Thermodynamik-Kolloquium, Bayreuth, 5. Oktober 2010

Transportgrößen wasserstoffbrückenbildender Reinstoffe und Mischungen aus molekularen Simulationen

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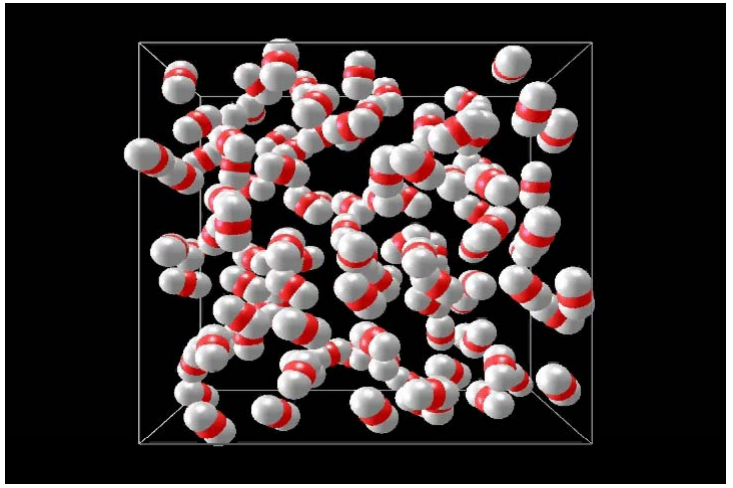
Computational
Molecular Engineering

Molekulare Simulation

- Ziel

  Berechnung makroskopischen Verhaltens
  aus molekularen Wechselwirkungen
  Hier: Transportgrößen



- Molekulardynamik (MD)

  Lösung der Bewegungsgleichungen

  ✓ statische Eigenschaften

  ✓ dynamische Eigenschaften

- Methoden zur Ermittlung von Transportgrößen

  ✓Gleichgewichts-MD (EMD)

  - Green-Kubo Methode
  - D_i, η

  ✓Nichtgleichgewichts-MD (NEMD)

  - Reverse BD – NEMD
  - λ

EMD: Green-Kubo Formalismus

Gleichgewichts-Schwankung ➡ $F_i = \sum_j L_{ij} Y_j$ Mikroskopischer Fluss ➡ Mikroskopisches Gleichgewicht

Transportkoeffizienten ⟷ Autokorrelationsfunktionen

- Selbstdiffusion

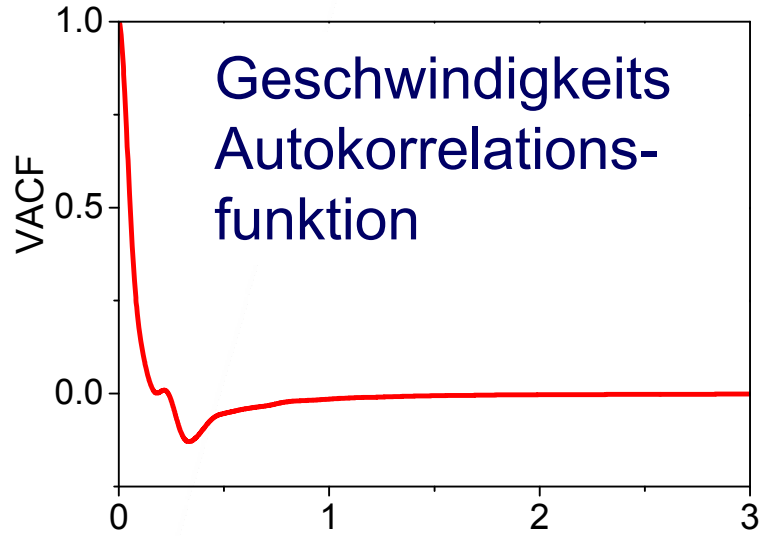
$$D_i = \frac{1}{3N_i} \int_0^\infty dt \left\langle \sum_i^N v_i(0) \cdot v_i(t) \right\rangle$$

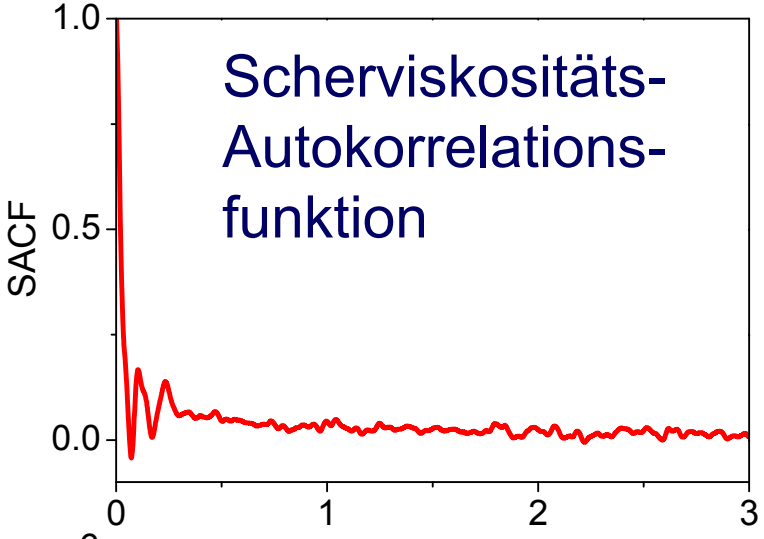
- Scherviskosität

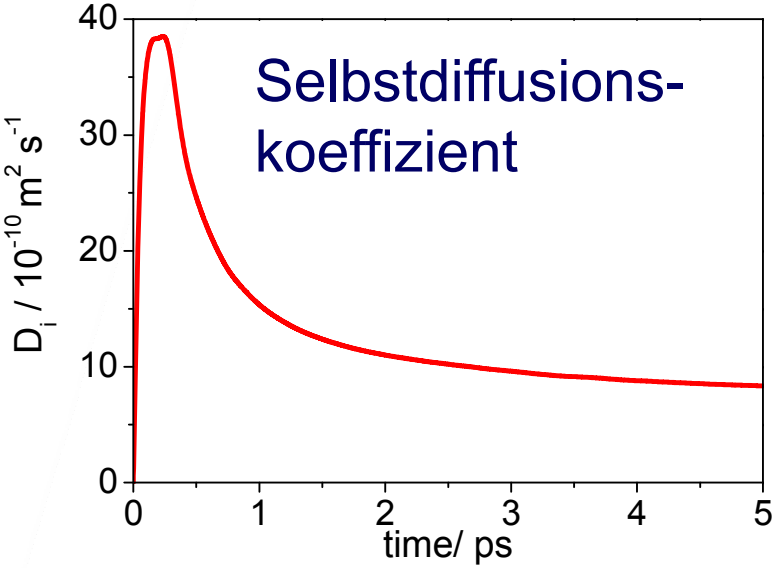
$$\eta_s = \frac{1}{Vk_BT} \int_0^\infty dt \left\langle J_P^{xy}(t) \cdot J_P^{xy}(0) \right\rangle$$

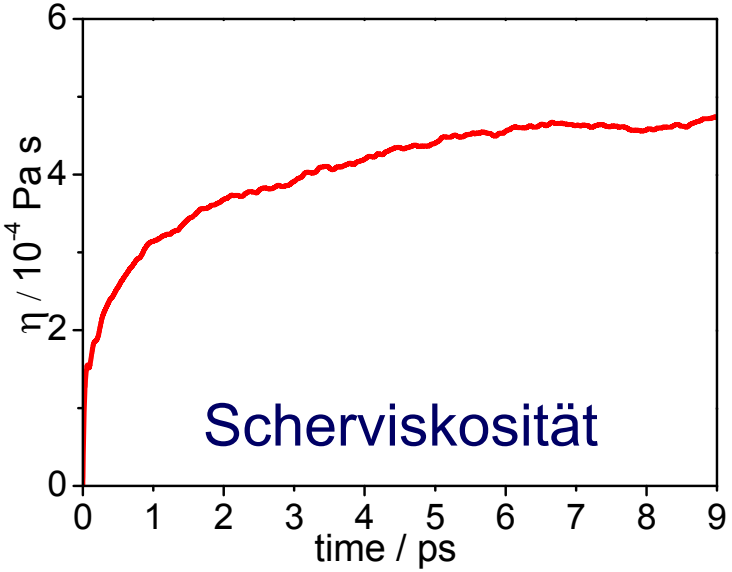
$$J_p^{xy} = \sum_{i=1}^N m_i \cdot v_i^x \cdot v_i^y - \sum_{i=1}^N \sum_{j>i}^N r_{ij}^x \frac{\partial \phi(r_{ij})}{\partial r_{ij}^y}$$

Autokorrelationsfunktionen

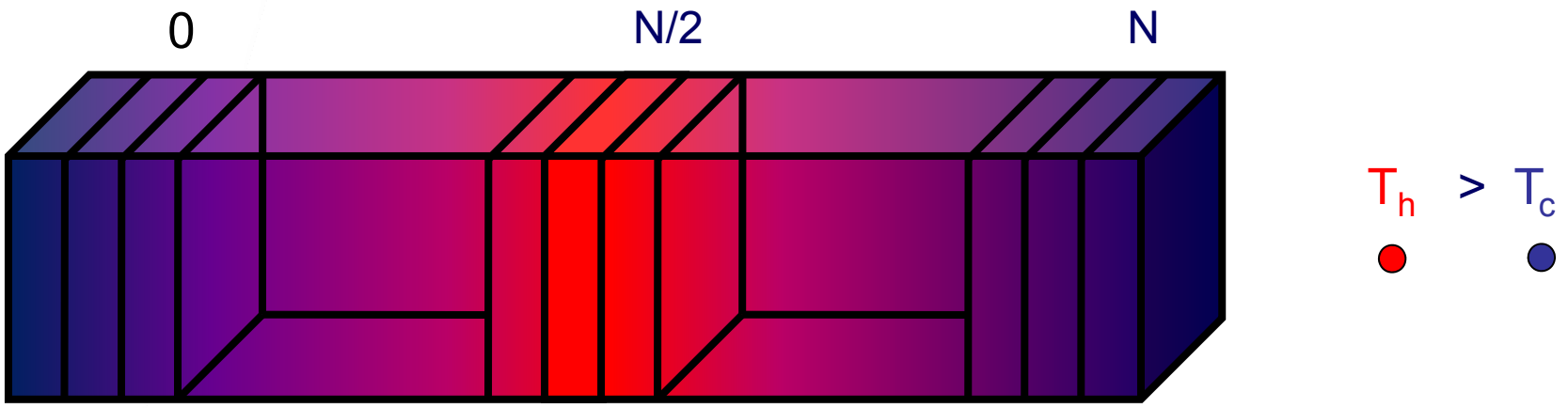








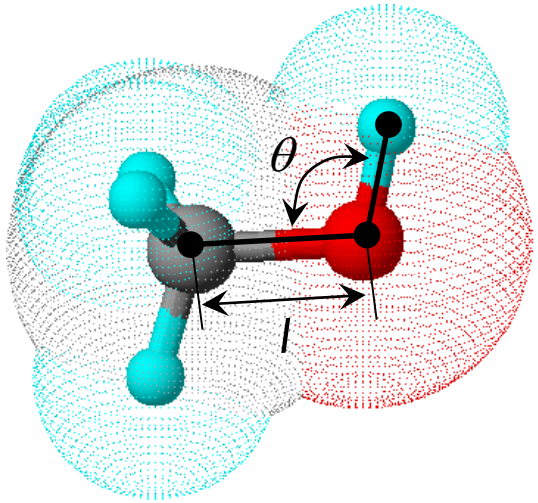
Nichtgleichgewichtsmethode (NEMD)

