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Thermodynamic study of working fluid pairs for an absorption refrigeration process

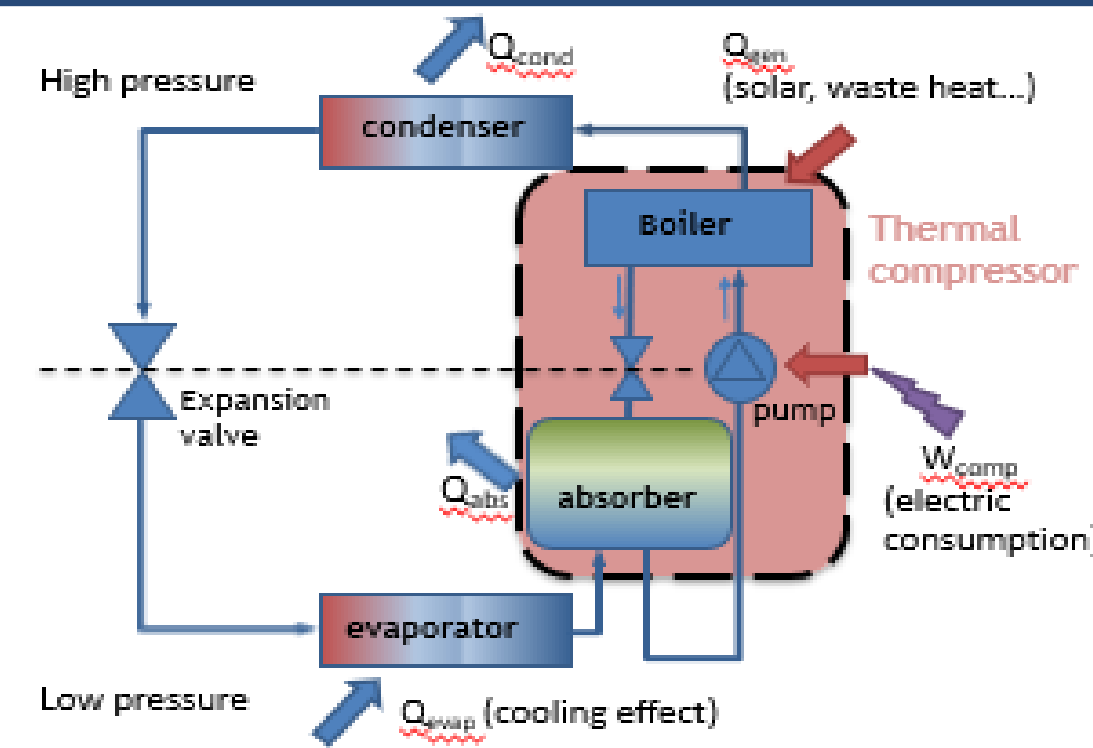
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Vapor absorption refrigeration (VAR) technology is a good alternative to conventional compression refrigeration. However, in addition to the low coefficient of performance of this technology, the fluids used have specific drawbacks that prevent wider use.

To promote this technology, the present work investigates new potential natural refrigerant/absorbent pairs. The detailed knowledge of the thermodynamic properties of the working fluid pairs is crucial to retrofit and modify VAR process.

