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Fluid phase behavior from molecular simulation: Hydrazine, Monomethyl-hydrazine, Dimethylhydrazine and binary mixtures containing these components

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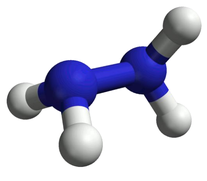
Synopsis

In the last years, molecular simulation has become a useful tool to accurately predict thermodynamic properties of fluids on the basis of molecular force field models. Especially in cases of industrially relevant hazardous and/or highly explosive substances, molecular simulation offers big advantages for the determination of pure substance and mixture properties. Hydrazine and its derivates, which are often used as high-energy propellants in rocket thrusters, are good examples for these safety-relevant substances.

In the present work, new molecular models for Hydrazine, Monomethylhydrazine and Dimethylhydrazine are developed. The models are based on a rigid set of Lennard-Jones sites with superimposed point charges. The parameterization of the molecular interaction models is carried out by using quantum chemical calculations and subsequent fitting to experimental vapor pressure and saturated liquid density data following a procedure that was proposed earlier [1]. To validate the molecular models, vapor-liquid equilibria of the pure substances and their binary mixtures with Water and Ammonia are calculated and compared with experimental data and molecular models from the literature. In addition, the Henry's law constant for the physical solubility of Argon and Nitrogen in liquid Hydrazine, Monomethylhydrazine and Dimethylhydrazine are computed.