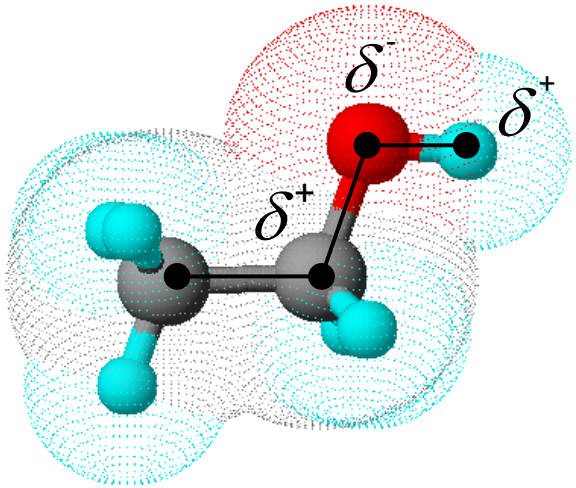


„Normale“ NEMD: Vorgabe $\Delta T \rightarrow$ Ermittlung des Wärmeflusses

„Reverse“ NEMD: Vorgabe des Wärmeflusses $\rightarrow$ Ermittlung ΔT

Molekulare Modelle



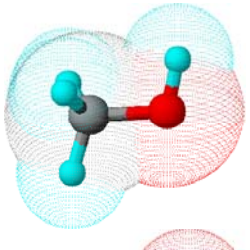
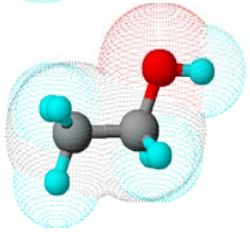
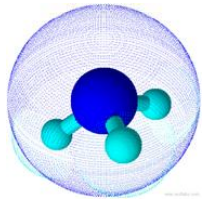
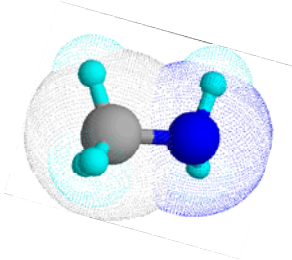
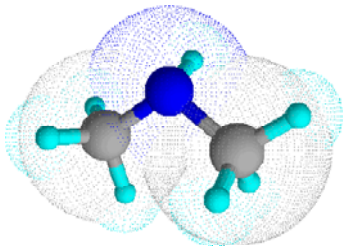
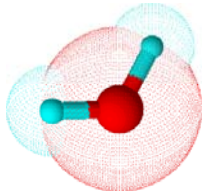


- ✓ Starre, United-Atom Mehrzentren Lennard-Jones (LJ) Modelle
- ✓ Modellierung der Wasserstoffbrücke/Polarität über Punktladungen

Geometriep[illegible]chemischen Rechnungen
Anpassung [illegible]modellparameter an experimentelle
Dampfdrücke, Sededichten, Verdampfungsenthalpien.

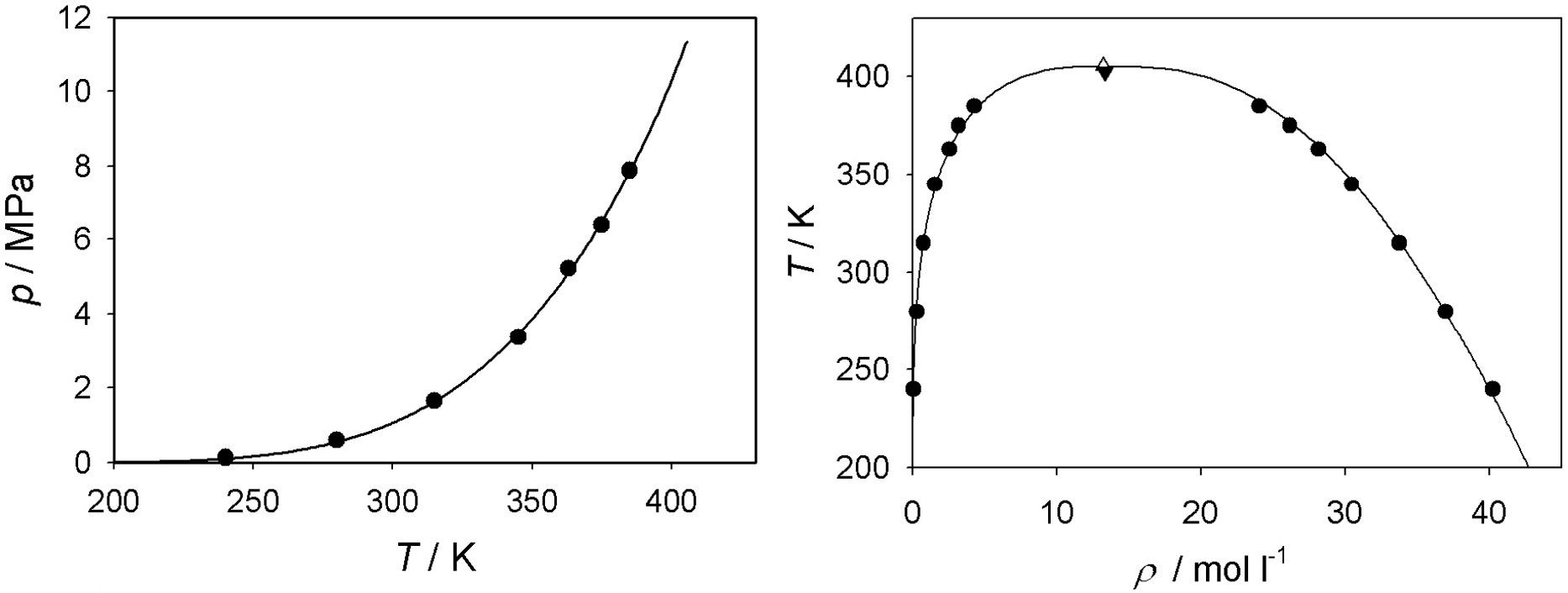
Keine Transporteigenschaften!

Betrachtete Reinstoffe

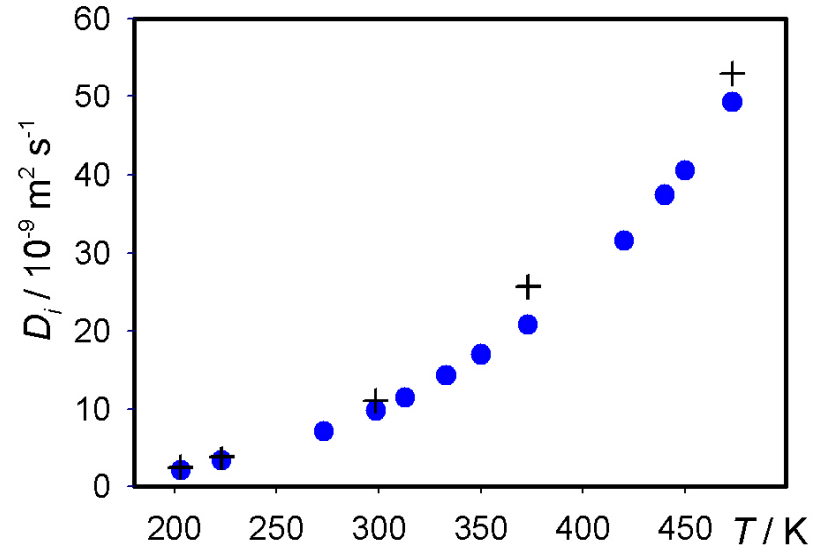
- Eigene Modelle
  - ✓ Methanol 
  - ✓ Ethanol 
  - ✓ Ammoniak 
  - ✓ Methylamin 
  - ✓ Dimethylamin 
- Modell aus der Literatur
  - ✓ Wasser: TIP4P/2005 

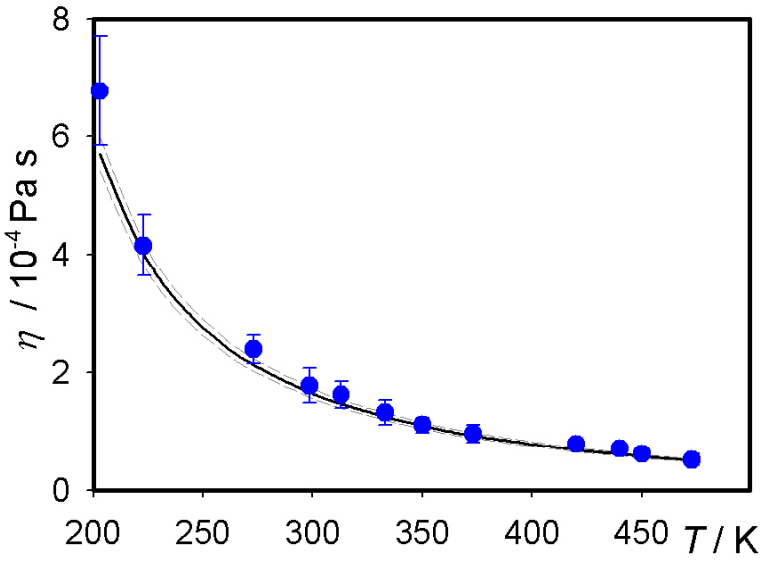
Ergebnisse VLE Daten mit eigenen Modellen

