Solubility and Diffusivity Studies

Research Objectives

- Develop methods to measure phase equilibrium and diffusivity in industrially important polymer-solvent systems

- Develop models to correlate and predict these properties

Applications

- Drying of films and coatings
- Polymer synthesis
- Devolatilization
- Foam production
- Supercritical extraction

Experimental Methods

Low pressure

- Gravimetric sorption
  - Quartz spring
- IGC
  - Capillary column
  - Packed column
- LLE - HPLC

High pressure

- Pressure decay
- Capsule
- IGC

Modeling Efforts

Thermodynamics of polymer systems

- Phase equilibria
  - Equations of state – developing a predictive model
  - Activity coefficient models

Diffusion

- Application of the Vrentas-Duda Free-Volume model
  - Multicomponent

Processes

- Film dryers – multicomponent solvent, multilayer
- Purge towers (devolatilization)
- Latex polymerization

Importance of Diffusion

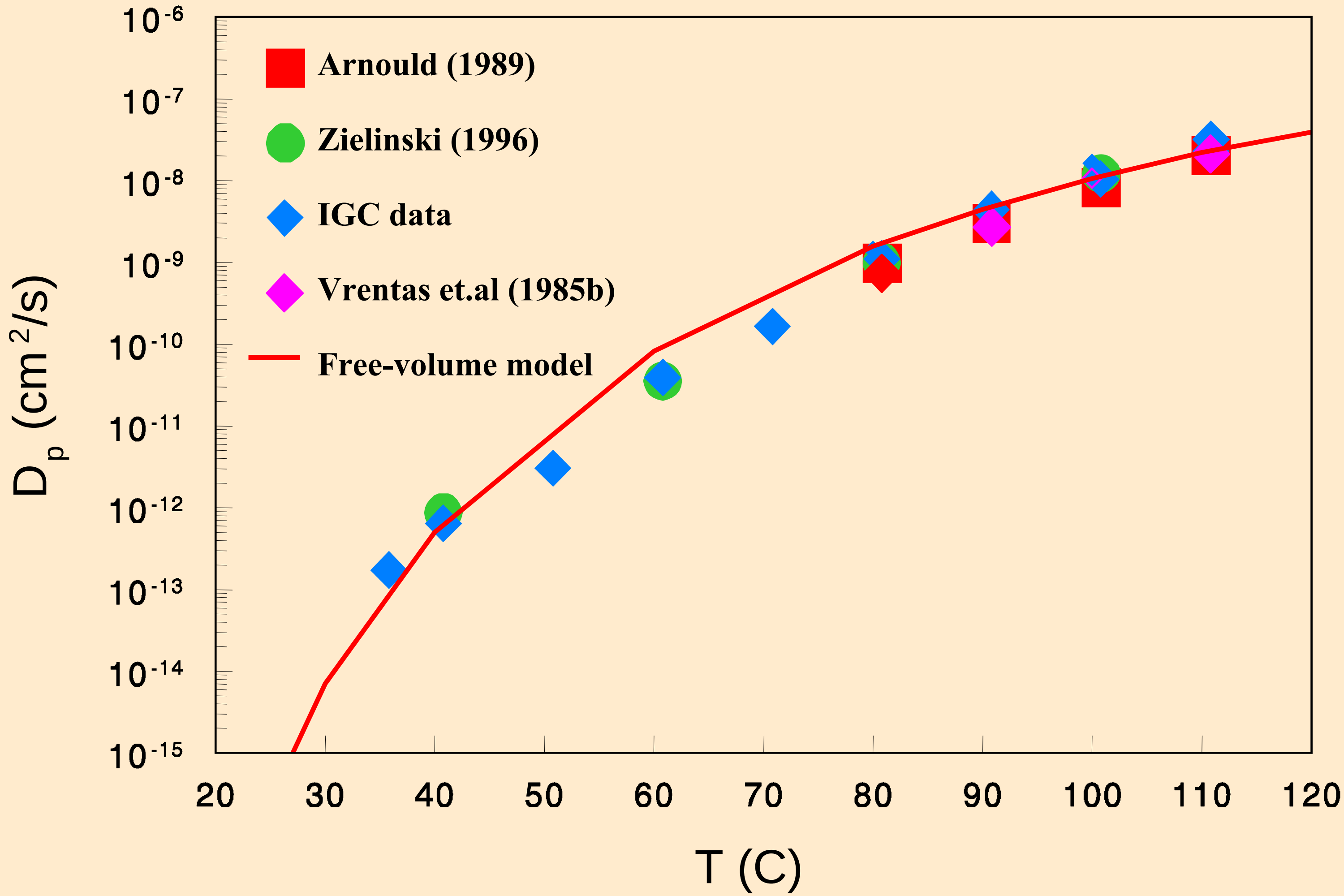
Diffusion characteristics are especially important in polymer-solvent systems at high concentrations of polymer.

Strong functions of concentration

Strong function of temperature

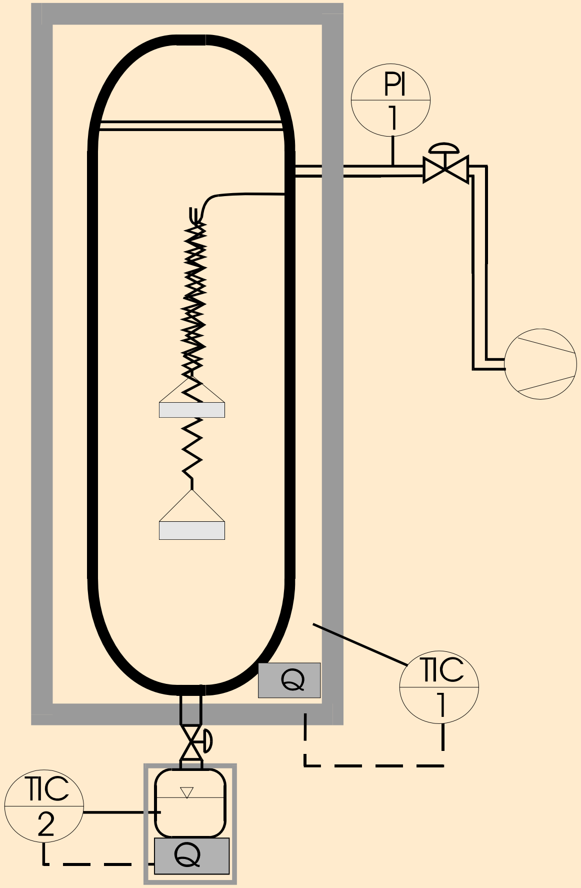
Frequently the controlling factor in the drying or devolatilization process.