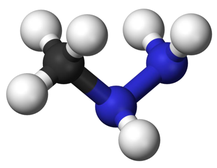
Developed molecular models

Hydrazine



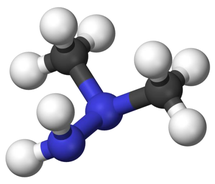
- ✓ 2 LJ sites
- ✓ 6 point charges

Monomethylhydrazine



- ✓ 3 LJ sites
- ✓ 3 point charges

Dimethylhydrazine



- ✓ 4 LJ sites
- ✓ 3 point charges

Simulation results: Pure fluid VLE

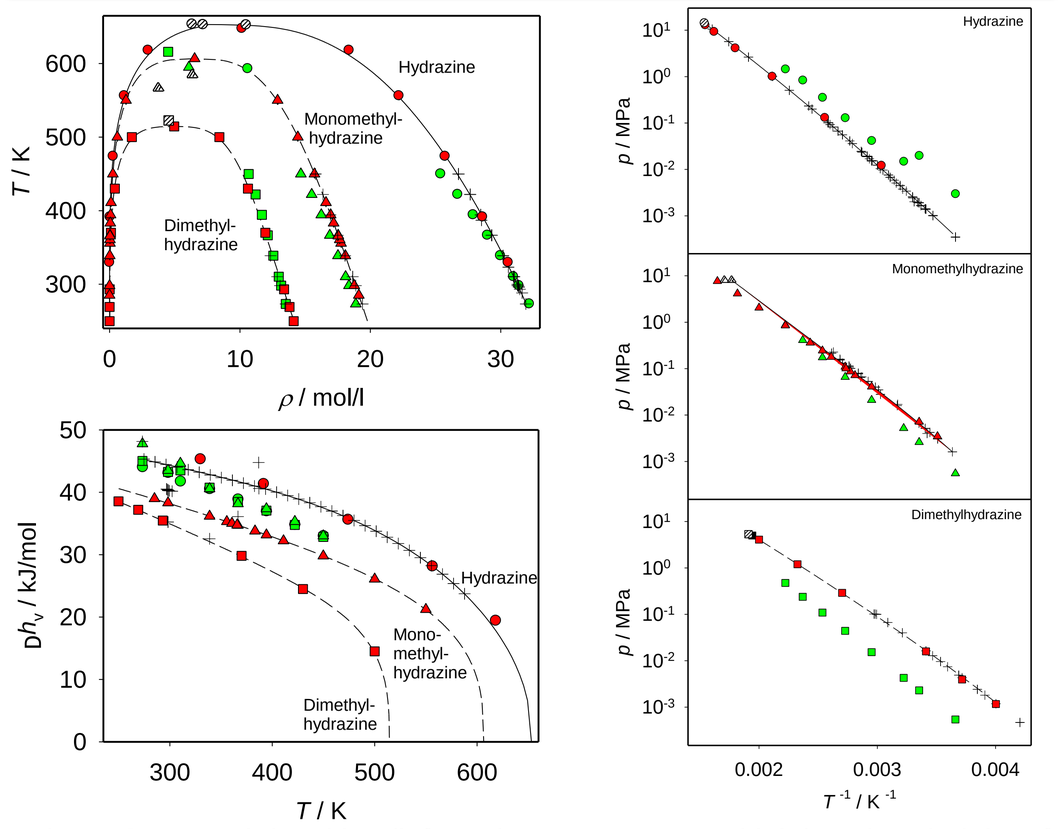


Fig. 1. Saturated densities (left, top), vapor pressure (right) and Enthalphy of Vaporization of Hydrazine, Monomethylhydrazine and Dimethylhydrazine.

Modeling strategy

Pure fluids

- Geometric data of the molecules (bond lengths, angles and dihedrals) were determined by quantum chemical calculations.
- Electrostatic and Lennard-Jones parameters optimized to experimental VLE data using a Newton scheme as proposed by Stoll [1], followed by the reduced unit method [2].

Mixtures

Modified Lorentz-Berthelot combination rule:

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

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

The unlike interaction parameter ξ can be adjusted to a single experimental binary vapor pressure or a Henry's law constant.

Simulation results: Mixtures

Simulated mixtures

- Hydrazine + Dimethylhydrazine
- Water + Hydrazine
- Water + Monomethylhydrazine
- Water + Dimethylhydrazine
- Ammonia + Hydrazine
- Ammonia + Monomethylhydrazine
- Ammonia + Dimethylhydrazine

