The ZLC Method

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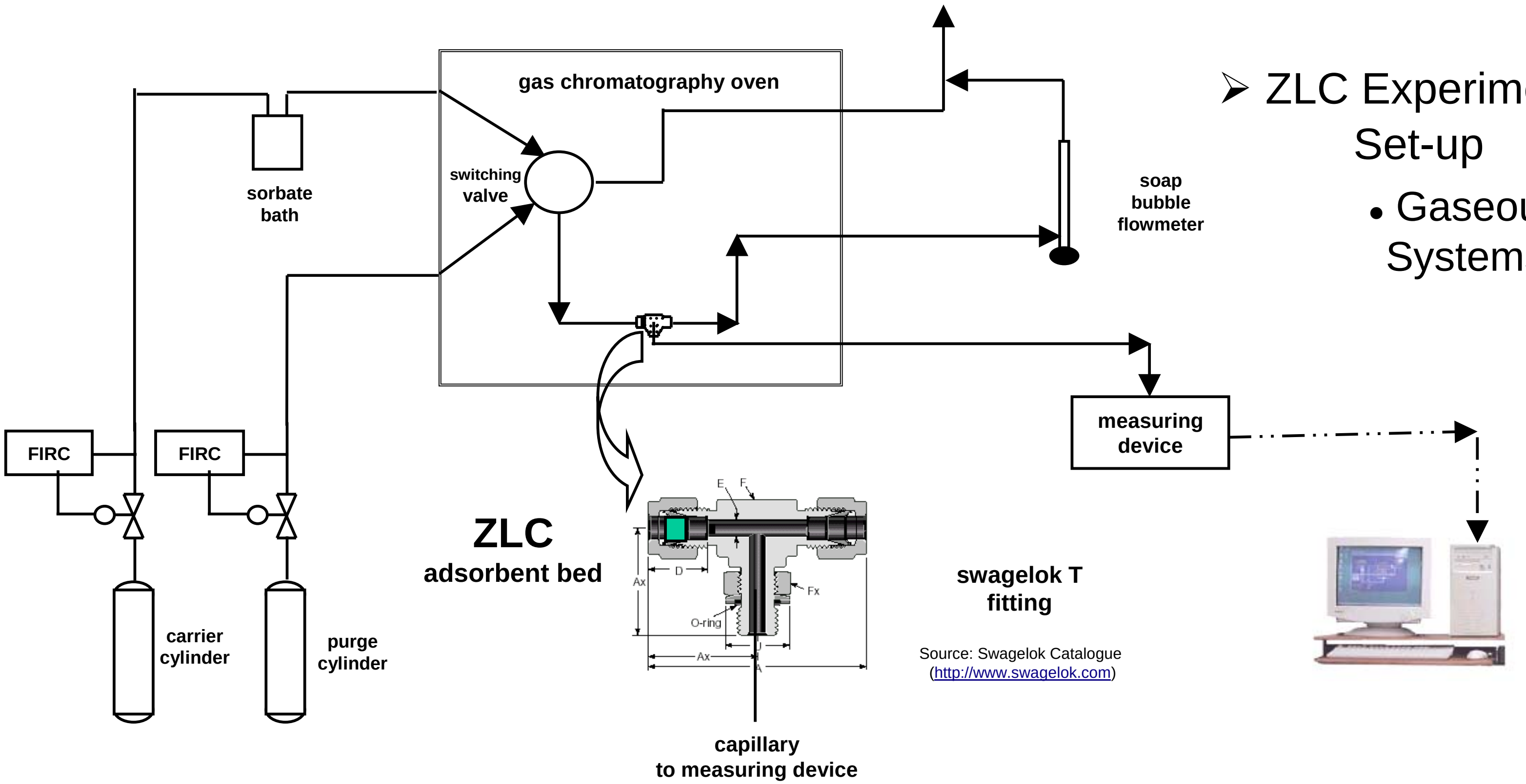
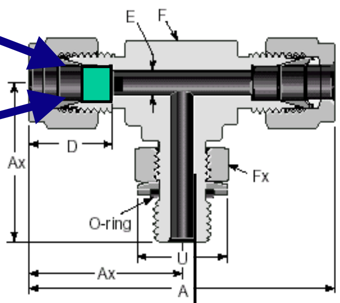
The ZLC apparatus