D_p for Toluene in PVAC

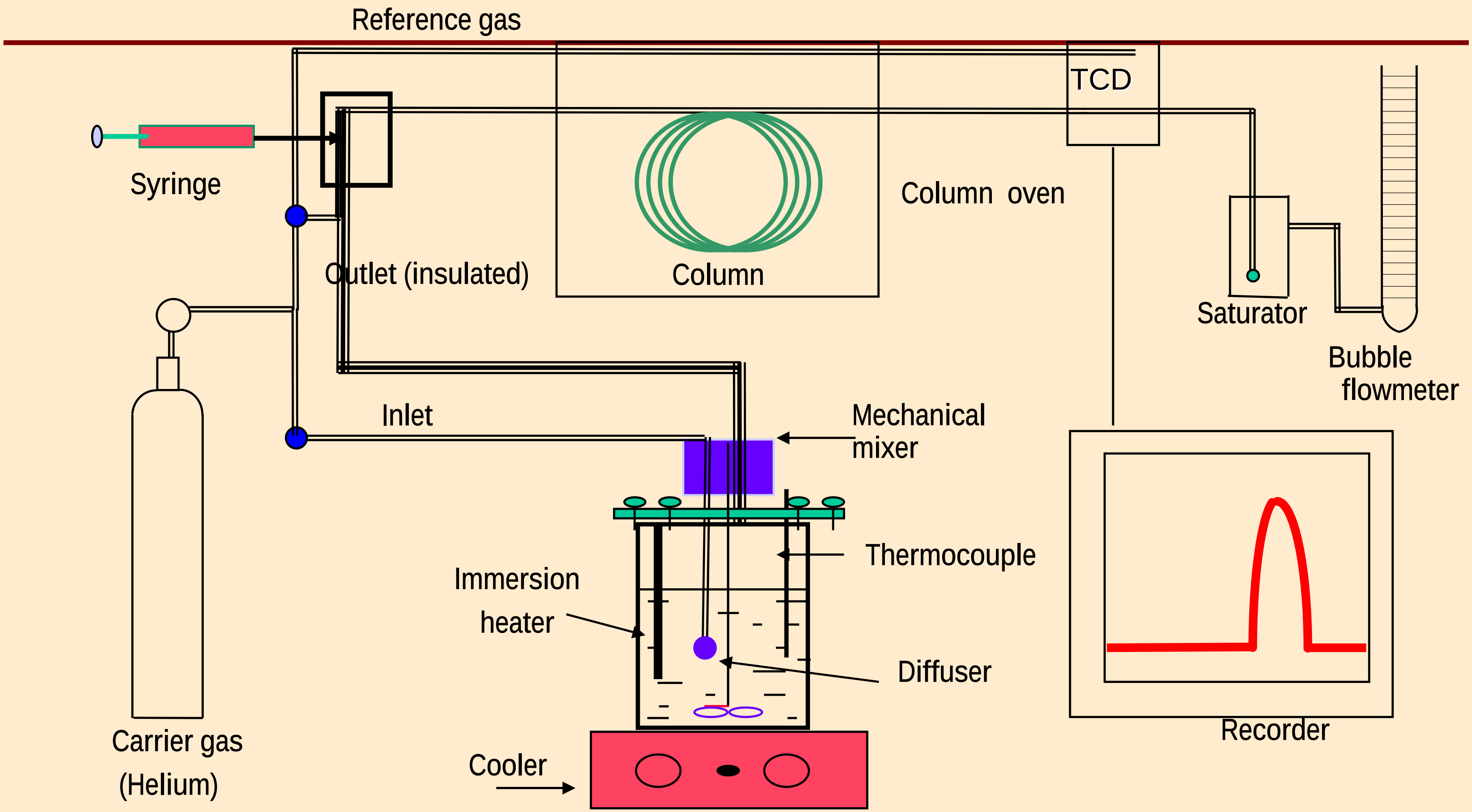


EXPERIMENTAL METHODS

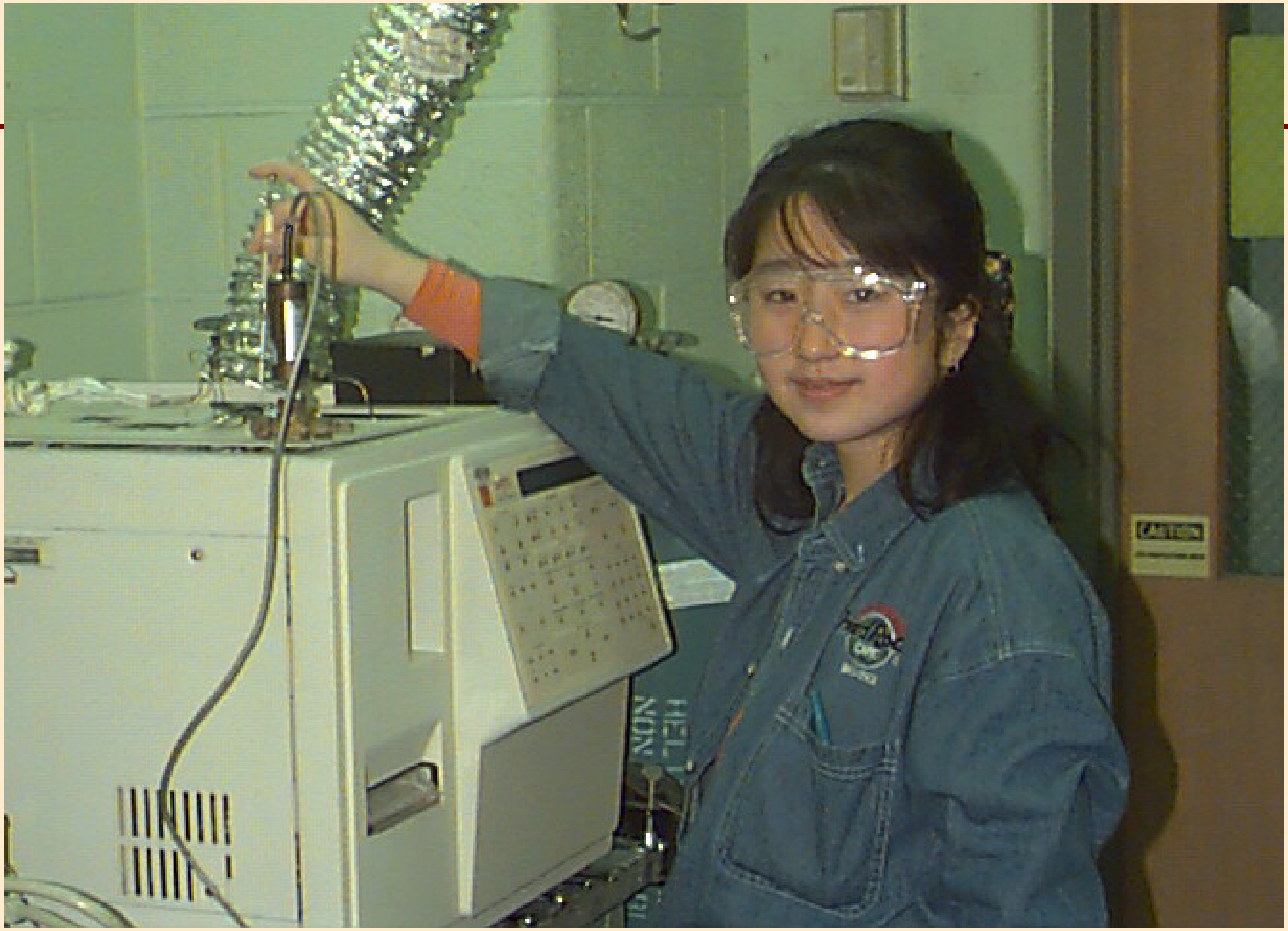
Quartz Spring Gravimetric



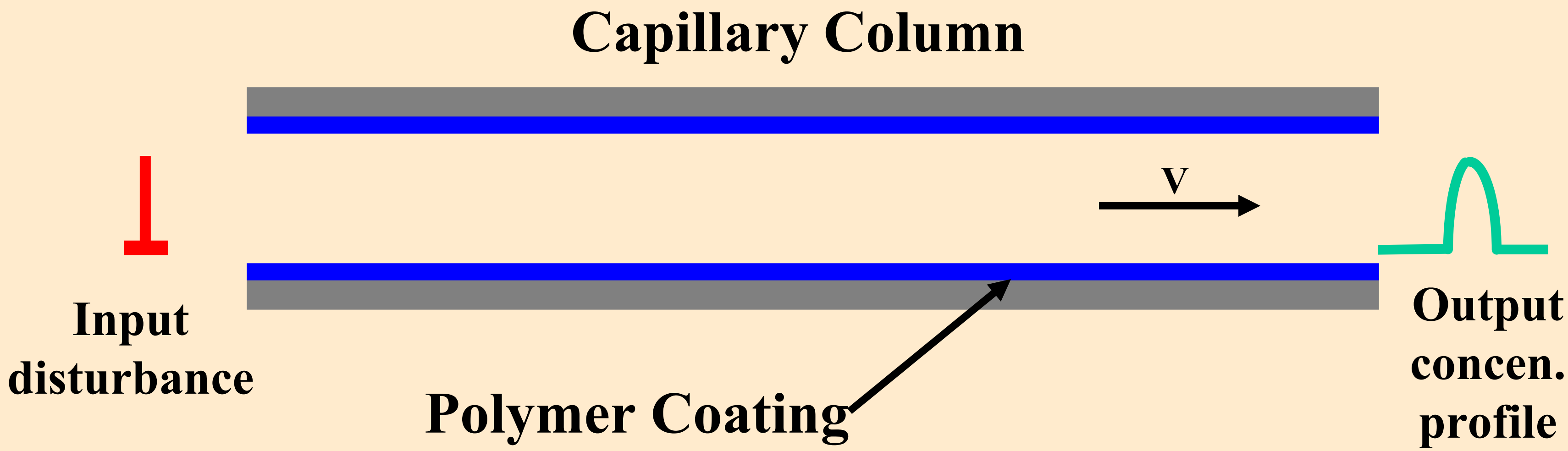
IGC Method