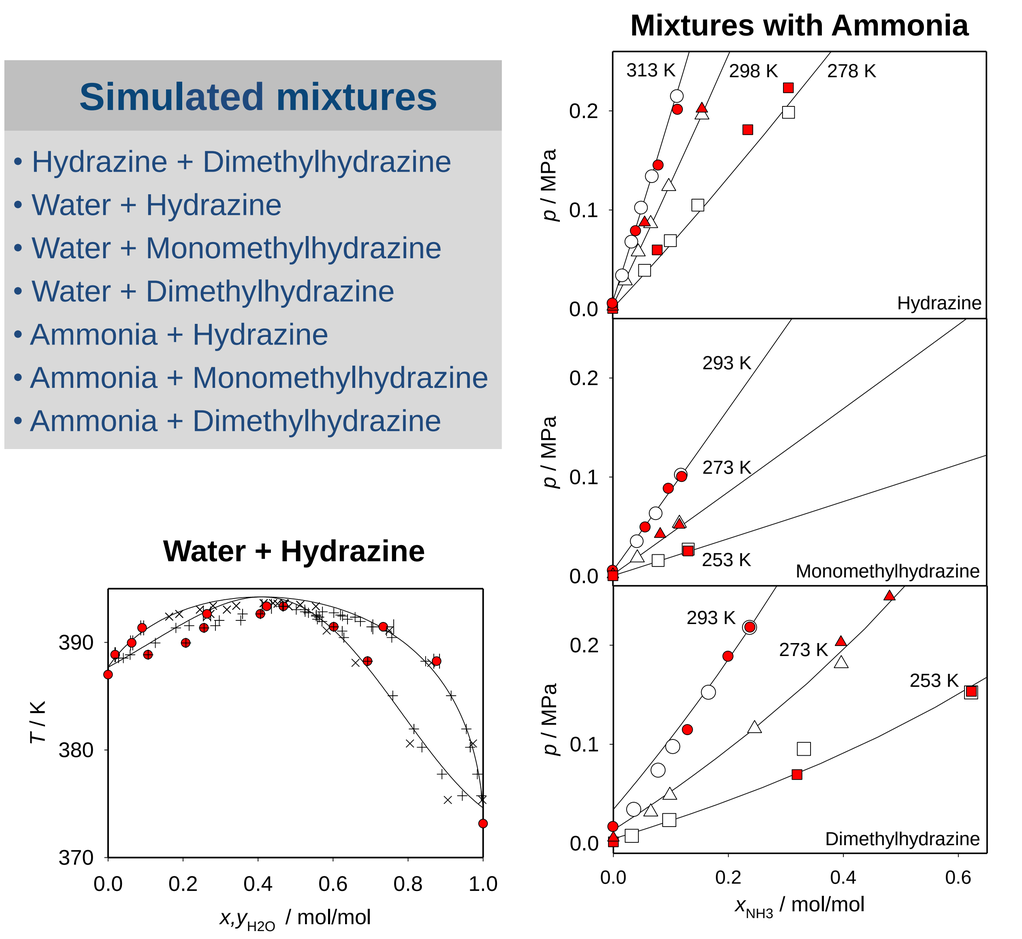


Fig. 2. Isobaric vapor-liquid phase diagram of Water + Hydrazine at 0.1013 MPa (left) and Isothermal vapor-liquid phase diagrams of binary mixtures containing Ammonia and the hydrazines at different temperatures (right).

Henry's law constant

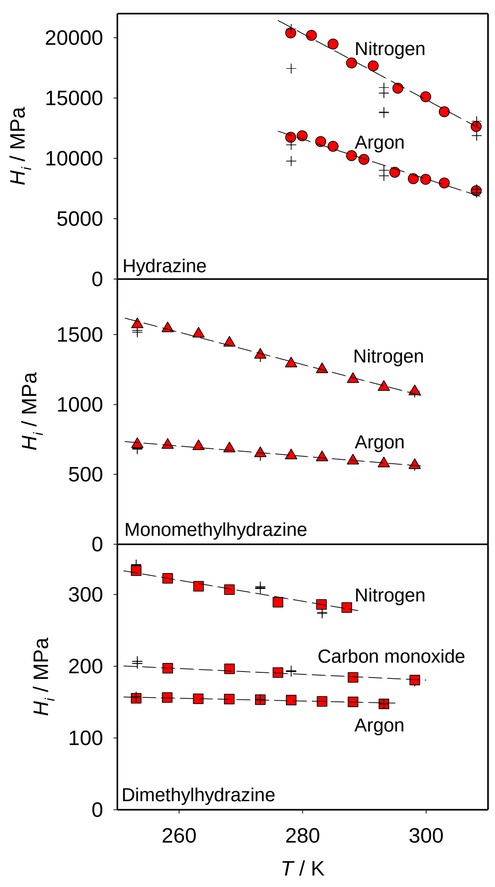


Fig. 3. Henry's law constant of gases in liquid Hydrazine, Monomethyl-hydrazine and Dimethylhydrazine.

Results

- Molecular models for the three pure fluids were developed.
- The unlike interaction parameter ξ were adjusted for 14 binary mixtures.

➡ These new models for pure fluids and mixtures could be valuable for the prediction of properties under different conditions and for systems, where no experimental data are available.

References

[1] Stoll, J. VDI-Verlag, Düsseldorf (2005), Reihe 3, Nr. 836.
[2] Merker, T.; Vrabec, J.; Hasse, H. Soft Materials 10: 3-24 (2012).
[3] K.E. Gutowski, B. Gurkan, E.J. Maginn, Pure Appl. Chem. 81 1799-1828 (2009).

Symbols

● ▲ ■ Simulation, present work

○ △ □ + Experimental data from the literature

● ▲ ■ Simulation, Gutowski et al. [3]

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