- ZLC Experimental Set-up
  - Gaseous Systems

The ZLC column

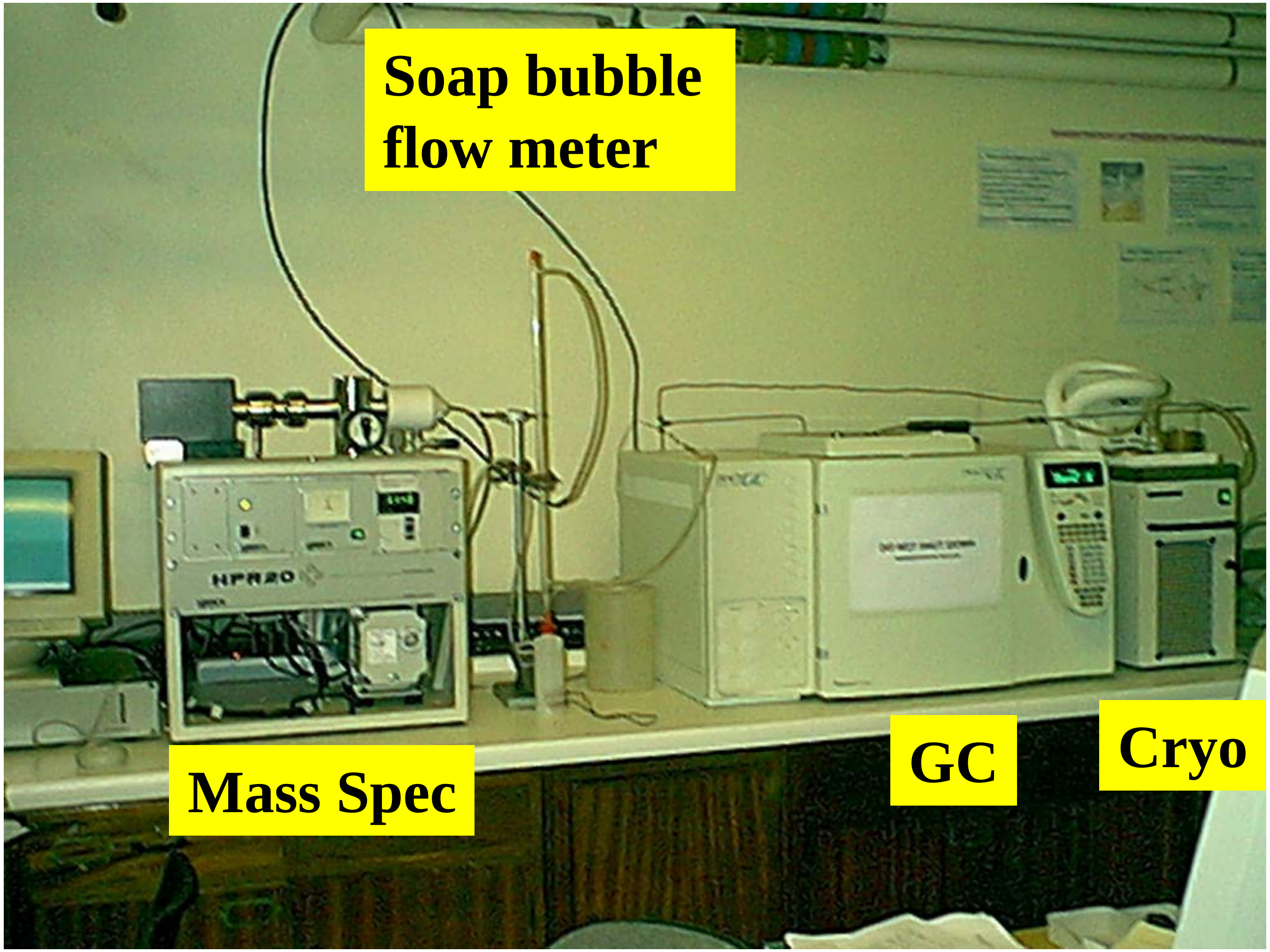
Packing: 0.5 – 2 mg



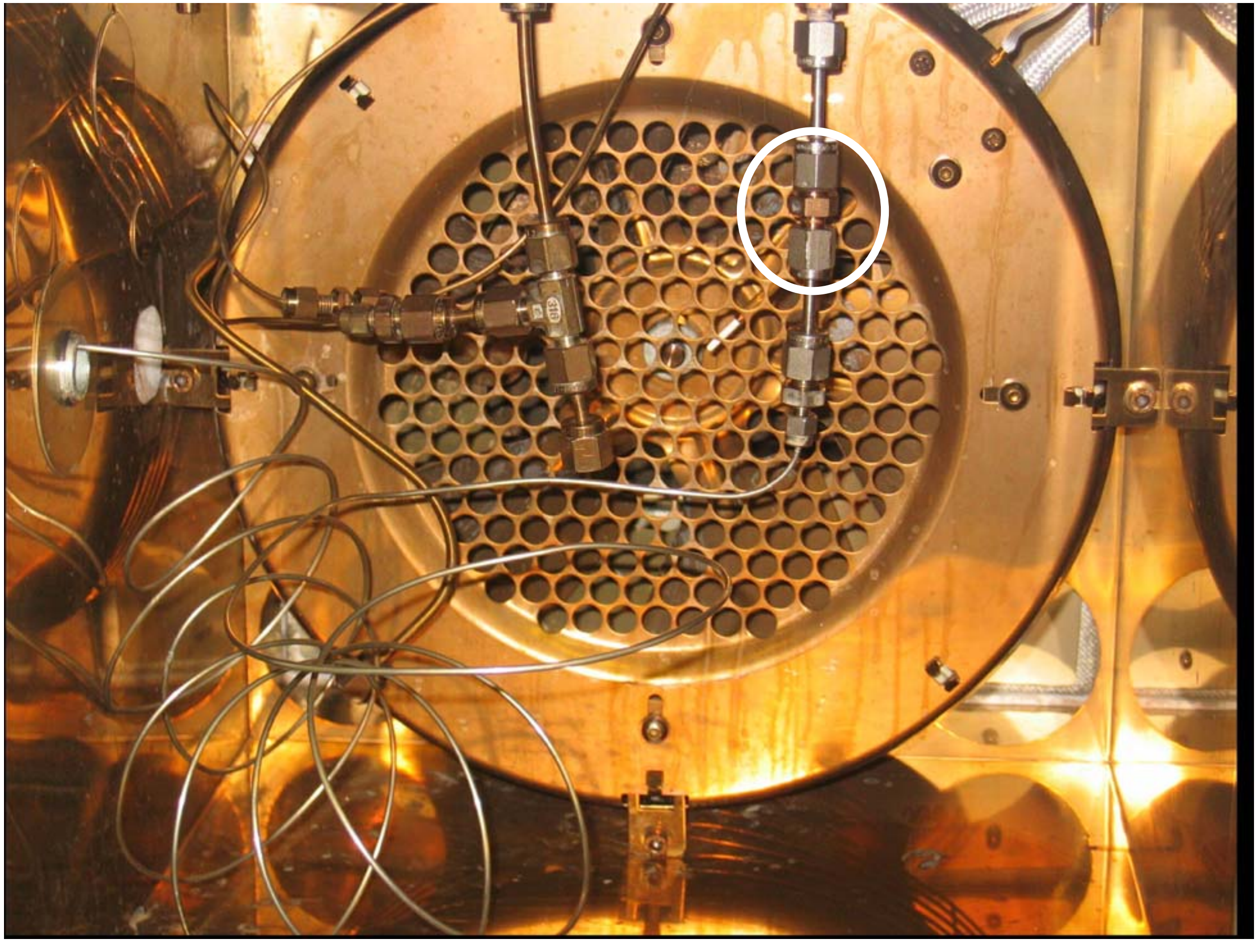
swagelok
T fitting

capillary
to measuring
device

The (Tracer) ZLC apparatus



ZLC column inside GC oven



What can be measured?
Kinetics

- The *transport diffusivity* at zero loading

  Eic M. and Ruthven D.M., *Zeolites*, **1988**, *8*, 40–45.
- *Liquid phase counter diffusion*

  Ruthven D.M. and Stapleton P., *Chem. Engng Sci.*, **1993**, *48*, 89-98.
- The *tracer diffusivity* – Tracer ZLC

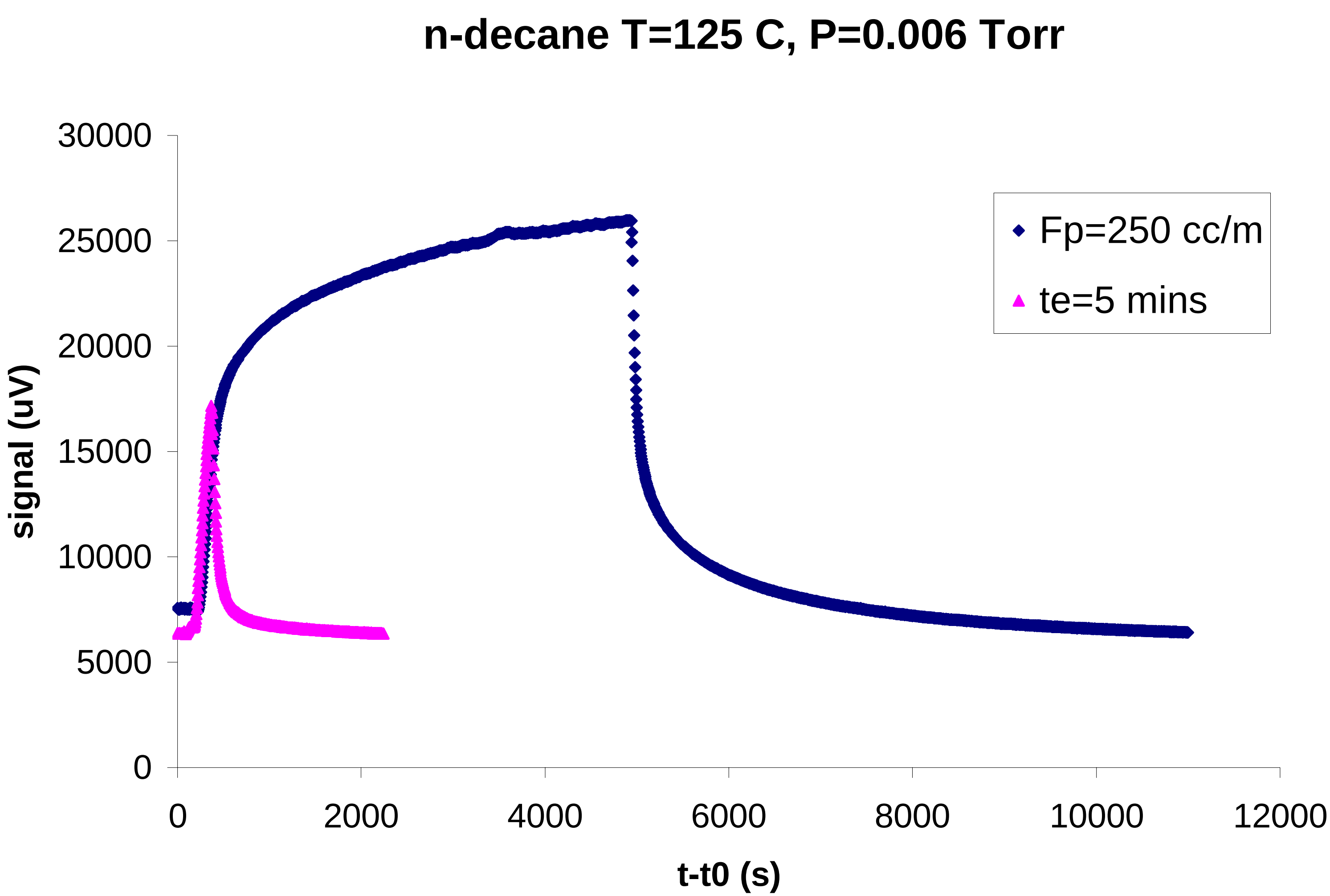
  Brandani S., Hufton J.R. and Ruthven D.M., *Zeolites*, **1995**, *15*, 624–631.
- The *transport diffusivity in mixtures*

  Brandani S., Jama M. and Ruthven D.M. , *Ind. & Eng. Chem. Res.*, **2000**, *39*, 821-828.

