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Thermodynamic Properties for the Heterogeneously Catalyzed Selective Oxidation of Cyclohexane in Carbon Dioxide Expanded Media by Experiment and Molecular Simulation

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Computational Molecular Engineering

Synopsis

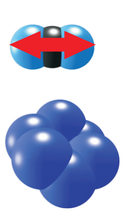
The development of novel octahedral molecular sieves is of particular interest for the catalytic oxidation of cyclohexane in carbon dioxide expanded media. In this project gas solubilities relevant in this process were studied. A literature survey shows a lack of gas solubility data for carbon dioxide and especially oxygen. Therefore, the Henry's law constants of carbon dioxide in pure cyclohexane and in pure cyclohexanone as well as in mixtures of these components is measured between 298 and 393 K [1]. Furthermore, the gas solubility of oxygen in pure cyclohexanol is measured. A synthetic method is used for the experiments.

Molecular simulations of the gas solubilities in the systems that were studied experimentally are performed with multi-center Lennard-Jones models with superimposed electrostatic sites. Only for some of the components of interest, molecular models are available in the literature [2]. For cyclohexane [3], cyclohexanol [4] and cyclohexanone [3] new molecular models are developed in this work. Furthermore, a new, improved carbon dioxide model is developed [5]. Unlike interactions are modeled with the modified Lorentz-Berthelot combination rule. The predictions from the molecular simulations are compared to the present experimental Henry's law constant data. Good agreement is observed. Additionally, high pressure vapor-liquid equilibira of the mixtures are predicted. Finally, predictive results for transport properties are presented.

Molecular Models Developed in This Work

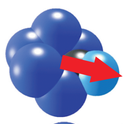
Parametrization Strategy

- Geometric parameters from quantum chemical calculations.
- Electrostatic and Lennard-Jones parameters optimized to experimental VLE data using a Newton scheme as proposed by Stoll [6], followed by the reduced unit method [4].

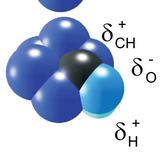


Carbon Dioxide
3 LJ sites plus point quadrupole

Cyclohexane
6 LJ sites



Cyclohexanone
7 LJ sites plus point dipole



Cyclohexanol
7 LJ sites plus 3 point charges

Vapor-Liquid Equilbiria

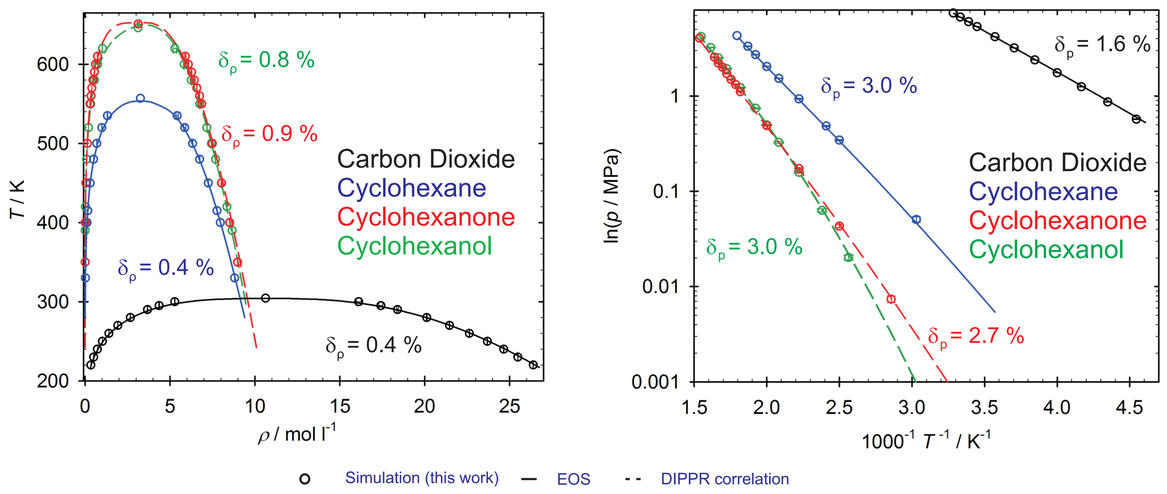


Fig. 1: Saturated densities (left) and vapor pressure (right) of carbon dioxide, cyclohexane, cyclohexanone and cyclohexanol.

