Regular Solution Approach to Modeling Asphaltene Precipitation

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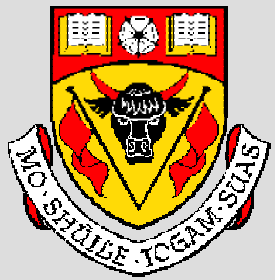
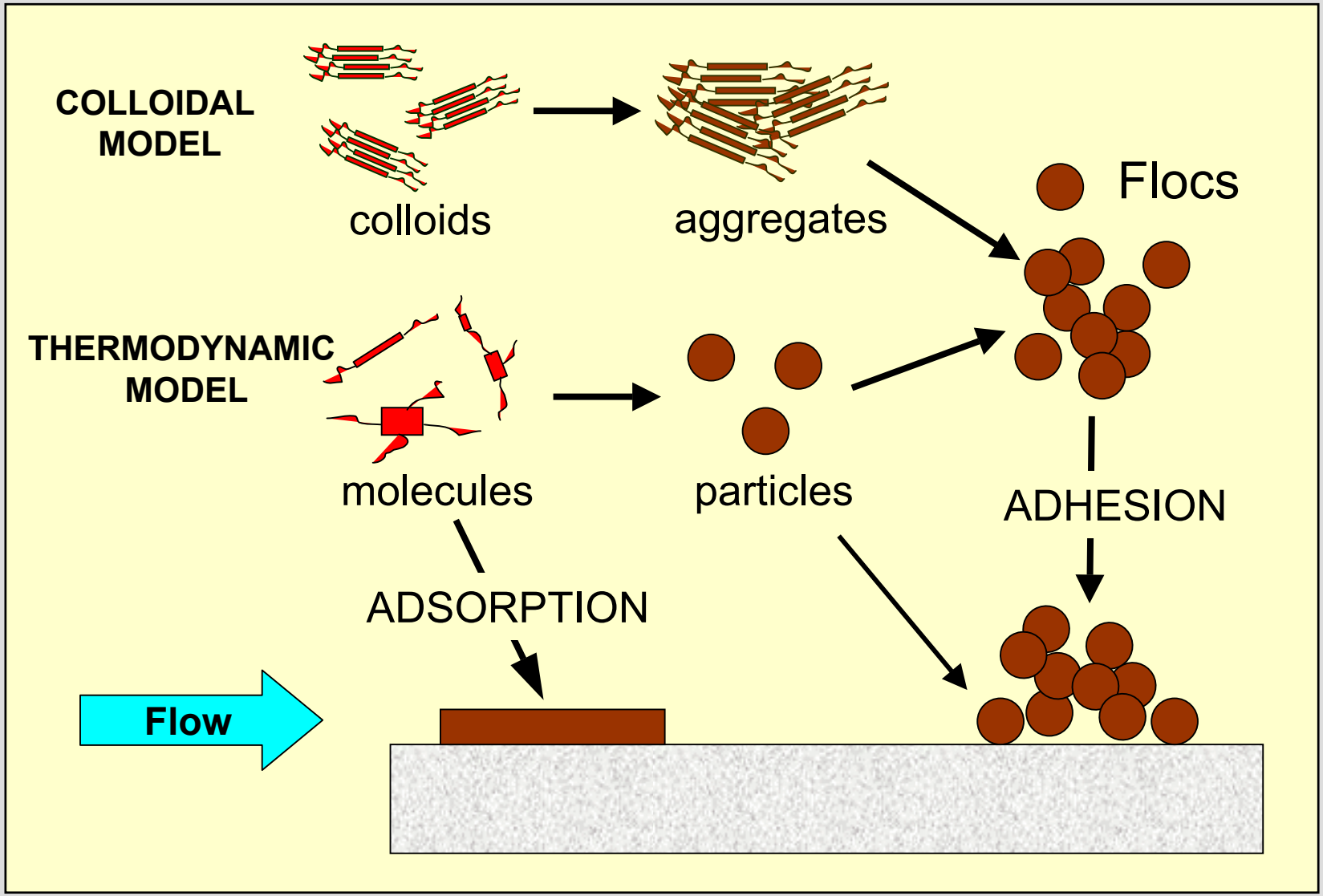


Asphaltene Deposition



Thermodynamic Approach

Divide fluid into (pseudo)components
Find equilibrium ratio for each component
Perform equilibrium calculation

Regular Solution Theory

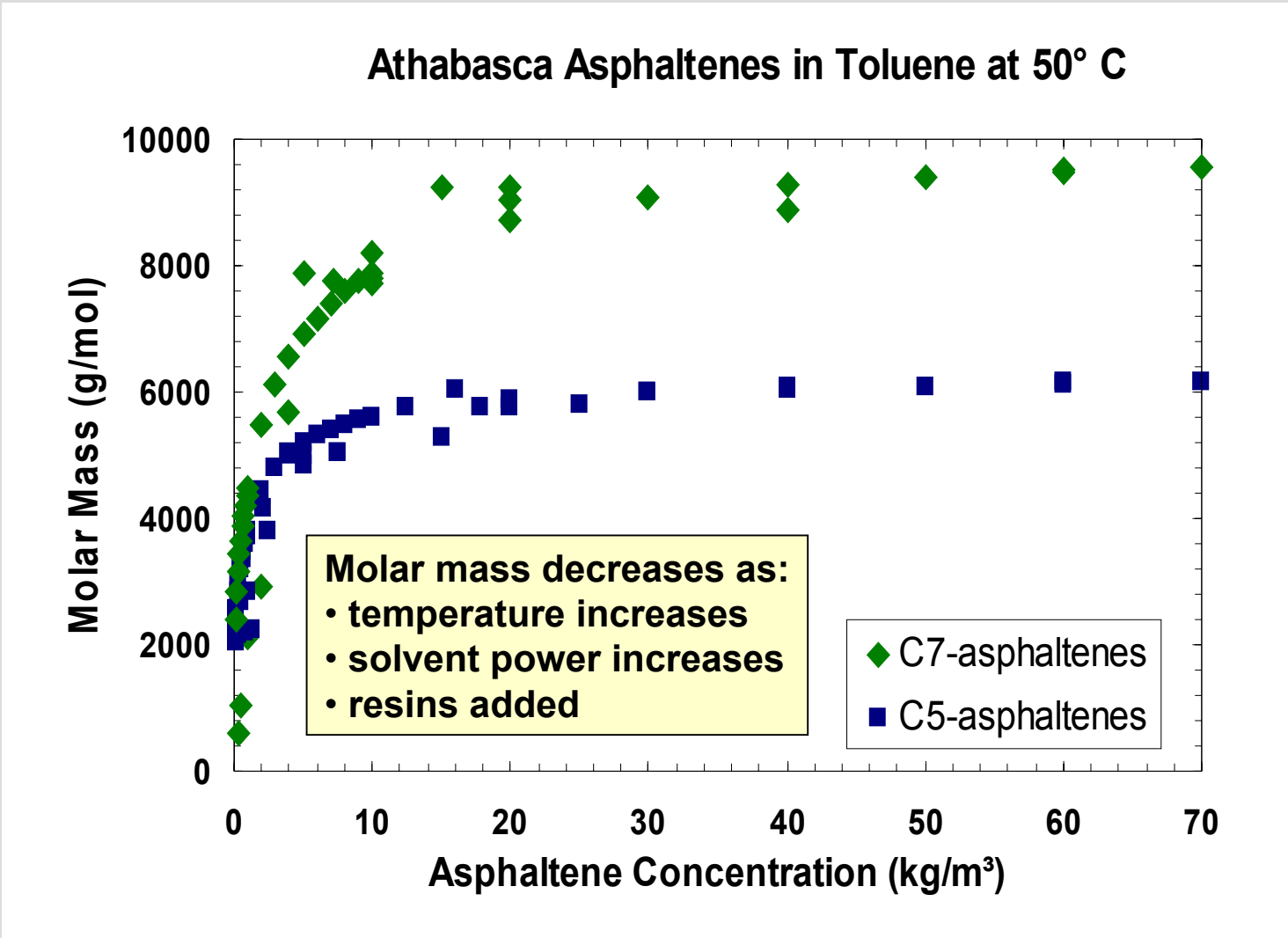
$$K_i^{hl} = \frac{x_i^h}{x_i^l} = \exp\left\{ \begin{array}{l} \dfrac{v_i^h}{v_m^h} - \dfrac{v_i^l}{v_m^l} + \ln\left(\dfrac{v_i^l}{v_m^l}\right) - \ln\left(\dfrac{v_i^h}{v_m^h}\right) + \\ \dfrac{v_i^l}{RT}\left(\delta_i^l - \delta_m^l\right)^2 - \dfrac{v_i^h}{RT}\left(\delta_i^h - \delta_m^h\right)^2 \end{array} \right\}$$