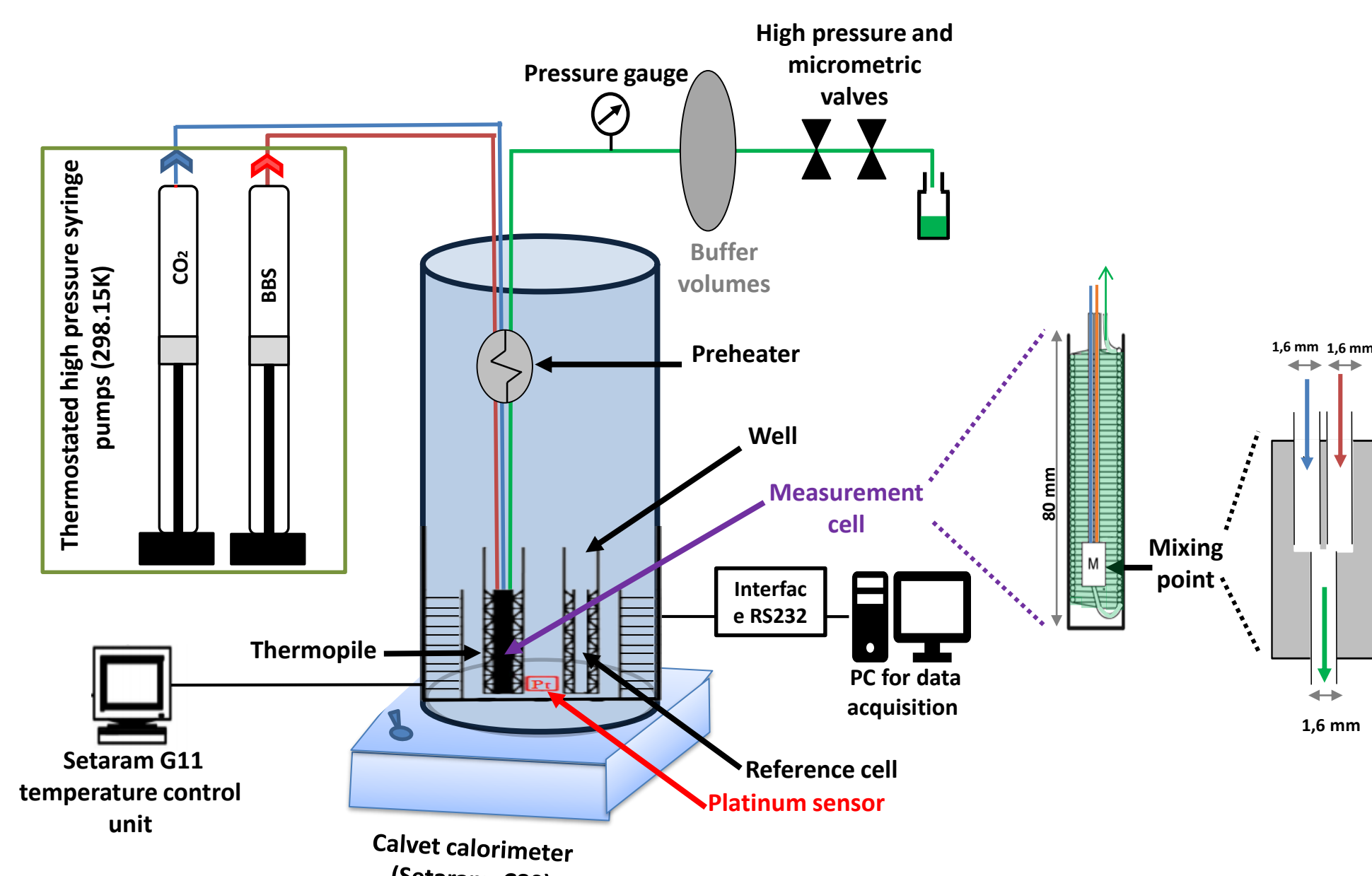


In this study, carbon dioxide (CO₂) has been selected as the natural refrigerant and the absorbent is a bio-based solvent (BBS) with low volatility and strong affinity to the former. Four BBSs are investigated namely cyrene (CYR), propylene carbonate (PC), anisole (ANI) and γ-valerolactone (GVL). New experimental vapor-liquid-equilibria data for {CO₂+BBS} systems are determined, using a calorimetric and a spectroscopic technique. The experimental results are then used to develop an appropriate thermodynamic model capable of reproducing phase equilibria in order to compare the CO₂ solubility in the different BBSs at the operating conditions of VAR cycle in the future.