Infinite dilution / Finite concentration



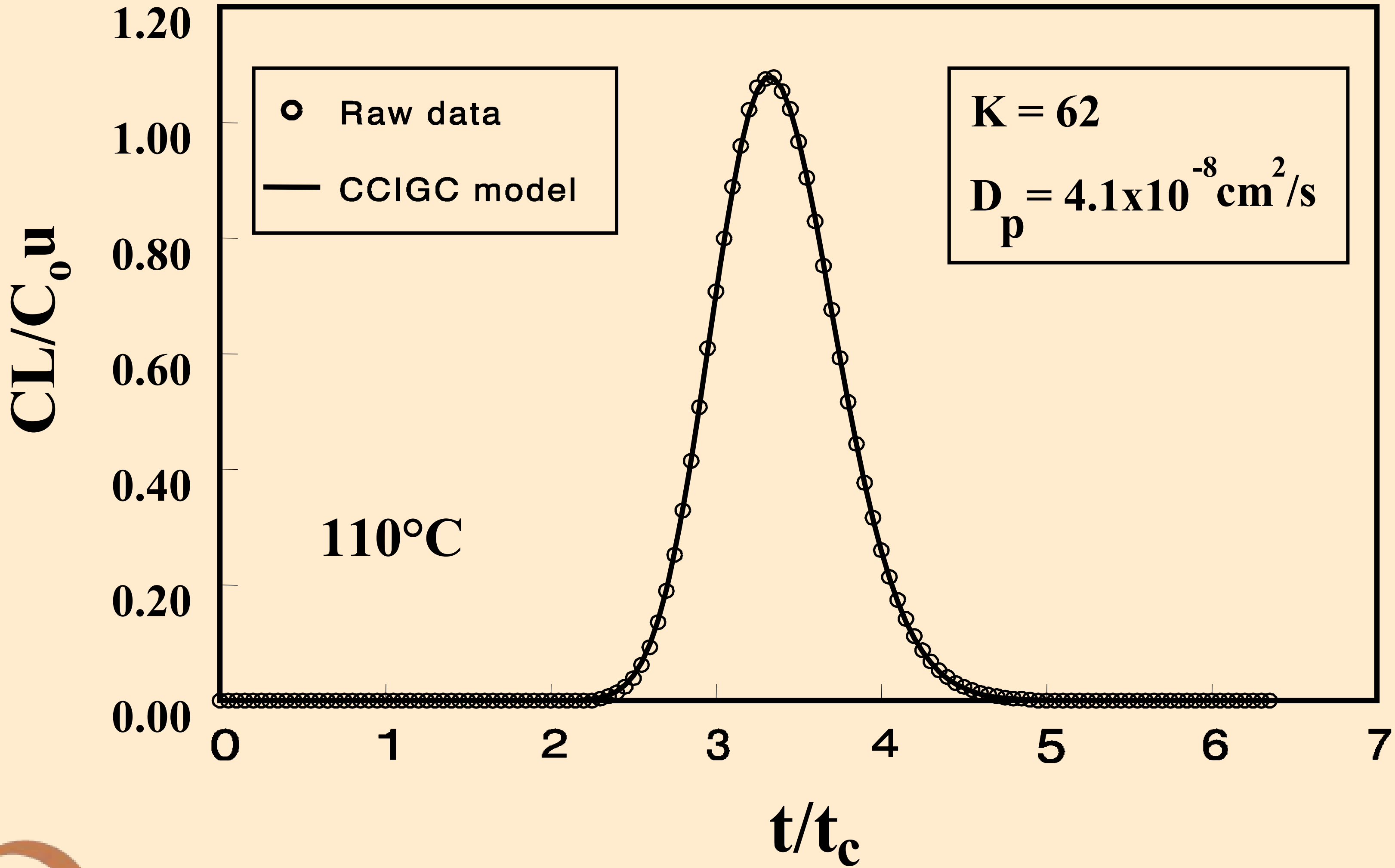
Inverse Gas Chromatography



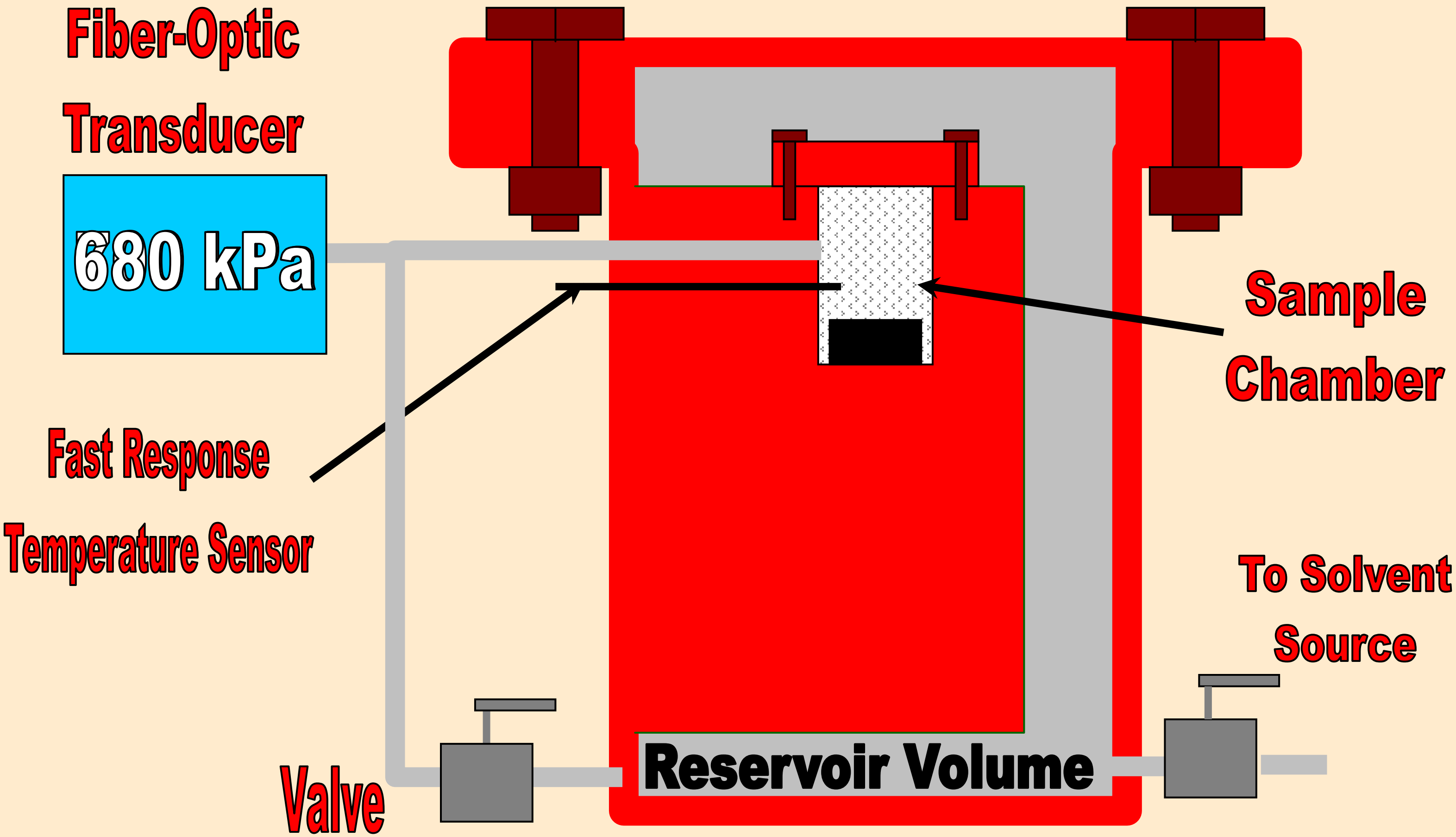
Contributions to zone broadening

- Longitudinal diffusion in the gas phase