K **= equilibrium ratio**
v **= molar volume**
δ **= solubility parameter**

Fluid Characterization

- Components: SARA (saturates, aromatics, resins, asphaltenes) and pure solvents
- find x, v, and δ for each component using SARA analysis, molar mass, density, and solubility measurements
- Step 1: asphaltene characterization based on data from asphaltene solvent systems
- Step 2: bitumen characterization based on SAR-solvent and bitumen-solvent systems

Asphaltene Self Association

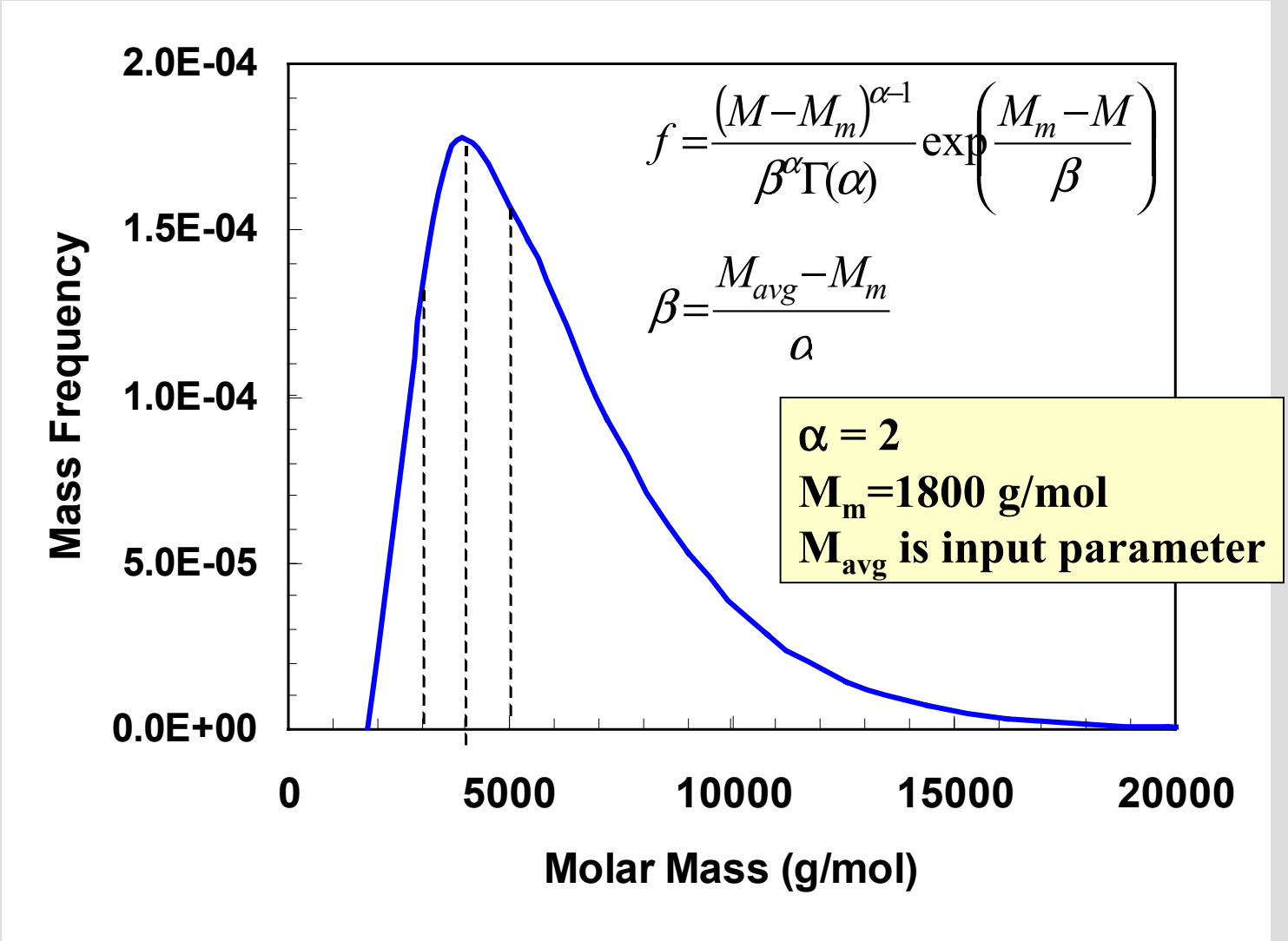


Yarranton et al., *Ind. Eng. Chem. Res.*, 2000, **39**, 2916

Asphaltene Characterization

- Divide asphaltenes into fractions of different molar mass
- Estimate asphaltene molar mass distribution at different T, P, X
- Develop correlations for asphaltene ν and δ
- Test precipitation model on asphaltene solvent systems at ambient conditions

Asphaltene Molar Mass Distribution



Model Parameters for Asphaltenes

updated from Yarranton et al, AIChEJ, 1996

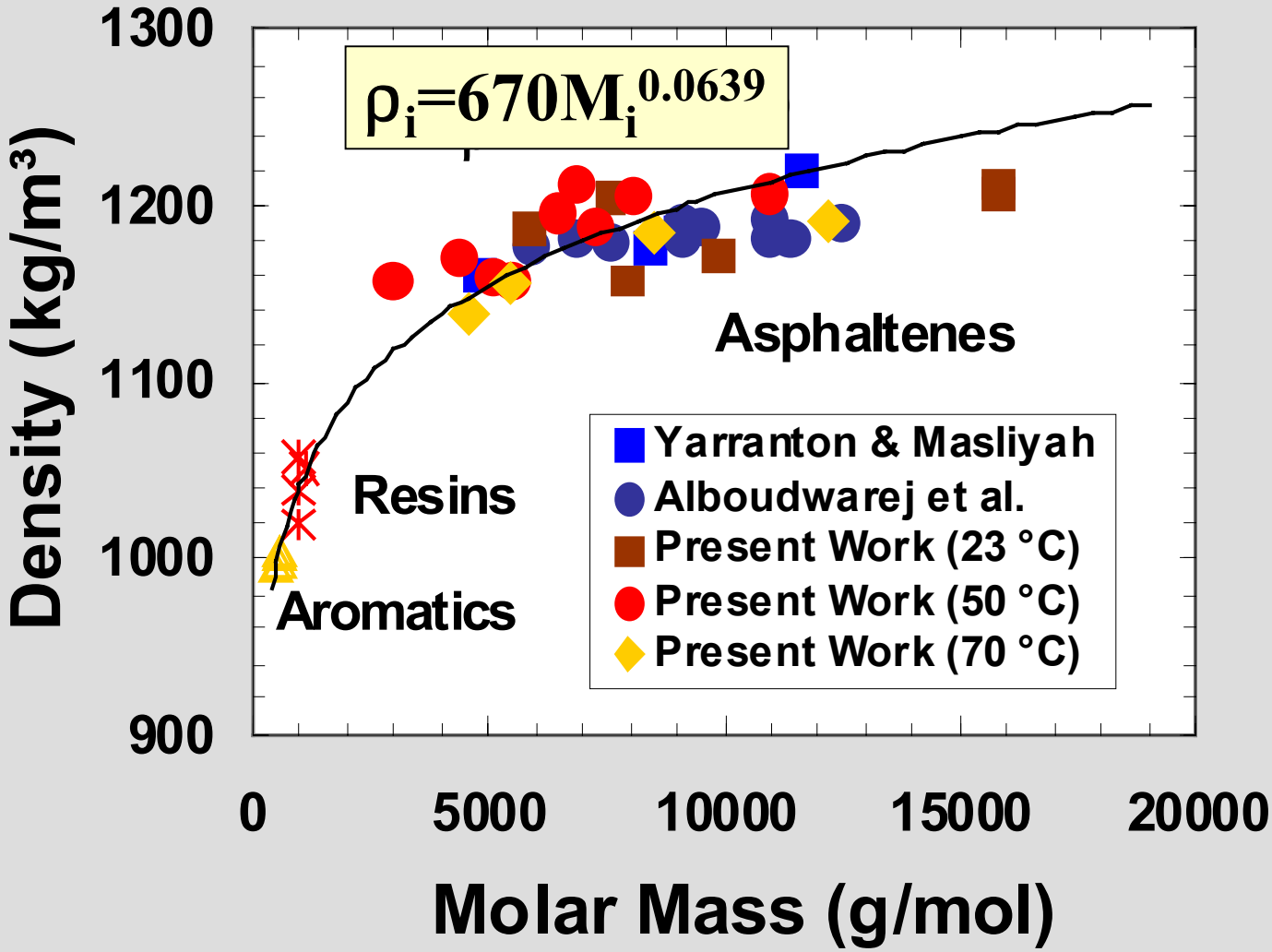
Molar Volume (cm^3/mol)

$$v_i = \frac{M_i}{\rho_i}$$

Solubility Parameter ($MPa^{0.5}$)

