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Predicting vapor-liquid equilibria from the densities of binary non-saturated mixtures of CO2 and organic solvent at elevated pressures

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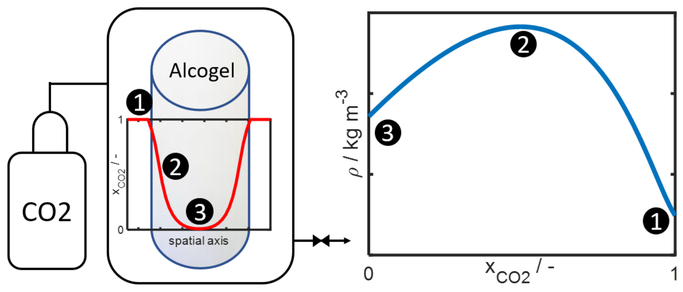
INTRODUCTION

Motivation:

- Modeling of extraction processes of organic solvents from porous media (e.g. aerogels) with compressed CO_2 requires precise mixture density data
- Extraction processes are typically isobaric and isotherm and span the whole composition range
- Literature data of organic-solvent/CO_2 mixture densities are overwhelmingly saturated densities



Drying of aerogels

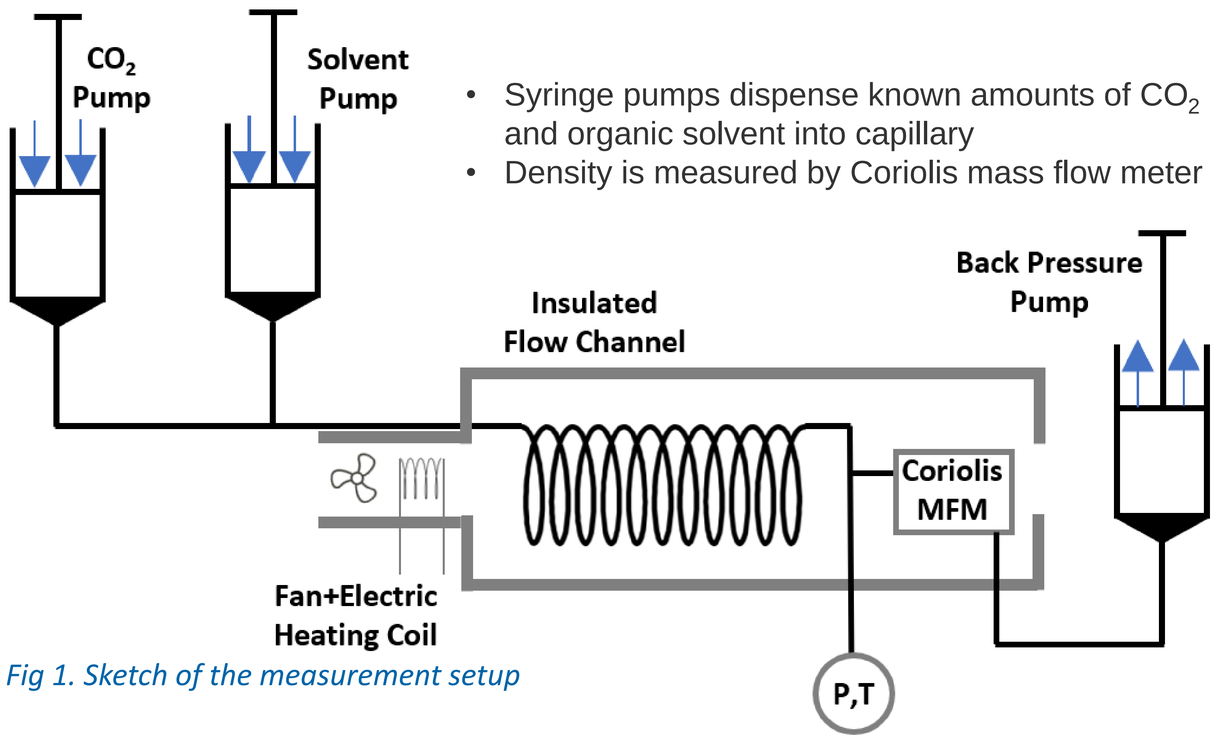
Proceeding:

- Binary mixture densities are measured at isobaric and isotherm conditions
- NRHB-parameters are fitted to binary density data

Can NRHB-parameters fitted solely to density data also predict vapor-liquid equilibria?