Vapor-liquid equilibrium measurements

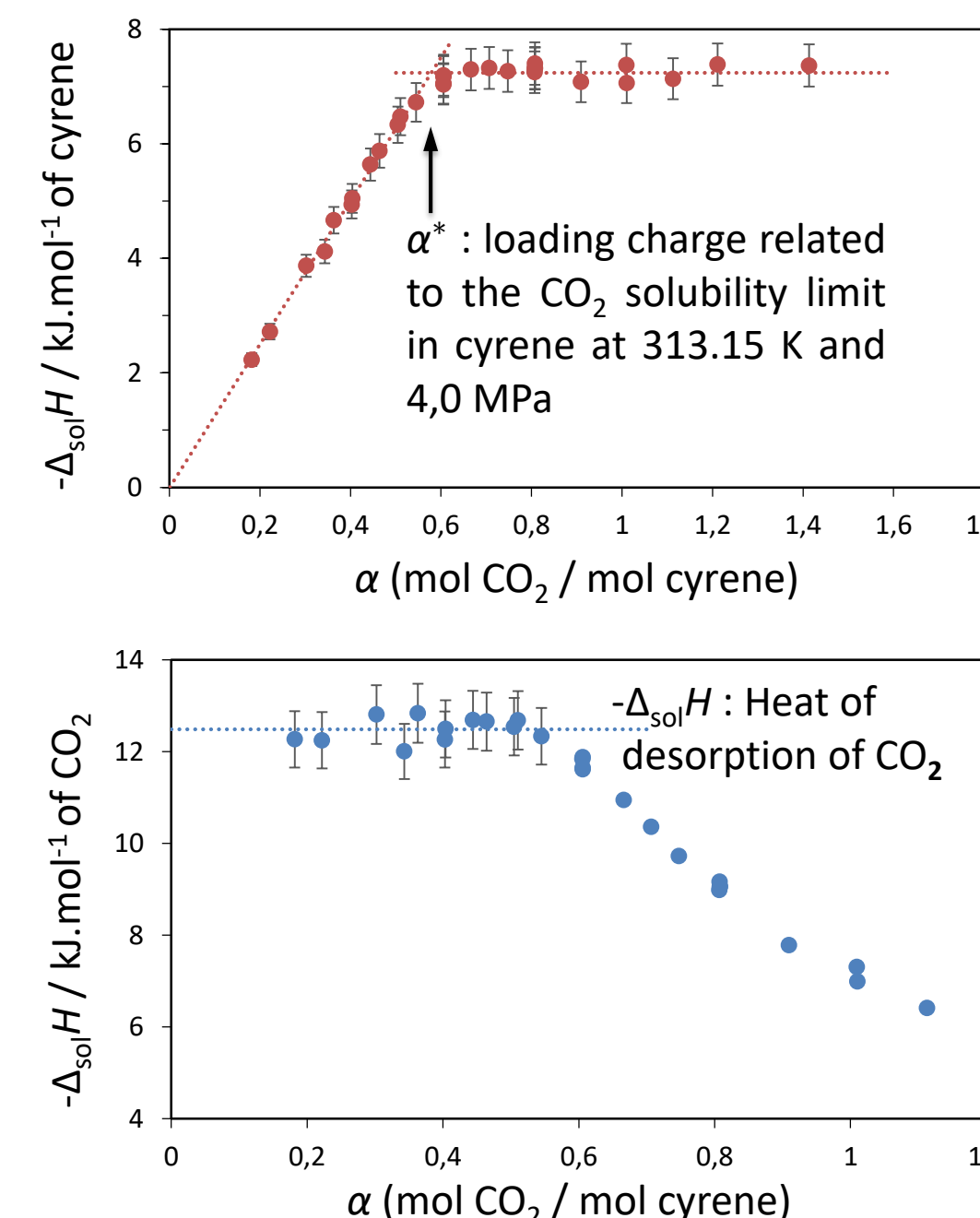
Calorimetric technique

Enthalpies of solution of CO₂ in the BBS are determined using a customized mixing flow unit adapted to a SETARAM C80 heat conduction differential calorimeter at constant temperature and pressure.