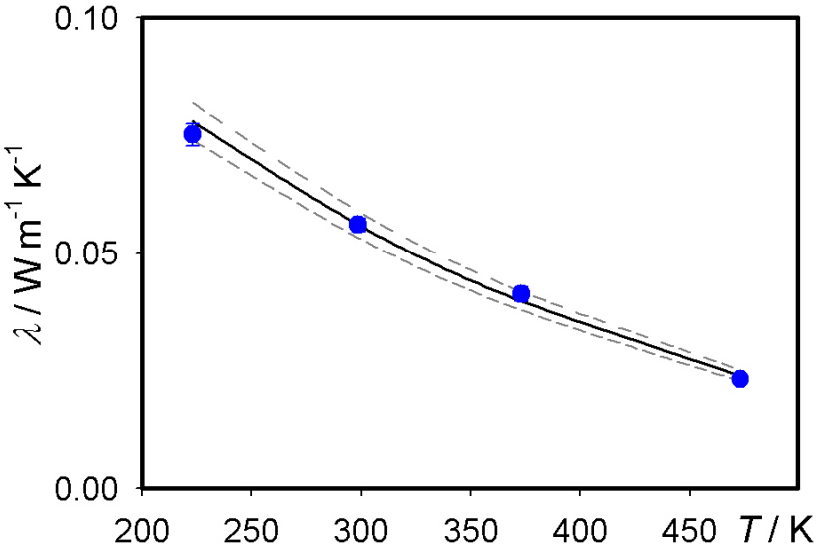
Beispiel: Ammoniak



Vorhersagen Transportgrößen: Ammoniak

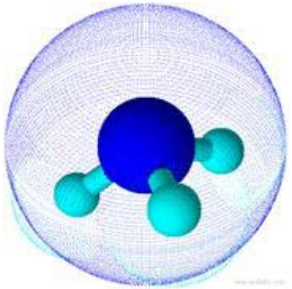




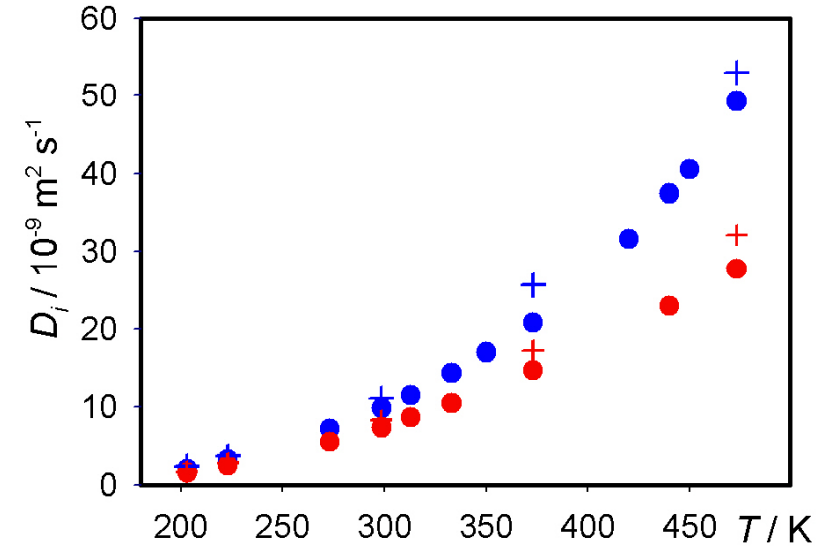


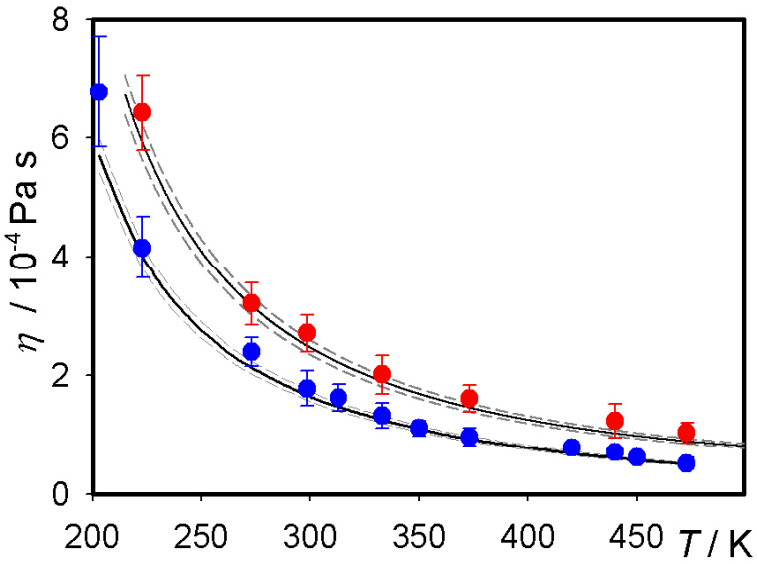
- Vorhersage Simulation
- \+ Experiment (Literatur)
- — Korrelation (REFPROP)

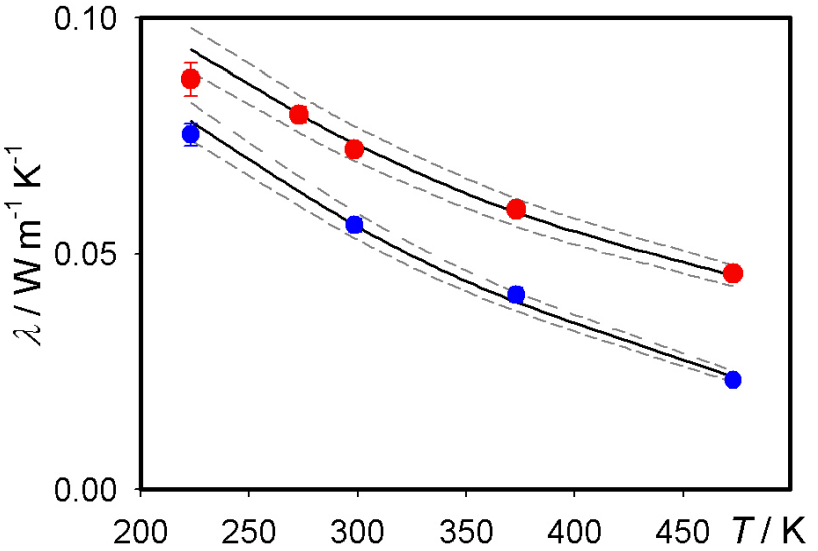
alle Angaben: **50 MPa**



Vorhersagen Transportgrößen: Ammoniak

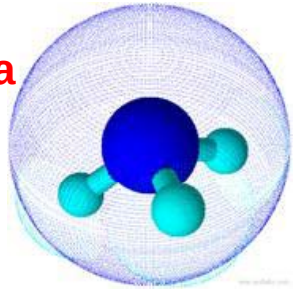




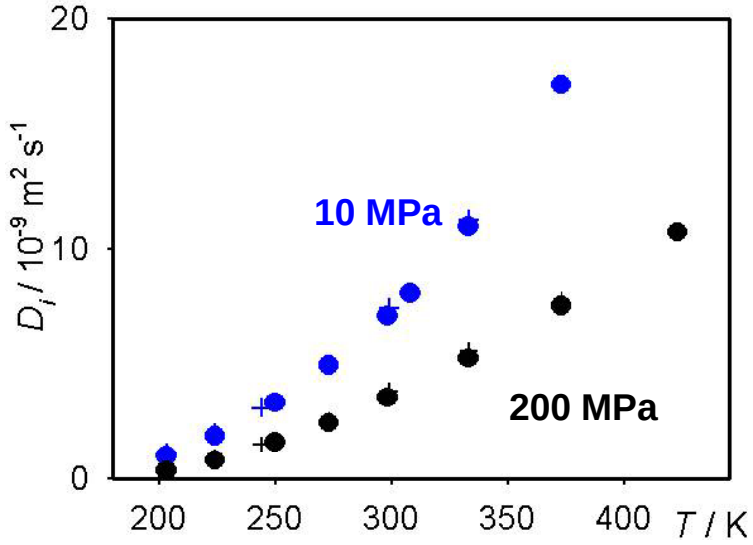


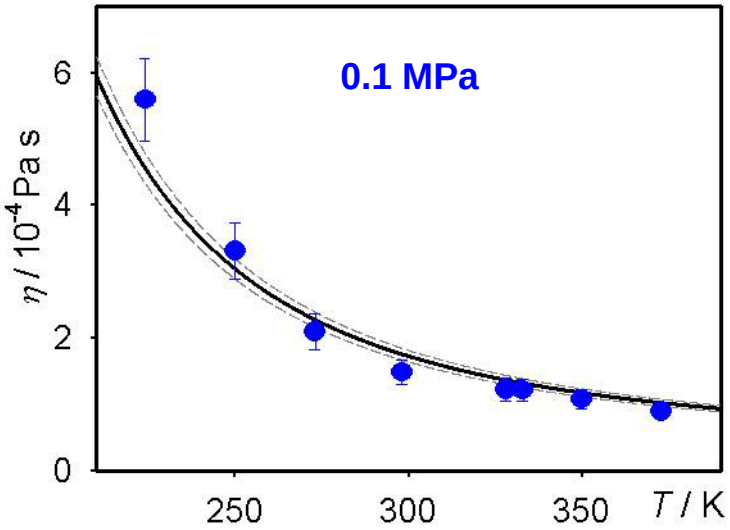
- Vorhersage Simulation
- \+ Experiment (Literatur)
- — Korrelation (REFPROP)