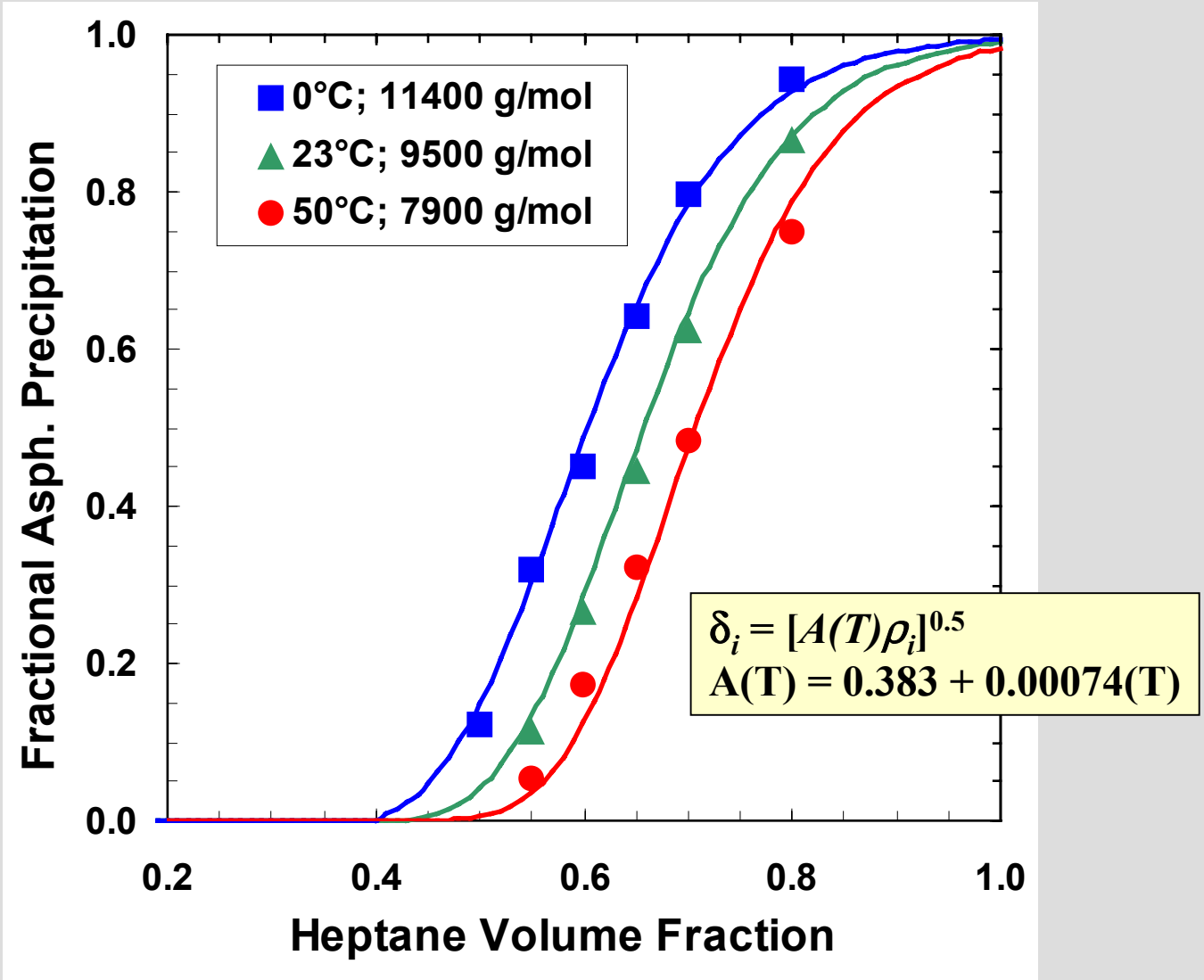
$$\delta_i = \left[\frac{\left(\Delta H^{vap} - RT\right)\rho_i}{M_i}\right]^{1/2} \approx \left[A(T)\rho_i\right]^{1/2}$$

Asphaltene Density



Asphaltene Solubility Parameter

10 kg/m³ asphaltenes in heptane/toluene solution



Model Parameters for Asphaltenes

Molar Volume (cm^3/mol)

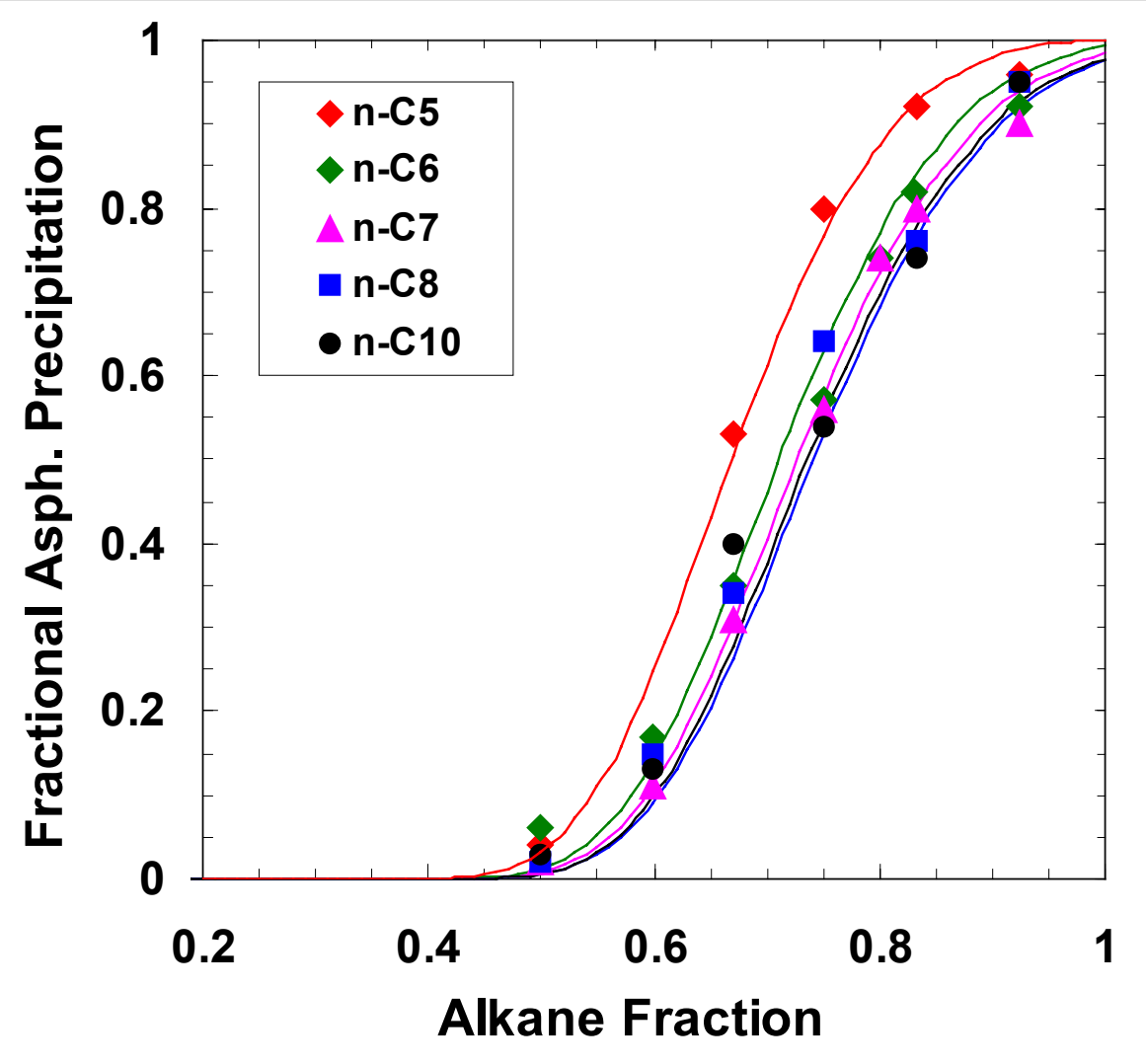
$$v_i = \frac{M_i}{\rho_i}; \quad \rho_i = 670 M_i^{0.0639}$$