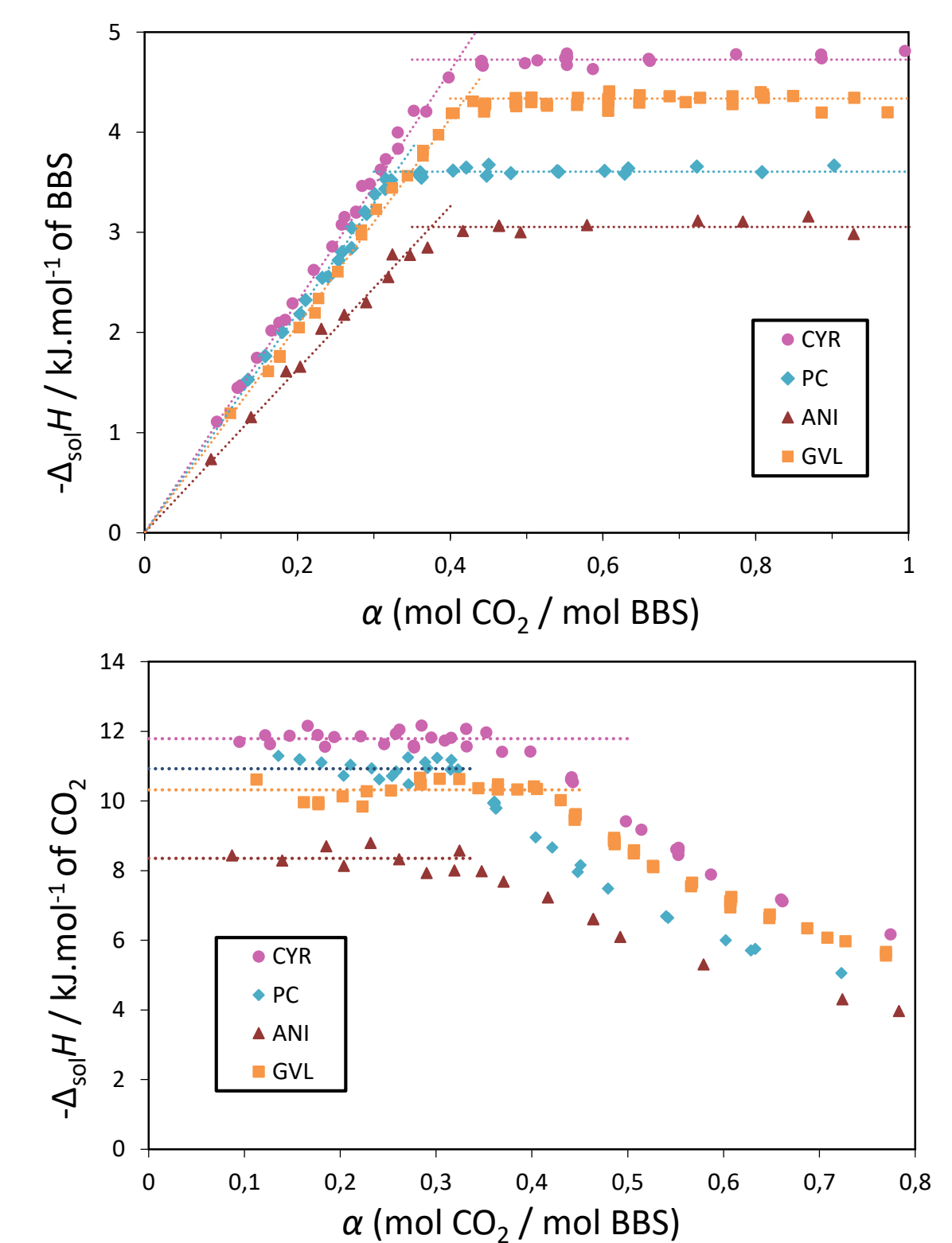
Schematic view of the calorimetric device for mixing enthalpies

Enthalpies of solution allow us to obtain two information; CO₂ solubility limit in the BBS and the heat of desorption.



Enthalpy of solution (-Δ_{sol}H) of CO₂ in cyrene vs loading charge (α) at 313,15 K and 4,0 MPa

