Computational Assignment Report

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Equation of State: **Soave-Redlich-Kwong**
System: **Acetonitrile**

The SRK EOS is given as $P = \frac{R \cdot T}{v - b} - \frac{a \cdot \alpha}{v \cdot (v + b)}$, where the different parameters are,

- P : Pressure (in Pa)
- v : Molar Volume (in m^3/mol)
- T : Temperature (in K)
- R : Universal Gas Constant
- $a = 0.42748 \cdot \frac{R^2 \cdot T_c^2}{P_c}$
- $b = 0.08664 \cdot \frac{R \cdot T_c}{P_c}$
- $\alpha_{\mathrm{SRK}}(T_r; \omega) = \left[1 + (0.480 + 1.574\,\omega - 0.176\,\omega^2)(1 - T_r^{1/2})\right]^2$

The values of the constants are

- P_c = 4.83 MPa
- T_c = 545.5 K
- R = 8.314 J K^{-1} mol^{-1}
- a = 1.8204 Pa m^6 mol^{-2}
- b = 0.0000813 m^3 mol^{-1}
- $\omega = 0.338$

Source: Perry's Chemical Engineers' Handbook

Expression used for calculating Saturated Pressure is given as

$P_{sat} = exp(C_1 + \frac{C_2}{T} + C_3\, ln(T) + C_4 T^{C_5})$ (in Pa), where the constants are

- C_1 = 58.302
- C_2 = -5385.6
- C_3 = -5.4954
- C_4 = 5.3634E−06
- C_5 = 2

Valid for temperature range of 229.3 - 545.5 K

Source: Perry's Chemical Engineers' Handbook

Algorithm

- For **critical.m** (code tested only on Matlab Online)
  1. Initialize a symbolic function for the equation of state as P = f(v,T).
  2. The critical point is an inflection point on the isotherm. Therefore the first order partial derivative of P w.r.t v and the second order partial derivative of P w.r.t. v both must be equal to zero.
  3. Solve the given equations simultaneously and look at the real roots.
  4. The real roots give the critical temperature and critical volume for the system.

- For **assign.m** (code tested on Octave)
  1. Get saturated pressure for a particular temperature using the given expression.
  2. Use this pressure to calculate the chemical potential of the liquid phase and the vapor phase and get their difference.
  3. Adjust the pressure accordingly and iterate to minimize the difference in the chemical potentials (upto a certain tolerance value).
  4. Use the adjusted saturated pressure value to calculate the volume from the cubic equation of state. Consider only the largest and smallest values of volume (largest corresponds to vapor and smallest to liquid).
  5. Iterate through steps 1-4 for different values of temperature below critical temperature.
  6. Plot these points to get the dome shaped curve for vapor liquid coexistence, and also plot the isotherms.

Analysis

- For temperatures above critical temperature, acetonitrile exists in a superheated state.
- At critical temperature, acetonitrile as a single phase (vapor and liquid are difficult to distinguish).
- For temperatures below critical temperature, acetonitrile exists as liquid and vapor.
- On comparing, we find that the critical temperature obtained from the EOS is consistent with the experimental value, but the critical volume is not. It is about 1.8 times higher than the experimental value. Critical pressure is also consistent with the experimental value.

Plot is attached as **Plot.pdf**