Solubility Parameter ($MPa^{0.5}$)

$$\delta_i = \left[A(T) \rho_i \right]^{1/2}$$

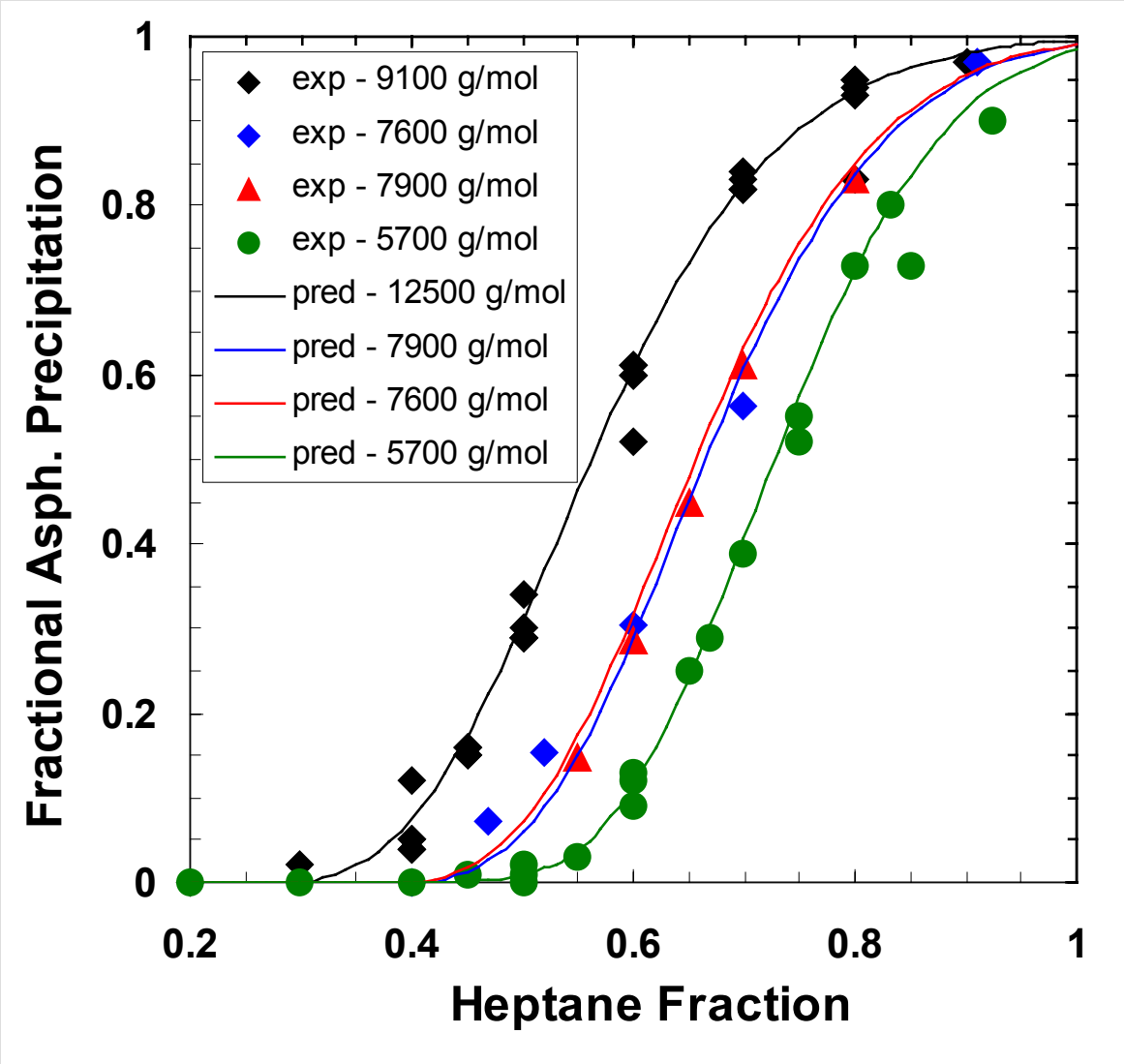
$$A(T) = 0.383 + 0.00074T$$

Asphaltene Precipitation
in Alkane-Toluene Solutions



Asphaltene Precipitation

different asphaltene fractions in heptol



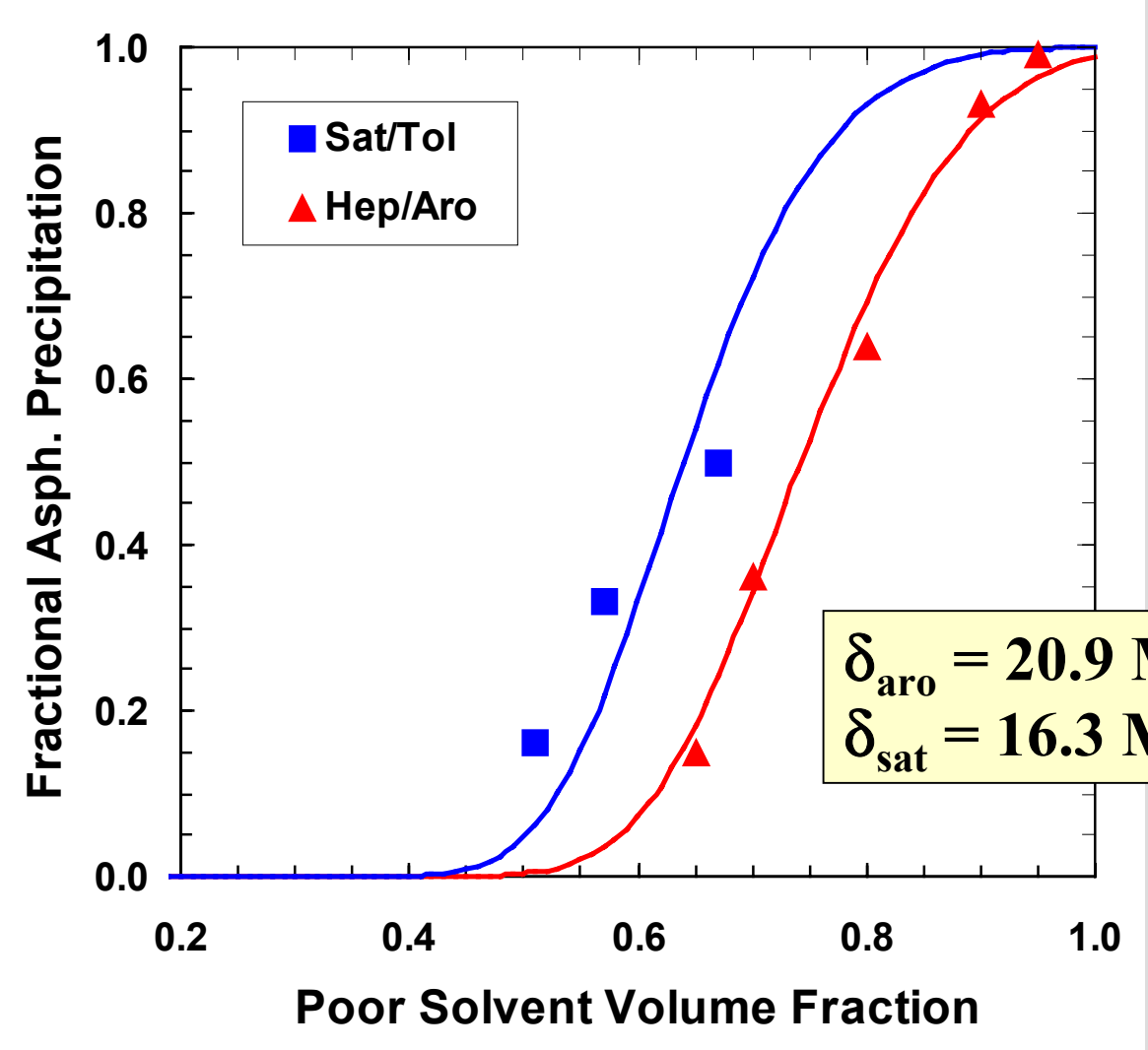
Bitumen Characterization

Bitumen Component	Molar Mass (g/mol)	Density (kg/m^3)	Sol. Par. ($MPa^{0.5}$)
Saturates	480 – 530	880 – 900	16.3
Aromatics	520 – 550	995 – 1000	20.9
Resins	860 – 980	1020 – 1060	19.5
Asph.	1800+	1080+	20.1+

Asphaltene monomer molar mass = 1800 g/mol.