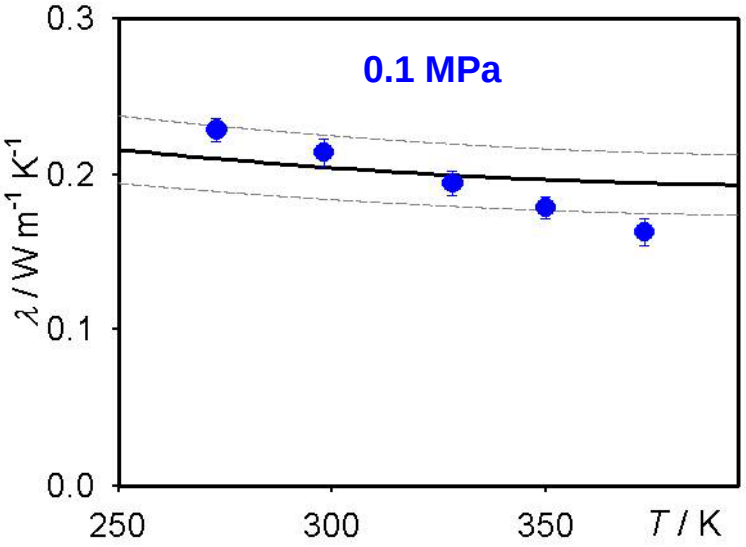
neue Angaben: **200 MPa**



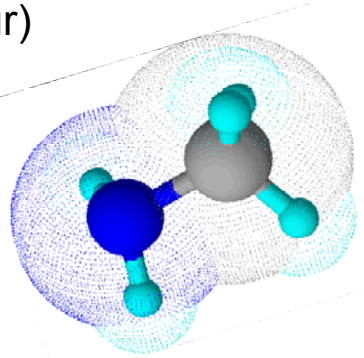
Vorhersagen Transportgrößen: Methylamin



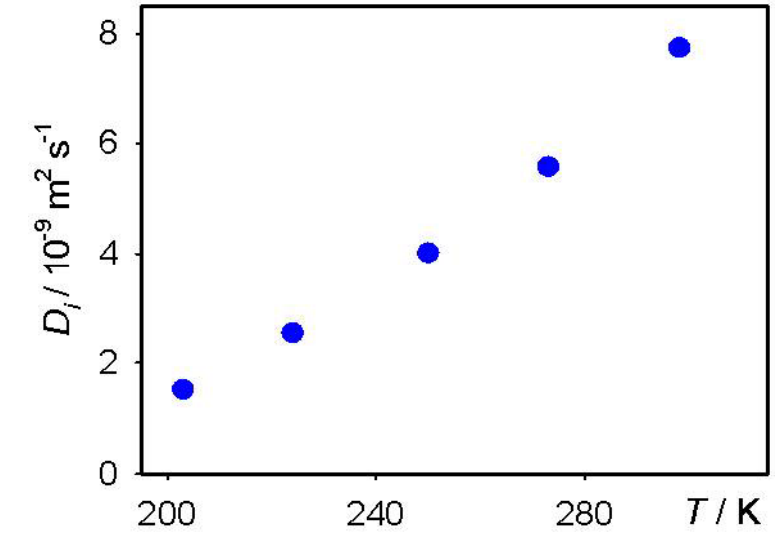


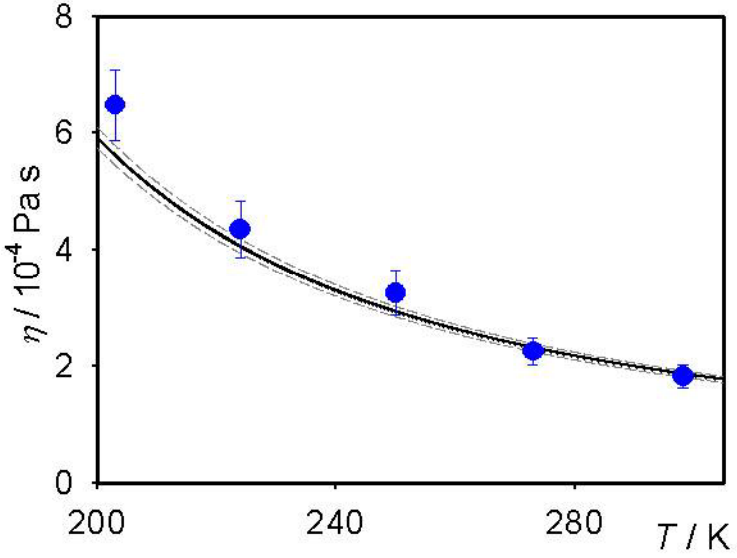


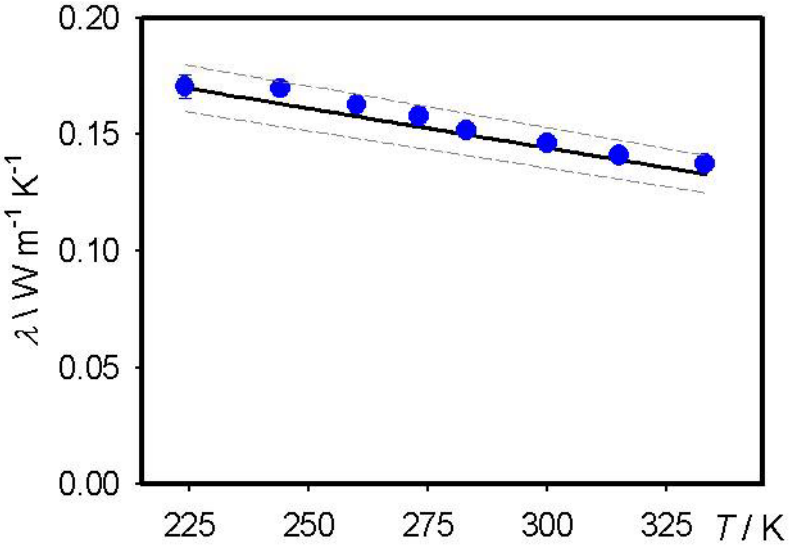
- ● Vorhersage Simulation
- \+ Experiment (Literatur)
- — Korrelation (DIPPR)



Vorhersagen Transportgrößen: Dimethylamin

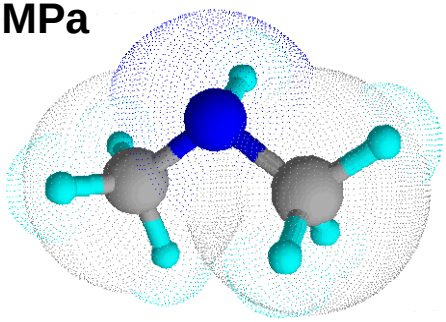




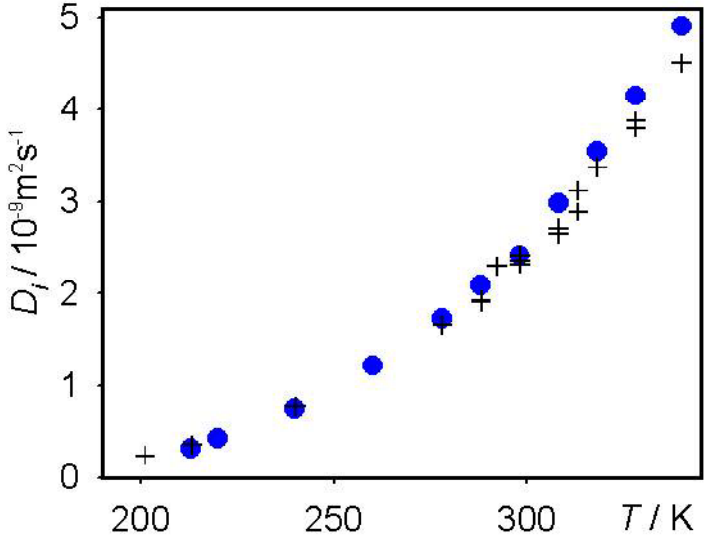


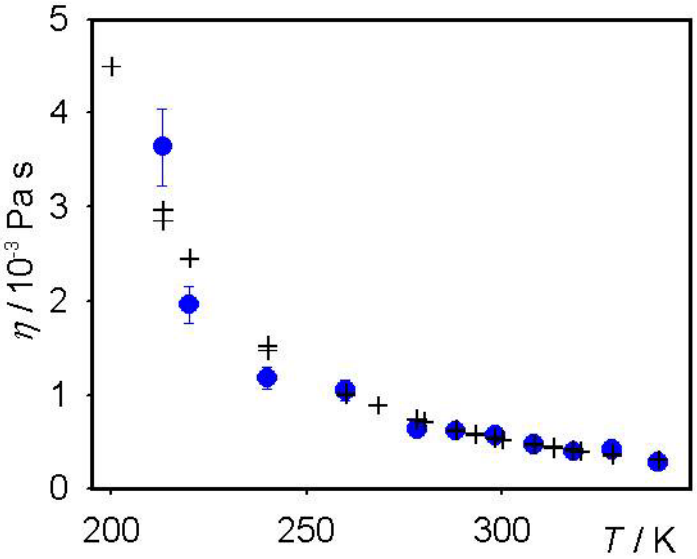
- Vorhersage Simulation
- Korrelation (DIPPR)