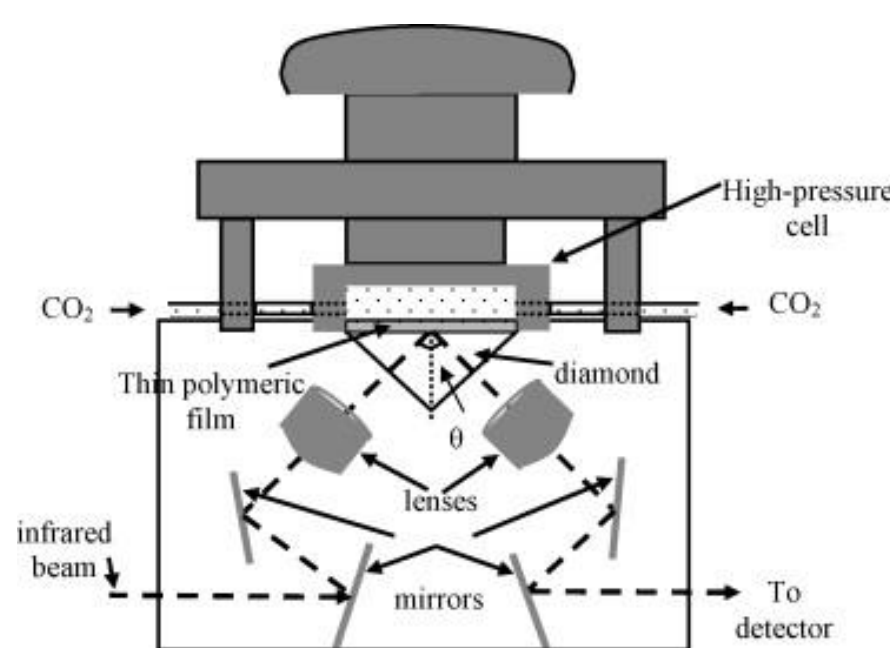
Results



Enthalpy of solution (-Δ_{sol}H) of CO₂ in four different BBS vs loading charge (α) at 333,15 K and 4,0 MPa

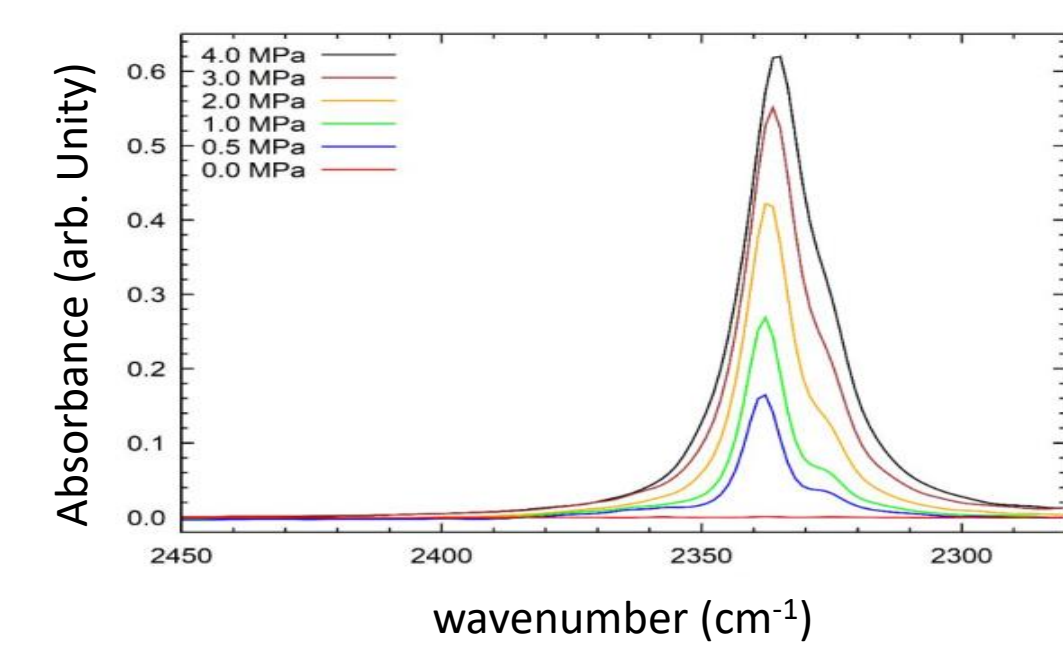
Spectroscopic technique

Knowing CO₂ solubility in the solvent at a given pressure and temperature, the spectroscopic technique allows us to determine the solubility at that same temperature and at various pressures.



