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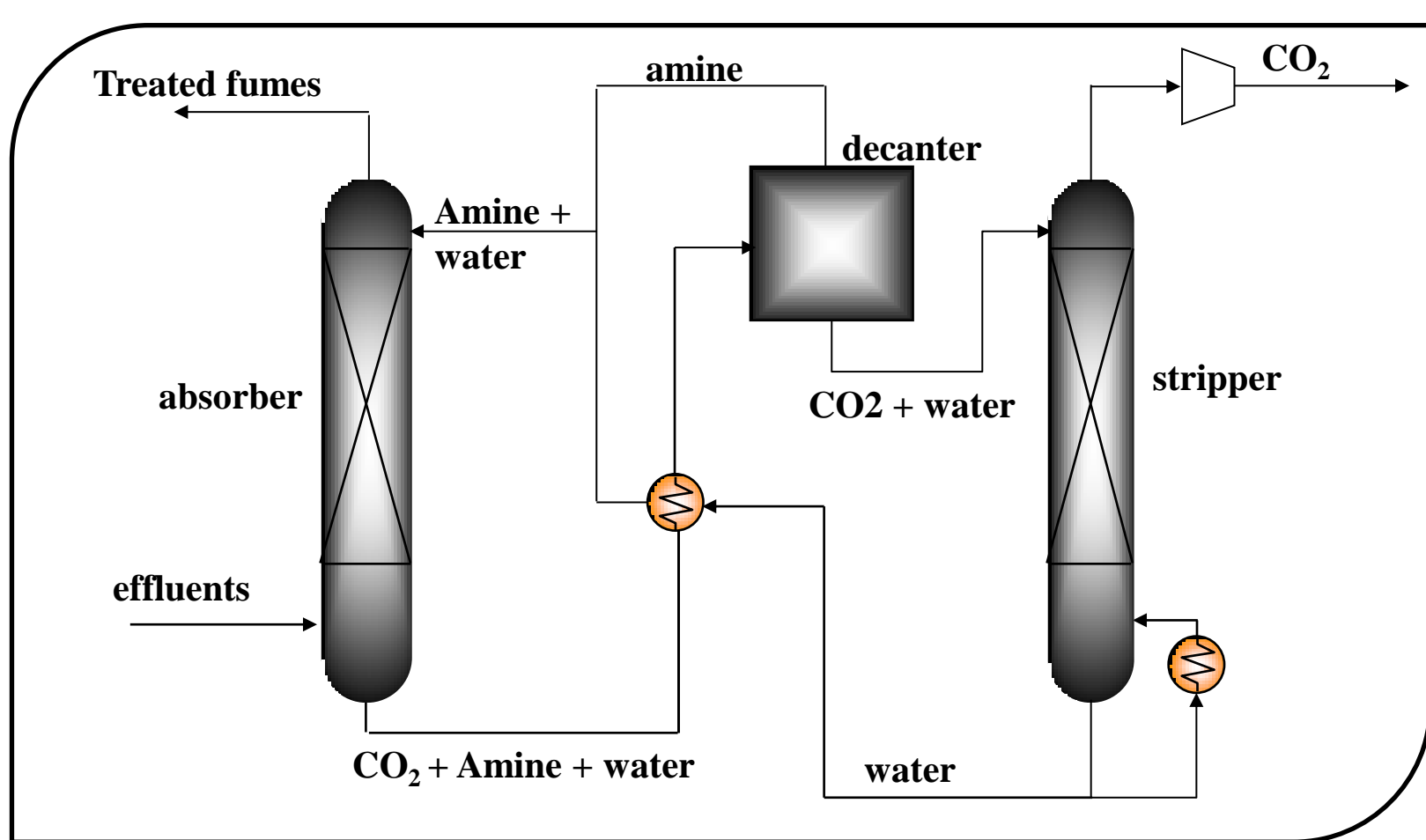
# Liquid-liquid equilibria in aqueous solutions of demixing amines loaded with gas for CO<sub>2</sub> capture processes