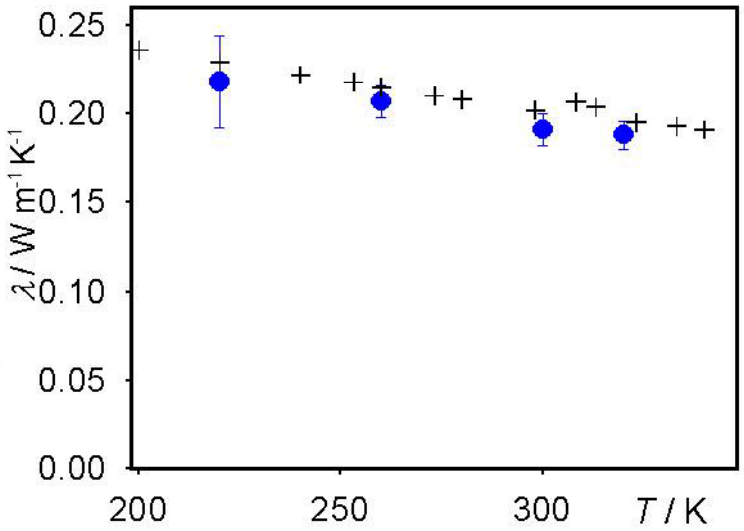
alle Angaben: **0.1 MPa**



Vorhersagen Transportgrößen: Methanol

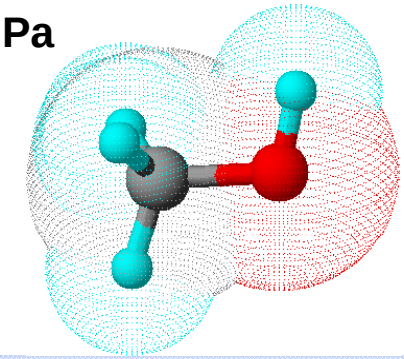




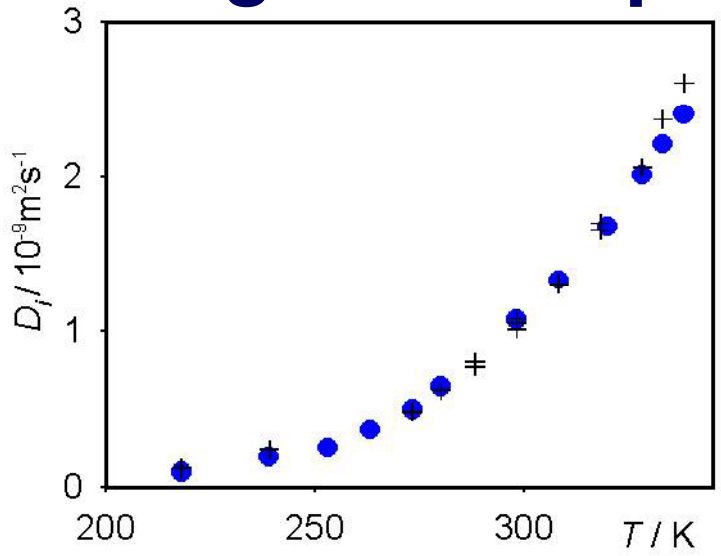


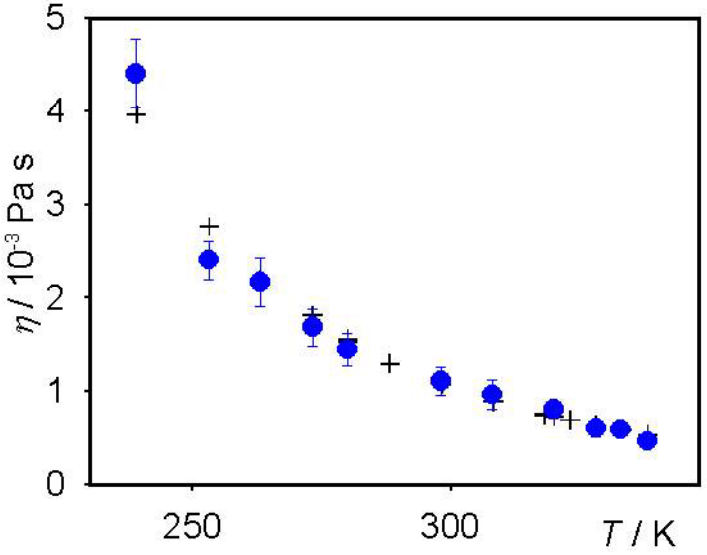
- Vorhersage Simulation
- \+ Experiment (Literatur)

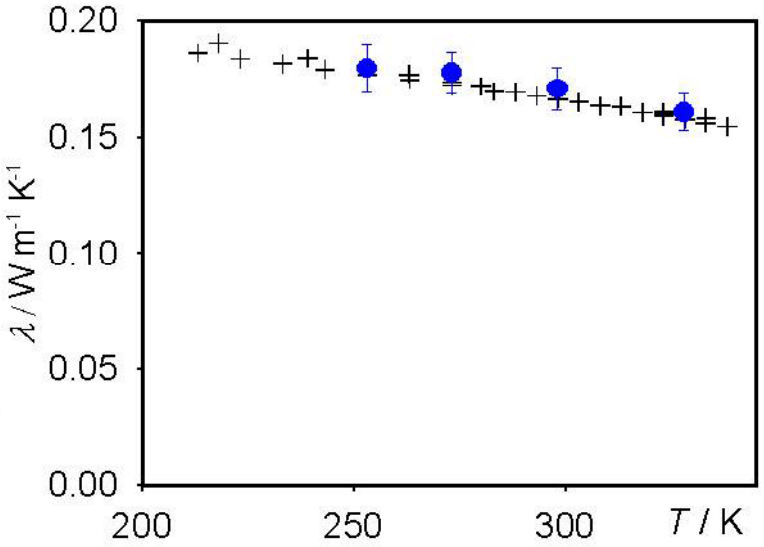
alle Angaben: **0.1 MPa**



Vorhersagen Transportgrößen: Ethanol

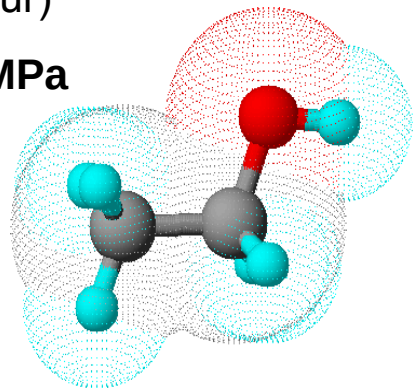




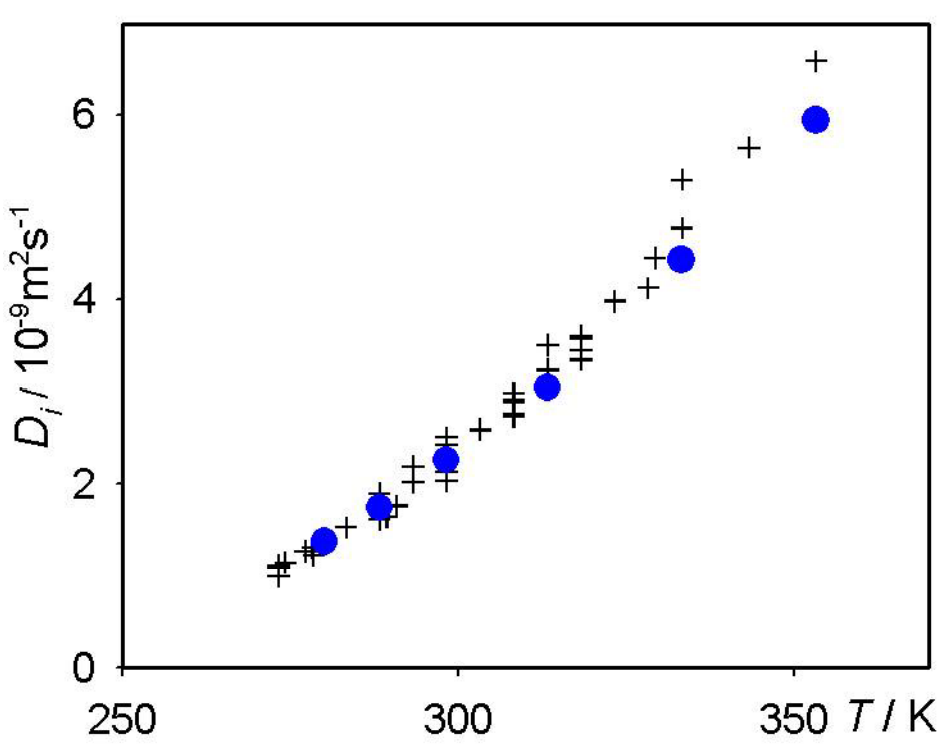


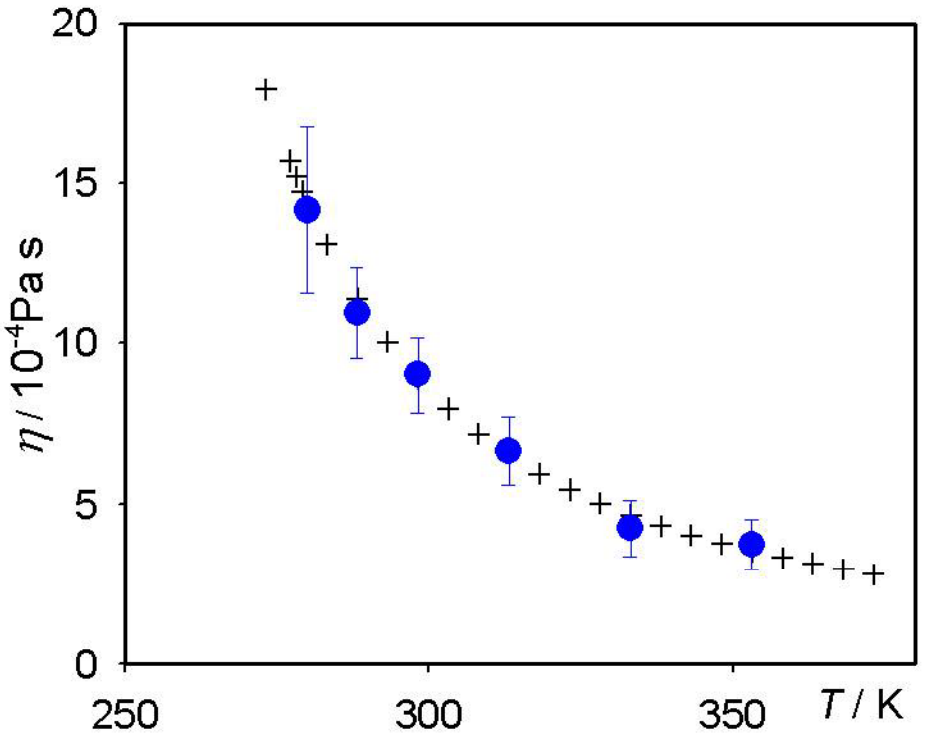
- Vorhersage Simulation
- \+ Experiment (Literatur)

