. Ternary mixtures are prepared below the temperature of liquid-liquid phase separation.

Uncertainties

- composition : $\alpha : \pm 0.01$
 $x : \pm 0.001$

- Pressure : ± 0.1 bar, - Temperature : ± 0.3 K

| | Water + amine | Water + amine + CO ₂ (α = 0.2) | Water + amine + CO ₂ (x = 0.05) |
|--------------------|--------------------------|---|--|
| 2-methylpiperidine | LCST = 341 K x = 0.07 | LCST = 343 K x = 0.04 | ----- |
| N-methylpiperidine | LCST = 318 K x = 0.07 | ----- | LCST = 303 K α = 0.33 |

- Good agreement between the two methods
- LCST is strongly influenced by the presence of the dissolved gas
- N-methylpiperidine cannot be used in a process at high concentration (40%wt) as the CO₂ drastically lowered the LCST; 2-methylpiperidine is a better candidate.

ANR – NSERC joint program DACOOTA

References

The objective of the project, co-supported by ANR in France and NSERC in Canada, is to analyze the structure-properties relationships for different substituted piperidines.

Thermodynamic properties (enthalpies, heat capacities, volumes, phase equilibria) are measured in Clermont-Ferrand (France). [6]

Speciation in solution using Raman spectroscopy at high temperature and pressure are determined in Guelph (Canada).

Modeling using activity coefficient models and molecular simulation will complete the program.

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