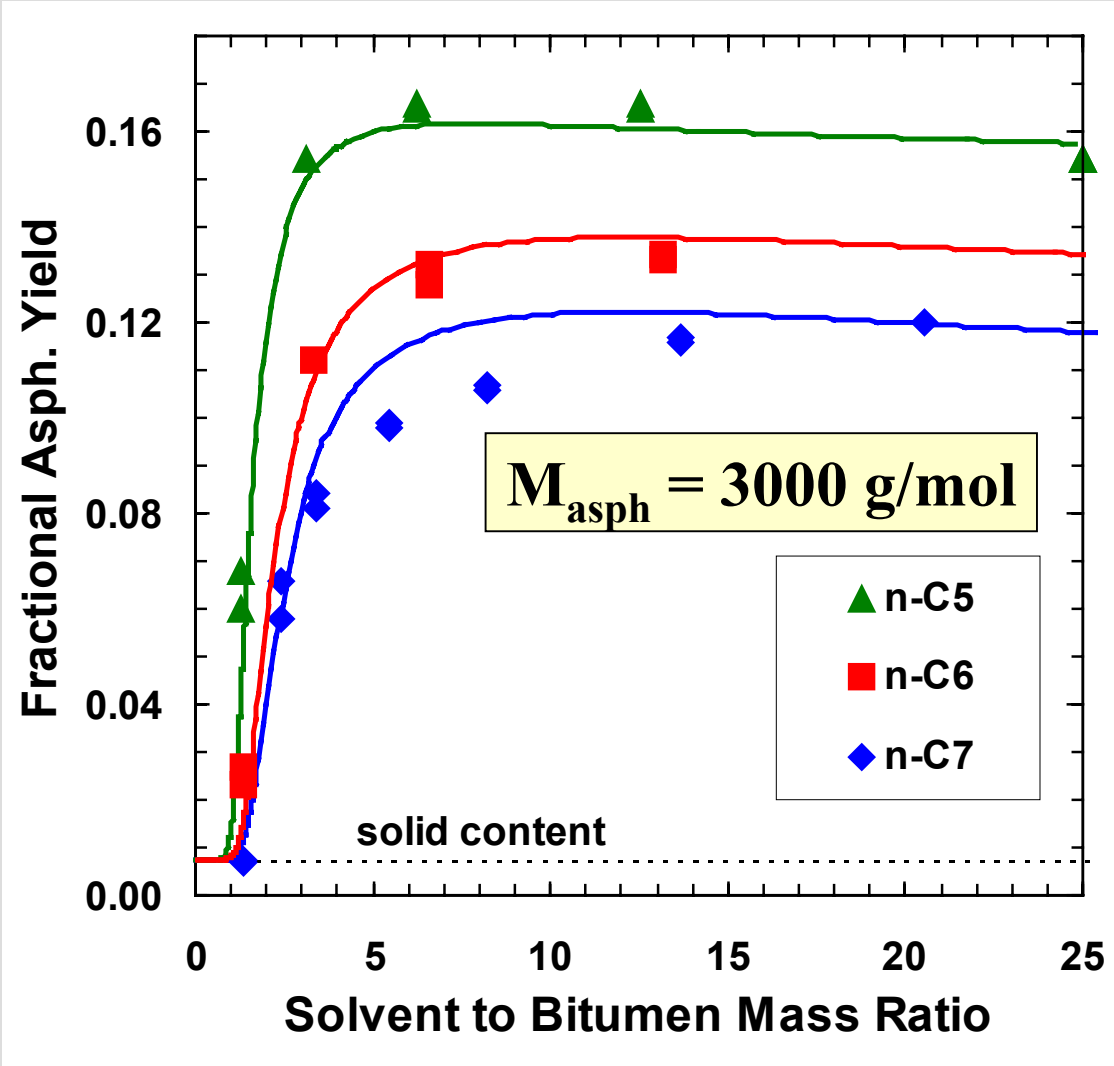
Asphaltene Precipitation

SARA Fractions



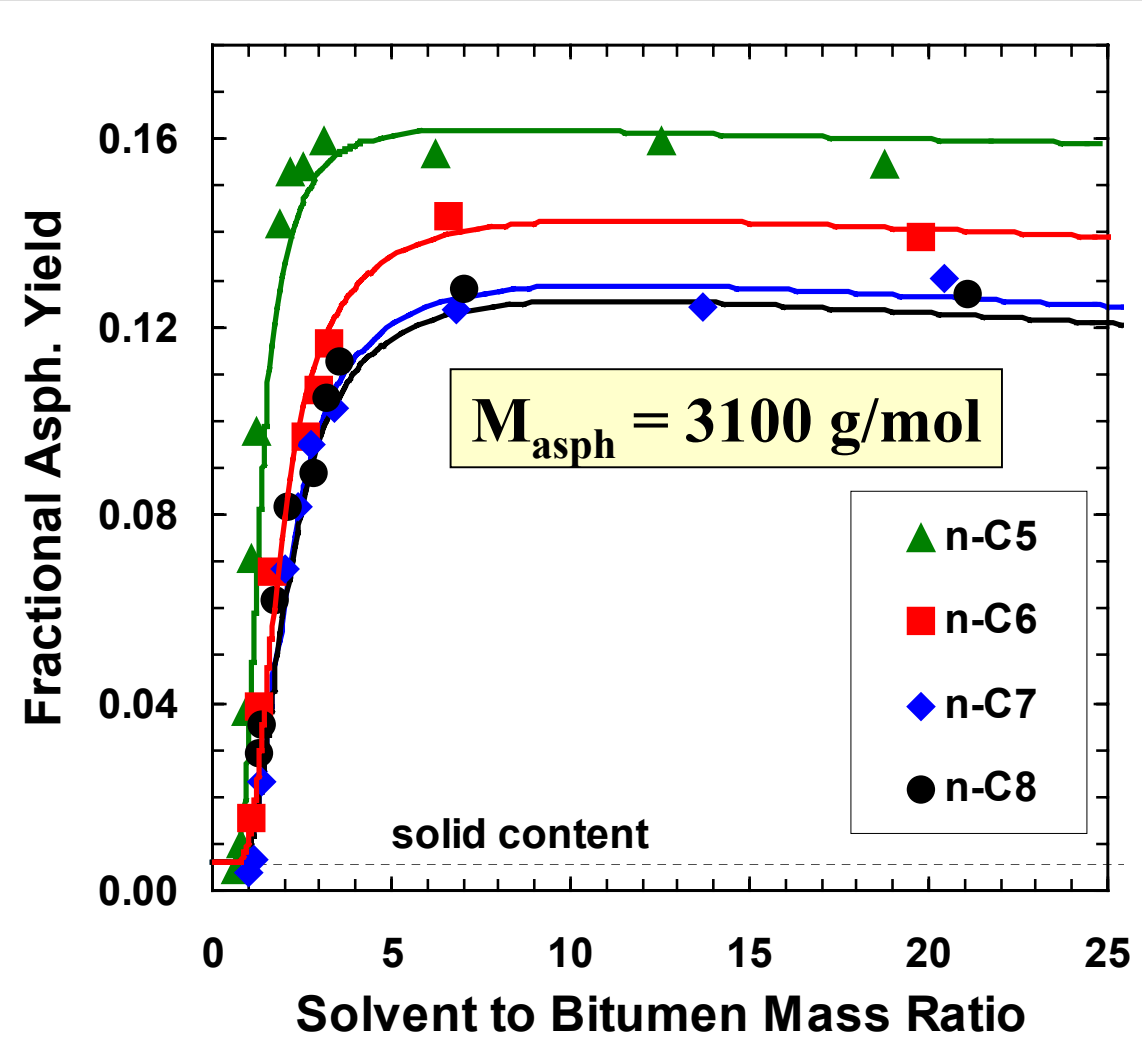
Asphaltene Precipitation

Athabasca Bitumen and Heptane at 23°C, 0.1MPa



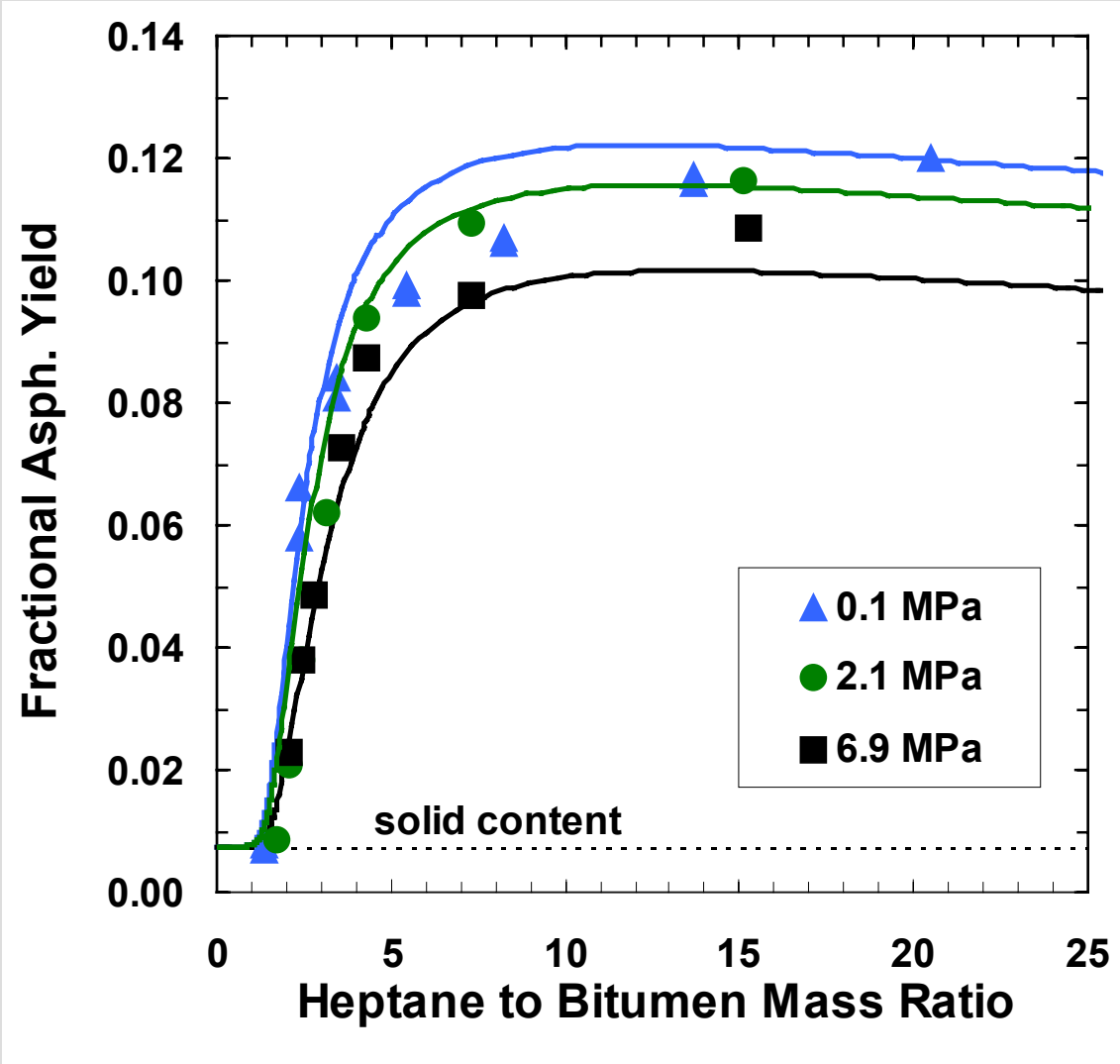
Asphaltene Precipitation

Lloydminster Heavy Oil and Alkanes at 23°C, 0.1 MPa



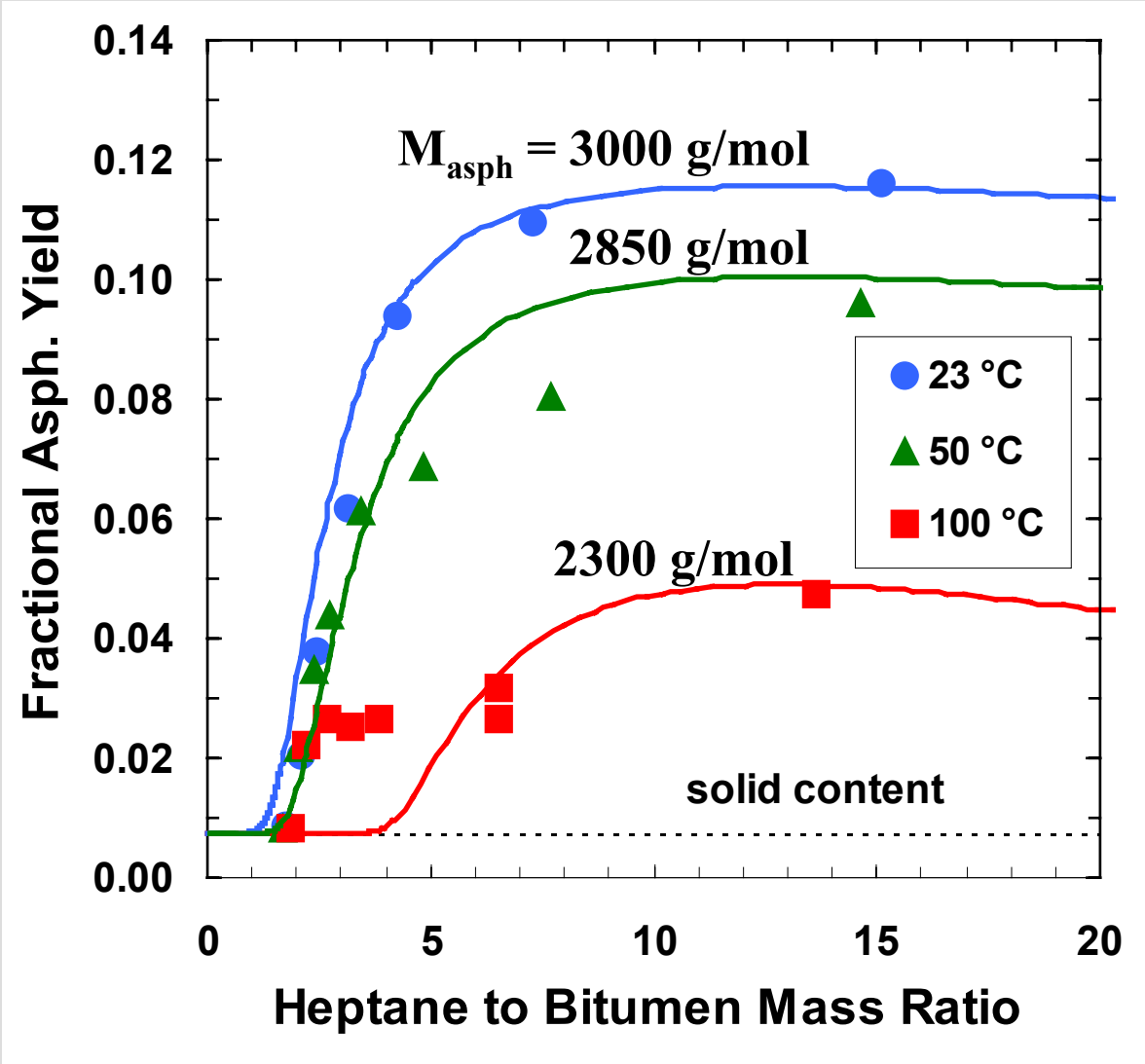
Asphaltene Precipitation - Pressure