- Mass-transfer resistance in the polymer phase

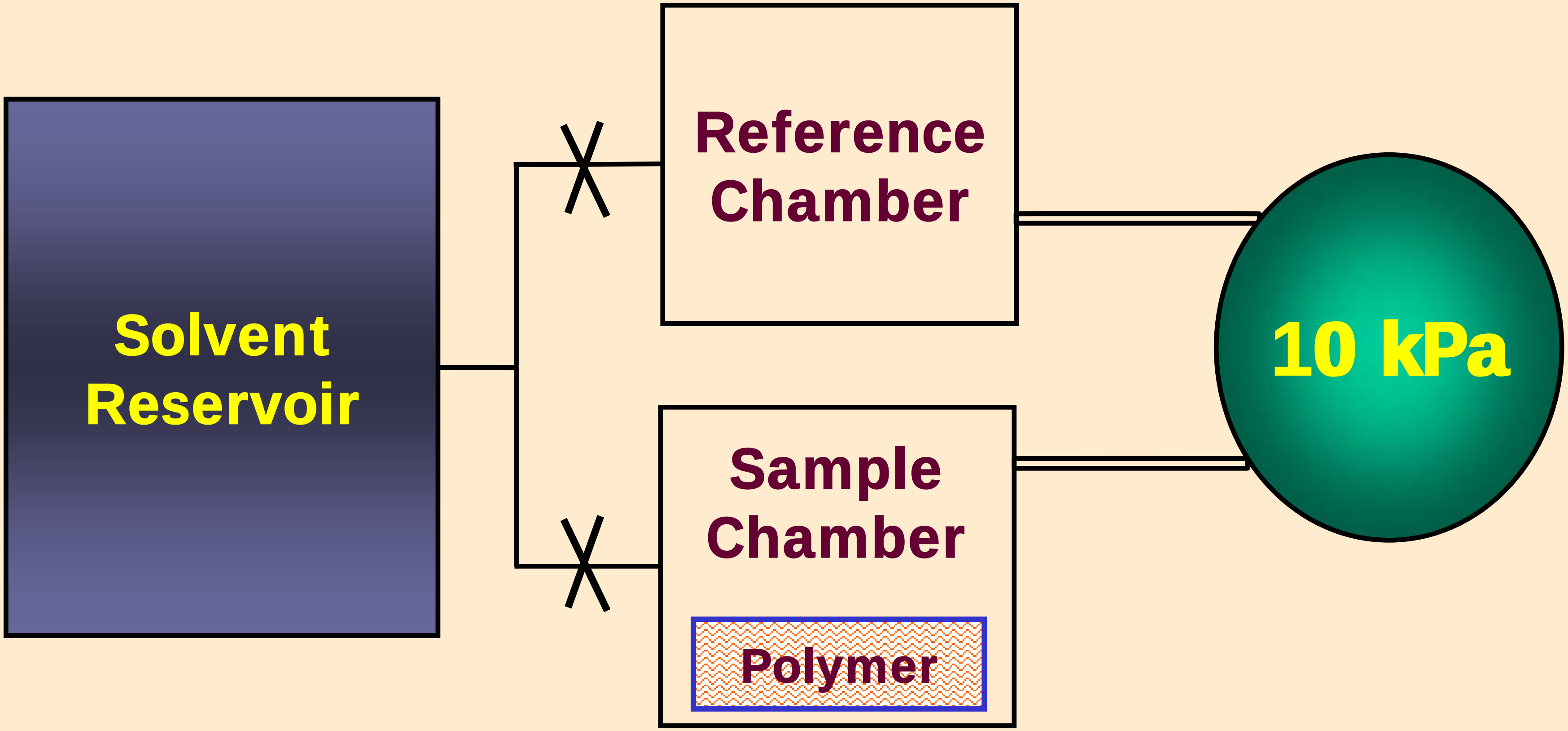
Elution Profile - Toluene through PVAC



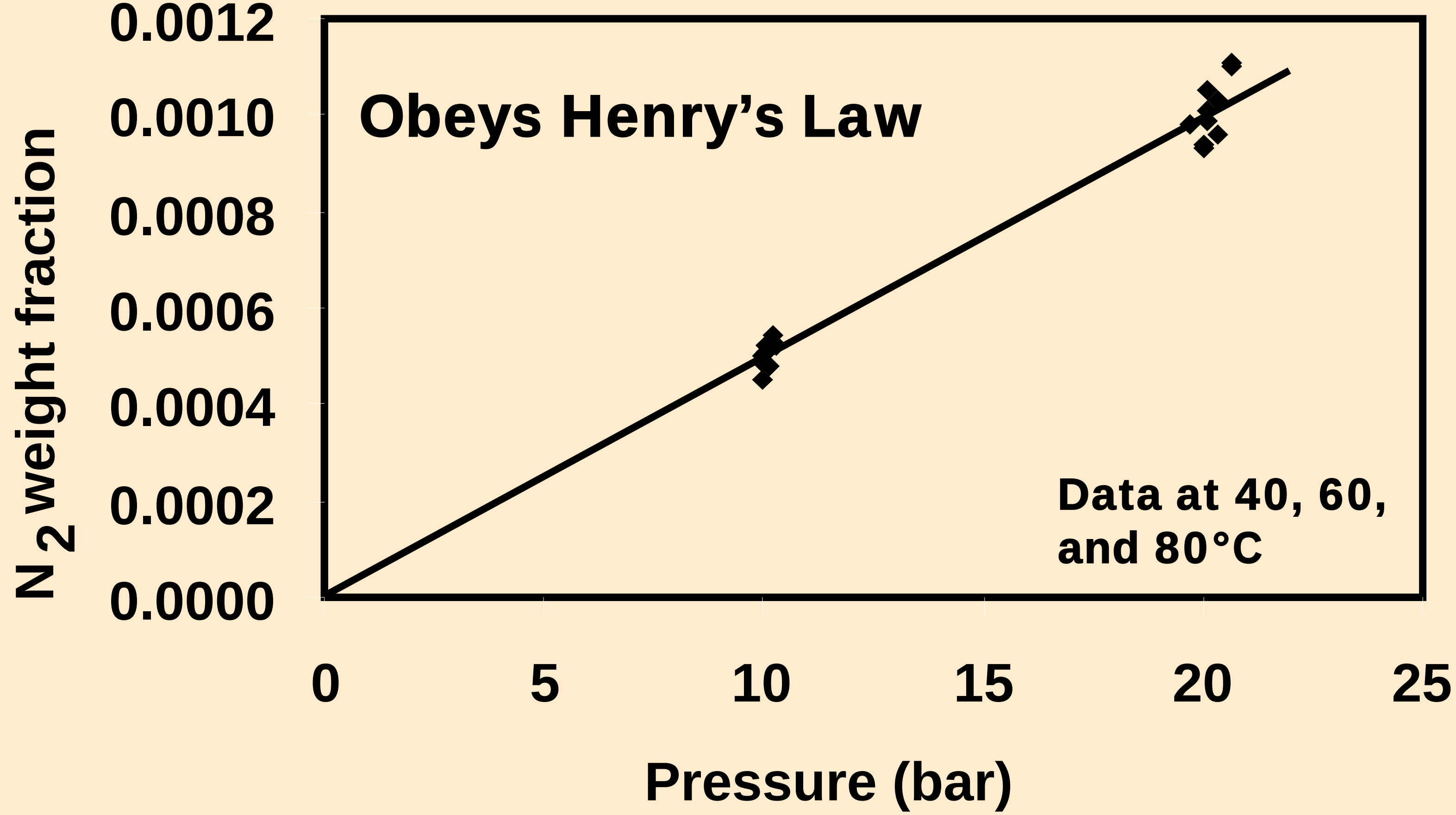
Pressure Decay
Absolute Pressure Apparatus



