Mutual diffusion of binary liquid mixtures containing methanol, ethanol, acetone, benzene, cyclohexane, toluene and carbon tetrachloride

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Motivation

The knowledge of diffusion coefficients and other transport properties of fluids is essential for the modeling of complex systems and processes in science and engineering. Since the experimental estimation of diffusion coefficients can be very challenging and time consuming, there is a growing need for accurate predictive methods. Due to the rapid development of computing power, molecular modeling and simulation has emerged as an alternative for empirical correlations, especially when dealing with complex and strongly non-ideal liquid mixtures.

Description of mutual diffusion

Fick: \( J_i = -\rho_i \frac{d}{dt} \int_{x_i} x_i \, dx_i \) → coefficients from experiment

Maxwell-Stefan:

\[
\frac{d}{dt} \rho_i \nabla_i \nabla_i \sum_j \frac{x_j}{x_i} \left( \Lambda_{ij} x_j - \Lambda_{ij} x_i \right)
\]

→ coefficients from molecular simulation

\( x_i u_i = \frac{1}{n} \sum_{j=1}^{n} \Lambda_{ij} x_j \) In binary mixture: \( \Delta_{ij} = \frac{\Lambda_{ij} x_j - \Lambda_{ij} x_i}{x_i} \)

Onsager reciprocal relation: \( \Lambda_{ij} = \Lambda_{ji} \sum_{l=1}^{n} M_i M_j = 0 \)

Thermodynamic factor \( \Gamma \):

- Binary mixture: \( D = D^0 \Gamma = 1 + x_1 \frac{d \ln y_1}{d x_1} \)
- Ideal mixture: \( \Gamma = 1 \)
- Thermodynamic instability (phase separation): \( \Gamma < 0 \)
- Can be calculated by G0 models (e.g. Wilson, NRTL, UNIQUAC)
- Fitting of model parameters to experimental VLE data or simulation data

Method

Molecular simulation

Molecular simulation of thermodynamic properties:

- Macroscopic behavior of fluids results directly from intermolecular interactions.
- Prediction of transport properties
- Equilibrium molecular dynamics: numerical solution of Newton’s equations of motion to obtain molecular trajectories
- Autocorrelation functions according to the Green-Kubo formalism

Tool: ms2

Molecular models defined by force fields

Molecular dynamics (MD) / Monte Carlo (MC)

Several classical ensembles:

All static properties (therm, calor, entropic)

Code: FORTRAN90

Parallelization: MPI / OpenMP

Green Kubo formalism

Microscopic fluctuations around equilibrium

- Description of non-equilibrium phenomena
- Transport coefficients from time dependent autocorrelation functions of corresponding fluxes

Self diffusion:

\[
\begin{align*}
\langle J_i \rangle &= \frac{1}{3N_i} \int_0^\infty dt \sum_{j=1}^n v_j(0) \cdot v_i(t) \\
\end{align*}
\]

Onsager coefficients:

\[
A_{ij} = \frac{1}{3N} \int_0^\infty dt \sum_{k=1}^N v_{ik}(0) \sum_{l=1}^N v_{1l}(t)
\]

Shear viscosity:

\[
\eta = \frac{1}{V_k B R} \int_0^\infty dt \left( f_{x x}^{(0)}(0) - f_{x x}^{(t)}(t) \right)
\]

Thermal conductivity:

\[
\lambda = \frac{1}{V_k B R} \int_0^\infty dt \left( f_{x x}^{(0)}(0) - f_{x x}^{(t)}(t) \right)
\]

Simulation results

Group I: Benzene + Toluene

Group II: Acetone + Benzene

Group III: Methanol + Toluene

Studied mixtures

Molecular models:

- Rigid molecules (united atom)
- Lennard-Jones sites, point charges, point dipole, point quadrupole
- Non-polarizable
- LJ parameters optimized to saturated liquid density and vapor pressure, (self diffusion)
- Mixing behavior: predicted

20 binary mixtures

Three groups according to deviation of thermodynamic factor from ideal behavior.

References

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ms2: A Molecular Simulation Tool for Thermodynamic Properties, New Version Release

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