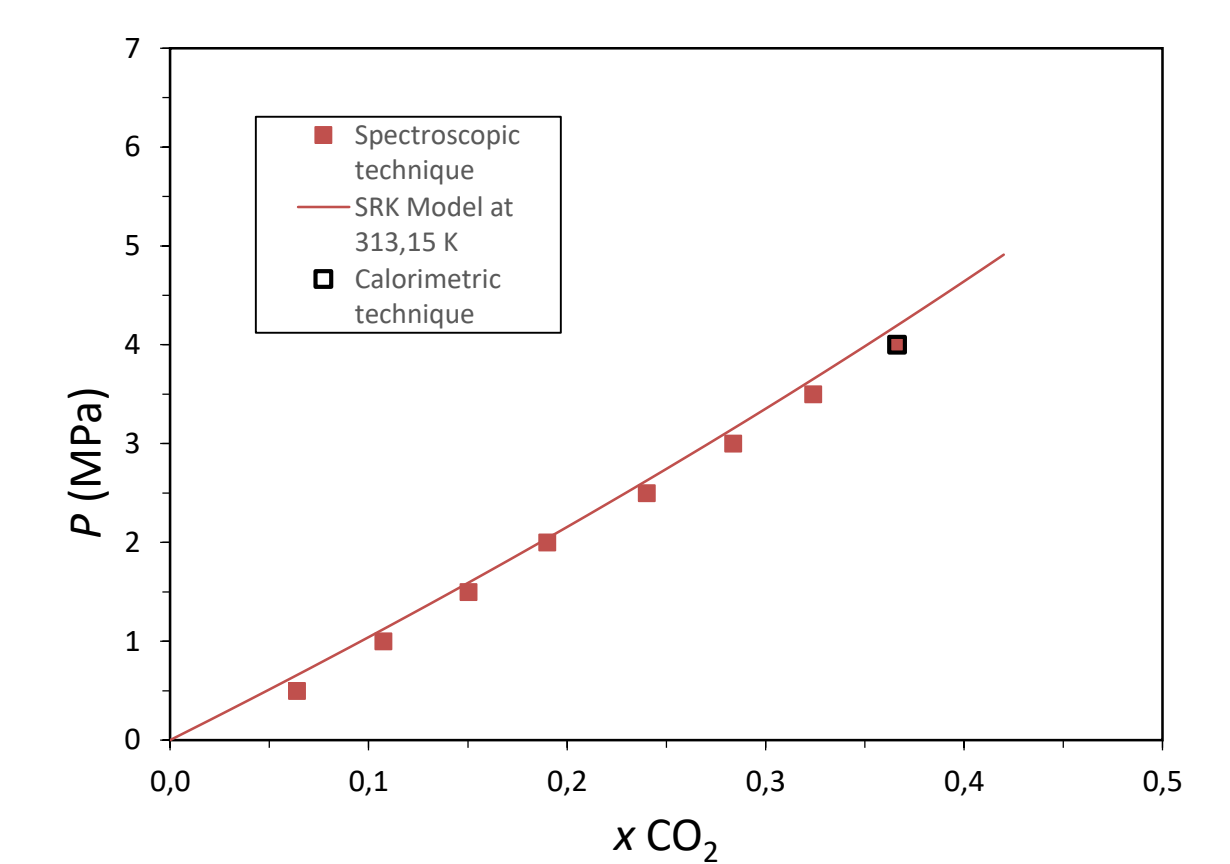
Schematic view of customized high pressure IR reactor

Spectroscopic measurements are performed at constant temperatures and pressures.



Part of the IR spectra of the binary mixture (cyrene + CO₂) at 313,15 K

Results



Solubility of CO₂ in cyrene at 313,15 K

Thermodynamic modeling

The experimental Vapor-Liquid-Equilibrium (VLE) data for CO₂-BBS system are described using the Soave-Redlich-Kwong (SRK) equation of state [1,2] :

$$P = \frac{RT}{v-b} - \frac{a\alpha(T)}{v(v+b)}$$

With :

- Soave alpha function $\alpha(T)$
- Van der Waals mixing rules and binary interaction parameters :