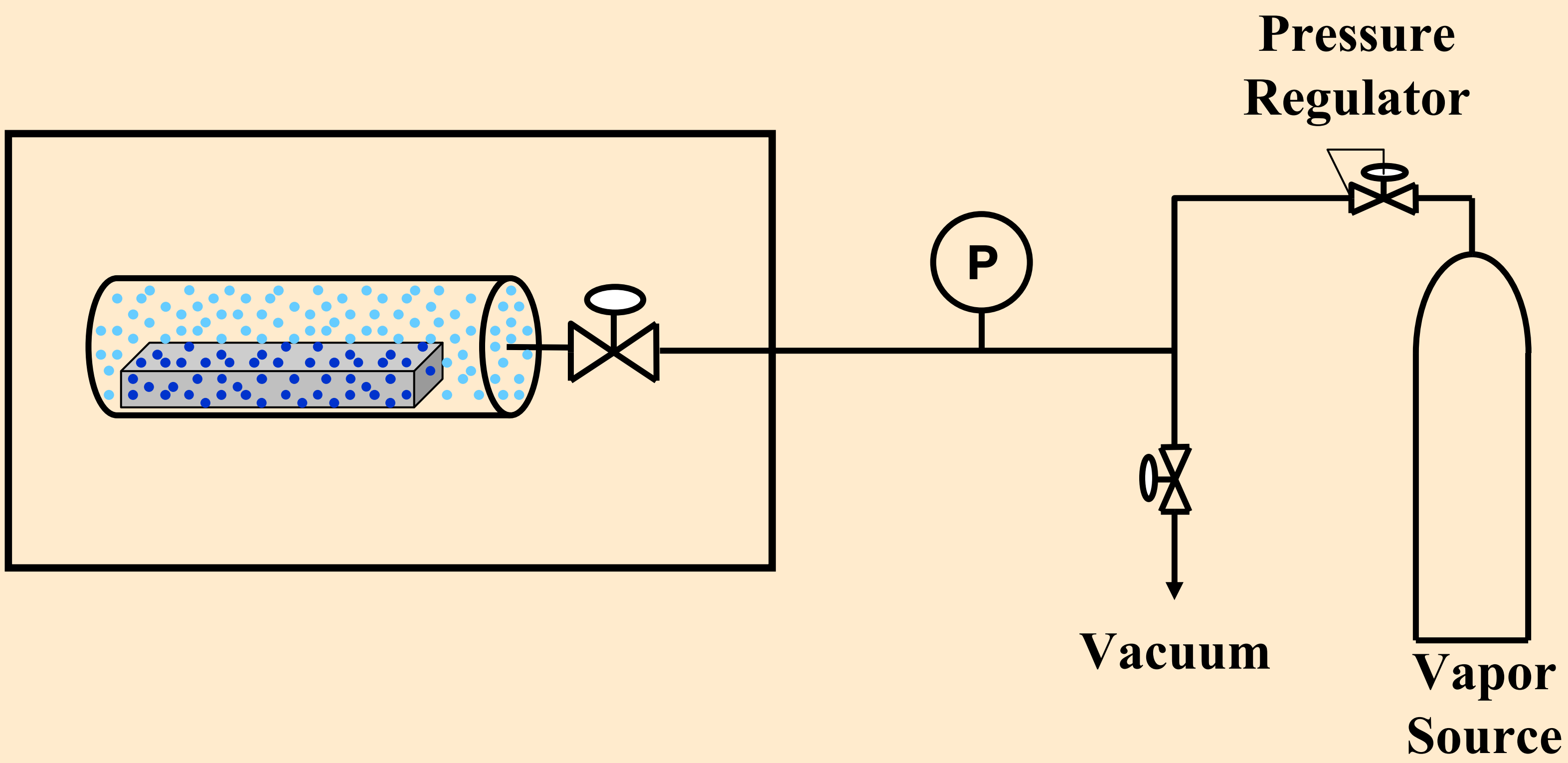
Pressure Decay
Differential Pressure Apparatus



