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Experimentelle Untersuchung und molekulardynamische Simulation der Gaslöslichkeit von Sauerstoff in Cyclohexanol

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Computational Molecular Engineering

Synopsis

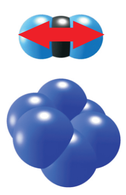
The development of novel octahedral molecular sieves is of particular interest for the catalytic oxidation of cyclohexane in carbon dioxide expanded media. In this project, the thermodynamic properties of the relevant mixtures are investigated. Therefore, the mixtures of interest are studied with respect to the gas solubility both by experiment and molecular simulation.

A literature survey shows a lack of gas solubility data for oxygen in cyclohexanol. Therefore, the Henry's law constant of oxygen in pure cyclohexanol is measured between 298 and 393 K. A synthetic method is used for the experiments.

Molecular simulations are performed with multi-center Lennard-Jones models with superimposed electrostatic sites. For all the components of interest, molecular models are available in the literature [1,2,3]. Unlike interactions are modeled with the modified Lorentz-Berthelot combination rule. The predictions from simulation are compared to experimental Henry's law constant data, which are in a very good agreement. Additionally, high pressure vapor-liquid equilibria of the mixtures are predicted.

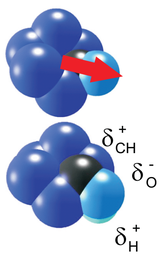
Molecular models developed in this work

The parameters are fitted in the optimization process to yield the correct VLE behavior of the modeled pure substance. The optimization is performed using a Newton scheme as proposed by Stoll [4]. It relies on a least-square minimization of a weighted fitness function that quantifies the deviations of simulation results from a given molecular model compared to experimental data.



Carbon dioxide
3 LJ sites plus point quadrupole

Cyclohexane
6 LJ sites



Cyclohexanone
7 LJ sites plus point dipole

Cyclohexanol
7 LJ sites plus 3 point charges

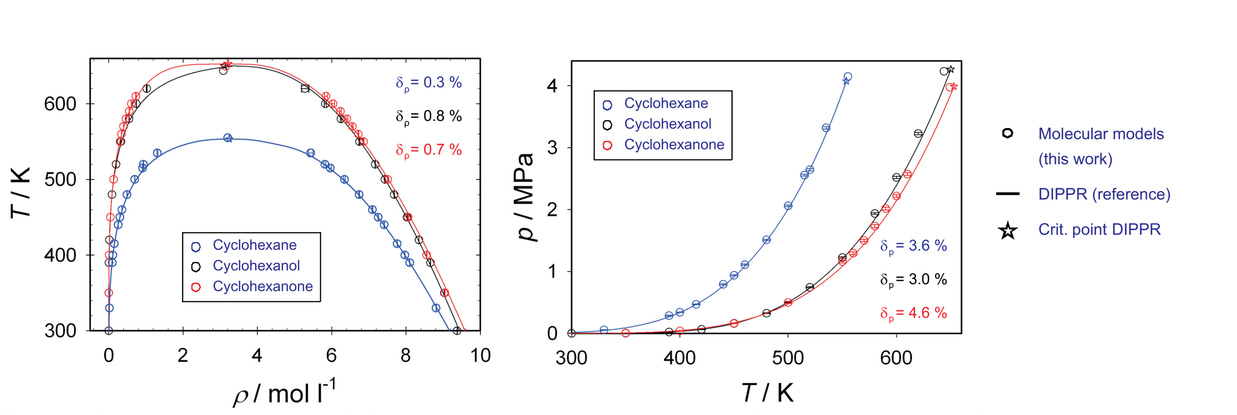


Fig. 1: Saturated densities (left) and vapor pressure (right) of cyclohexane, cyclohexanone and cyclohexanol