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## Introduction

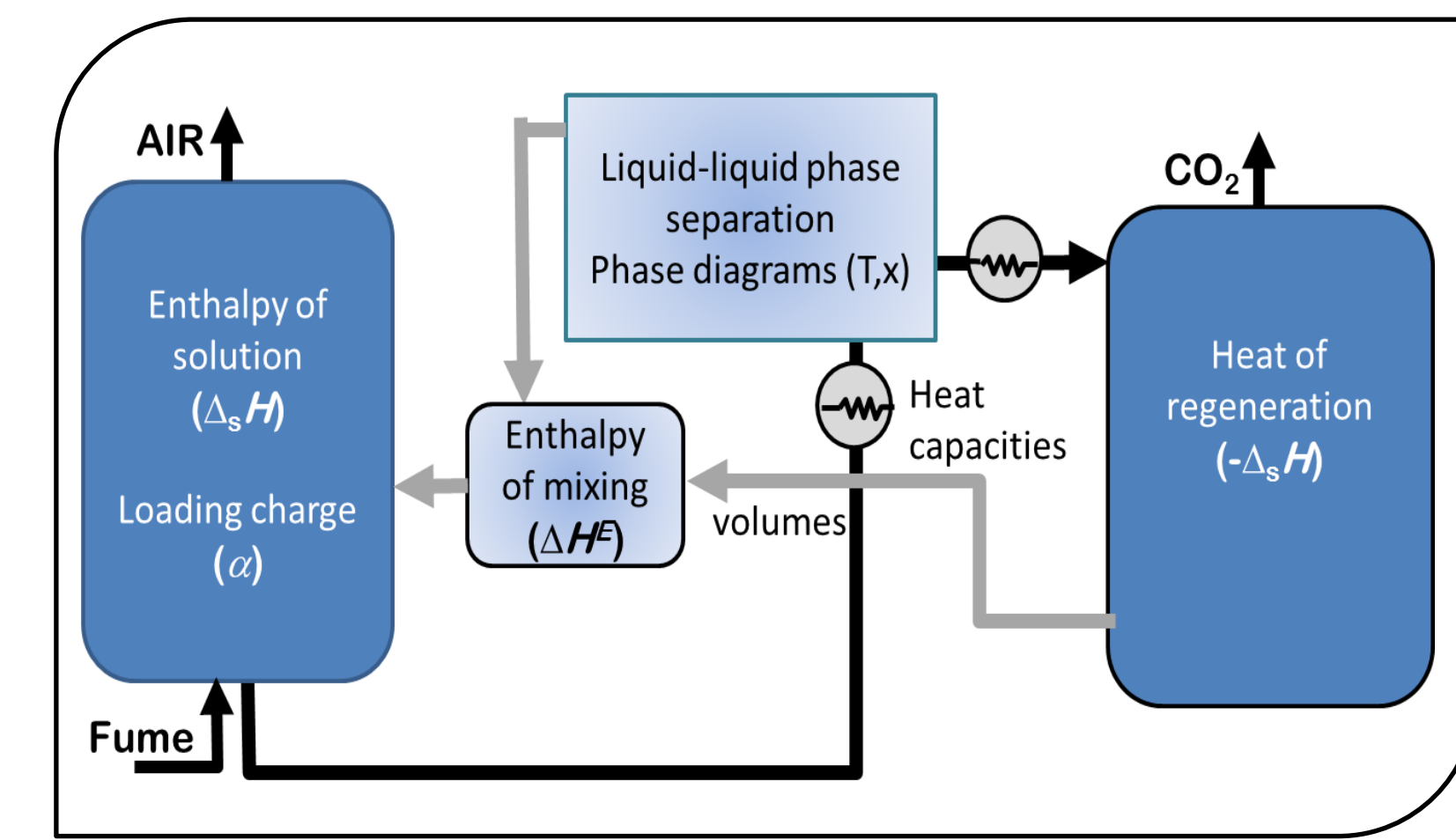
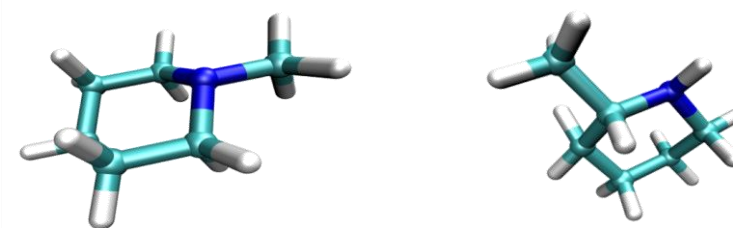


Aqueous solutions of amines are selective carbon dioxide (CO<sub>2</sub>) absorbents [1,2]. They are used in CO<sub>2</sub> capture processes working on absorption/desorption cycles.

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+CO<sub>2</sub>, as a function of the pressure and the CO<sub>2</sub> loading charge.