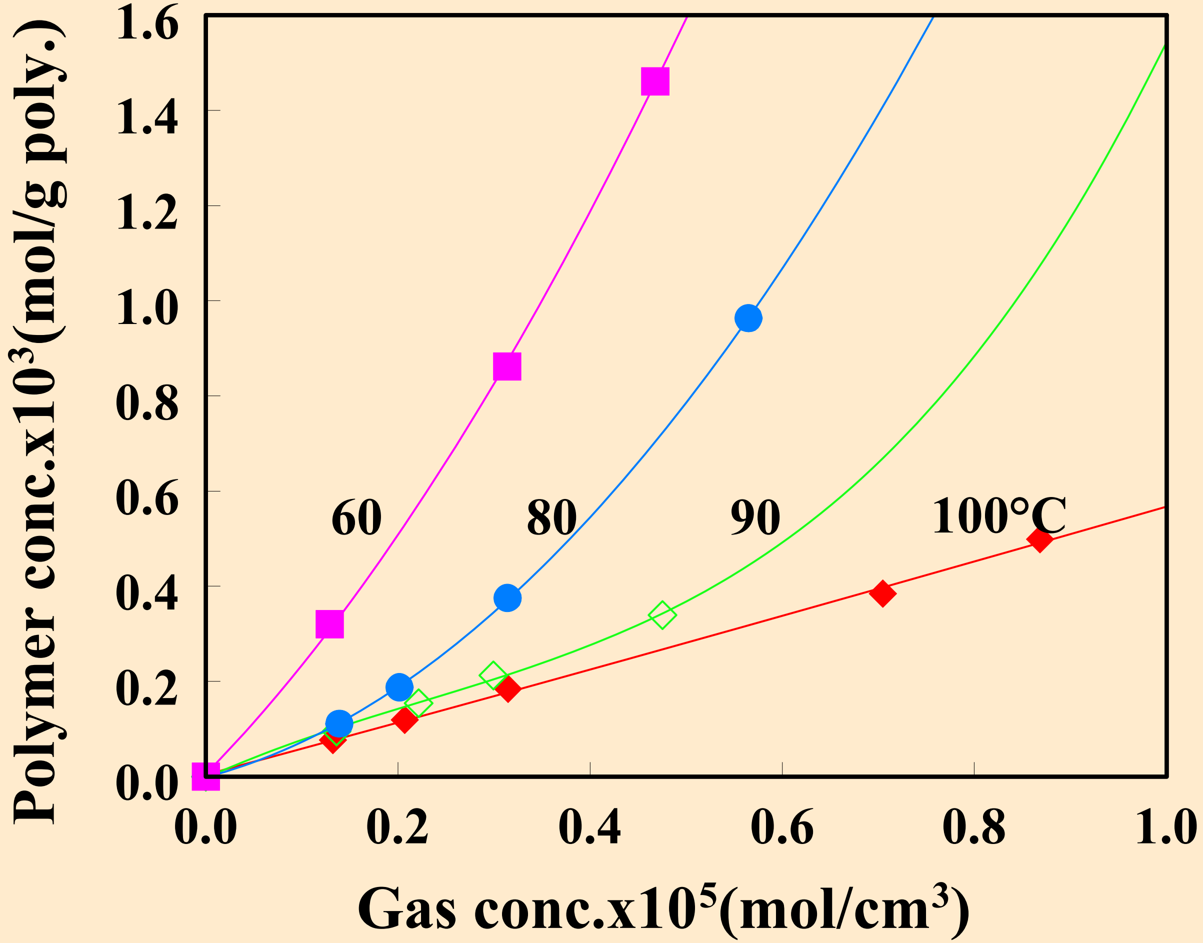
Pressure Decay
N_2 Solubility in PVB



Capsule Method



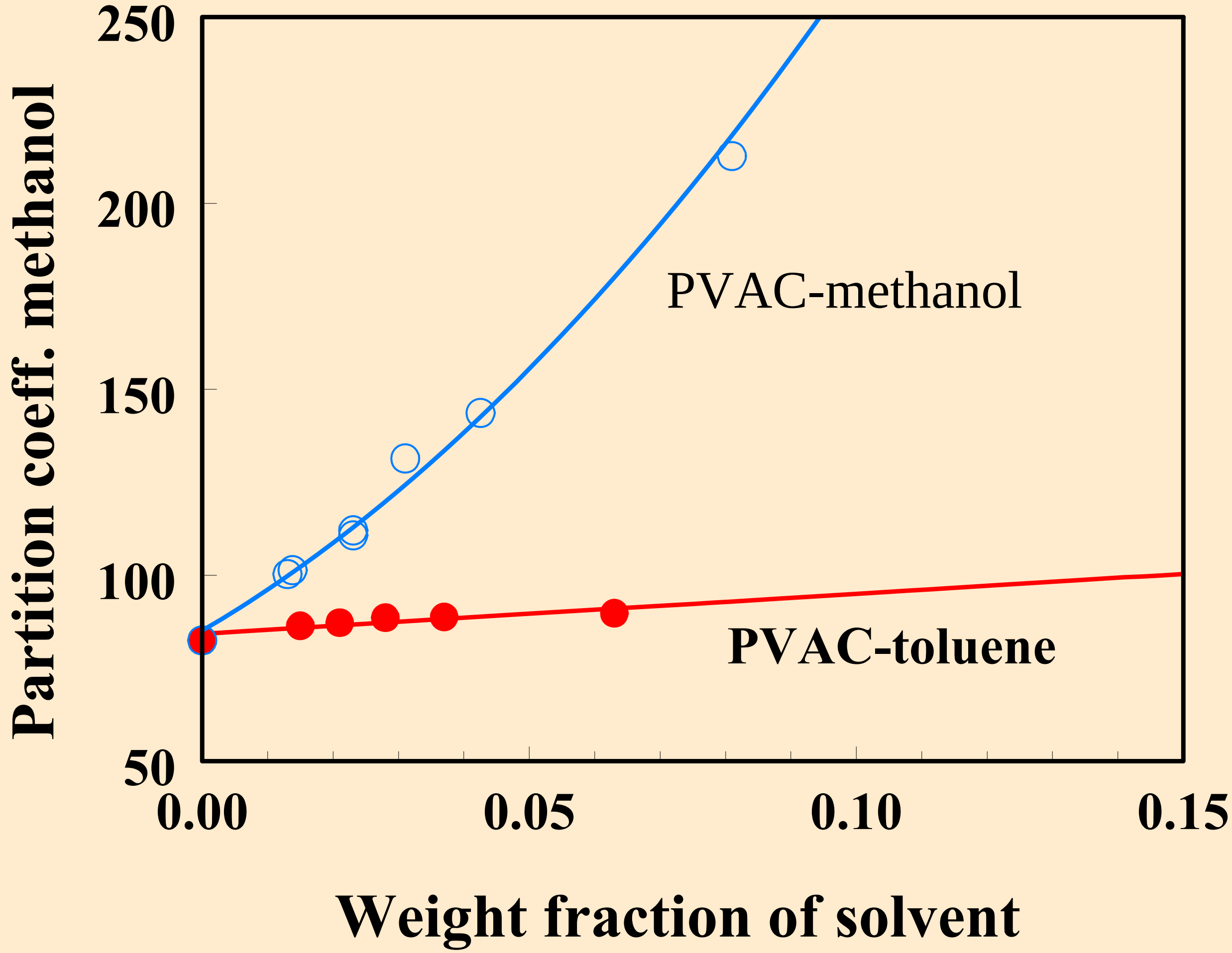
Sorption Isotherms for Toluene in PVAC



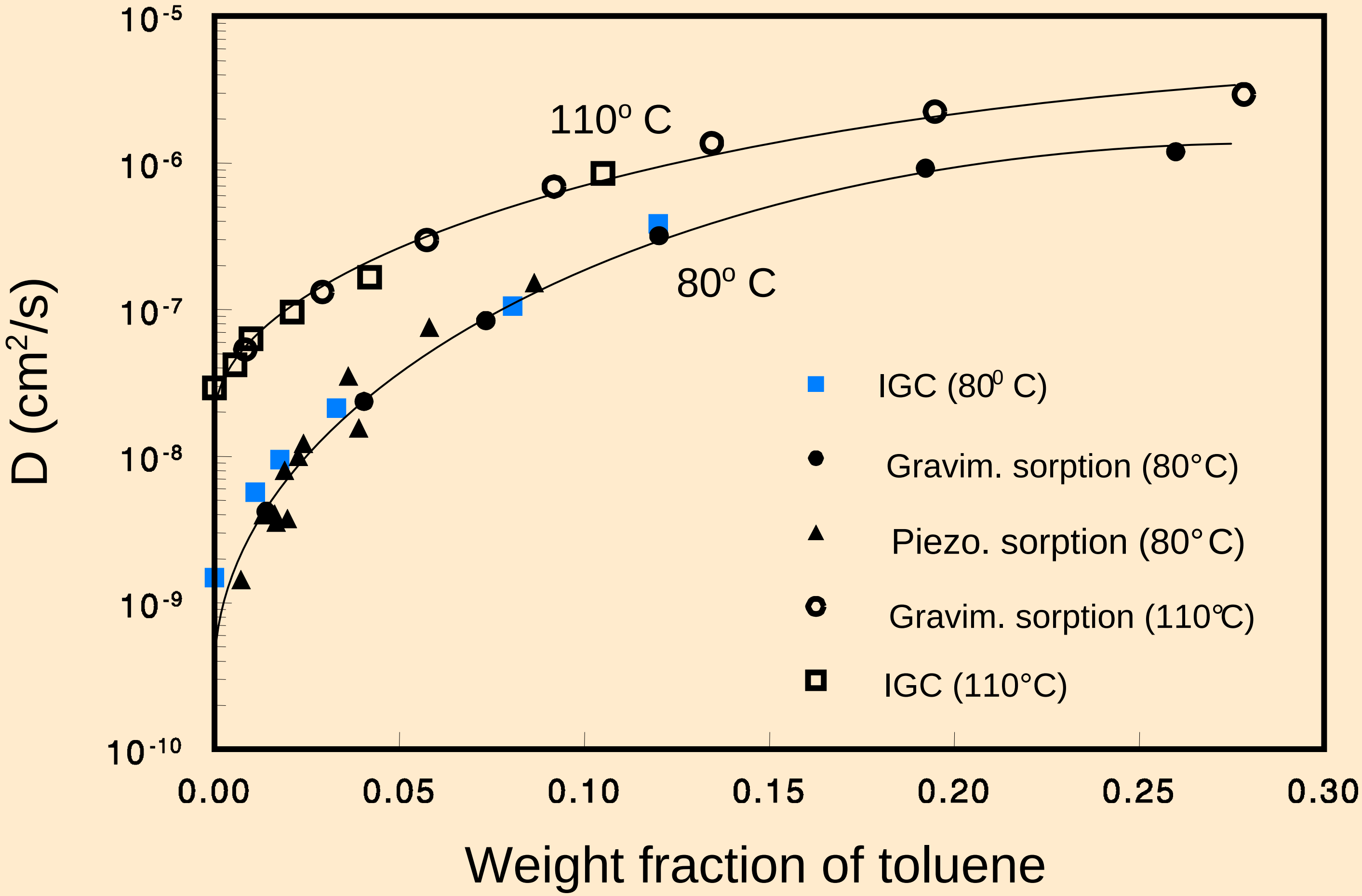
Partition Coefficient of Methanol in PVAC-Toluene and PVAC- Methanol at 60°C