Prediction of Transport Properties

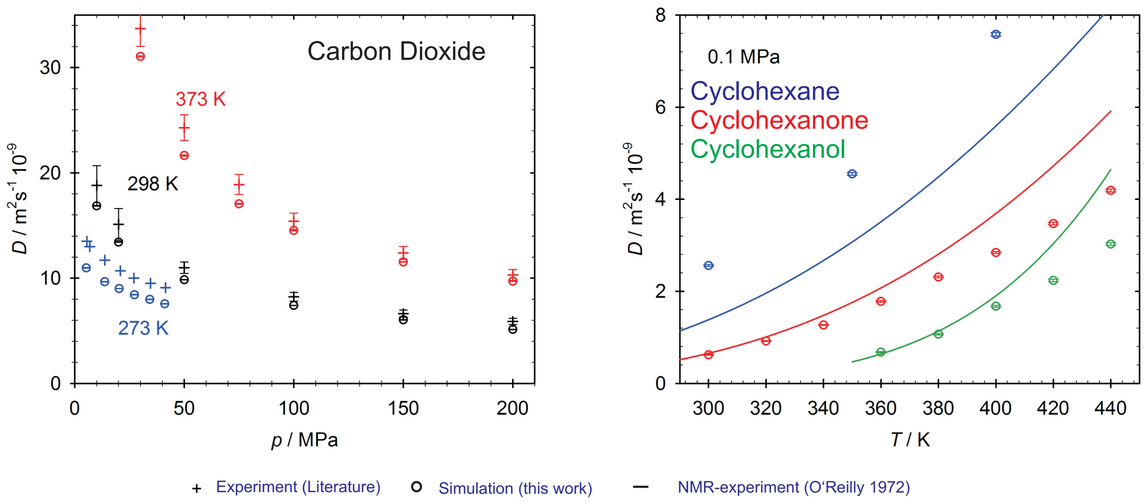


Fig. 2: Self-diffusion coefficient of carbon dioxide (left) and cyclohexane, cyclohexanone and cyclohexanol (right).

Gas Solubility Measurements

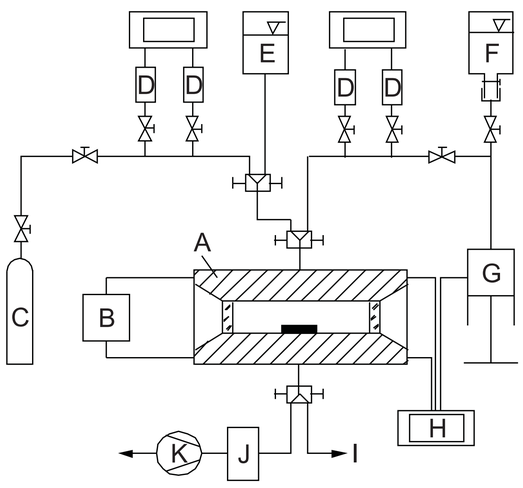
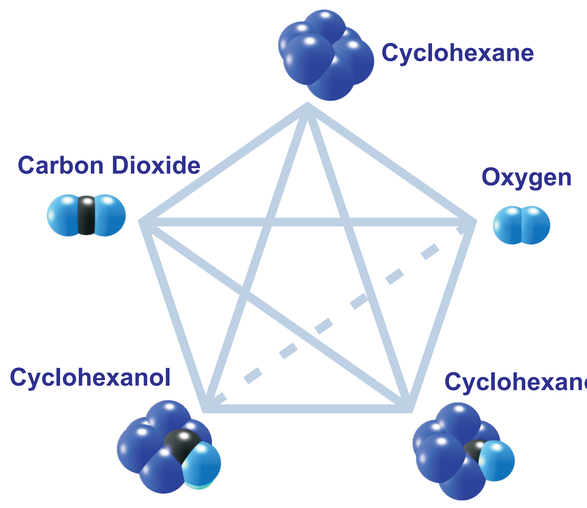