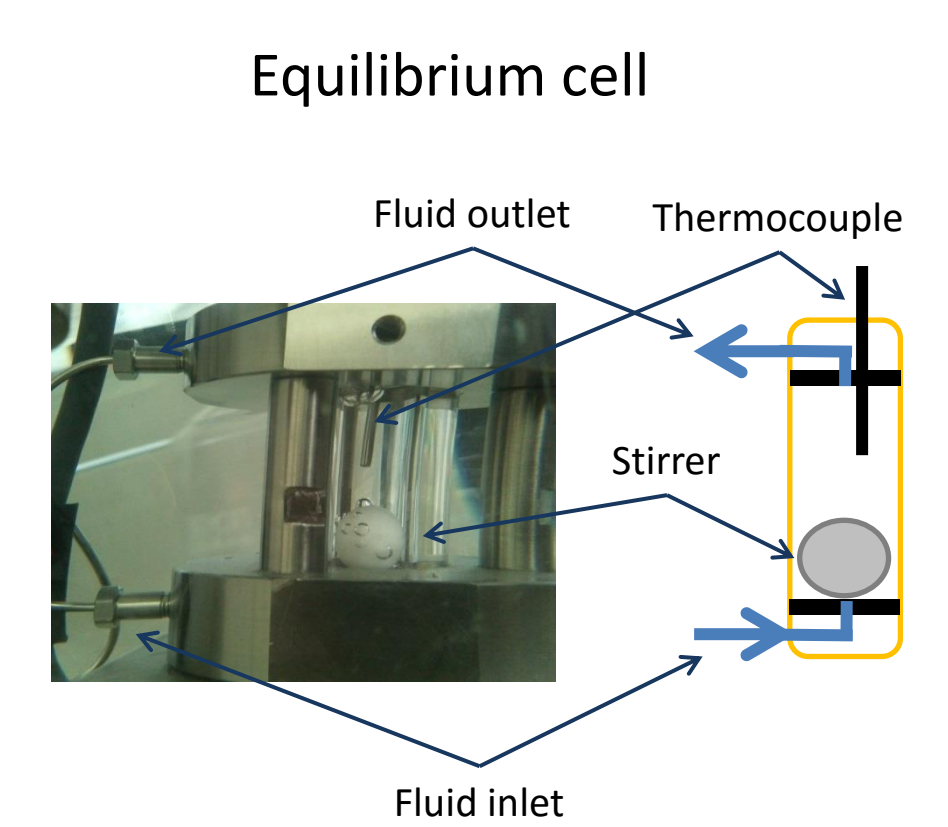
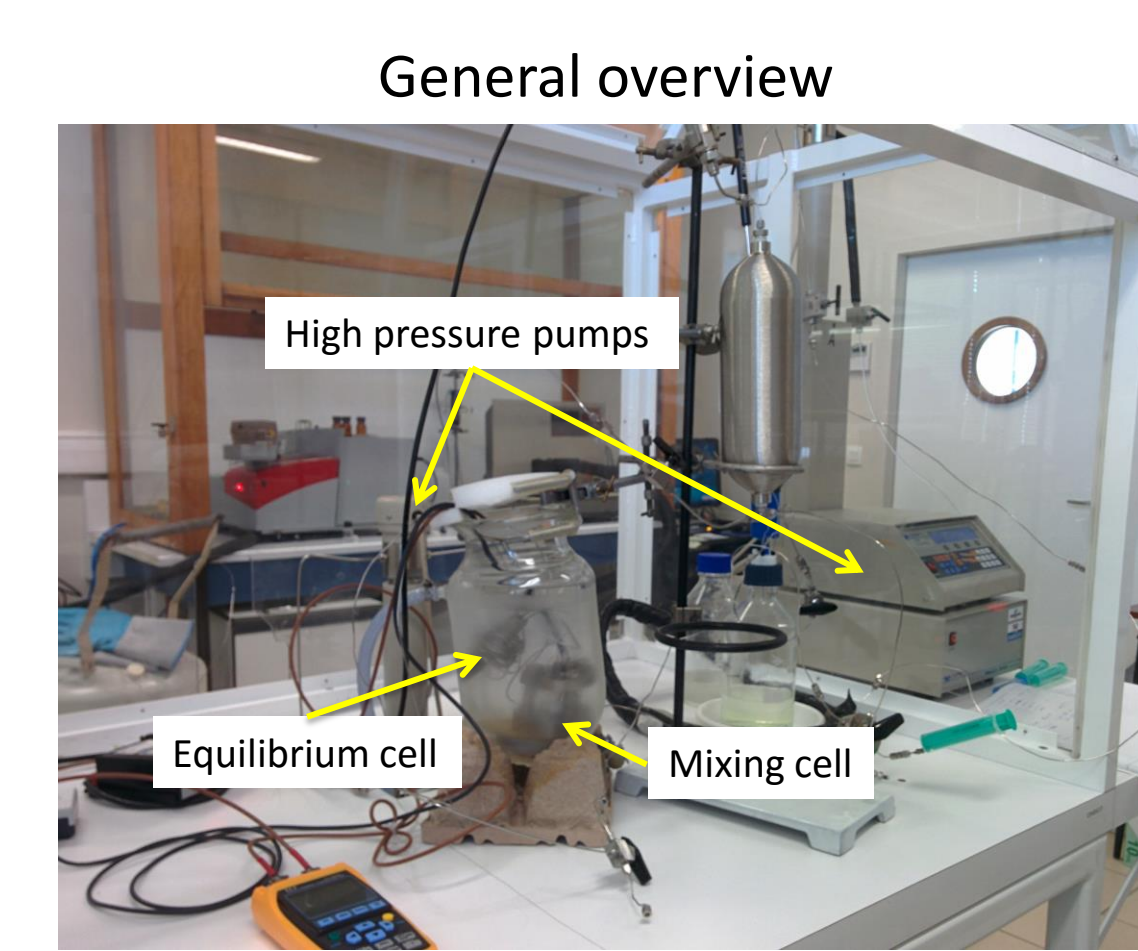