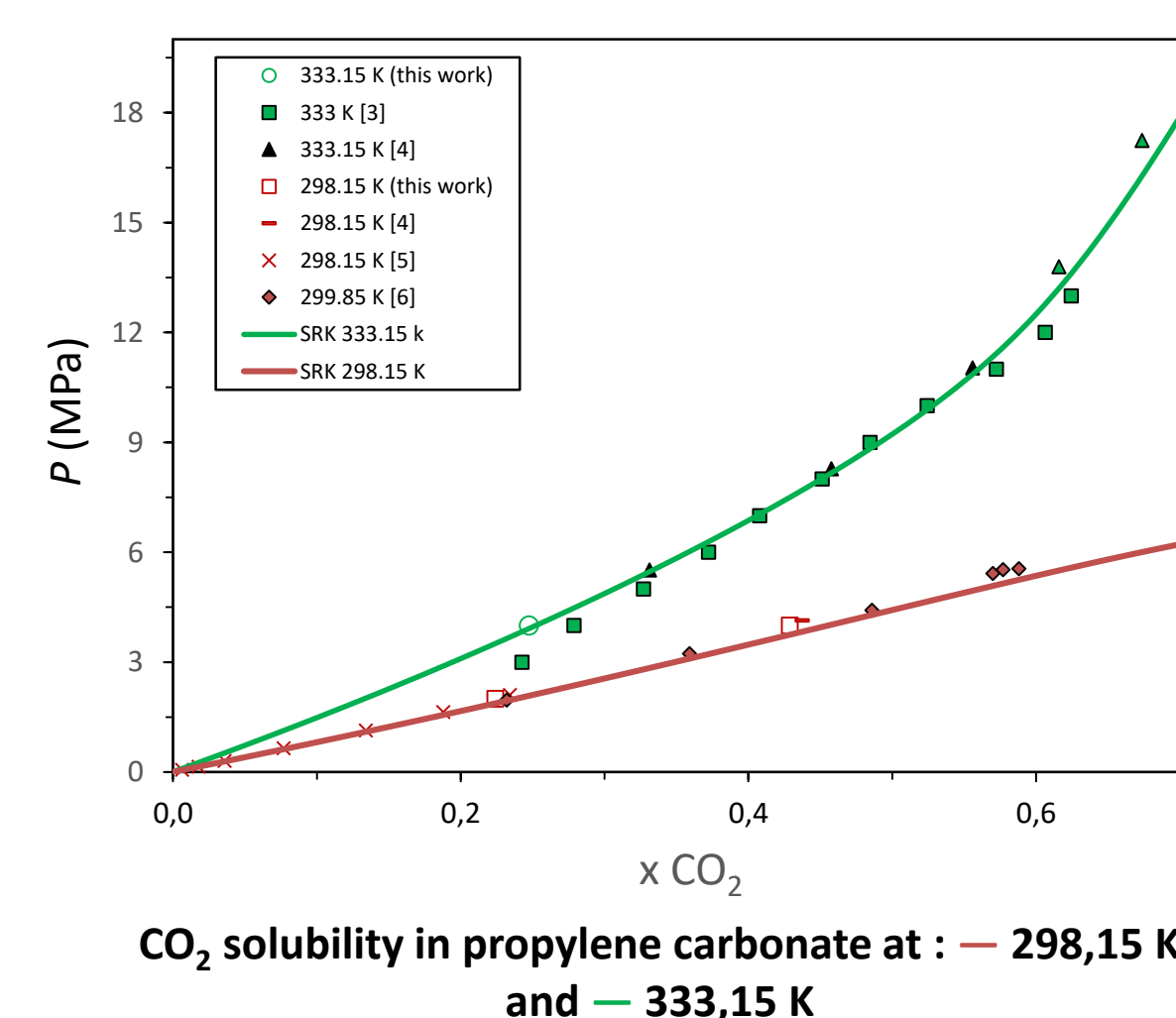
$$a\alpha = \sum_i \sum_j z_i z_j \sqrt{(a\alpha)_i (a\alpha)_j (1 - k_{ij})}$$