alle Angaben: **0.1 MPa**



Wasser TIP4P/2005: Transportgrößen

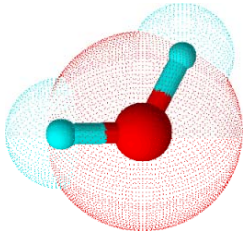




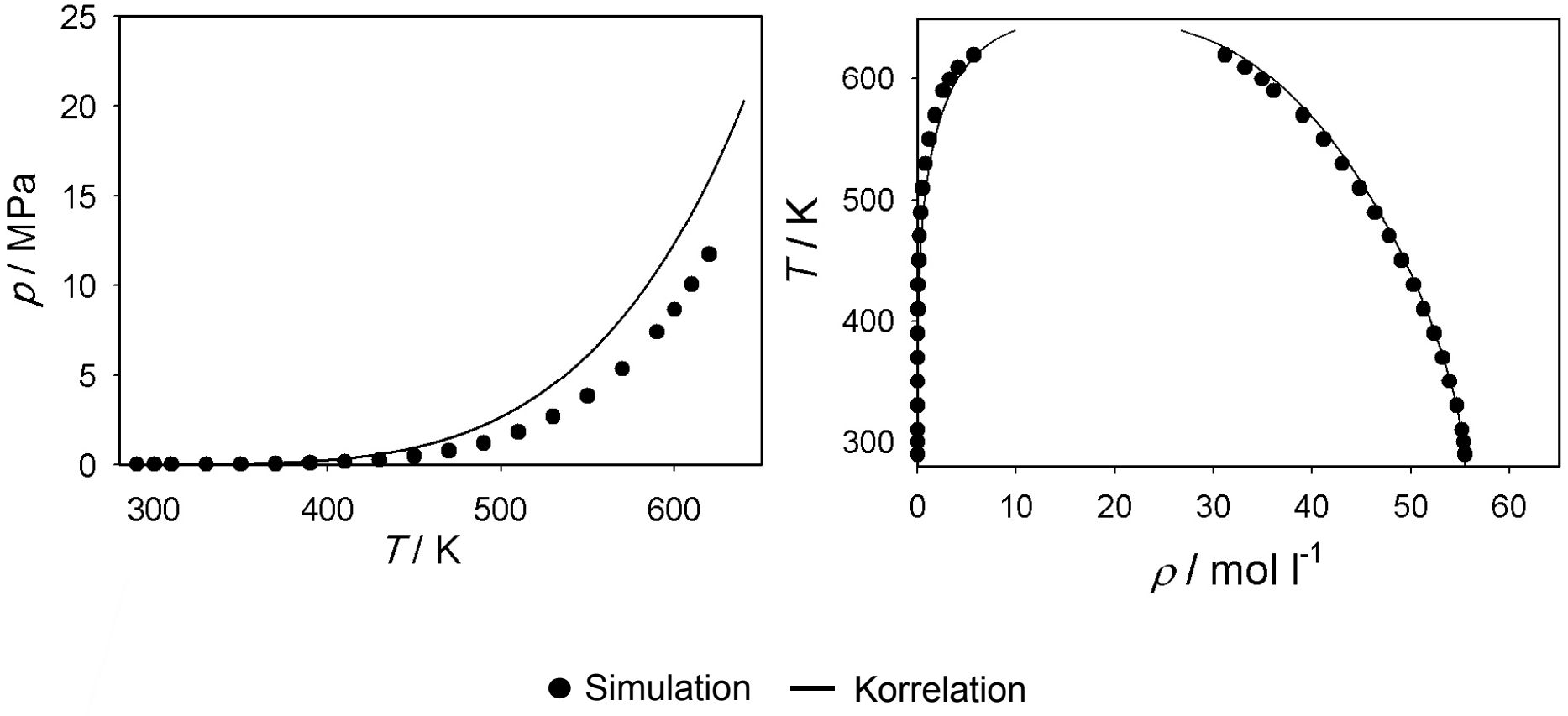
● Vorhersage Simulation

\+ Experiment (Literatur)

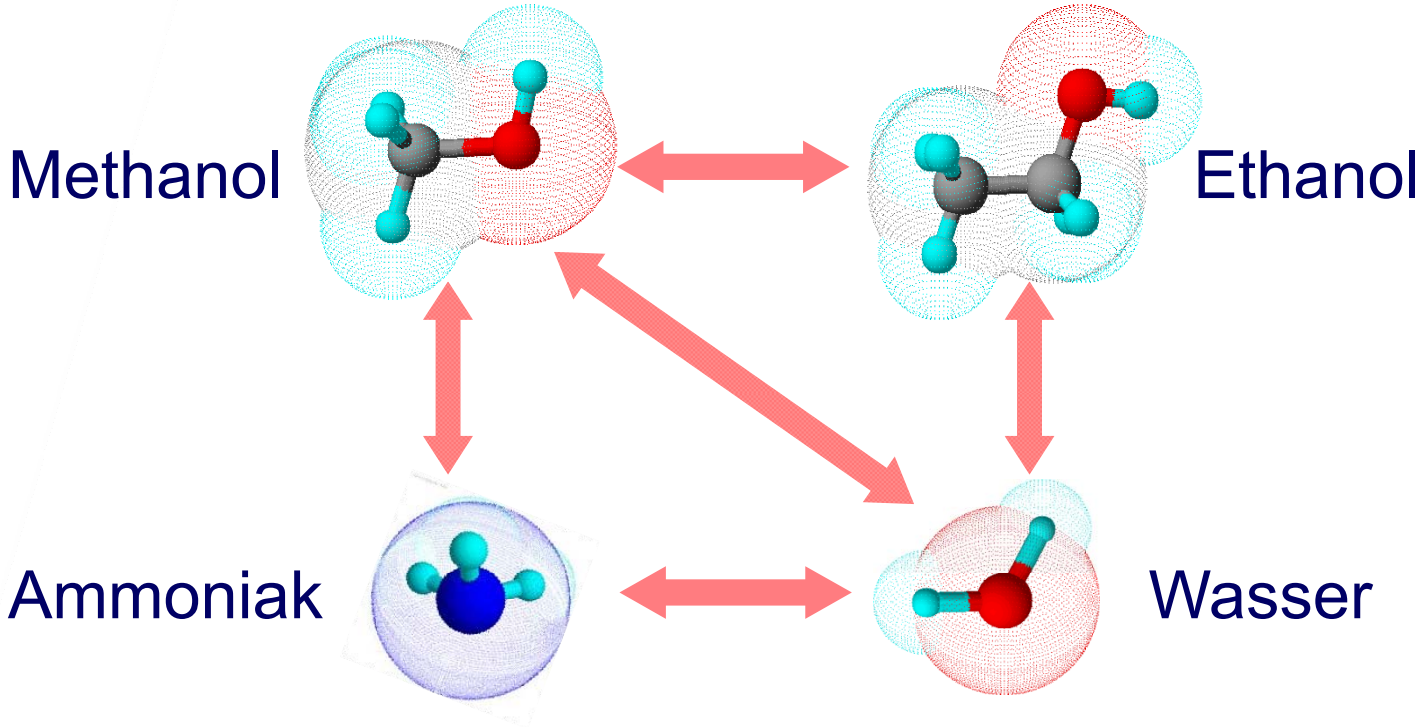
alle Angaben: **0.1 MPa**



Wasser TIP4P/2005 : Dampf-Flüssigkeits Gleichgewicht



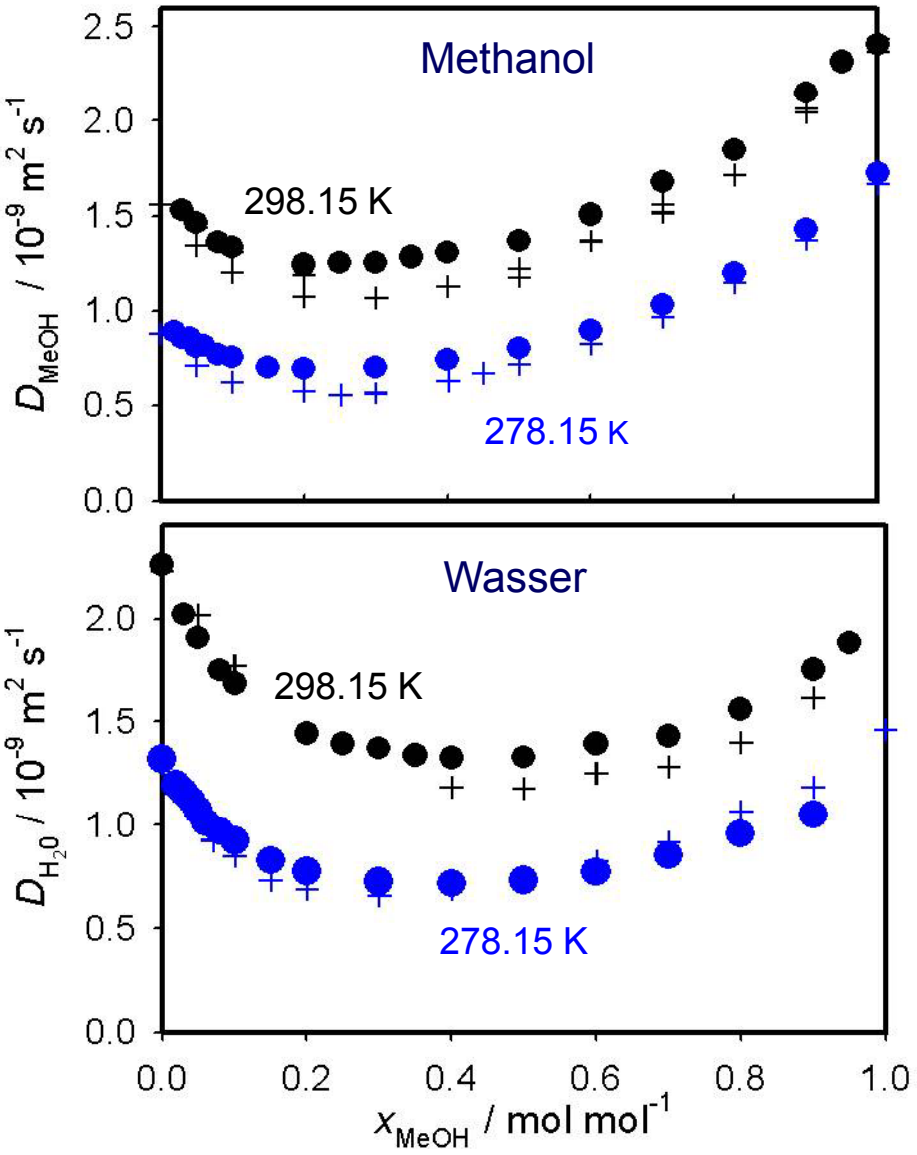
Betrachtete Mischungen

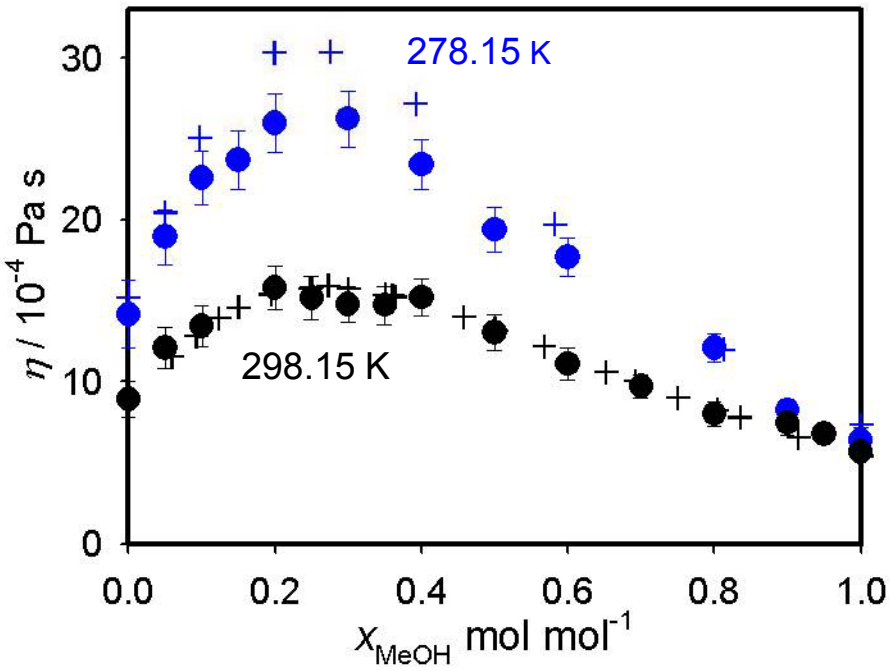


Ungleiche LJ Parameter:
Lorentz- Berthelot

$$\sigma_{ab} = \left(\frac{\sigma_a + \sigma_b}{2} \right) \qquad \varepsilon_{ab} = \sqrt{\varepsilon_a \varepsilon_b}$$