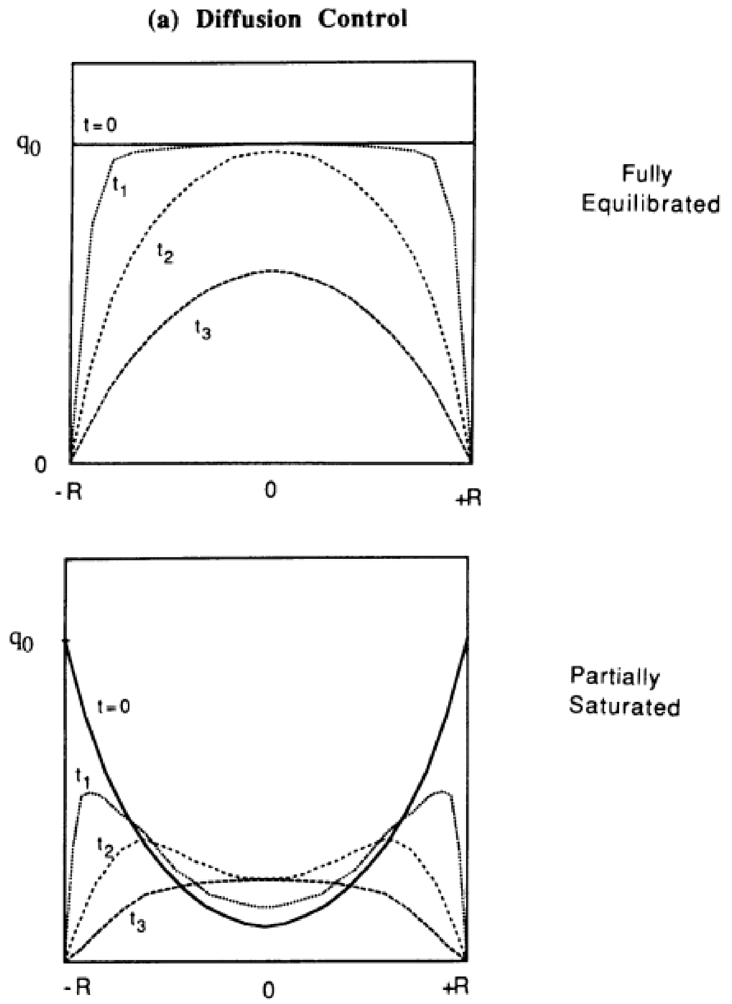
Tracer ZLC

- ZLC measurements are carried out using a tracer, such as a C_6D_6 for C_6H_6.
- Total concentration constant
- **ALWAYS LINEAR + ISOTHERMAL**
- **DIRECTLY COMPARABLE TO MICROSCOPIC MEASUREMENTS**
- Requires a mass spectrometer

Experimental Signals - Silicalite



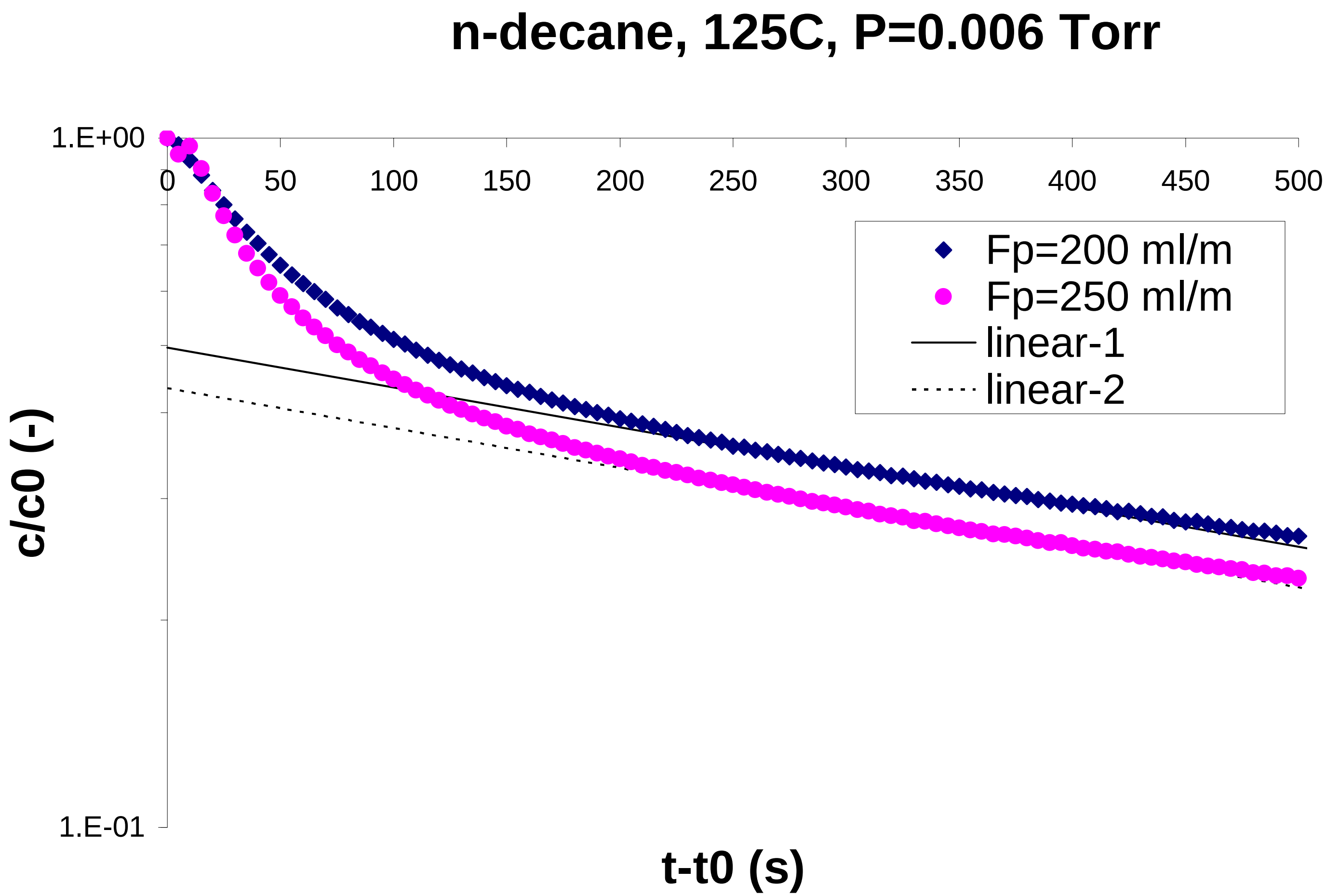
Partial Loading Experiment: surface barriers