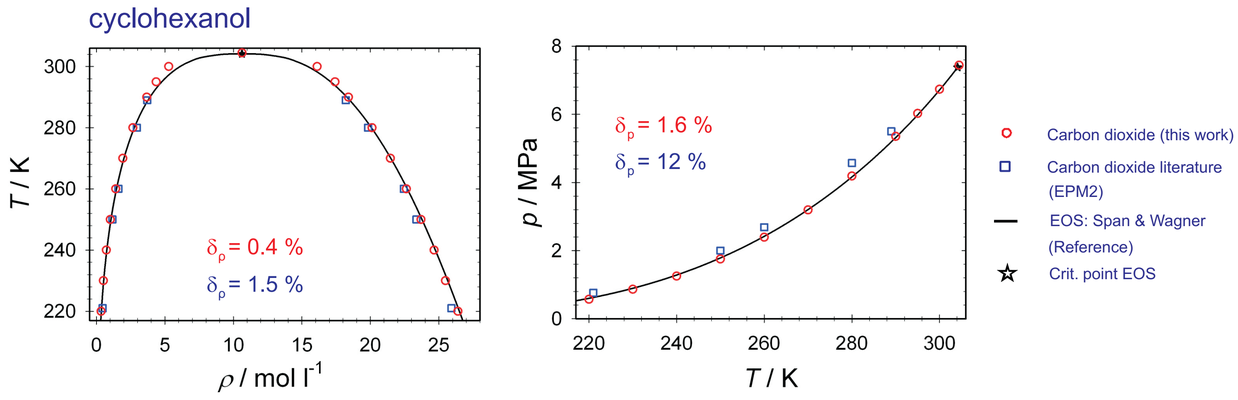
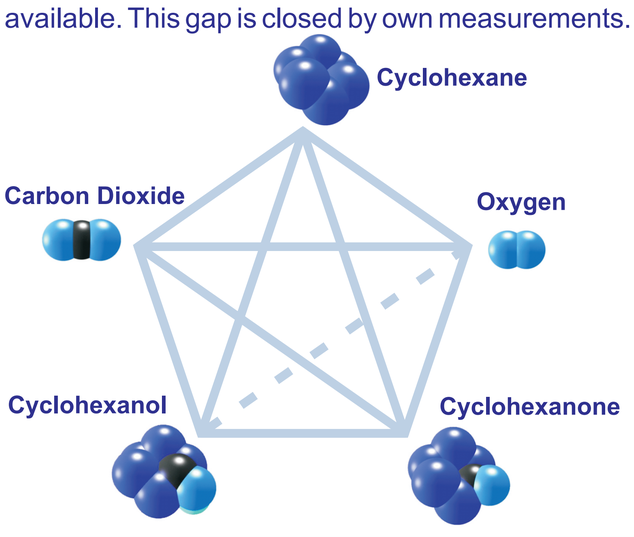


Fig. 2: Saturated densities (left) and vapor pressure (right) of carbon dioxide

Reacting system

Experimental data for binary mixtures, VLE or Henry's law constants, are needed to adjust the unlike interaction parameter ξ. Especially for the subsystem cyclohexanol + oxygen, no experimental data is available. This gap is closed by own measurements.



Modified Lorentz-Berthelot combination rule

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2$$

$$\varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \varepsilon_B}$$

Experimental data available (VLE or Henry's law constants)

Gas solubility measurements

Gas solubility measurements

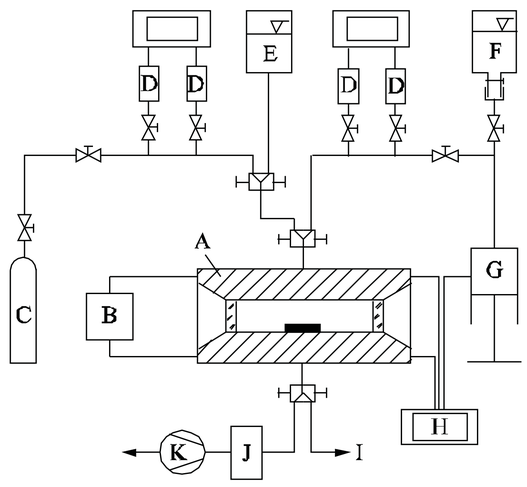


Fig. 3: Experimental setup

A: Cylindrical high-pressure equilibrium view cell with two sapphire windos and magnetic stirrer
B: Thermostat
C: Container for the gas
D: Pressure transducers
E: Tank for rinsing water
F: Tank for solvent mixture
G: High-pressure spindle press
H: AC-brigde with three platinum resistance thermometers
I: Solution outlet
J: Cooling trap
K: Vacuum pump