Partition Coefficient

$$= \frac{\text{conc. polym.}}{\text{conc. gas}}$$



Comparison of Methods: Toluene in PVAC at Finite Concentrations



MODELING EFFORTS

Diffusion

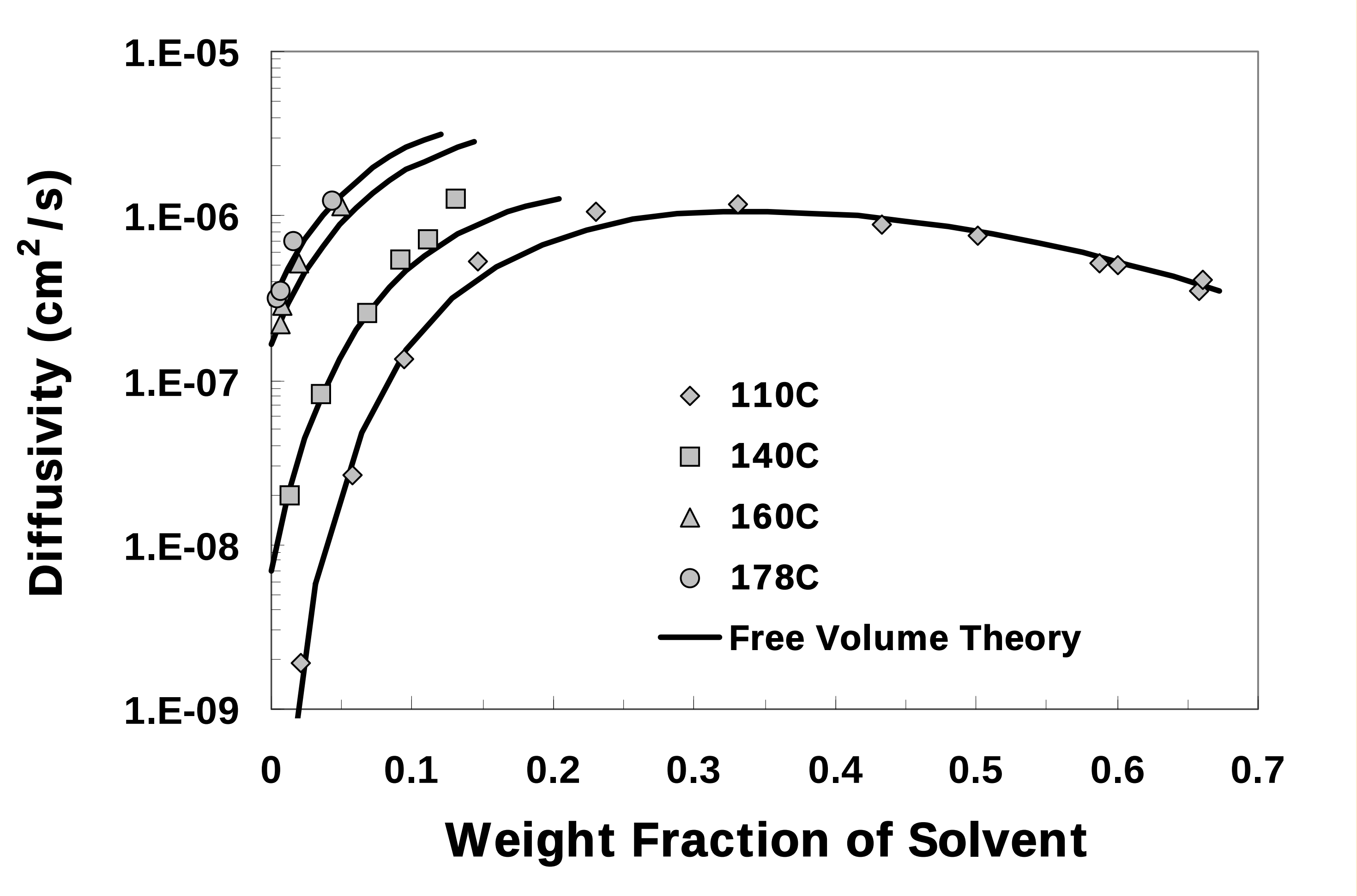
Vrentas-Duda Free-Volume Theory

Model based on free volume concept to describe molecular diffusion of solvents in polymers.

Necessary events for molecular transport:

- **Hole of sufficient size next to the molecule**
- **Molecule possesses enough energy to jump**

Polystyrene-Toluene



Implications of Free-Volume Theory

Addition of solvent or a temperature increase will increase D more strongly close to the T_g

Larger molecules increase the T and concentration dependence of D.

Elastomers far above their T_g have large fraction of hole free volume - large D with weak T and concentration dependence.

In region of high polymer concentration, D is very weak function of the molecular weight.

Addition of additives effect D according to their free-volume contribution

Phase Equilibria

UNIFAC-vdw-Free Volume

Activity coefficient approach (low pressure)

Group-Contribution, Lattice-Fluid EoS

Equation of state approach

SAFT EoS

UNIFAC - FV

WFAC of a solvent in the polymer, Ω_i, is given by:

$$\ln \Omega_i = \ln \Omega_i^C + \ln \Omega_i^R + \ln \Omega_i^{FV}$$

GCLF-EoS

Panayiotou-Vera EOS

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+q/r-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}}$$

$\tilde{P}, \tilde{T}$ and $\tilde{v}$ are reduced quantities expressed as:

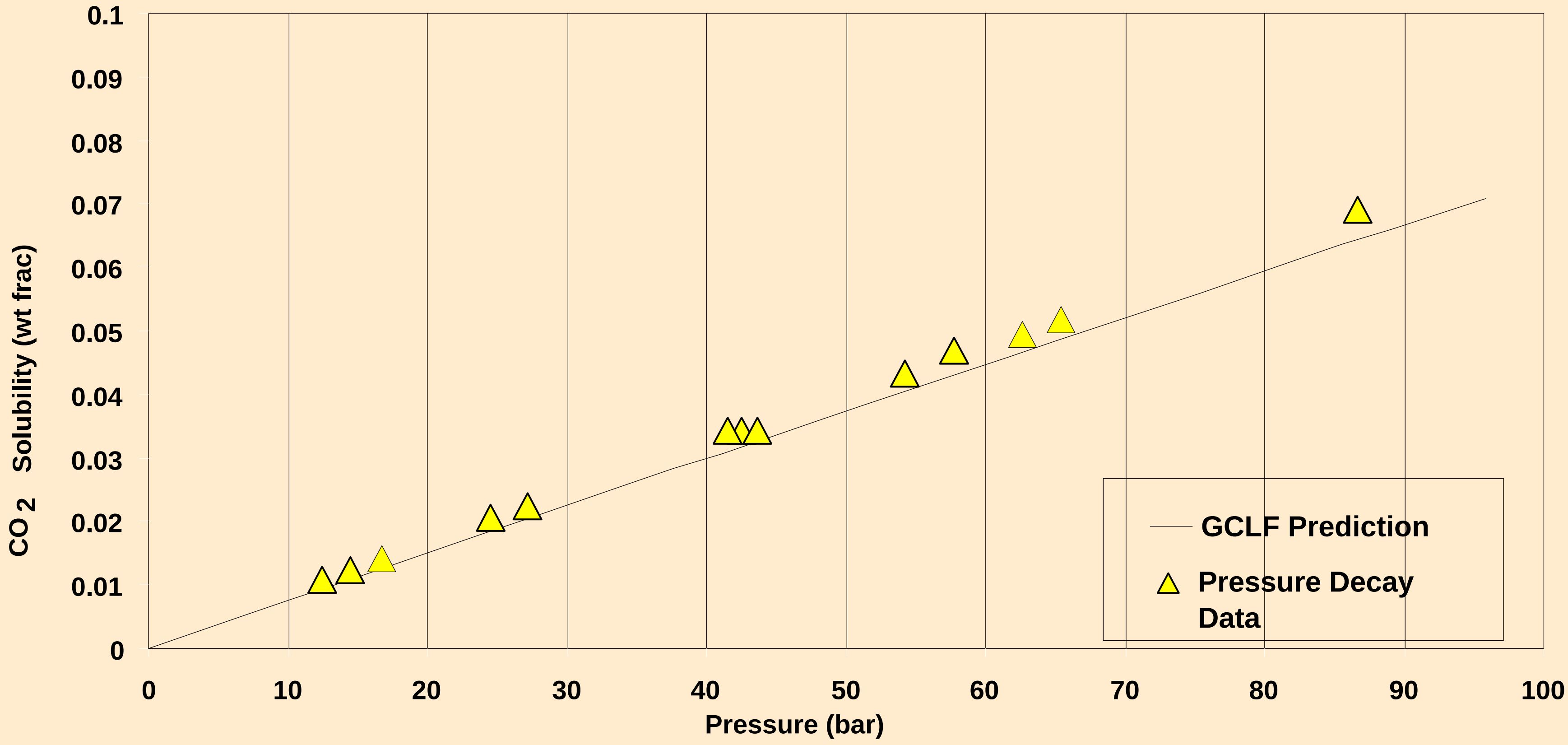
$$\tilde{P} = P/P^* \quad \text{where} \quad P^* = z\varepsilon_{11}/2v_h$$

$$\tilde{T} = T/T^* \quad \text{where} \quad T^* = z\varepsilon_{11}/2R \qquad \tilde{v} = v/v^*$$

Two scaling parameters per pure component: v^* and ε_{11} and an interaction parameter, k_{ij}, for mixtures. These parameters are obtained using the group contributions methods developed by Lee and Danner.

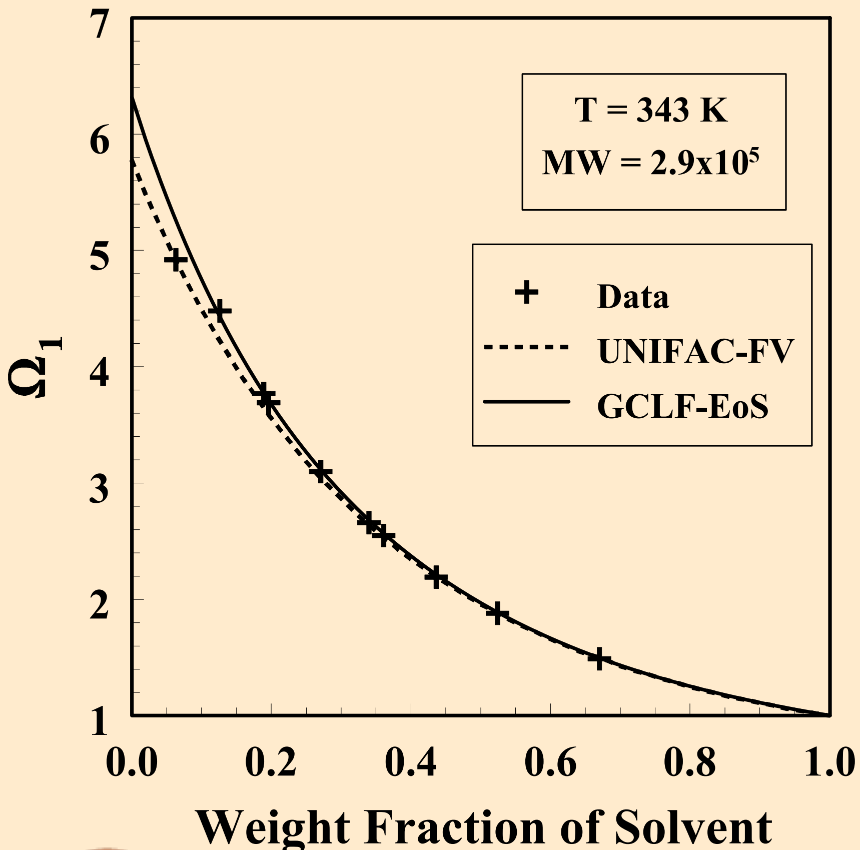
GLCF-EoS

CO_2 – PP at 170°C

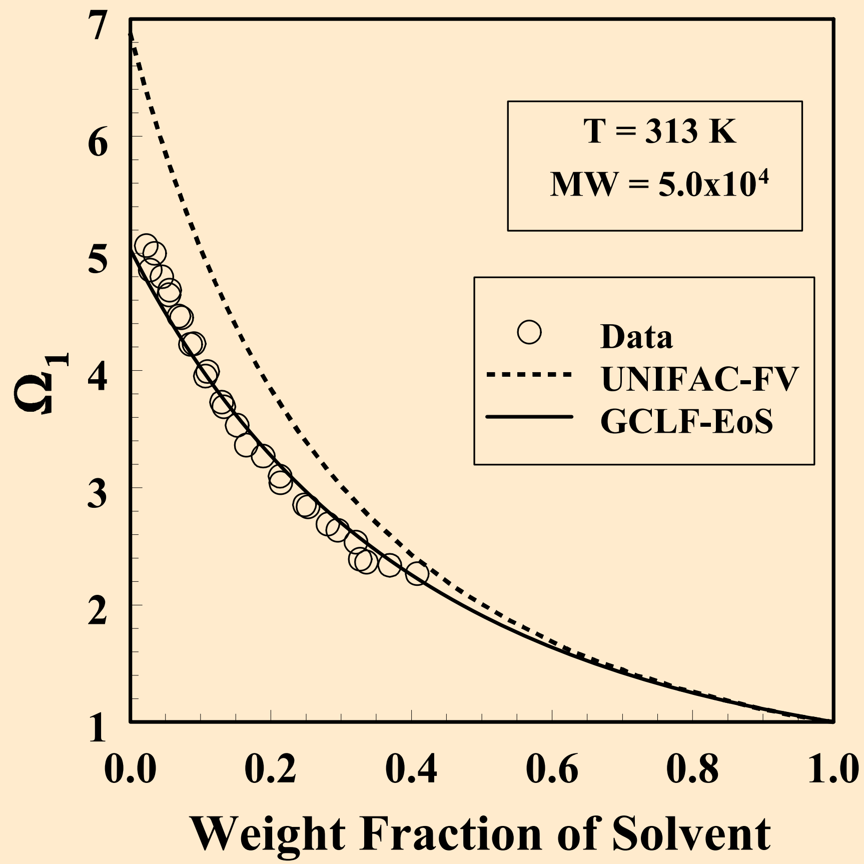


GCLF-EoS – UNIFAC-FV

PS/n-Propyl Acetate



PIB/Benzene



Conclusions

Extensive capabilities to measure and model:

Phase equilibria in polymer-solvent systems – primarily VLE

Mass transport in polymer-solvent systems

Wide application in polymer processing and production.