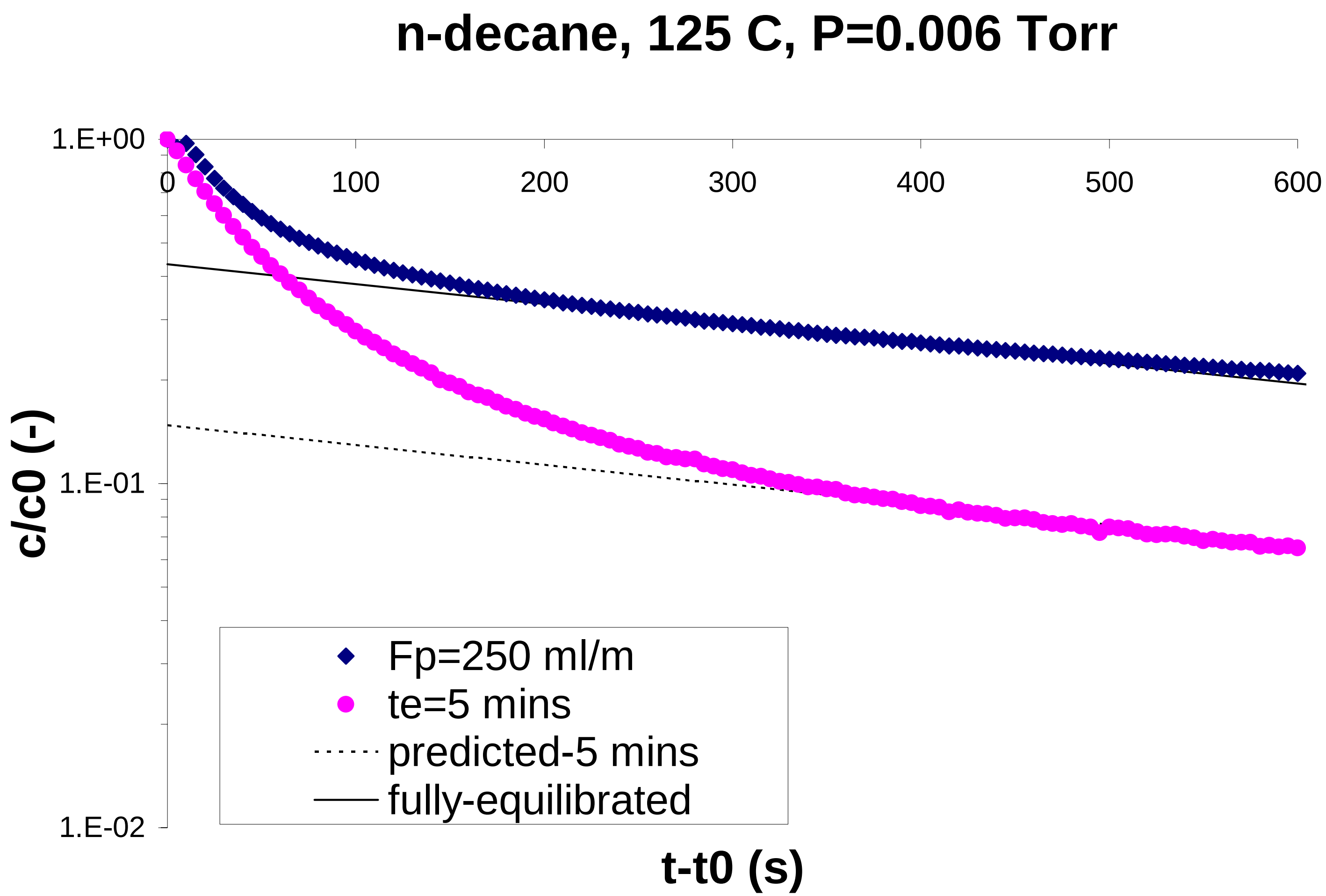
$$\tau_{Sat} \approx \frac{R^2}{D}$$

$$L > 10$$

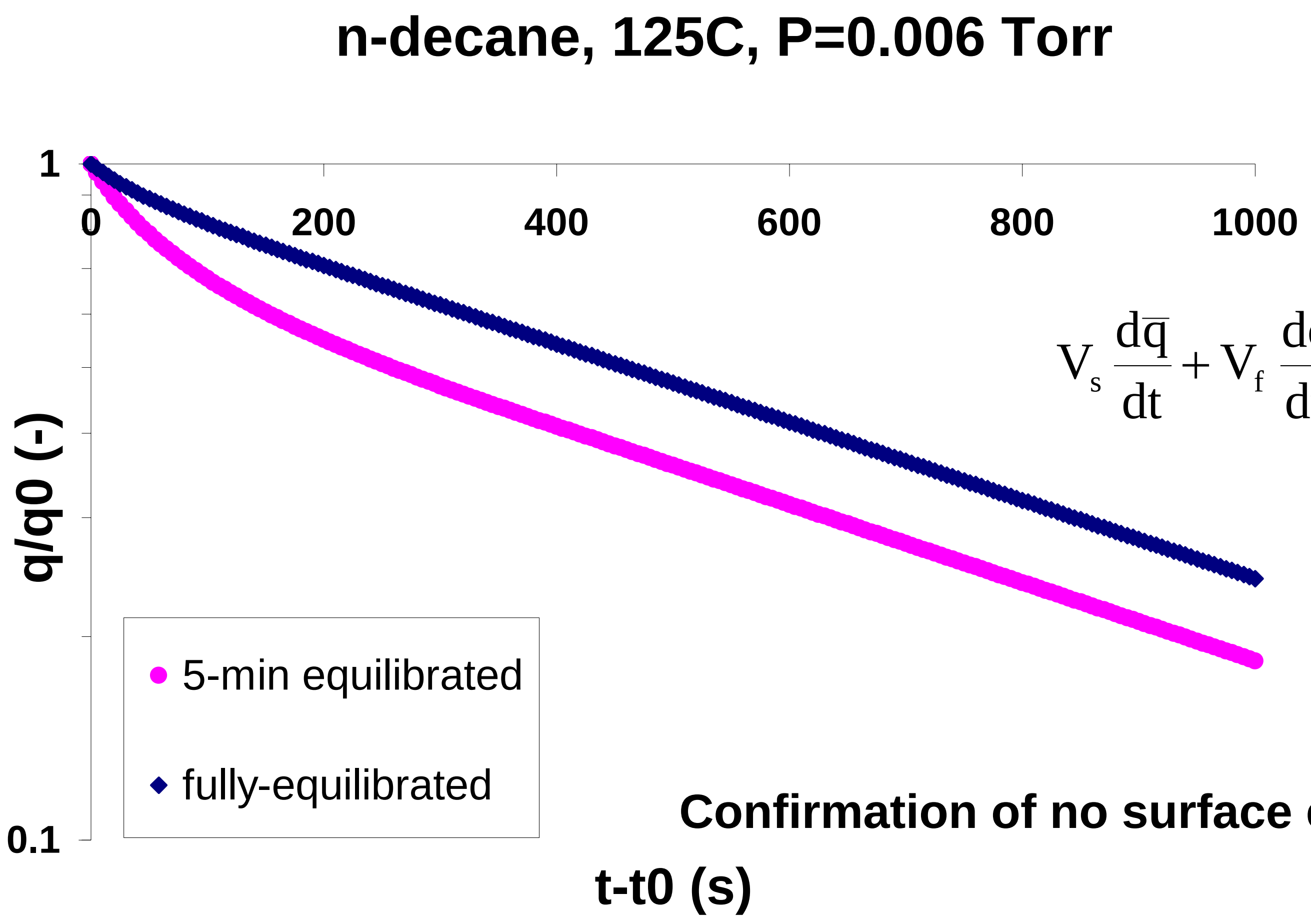
Determination of D_0



Check D_0 with Partial-Loading Experiment



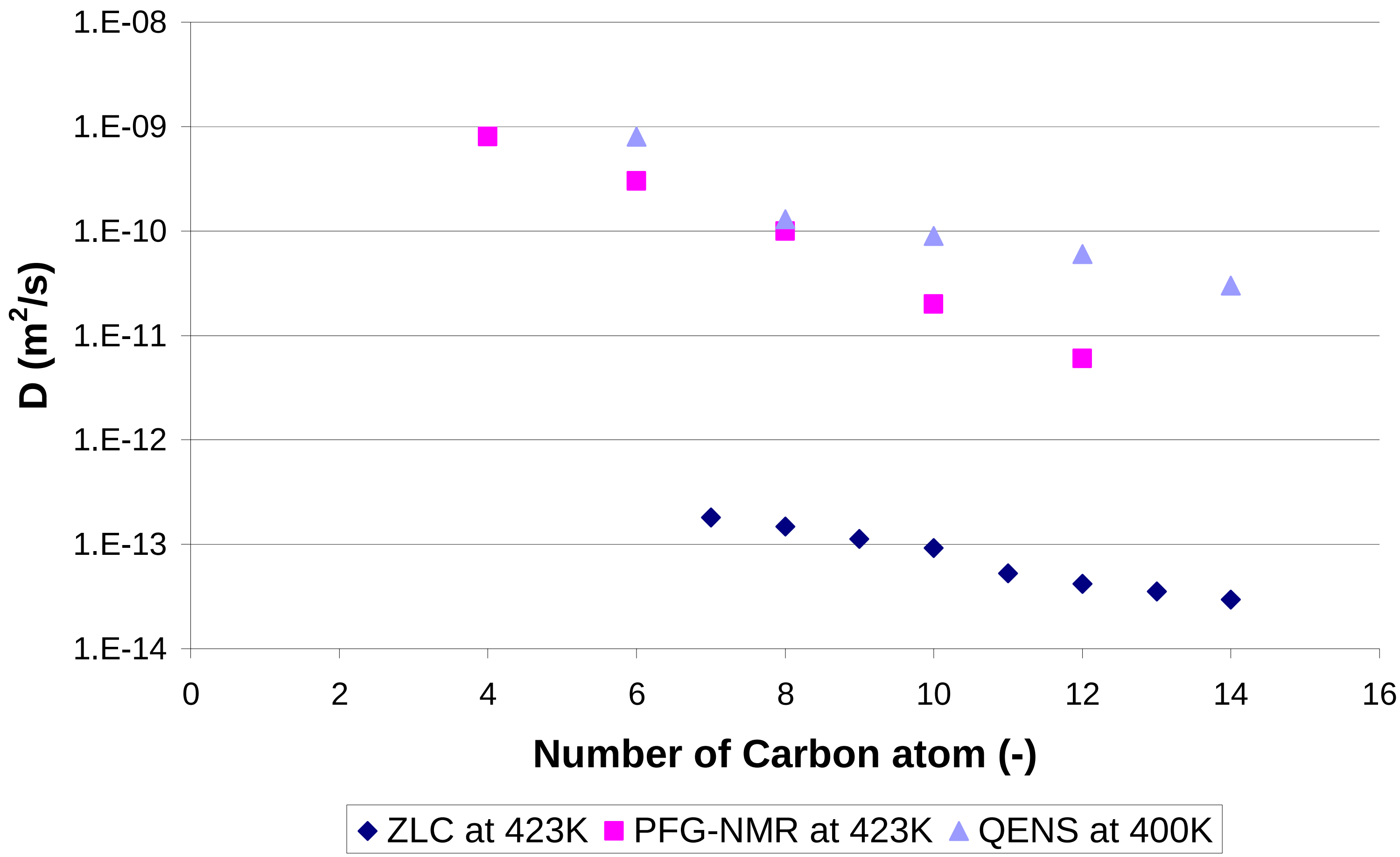
Adsorbed Phase Concentration



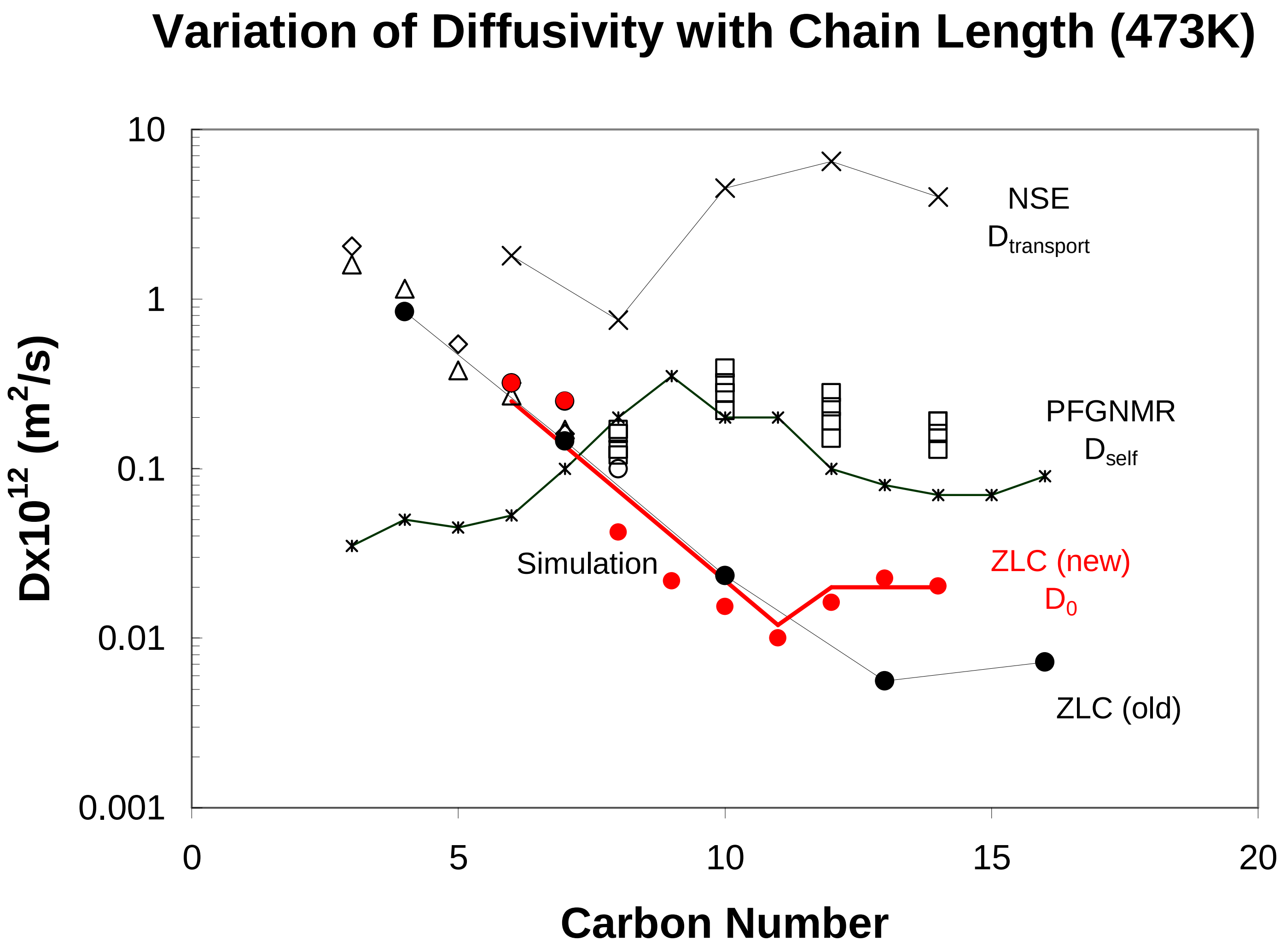
$$V_s \frac{d\overline{q}}{dt} + V_f \frac{dc}{dt} + Fc = 0$$

Confirmation of no surface effects

Results for silicalite – comparison with IRG



Comparison with IRG values – 5A



What can be measured? Equilibrium

- Henry law constants

Brandani F., Brandani S., Coe C.G. and Ruthven D.M., **2002**, *Fundamentals of Adsorption 7*, 21–28.

- Single component isotherms

Brandani F., Ruthven D.M. and Coe C., *Ind. Eng. Chem. Res.*, **2003**, *42*, 1451-1461.

- Multicomponent isotherms

Brandani F. and Ruthven D.M., *Ind. Eng. Chem. Res.*, **2003**, *42*, 1462-1469.