Mischung: Methanol + Wasser

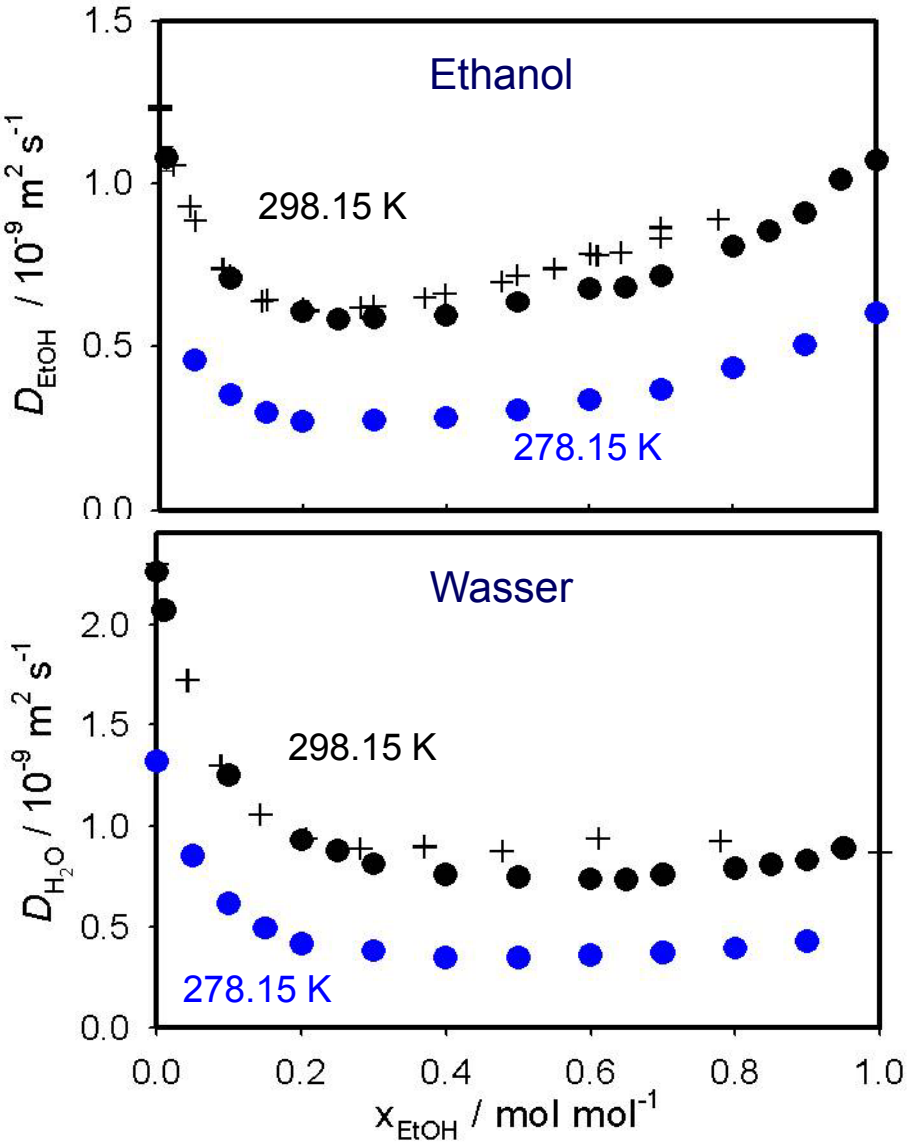


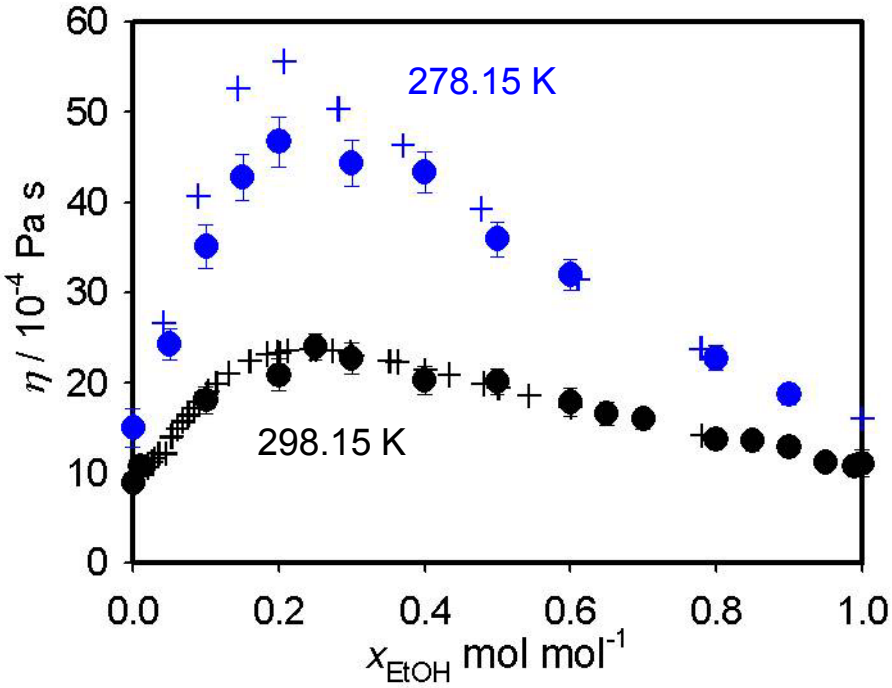


- ● Vorhersage Simulation
- \+ Experiment (Literatur)

alle Angaben: **0.1 MPa**

Mischung: Ethanol + Wasser



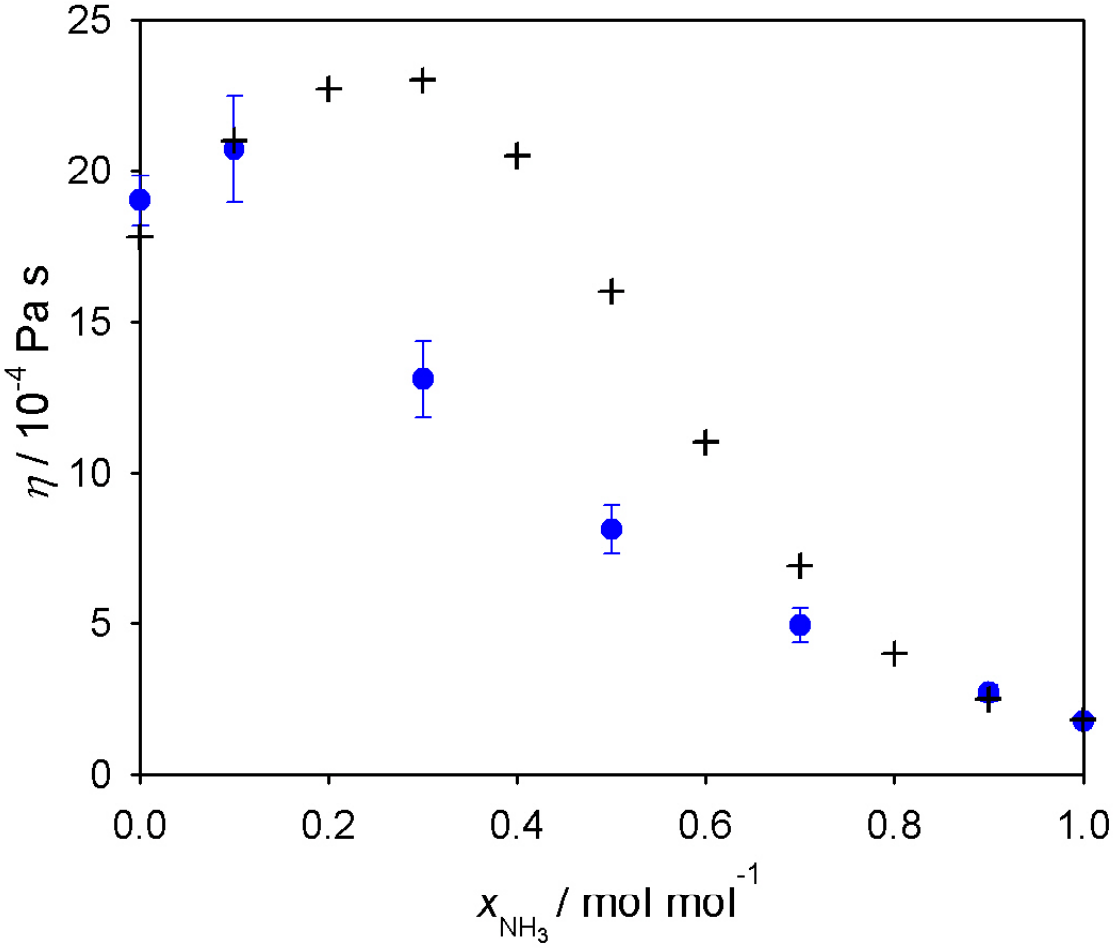


● Vorhersage Simulation

\+ Experiment (Literatur)