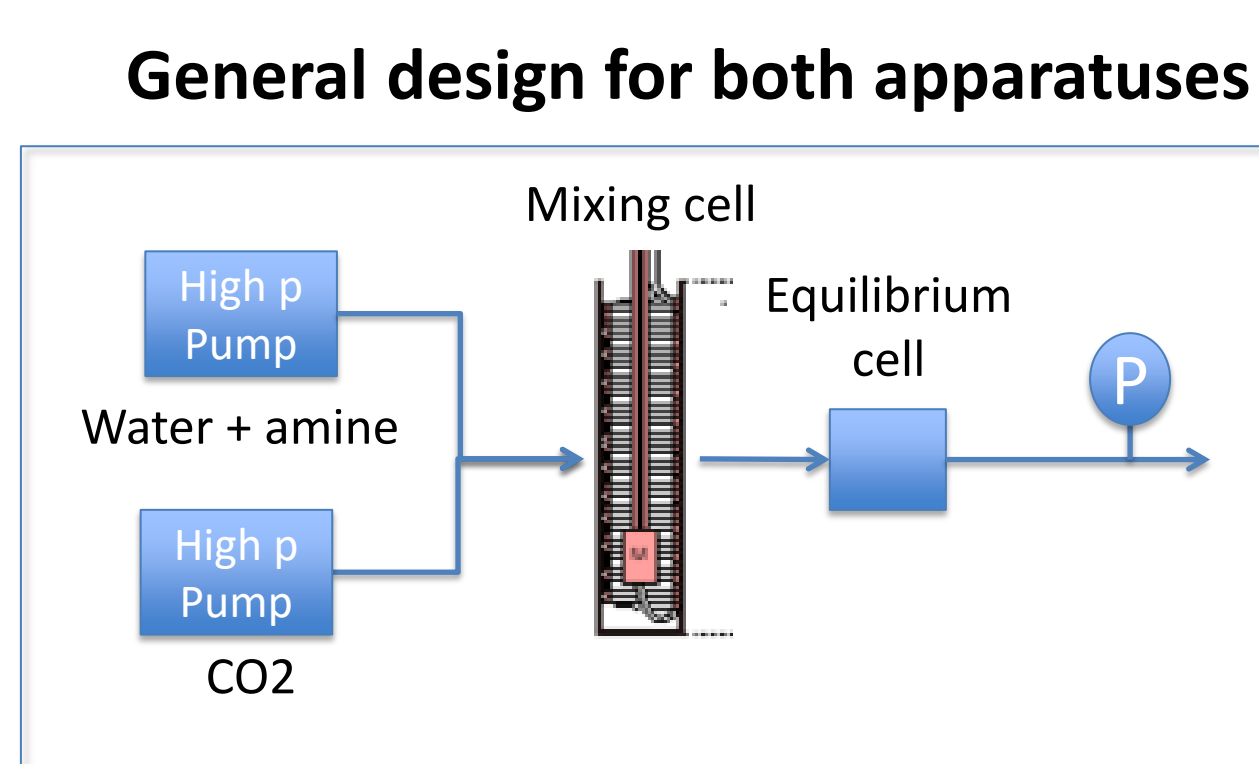
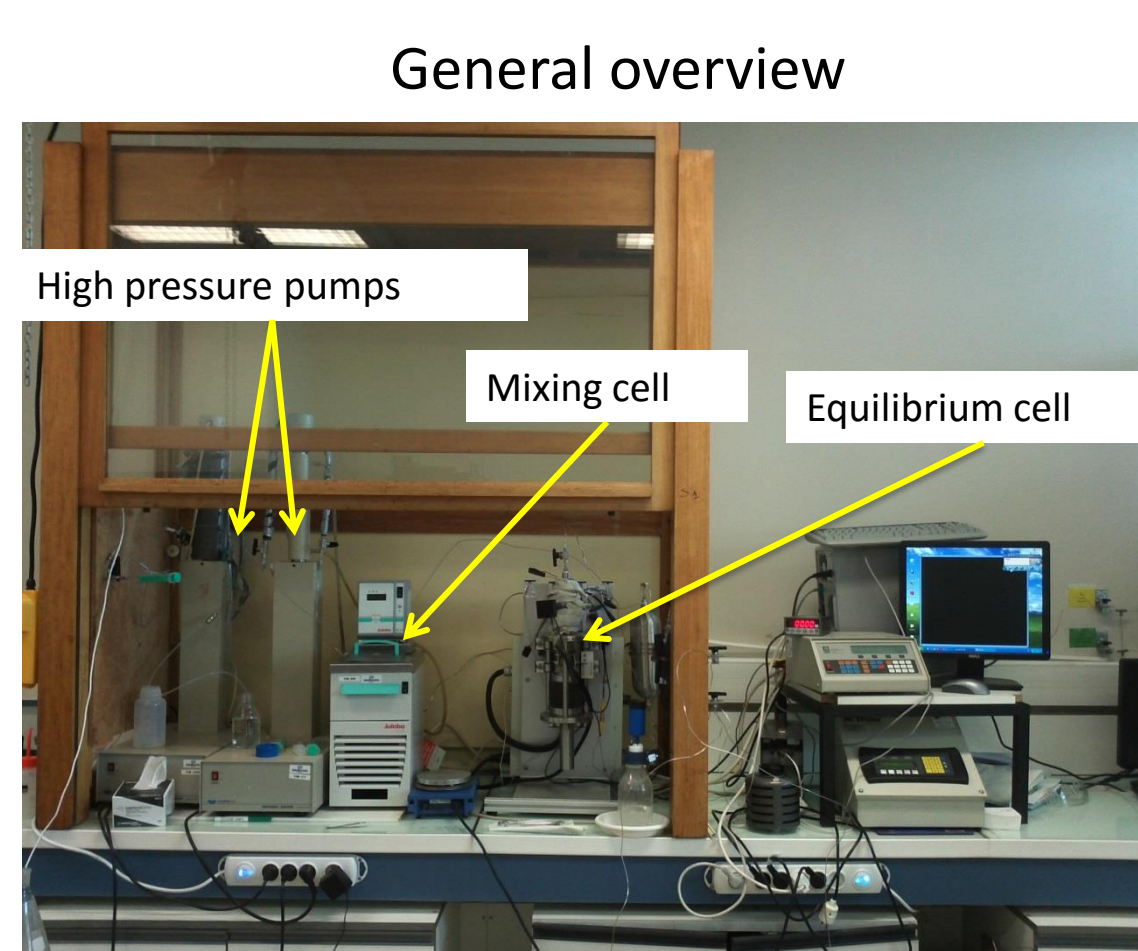