Fig. 3: Experimental setup

- 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

Reacting System

Experimental data for binary mixtures, i.e. 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

Henry's Law Constant

Carbon Dioxide

Oxygen

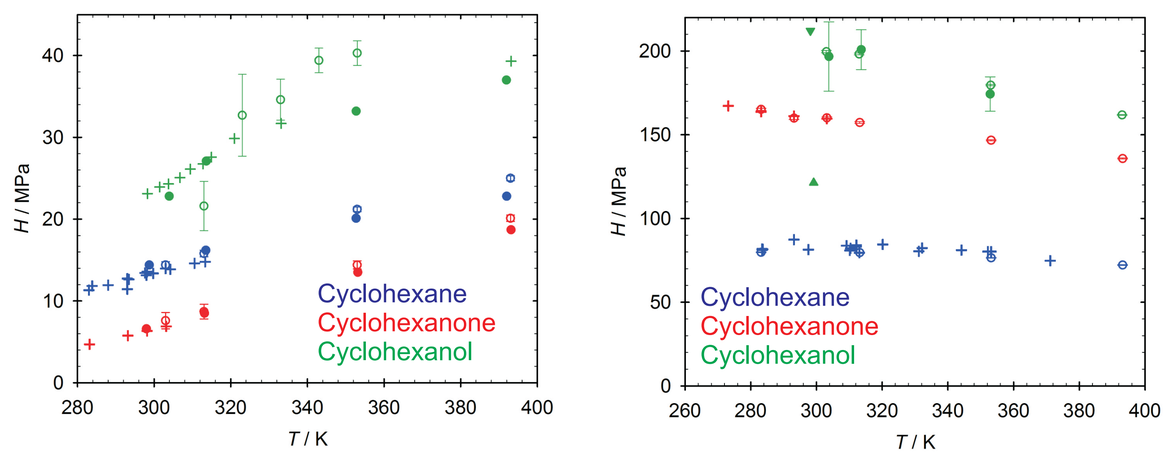


Fig. 4: Henry's law constant of carbon dioxide (left) and oxygen (right) in cyclohexane, cyclohexanone and cyclohexanol.

Cyclohexane + Cyclohexanone

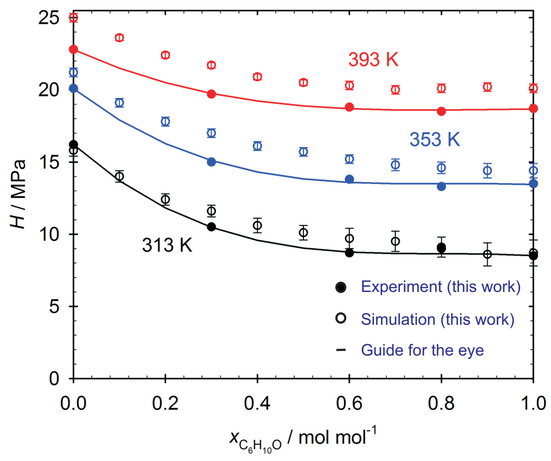


Fig. 5: Henry's law constant of carbon dioxide in mixtures of cyclohexane + cyclohexanone plotted over the liquid mole fraction of cyclohexanone.

Results

- Simulation in good agreement with experiment for Henry's law constants both for pure solvents and solvent mixtures.
- Henry's law constant of oxygen in cyclohexanol and of carbon dioxide in mixtures of cyclohexane and cyclohexanone is now known.

References

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