Athabasca bitumen and heptane at 23°C



Asphaltene Precipitation - Temperature

Athabasca bitumen and heptane at 2.1 MPa



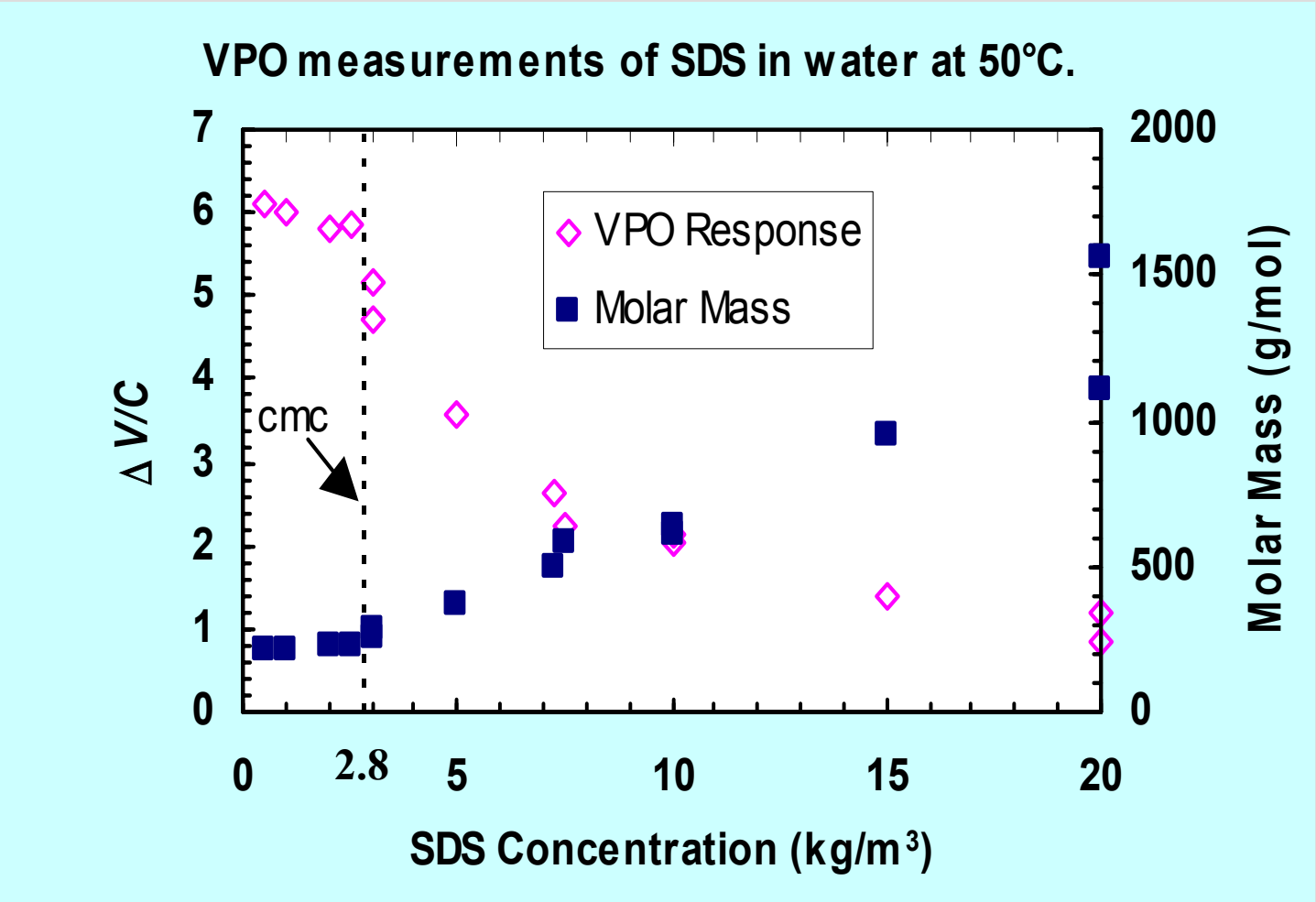
Future Work

- Extend model to higher T and P
  - correlate or predict average asphaltene molar mass in bitumens (function of resin content, temperature?)
  - test different asphaltene molar mass distributions