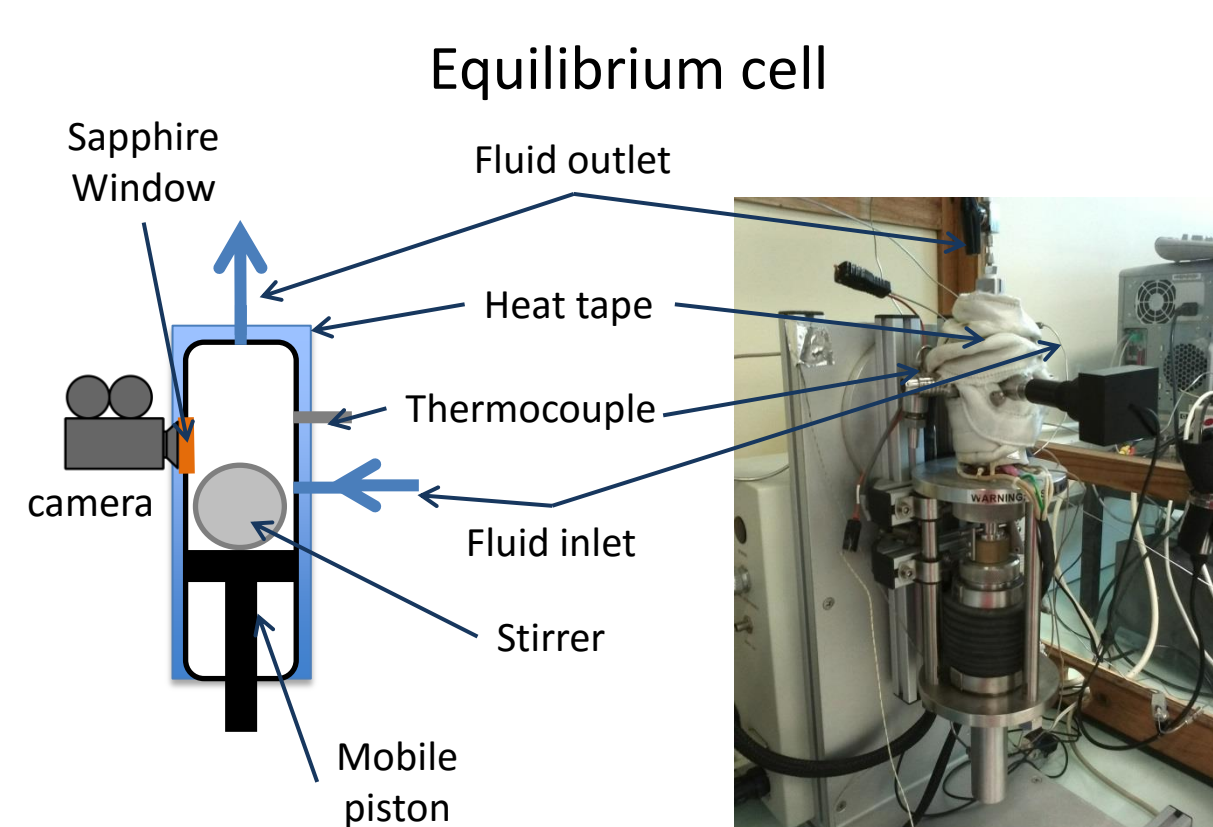
**Amines** : N-methylpiperidine  
2-methylpiperidine