$$b = \sum_i z_i b_i$$

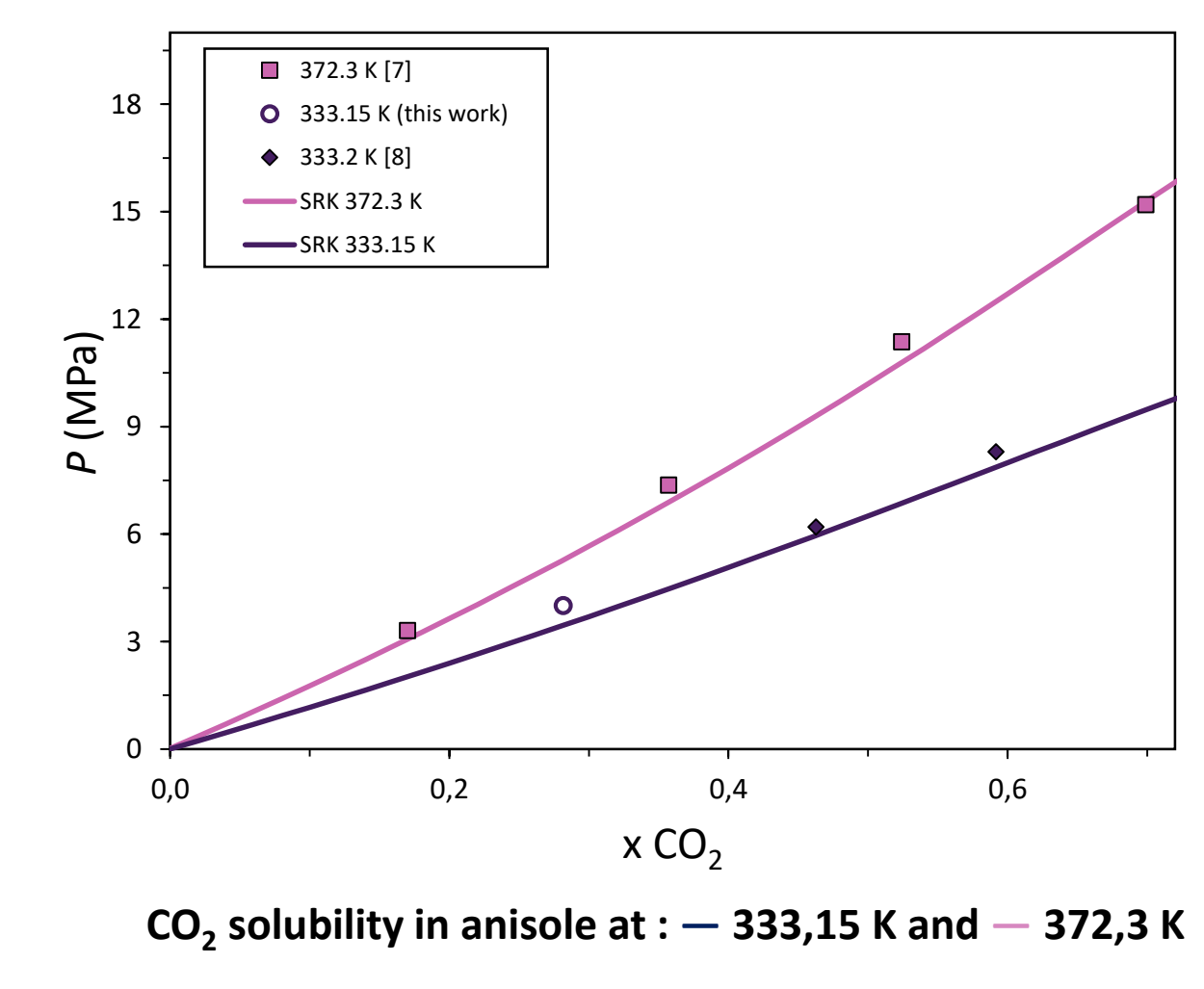
One parameter to determine using "Simulis Thermodynamic Software" by minimizing : $F = \sum \frac{(P_{exp} - P_{cal})^2}{P_{exp}}$

Our experimental measurements and those from the literature [3-8] are used for model parameter estimation.

Results



CO₂ solubility in propylene carbonate at : — 298,15 K and — 333,15 K



CO₂ solubility in anisole at : — 333,15 K and — 372,3 K

Conclusion

- The calorimetric technique allowed to determine simultaneously the solubility of CO₂ in BBS and the heat required to separate it from the absorbent.
- To avoid using large amounts of solvent and time consuming solubility measurements, an original approach combining the calorimetric technique and IR spectroscopy is used to rapidly evaluate BBS for VAR process.
- At 333,15 K and 4,0 MPa, the highest CO₂ solubility is observed for GVL and the lowest energy required to separate CO₂ from the solvent is obtained with anisole.
- SRK equation of state is capable of correlating experimental values and can be used process simulation.

Acknowledgement

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