  - account for phase split of resins in low carbon number alkane diluents
- Expand data base
  - consider butane and propane diluent
  - test international heavy oil/bitumens

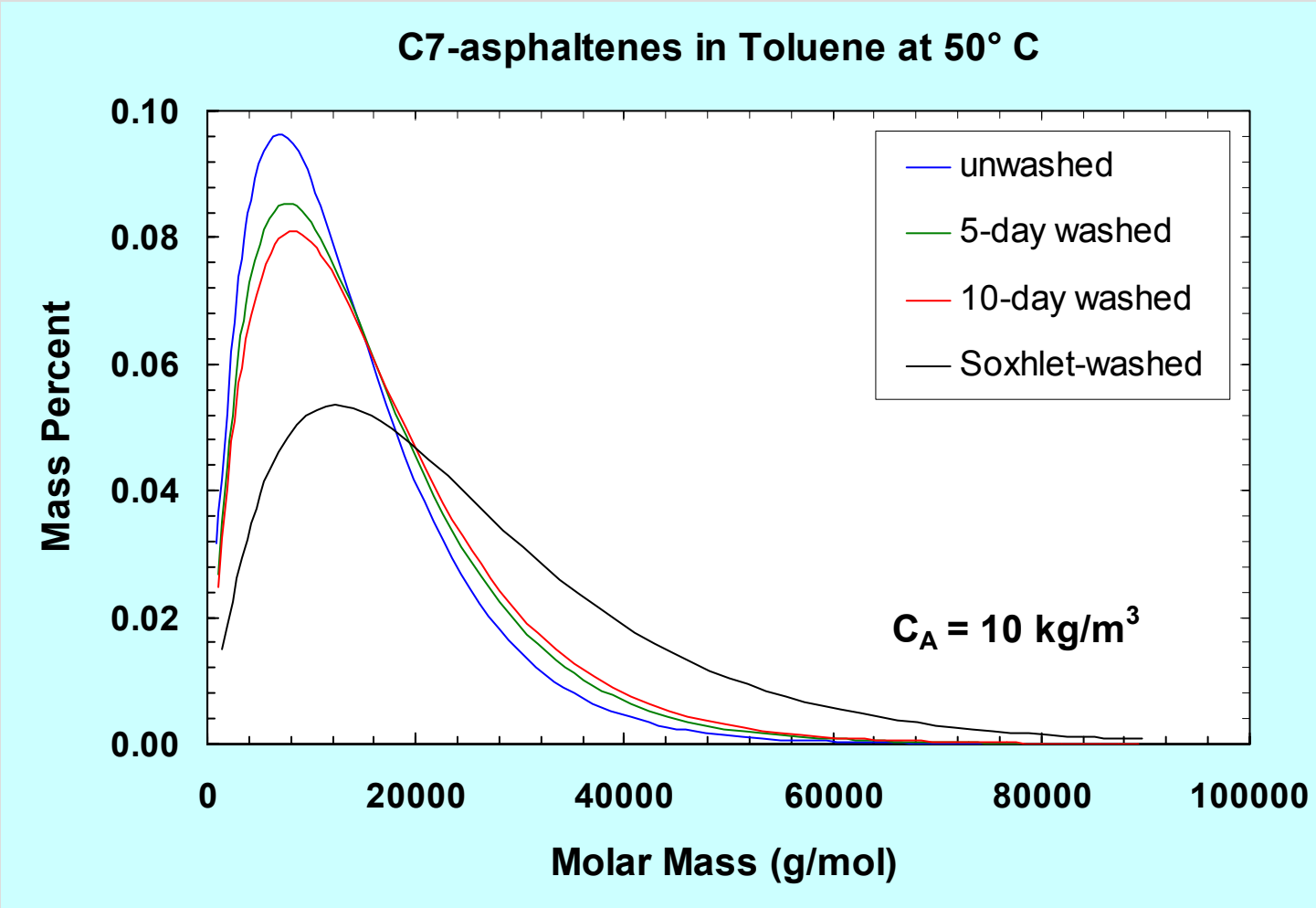
Acknowledgements

- NSERC
- CFI
- AERI
- DBR-Oilphase (Schlumberger)
- Shell Canada Ltd./Albian Sands Energy
- Syncrude Canada Ltd.
- Imperial Oil Ltd.
- Husky Oil Ltd.

