Test of activity coefficient models by direct molecular dynamics simulation of vapor–liquid equilibria

Knowledge of phase equilibria is essential to design and operate separators in chemical industry.

Relations of phase equilibria

- **vapor-liquid equilibria**
  \[ p y_i = \gamma_i x_i p^* \]

- **liquid-liquid equilibria**
  \[ \gamma_i^{I} x_i^{I} = \gamma_i^{II} x_i^{II} \]

\( p \); total pressure, \( p^* \); saturated vapor pressure, \( \gamma \); activity coefficient

Activity coefficient models

**advantage**
- NRTL
  It is possible to calculate multi component systems using parameters determined with the constituting binary systems.

**flaw**
- UNIQUAC
  The calculated results of ternary liquid-liquid equilibria are no good, when the binary parameters are determined with the constituting binary systems.

Schema of liquid-liquid extraction
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Activity coefficients can be calculated by the summation of interaction contribution and athermal contribution.

\[ \ln \gamma = \ln \gamma_{\text{interaction}} + \ln \gamma_{\text{athermal}} \]

When athermal term such as Flory-Huggins model is added to interaction term such as CDSAP model, the calculated results become worse than those of CDSAP model.

**Purpose**
- Test of athermal term of activity coefficient models by direct molecular dynamics simulation of vapor-liquid equilibria

**Methods**
- Activity coefficients are calculated for argon (1) + argon_dimer (2) system by direct molecular dynamics simulation.
- Contribution of athermal term is tested by comparing with athermal models.
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Flory-Huggins model

\[
\ln \gamma_1 = \ln \frac{\varphi_1}{x_1} + \varphi_2 (1 - \frac{1}{r}) \\
\ln \gamma_2 = \ln \frac{\varphi_2}{x_2} + \varphi_1 (1 - r)
\]

\(\varphi_i\): volume fraction

\(r\): molar volume ratio

Results

• The calculated results of activity coefficients are smaller than unity.

• The calculated results of activity coefficients are smaller than those of Flory-Huggins model.

Plan

• Effects of increasing number of segments on activity coefficients will be tested.

Calculated results of activity coefficients for argon(1) + argon_dimer(2) system at 100.048K. ●: \(\gamma_1\); ▲: \(\gamma_2\); ---: Flory-Huggins.