## methods

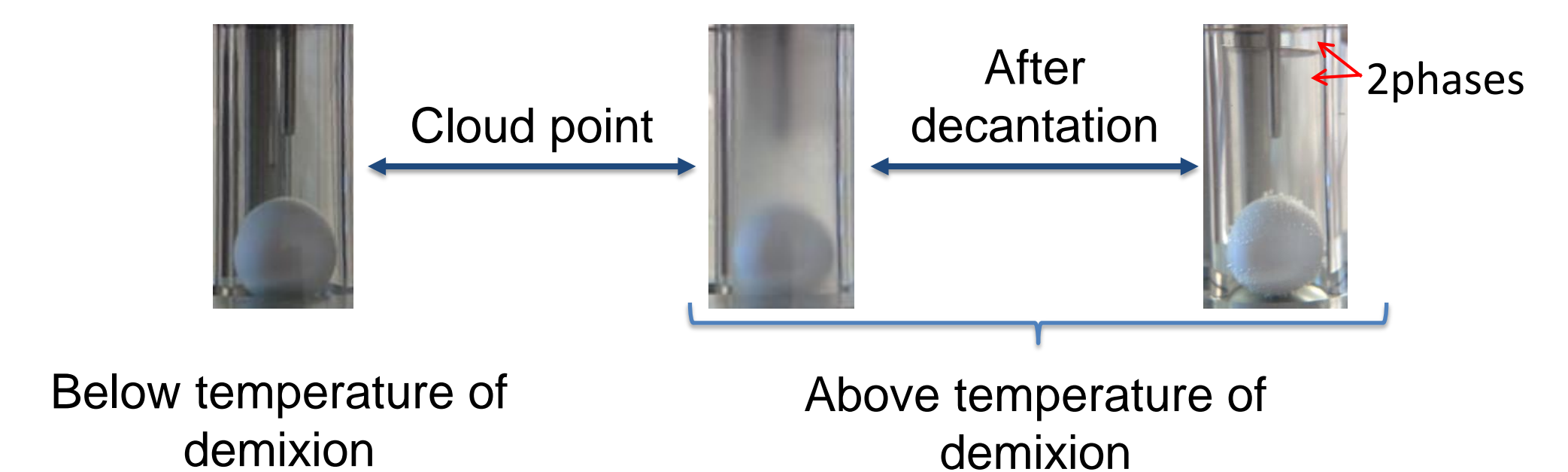
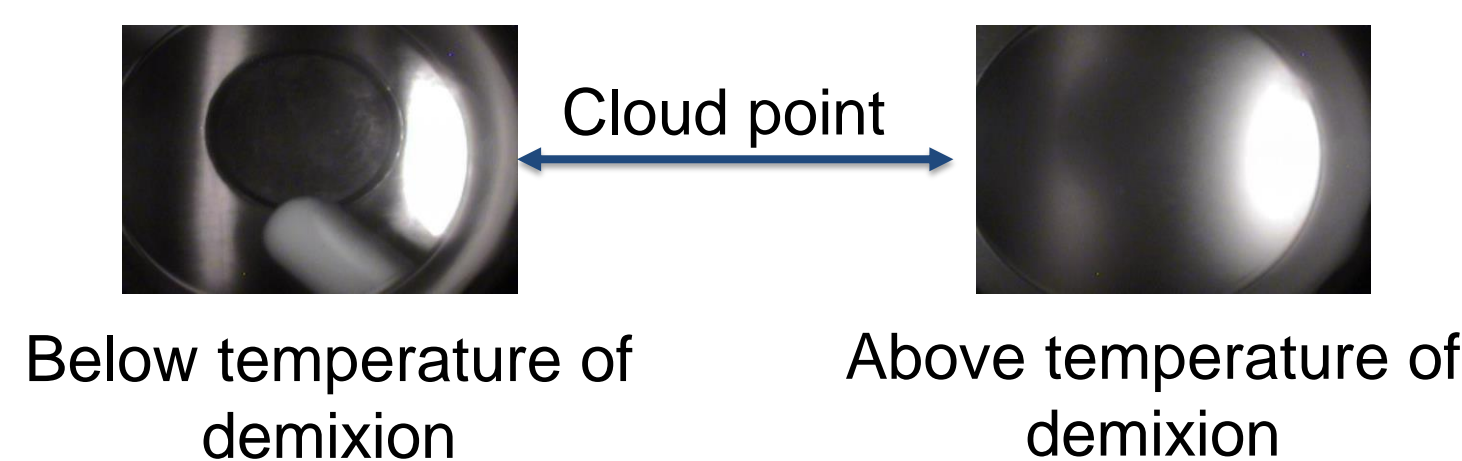
### Hastelloy cell : THAR SPM20