alle Angaben: **0.1 MPa**

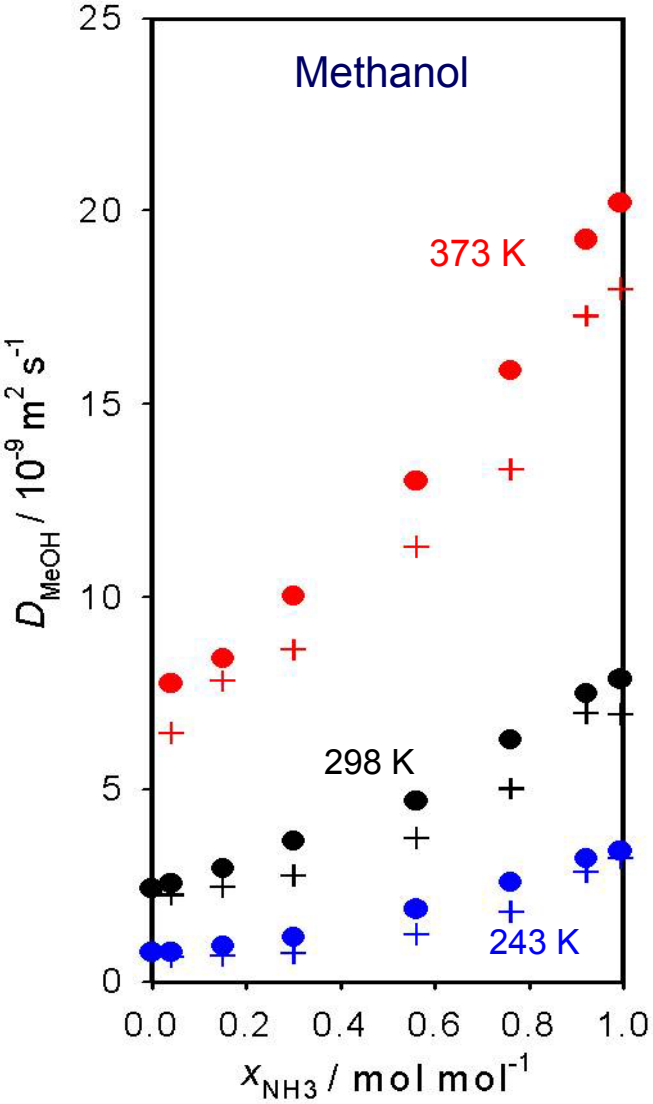
Mischung: Ammoniak + Wasser

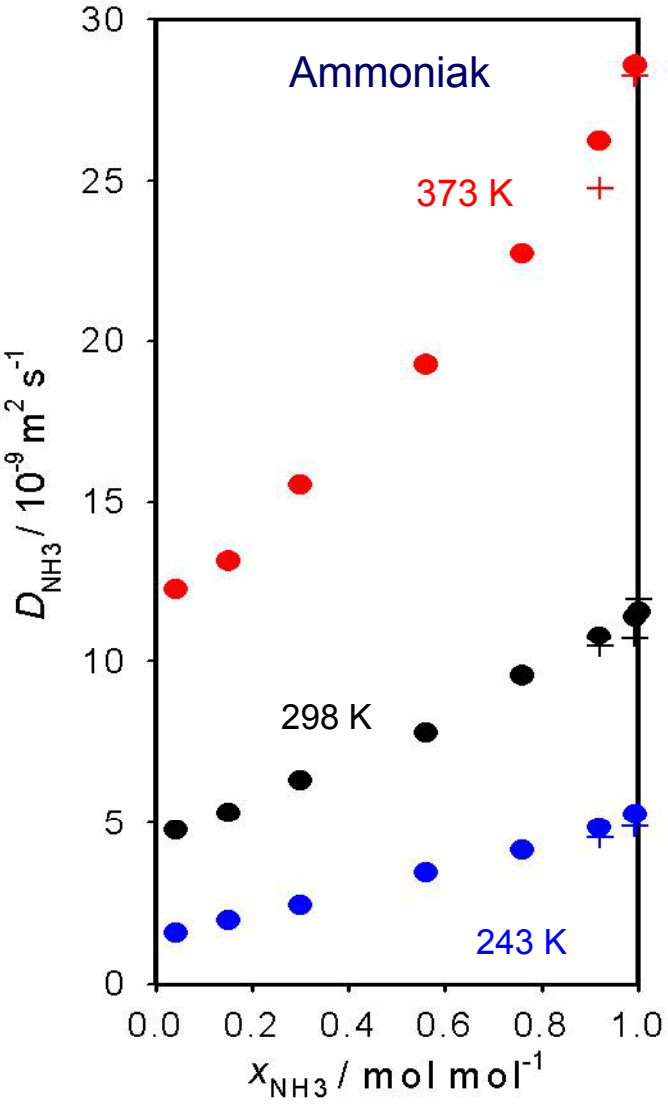


- Vorhersage Simulation
- \+ Experiment (Literatur)

alle Angaben: **273.15 K**
0.1 MPa

Mischung: Methanol + Ammoniak



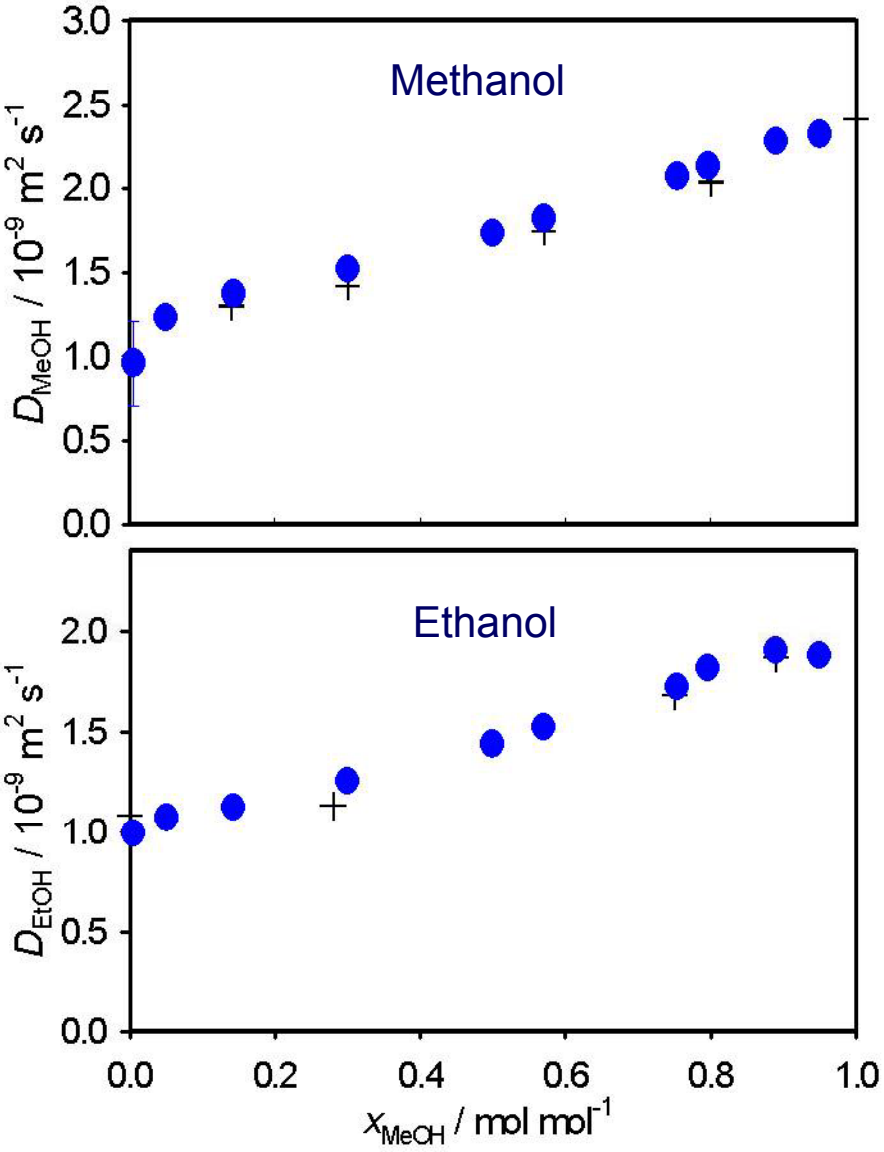


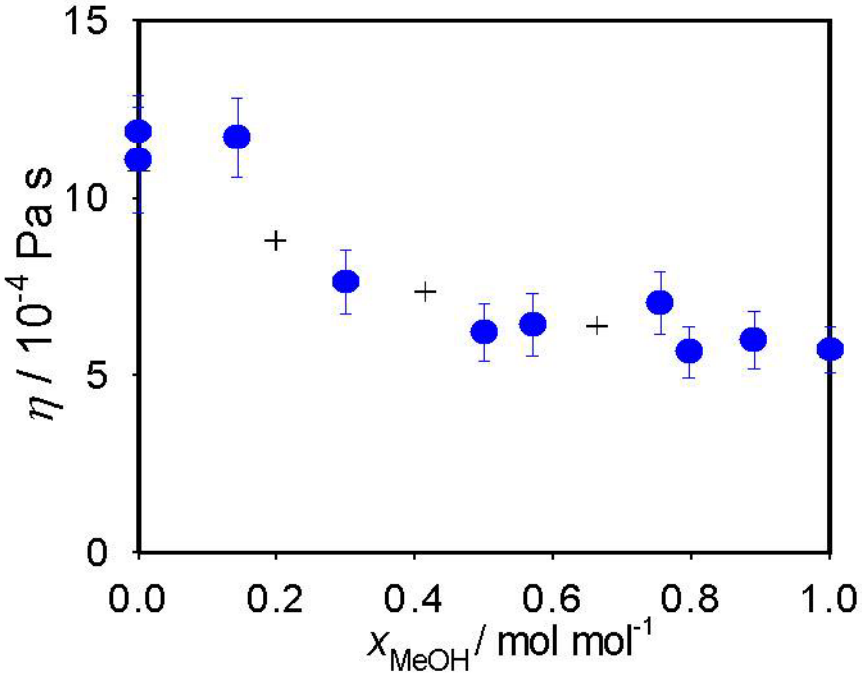
● Vorhersage Simulation

\+ Experiment (Literatur)

alle Angaben: **10 MPa**

Mischung: Methanol + Ethanol





- Vorhersage MD Simulation
- \+ Experiment (Literatur)

alle Angaben: **298.15 K, 0.1 MPa**

Zusammenfassung

- Vorhersage von Transportkoeffizienten H-brücken bildender Stoffe aus molekularen Simulationen
- Green-Kubo MD und Reverse-NEMD Methoden
- Selbstdiffusion, Scherviskosität, Wärmeleitfähigkeit
- Reinstoffe: Methanol, Ethanol, Ammoniak, MMA, DMA
- Wassermodell aus der Literatur: TIP4P/2005
- Mischungen: Methanol + Ethanol, Methanol + Wasser, Ethanol + Wasser, Ammoniak + Wasser, Methanol + Ammoniak
- Sehr gute Vorhersagen für Reinstoffe und Mischungen mit Modellen, die nur an Dampf-Flüssigkeits Gleichgewichtsdaten angepasst wurden

Vielen Dank für Ihre Aufmerksamkeit!