SETUP AND MEASUREMENT

Setup:



- Syringe pumps dispense known amounts of CO_2 and organic solvent into capillary
- Density is measured by Coriolis mass flow meter

Fig 1. Sketch of the measurement setup

Table 1. Measuring range

	Range	Increment
Organic solvent	EtOH, Acetone, Acetonitrile, DMSO	
P	6-12 MPa	1 MPa
T	308-333 K	5 K
x_{CO2}	0-1	0.05

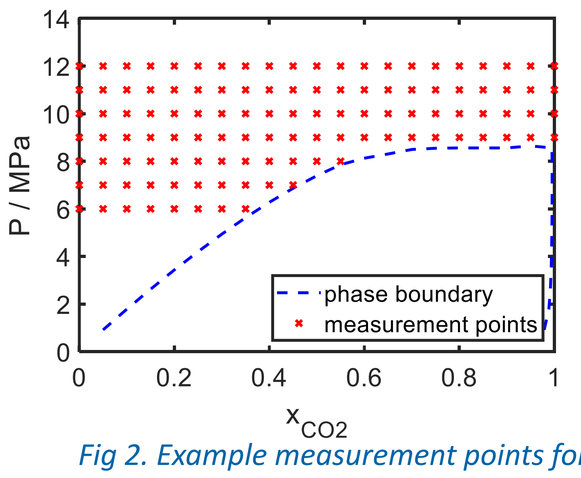


Fig 2. Example measurement points for one temperature step

MIXTURE DENSITY CORRELATION USING NRHB-EOS

Non-Random Hydrogen Bonding (NRHB) Model [1]:

- Compressible Lattice-Fluid based EoS that also accounts for non-random distribution of species and hydrogen bonding
- Three adjustable pure substance parameters fitted to pure substance densities: $\varepsilon^*_{h,i}$, $\varepsilon^*_{s,i}$, $v^*_{sp0,i}$
- One temperature independent binary interaction parameter: k_{ij}
- Equation of state:

$$\tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) - \tilde{\rho}\left(\Phi_1\frac{l_1}{r_1} + \Phi_2\frac{l_2}{r_2} - v_H\right) - \frac{z}{2}ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right] + \frac{z}{2}ln\Gamma_{00}\right] = 0$$

RESULTS

Mixture densities:

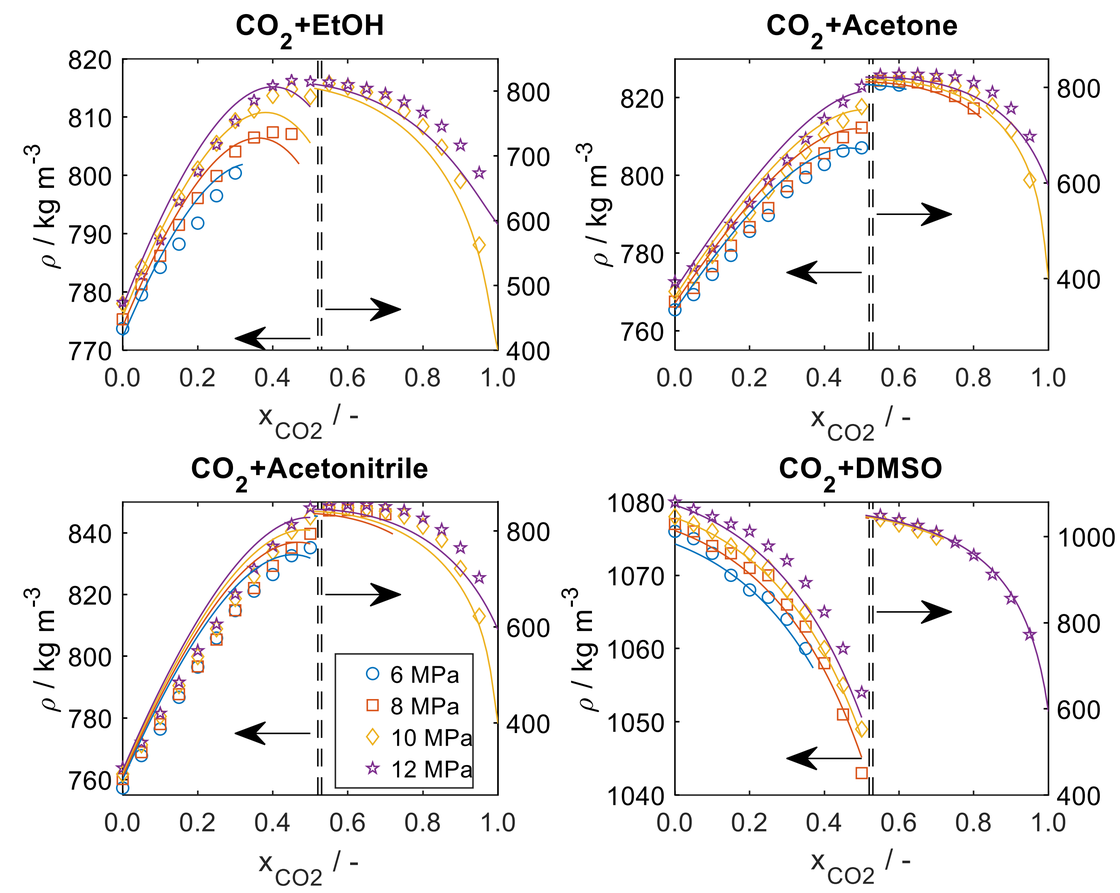


Fig 3. Measured mixture densities for 323 K. Lines show NRHB correlation

Table 2. Summary of density correlation using NRHB-EoS

Binary mixture	Number of measurement points	k_{ij}	AAD (ρ) %
CO_2+EtOH	665	0.115	1.28
CO_2+Acetone	809	0.0801	1.26
CO_2+Acetonitrile	757	0.1013	1.80
CO_2+DMSO	658	-0.187	0.67

VLE prediction:

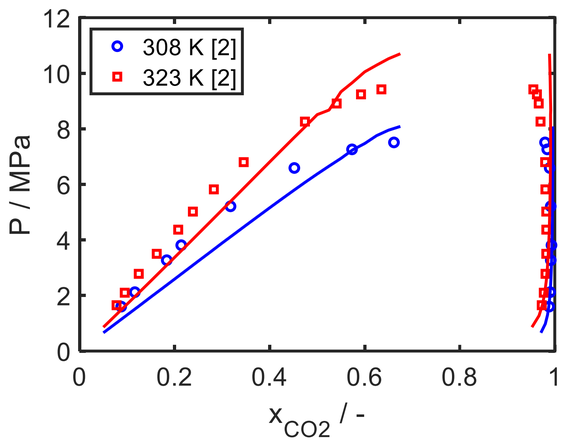


Fig 3. Phase Equilibria for CO_2+EtOH. Lines show NRHB prediction with k_{ij}=0.

CONCLUSION

- Mixture densities for the four binary systems consisting of CO_2 and EtOH, Acetone, Acetonitrile and DMSO were measured form 308-333K and 6-12 MPa
- Excellent correlation of mixture densities with the NRHB-EoS with one temperature independent binary parameter
- Parameters fitted to density data allow for prediction of the vapor-liquid equilibrium for the System of CO_2+EtOH

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[2] Fluid Phase Equilibria 2004 224 89–96

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