### Sapphire Cell



#### Comparison of the apparatuses

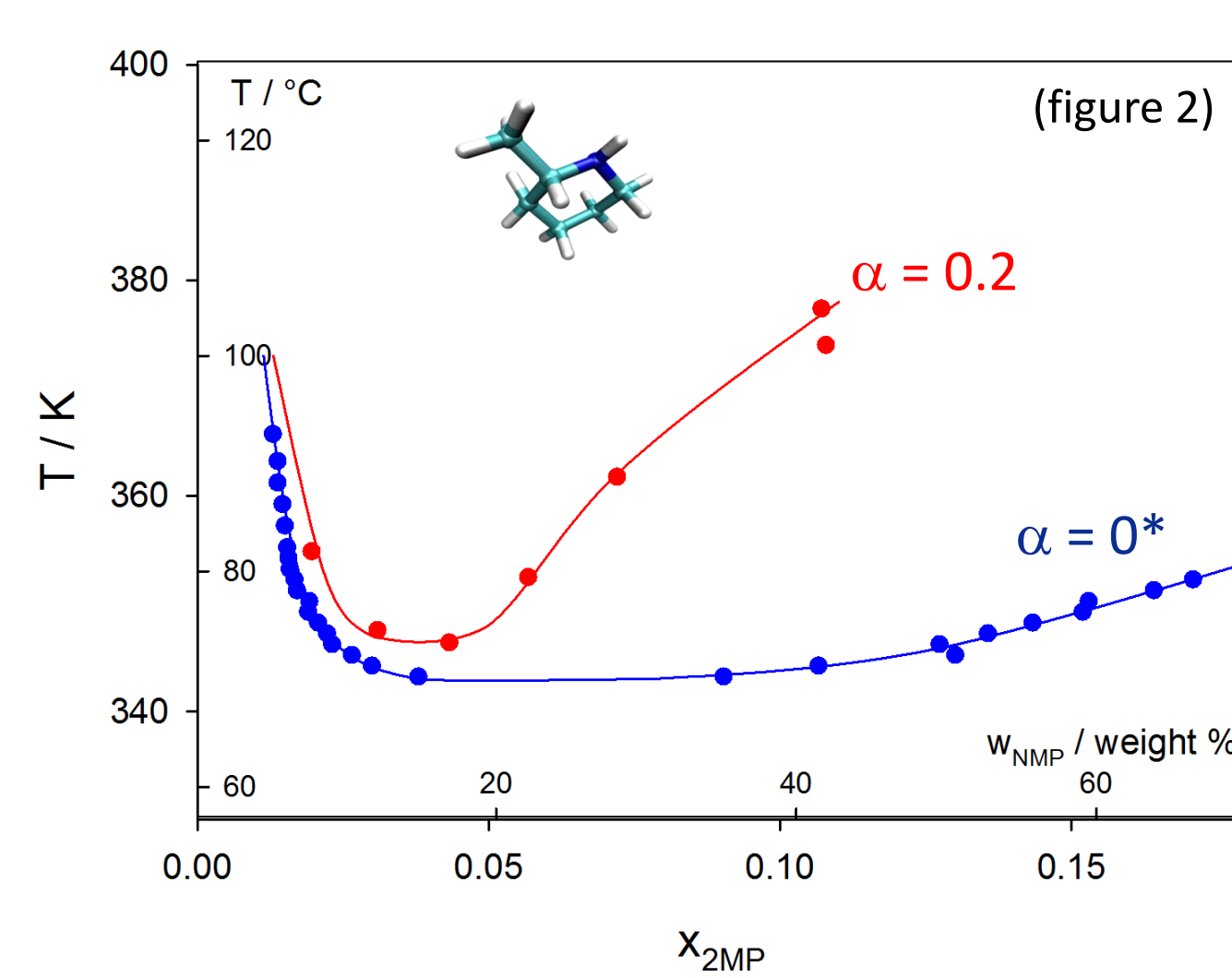
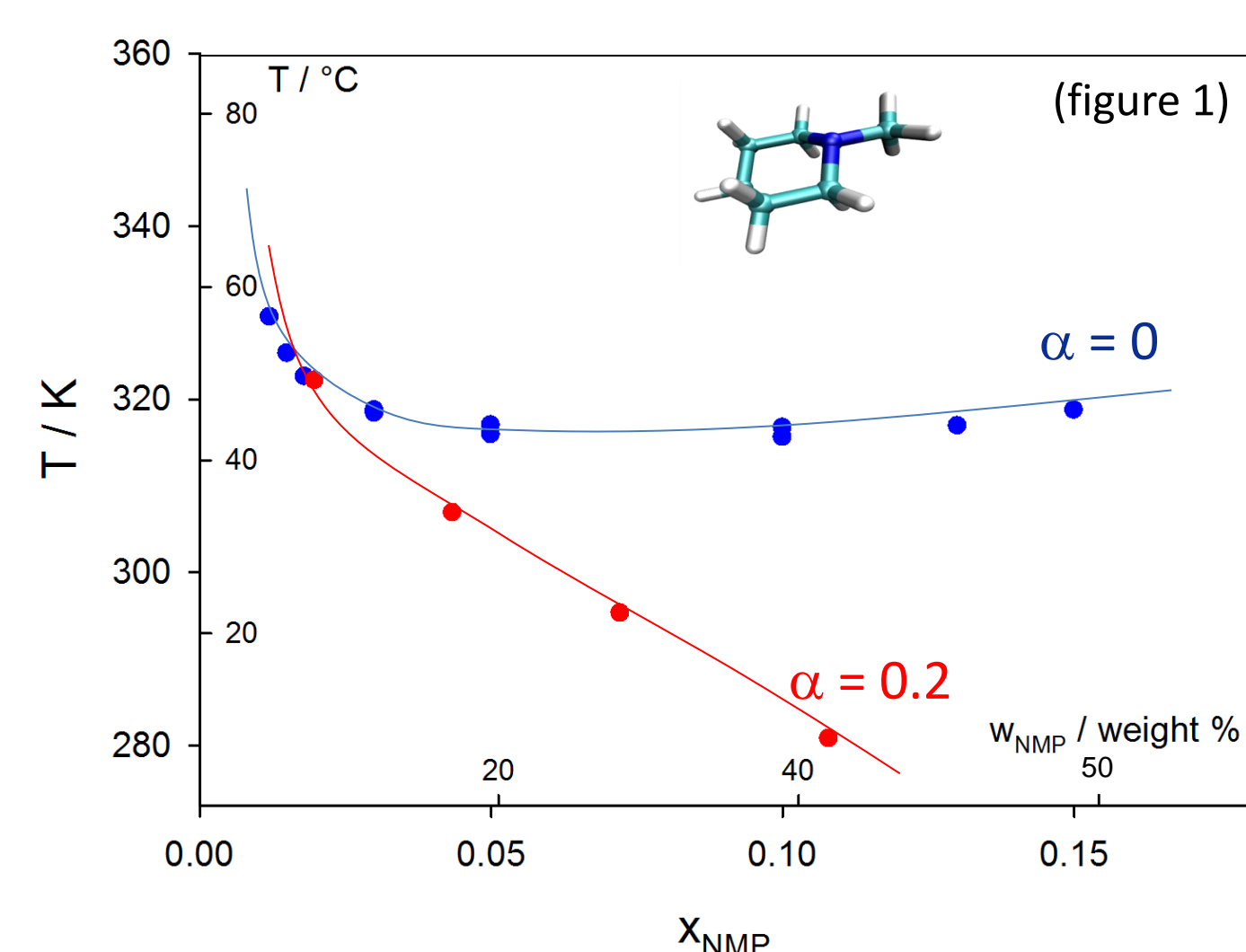
	Hastelloy cell	Sapphire cell
Temperature T	Room T – 428 K	263 – 423 K
Control of T	Heat tape	Thermostatic bath
Pressure p	0.1 – 40 MPa	0.1 – 8 MPa
Control of p	Buffer volume	Buffer volume
Volume of the cell	15 to 20 mL adjustable	5 mL
Visualization of the sample	Through the sapphire window	Full sample