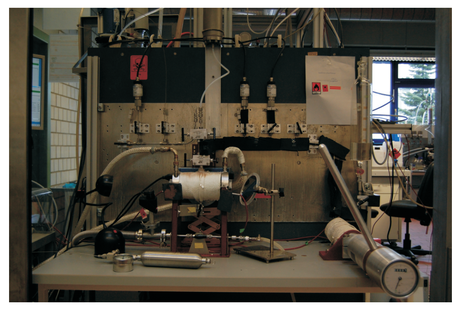


Fig. 4: Gas solubility apparatus

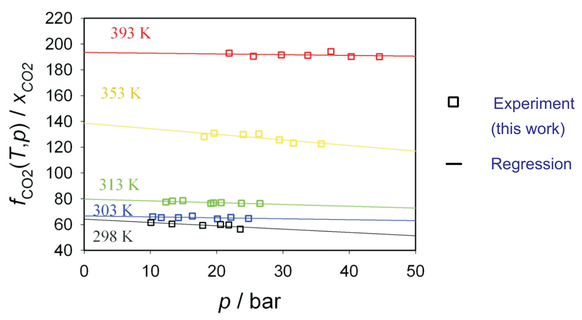


Fig. 9: Plot for determining the Henry's law constant

Carbon dioxide + cyclohexane + cyclohexanone

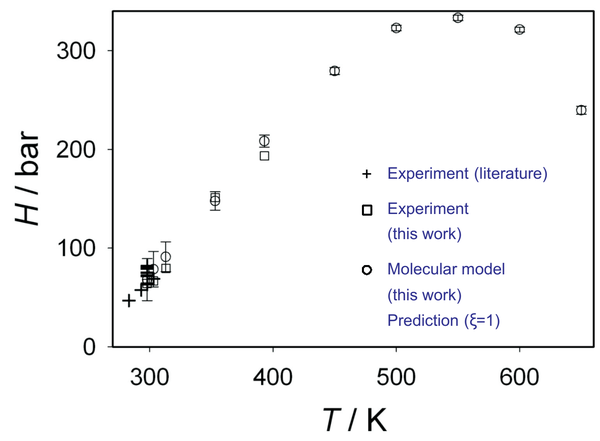


Fig. 5: Henry's law constant of carbon dioxide + cyclohexanone

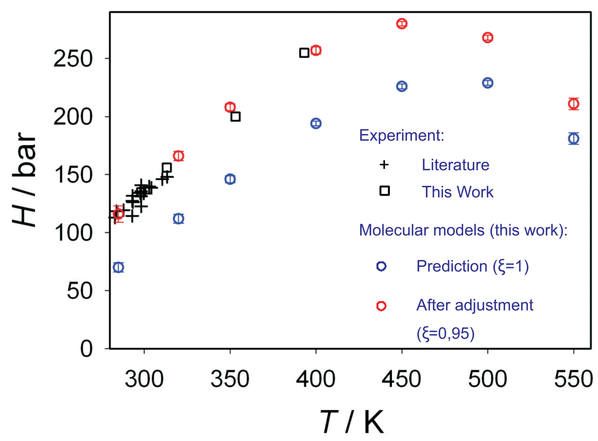


Fig. 6: Henry's law constant of carbon dioxide + cyclohexane

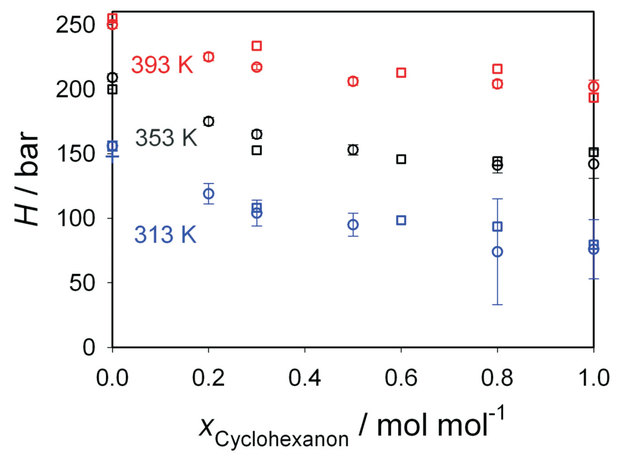


Fig. 7: Henry's law constant of carbon dioxide + cyclohexanone + cyclohexane

Extrapolation of the experimental Henry's law constant with:

$$H_{CO_2} = \lim_{p \to p^s_{liq.}} \left[\frac{f_{CO_2}(T,p)}{x_{CO_2}} \right]$$

$$f_{CO_2} = p \cdot y_{CO_2} \cdot \varphi_{CO_2}$$

Oxygen + cyclohexanol

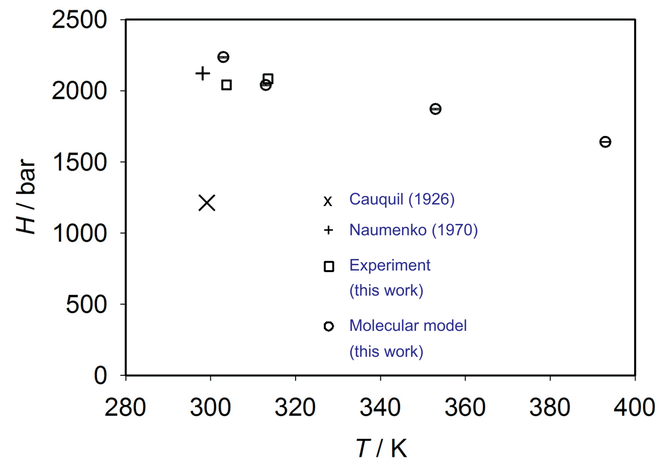


Fig. 8: Henry's law constant of oxygen + cyclohexanol

Only strongly contradictory data is available in the literature. This data can not be used for an adjustment of the binary interaction parameter ξ.

With the new experiments, the data point by Naumenko can be confirmed. The new Henry's law constants were used to adjust the binary interaction parameter ξ with a value of 0.908.

Literature

[1] Vrabec, J.; Stoll, J.; Hasse, H. J. Phys. Chem. B 105 (2001) 12126-12133.
[2] Merker, T.; Vrabec, J.; Hasse, H. Soft Materials, accepted (2010).
[3] Merker, T.; Engin, C.; Vrabec, J.; Hasse, H. J. Phys. Chem. 132 (2010) 234512.
[4] Stoll, J. VDI-Verlag, Düsseldorf (2005), Reihe 3.