- Zero loading heat of adsorption

Mass flux from chemical potential driving force

$$J_A = -\frac{D_0}{RT} q \frac{\partial \mu_A}{\partial z}$$

$$J_A = -D \frac{\partial q}{\partial z}$$

$$J_A = -D_0 q \frac{\partial \ln P_A}{\partial z}$$

At constant T, P

$$D = D_0 \frac{d \ln P_A}{d \ln q}$$

The transport diffusivity is a strong function of concentration

Corrected Diffusivity

Darken Correction Factor

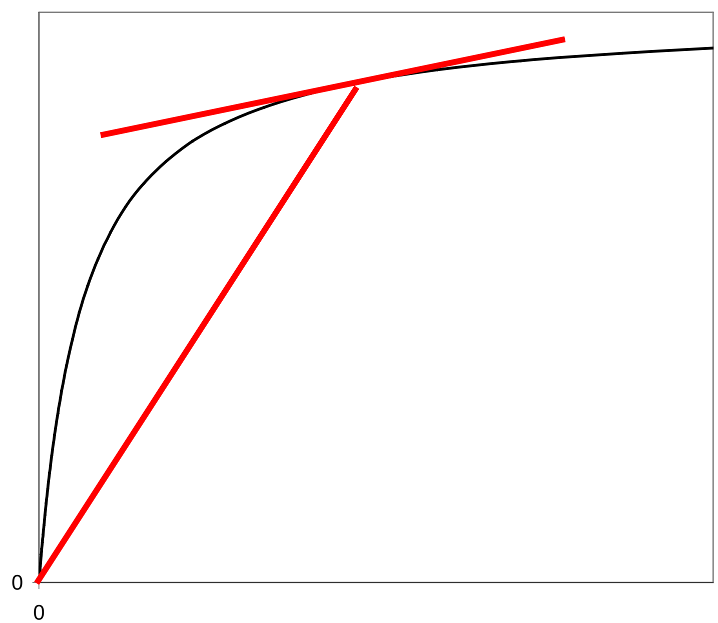
Darken Correction

Typically the corrected diffusivity is assumed to be constant, since the thermodynamic correction has a strong composition dependence.

$$\frac{d\ln P_A}{d\ln q} = \frac{q}{P_A} \Big/ \frac{dq}{dP_A}$$

Secant Tangent

Need VERY ACCURATE equilibrium data to evaluate the derivative.