## Results and Conclusions

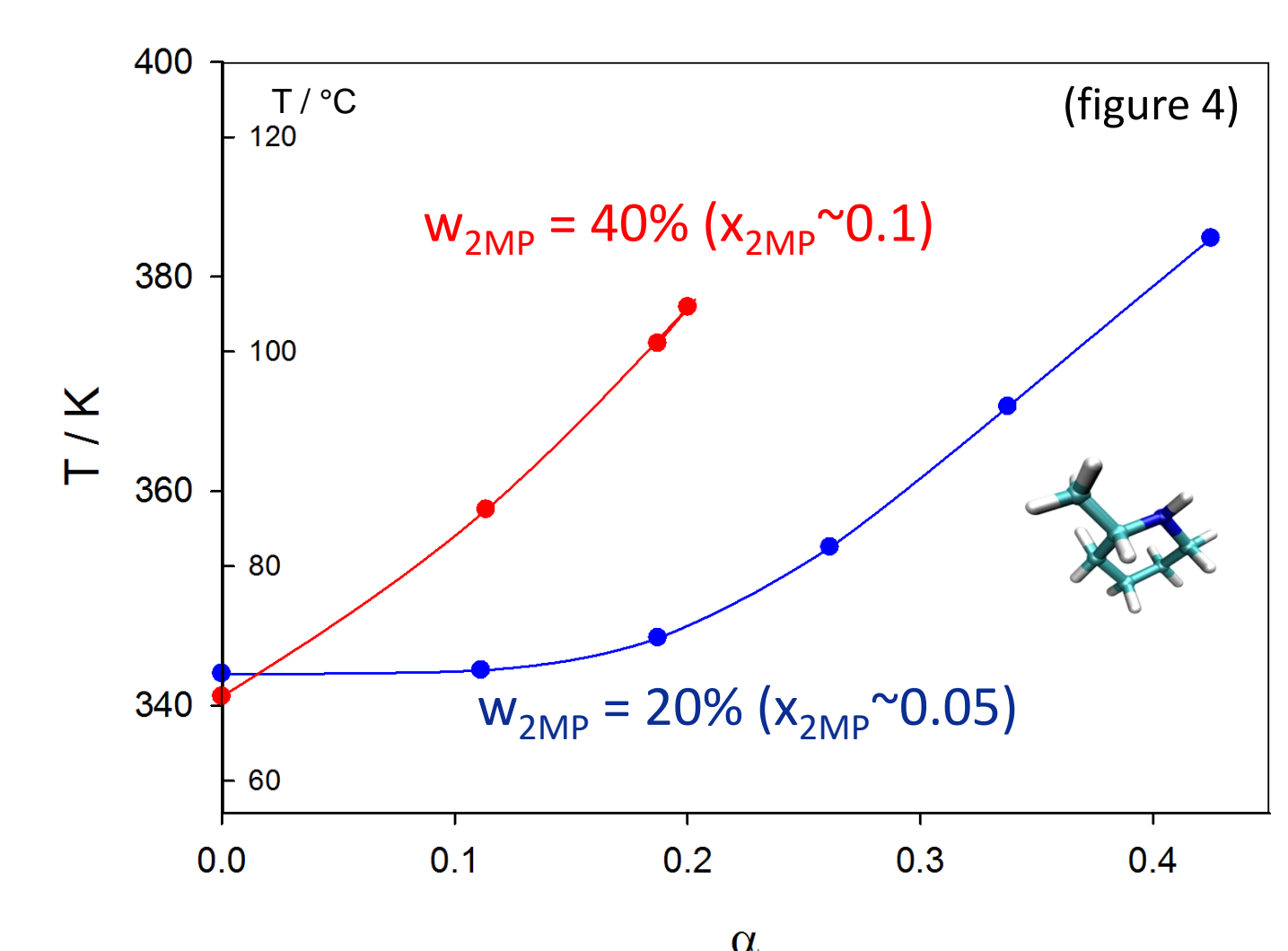
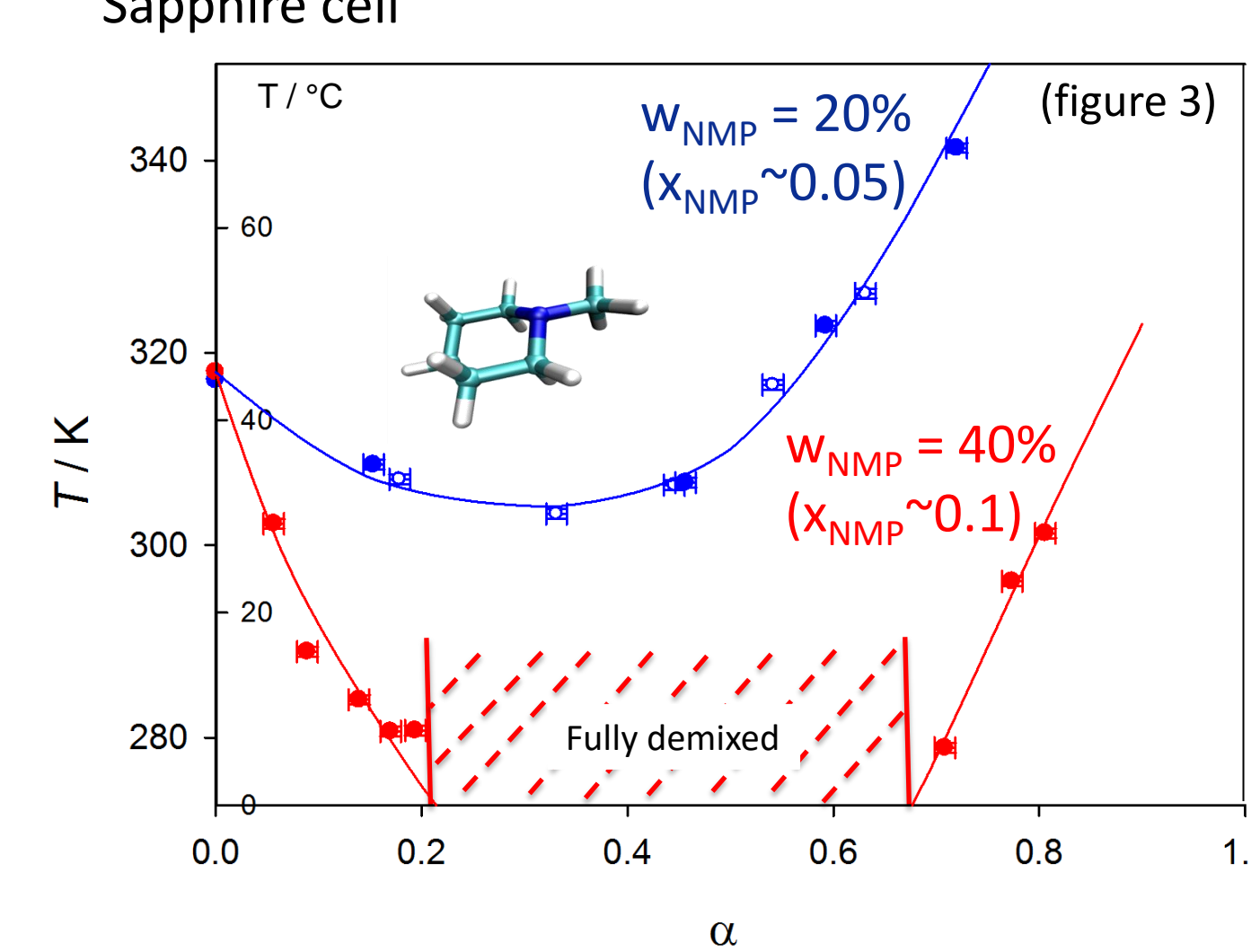
### Constant loading charge

Temperatures of liquid-liquid phase separation for solutions of water + N-methylpiperidine (NMP) + CO<sub>2</sub> (figure 1) and for solutions of water + 2-methylpiperidine (2MP) + CO<sub>2</sub> (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) + CO<sub>2</sub> (figure 3) and for solutions of water + 2-methylpiperidine (2MP) + CO<sub>2</sub> (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 :  $\pm 0.1$  bar, - Temperature :  $\pm 0.3$  K

	Water + amine	Water + amine + CO <sub>2</sub> (α = 0.2)	Water + amine + CO <sub>2</sub> (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 CO<sub>2</sub> 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.

- [1] L. Raynal, P-A. Bouillon, A. Gomez, P. Broutin, Chemical Engineering Journal 171 (2011) 742– 752;
- [2] L. Rodier, K. Ballerat-Busserolles, J-Y. Coxam, J. Chem. Thermodynamics, 42, 773-780 (2010).
- [3] Bouillon, P-A., M. Jacquin, and L. Raynal, IFP.Energies nouvelles, Editor. (2012)
- [4] Y. Coulier, K. Ballerat-Busserolles, L. Rodier, J-Y. Coxam, Fluid Phase Equilibria, 296, 206-212 (2010);
- [5] Stephenson, J. Chem. Eng. Data, 38, 428 (1993)
- [6] Y. Coulier, K. Ballerat-Busserolles, J. Mesones, A. Lowe, J-Y. Coxam, J. Chem. Eng. Data, 60, 1563–1571 (2015)