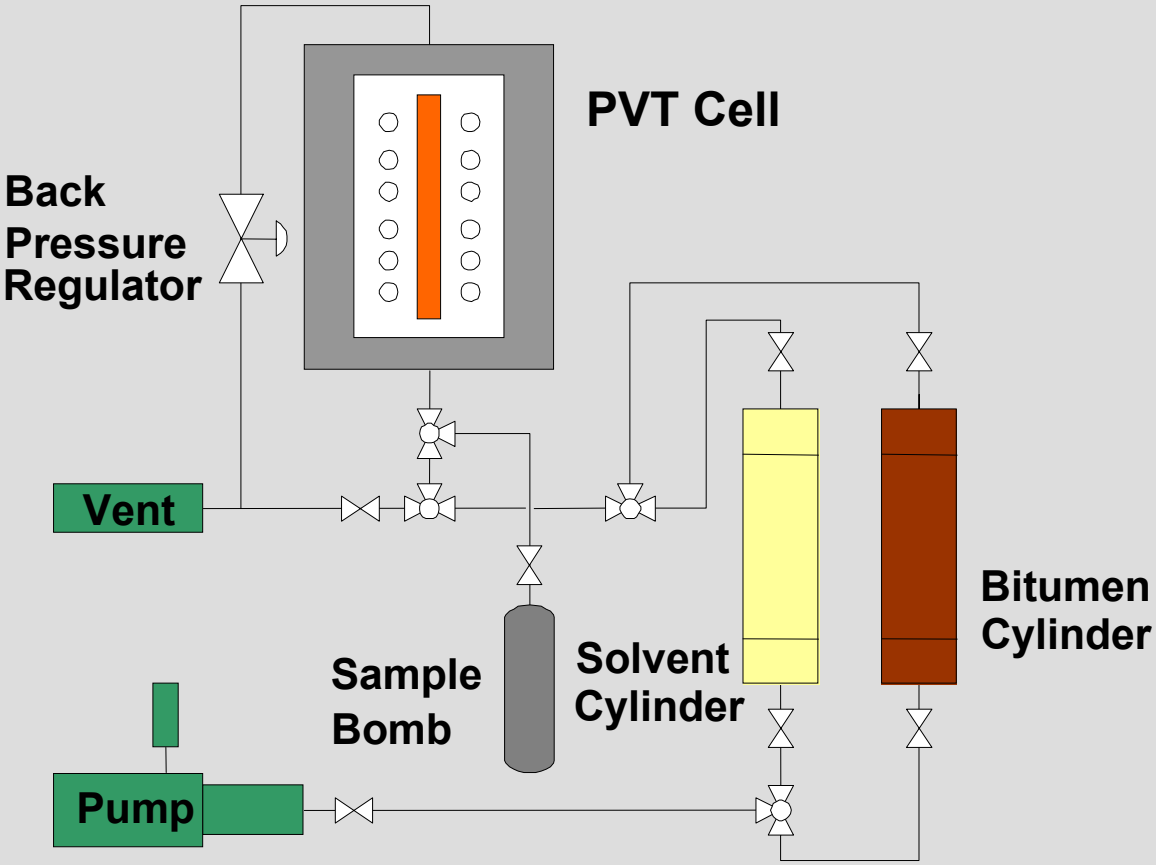
VPO of Micellar System



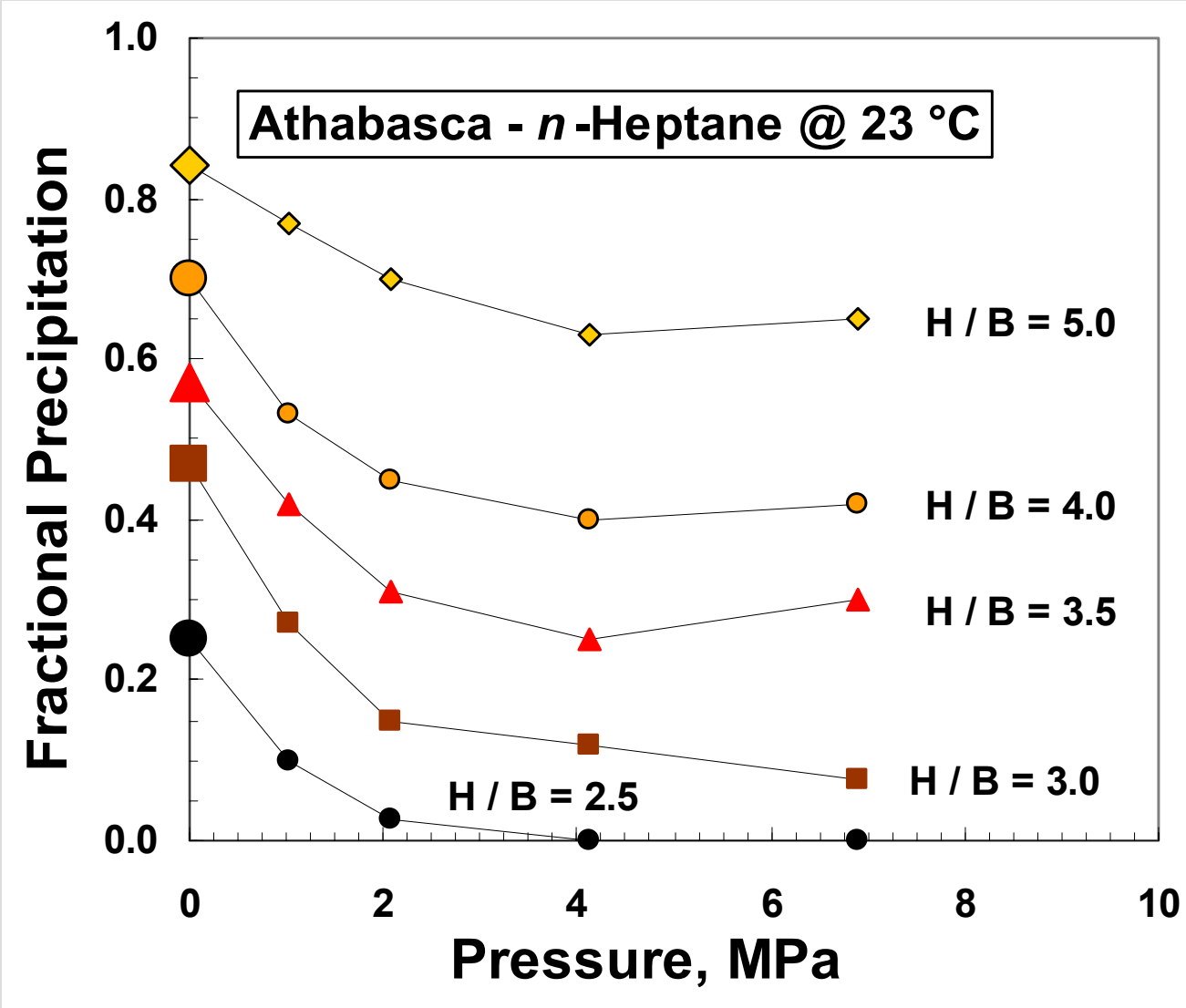
Molar Mass Distributions



PVT Cell


PVT Cell
Back
Pressure
Regulator
Vent
Sample
Bomb
Solvent
Cylinder
Bitumen
Cylinder
Pump

PVT Cell Data Validation



Asphaltene Precipitation

Cold Lake Bitumen and Alkanes at 23°C, 0.1 MPa