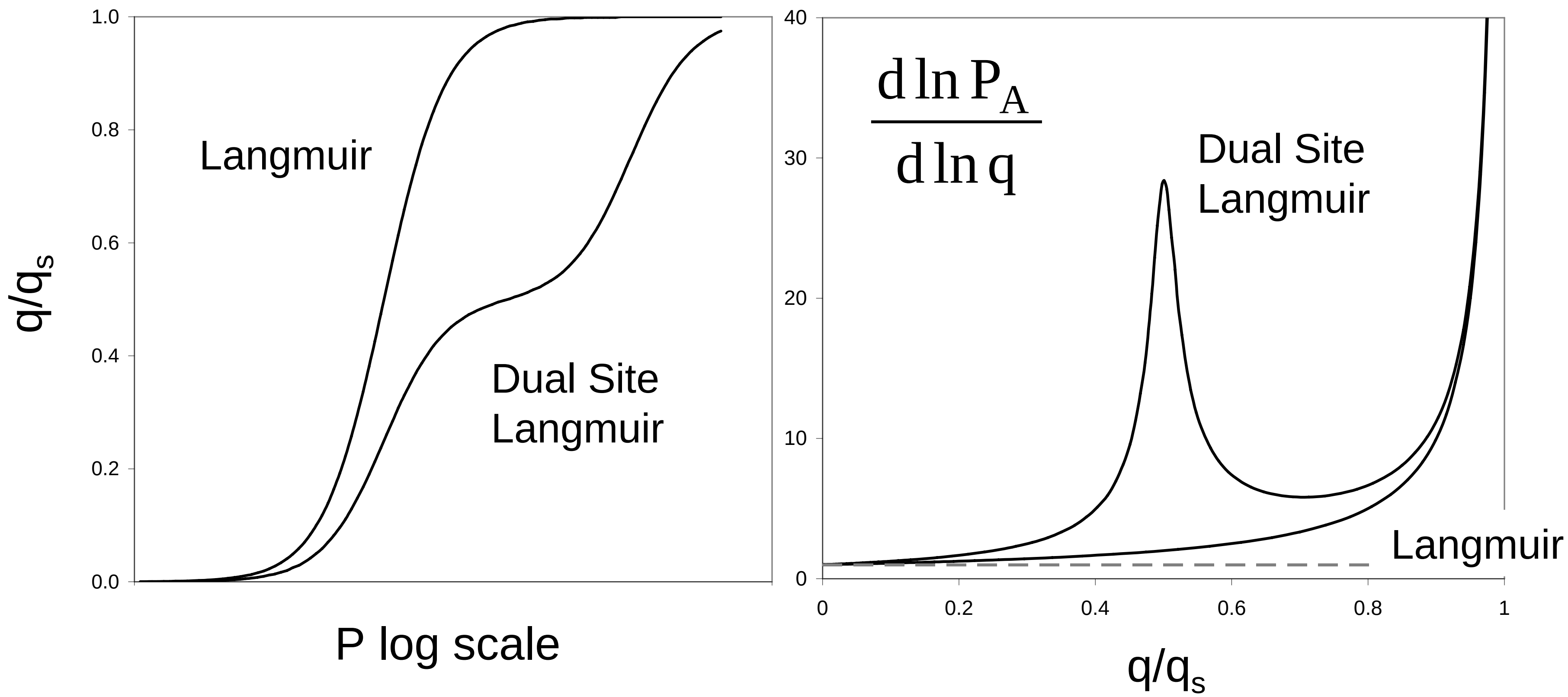
Langmuir

$$\frac{d\ln P}{d\ln q} = \frac{1}{1-q/q_S} =$$

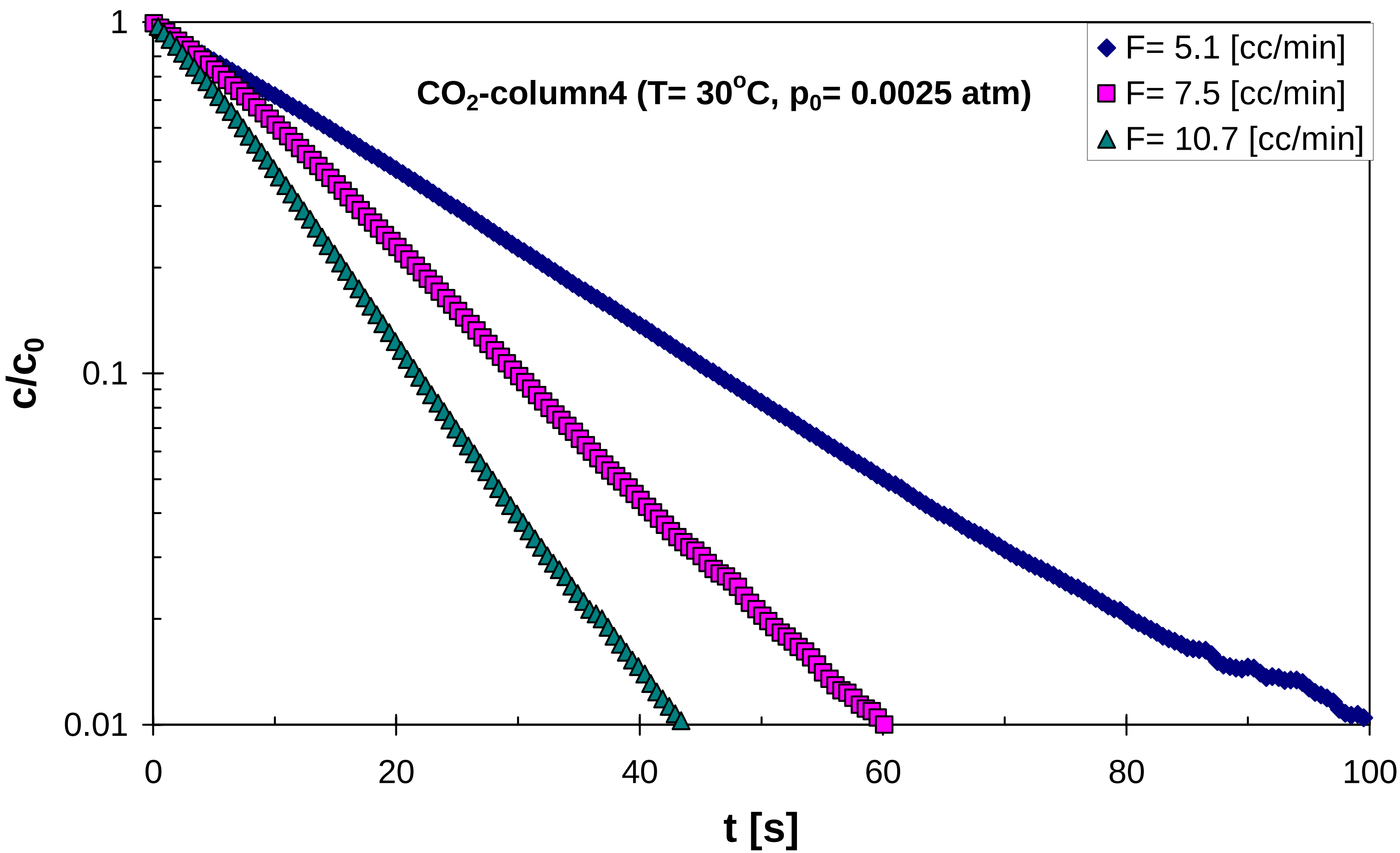
1 if P = 0

∞ if P = ∞

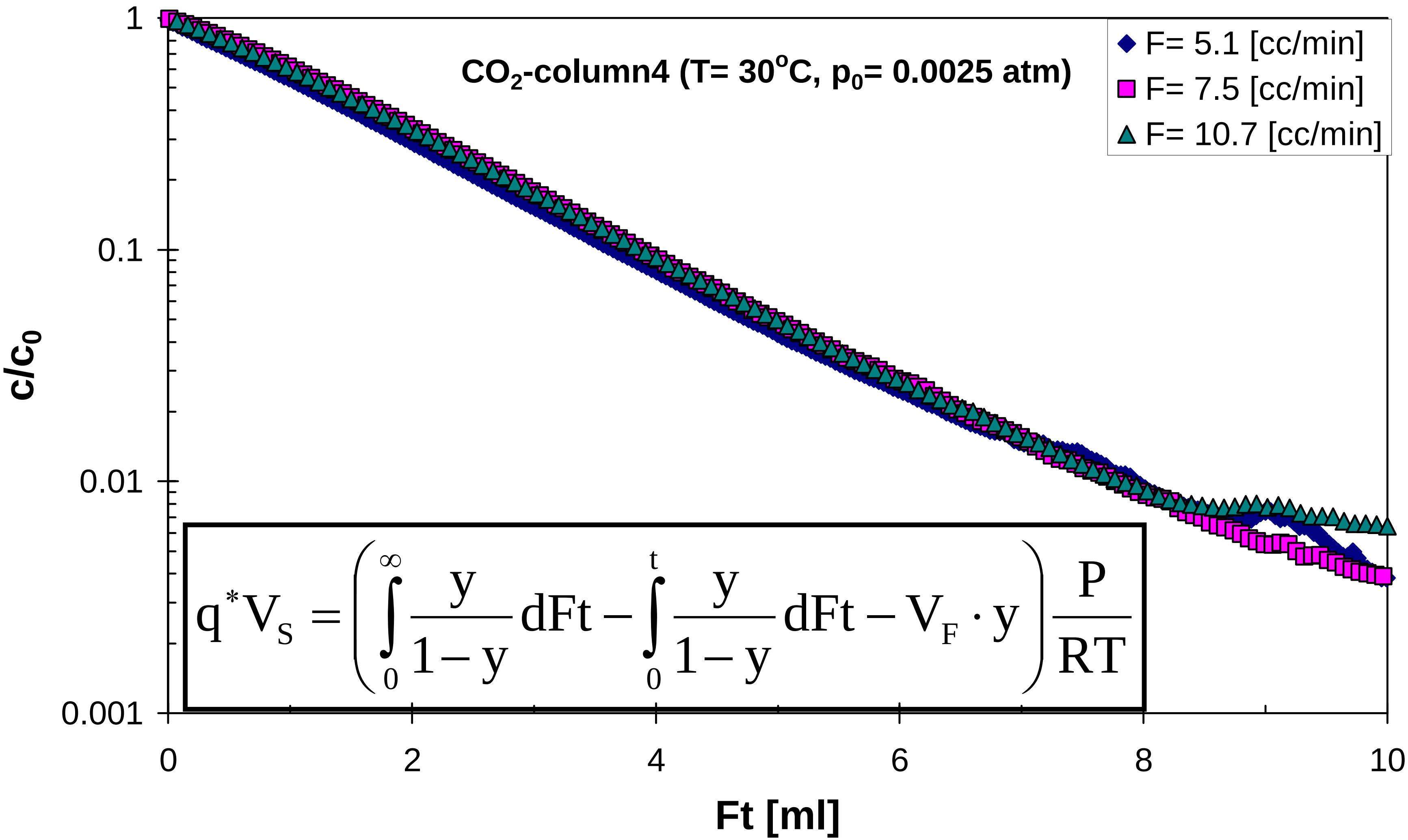
Darken Correction cont.



Equilibrium ZLC CO_2 - Silicalite.

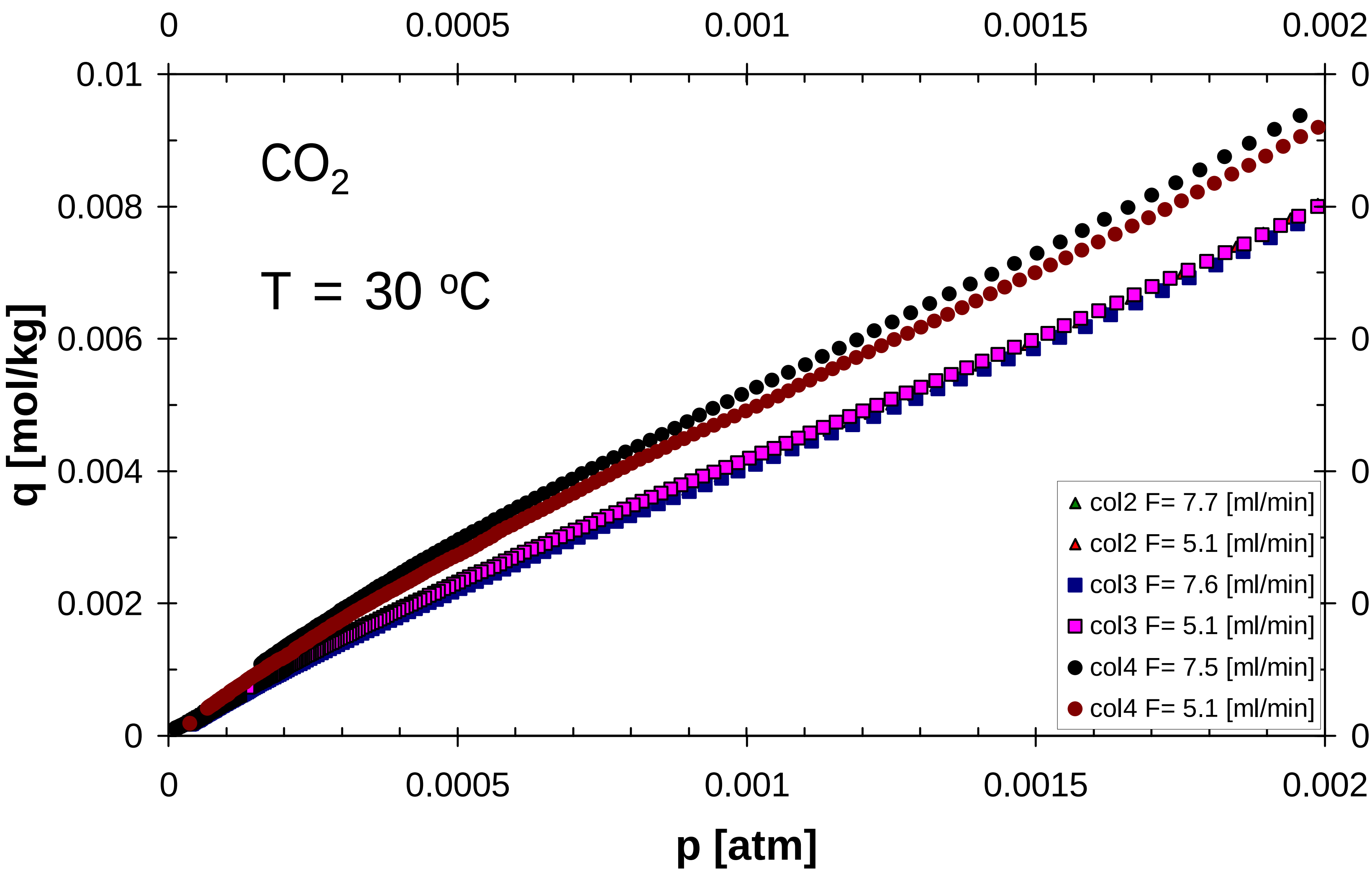


Experimental ZLC curves.

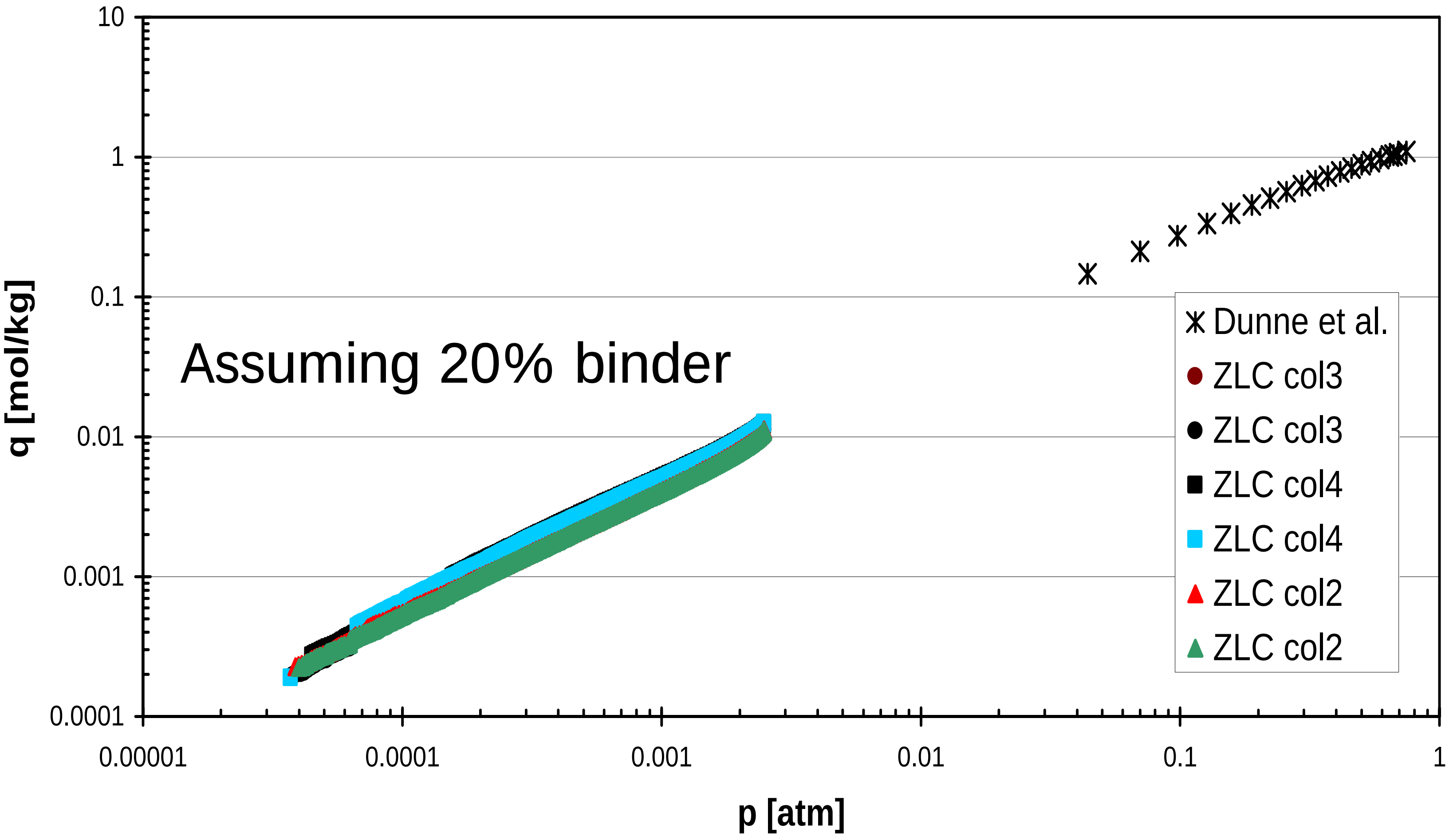


$$q^* V_S = \left(\int_0^\infty \frac{y}{1-y} dFt - \int_0^t \frac{y}{1-y} dFt - V_F \cdot y \right) \frac{P}{RT}$$

Adsorption isotherms.



Adsorption isotherms.



nC10 on NaCaA

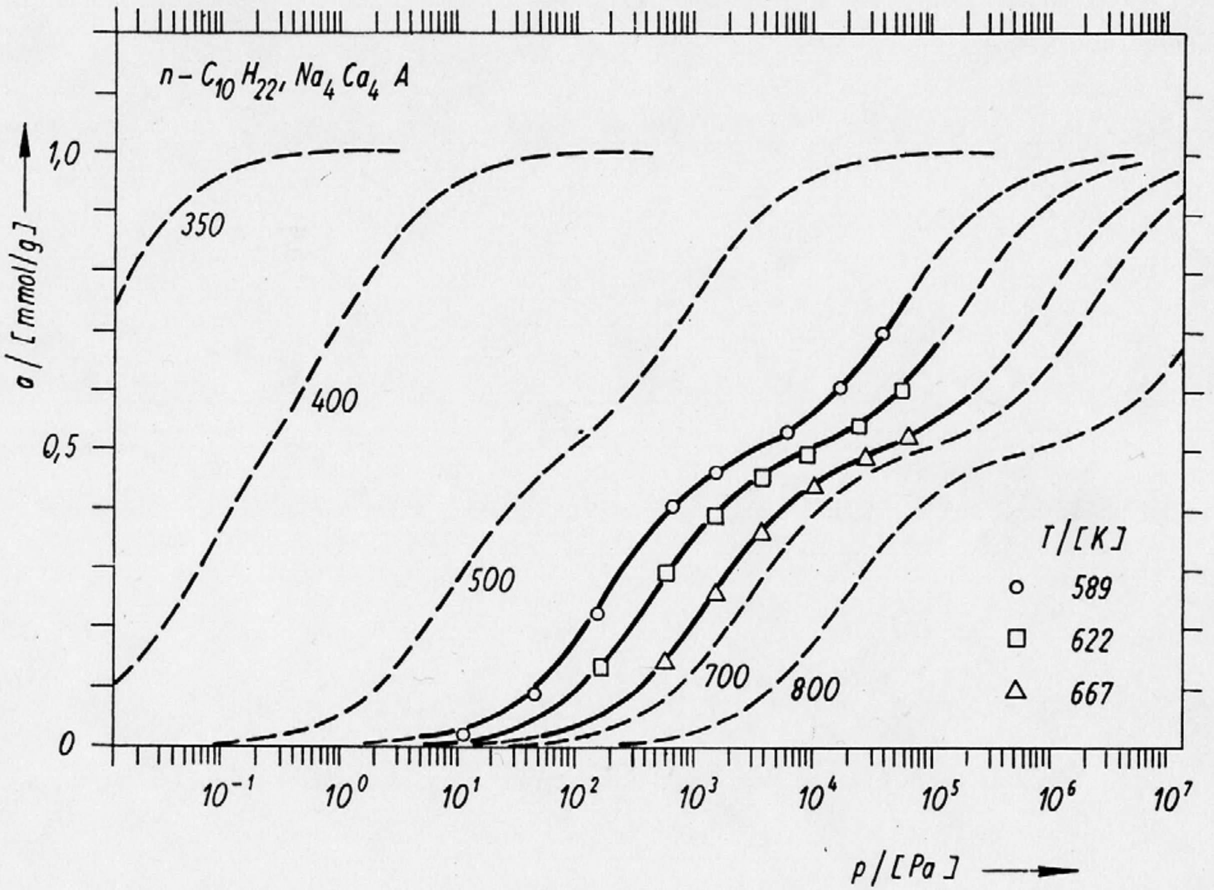


Abb. 2. Experimentelle (Symbole) und berechnete (——) Adsorptionsisothermen von n-Dekan am Zeolith NaCaA

Stach & Fiedler Z.Phys.Chemie Leipzig (1980), **261**, 246-257.