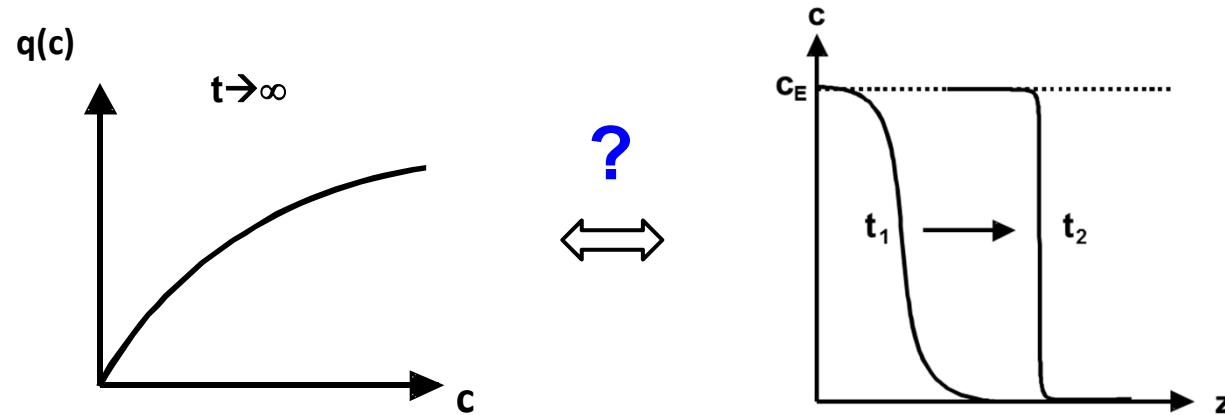
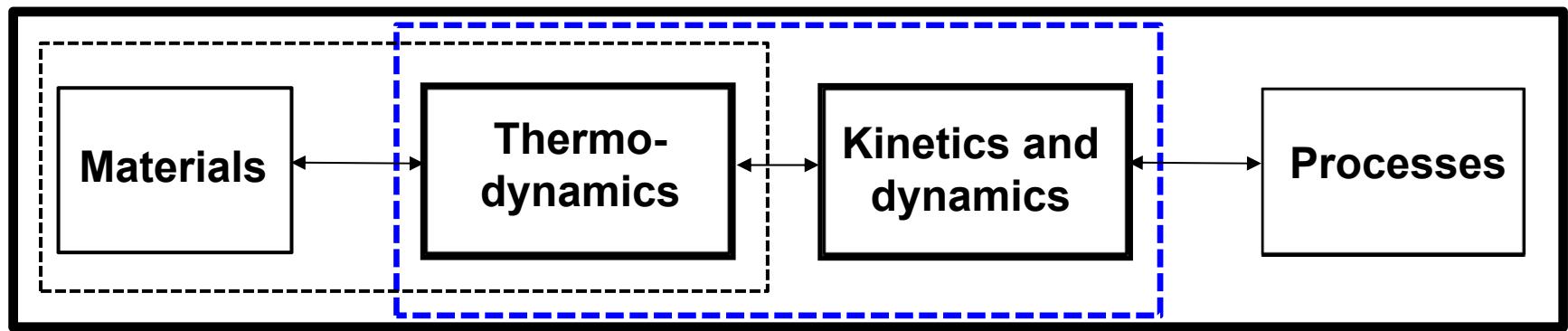


Dynamics of front propagation in fixed-bed adsorbers

Andreas Seidel-Morgenstern

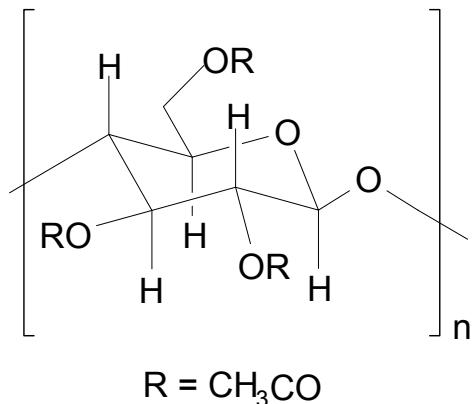
Max Planck Institute for Dynamics of Complex Technical Systems
Otto von Guericke University
Magdeburg



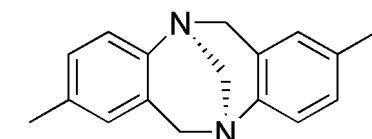
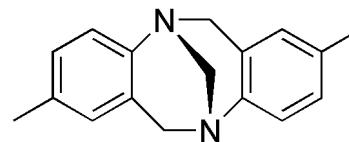
Personal experience

(Merck-Workshop „Preparative Chromatography“, Darmstadt, 1991)

Cellulose Triacetate (CTA)



Enantiomers of Tröger's base (TB)

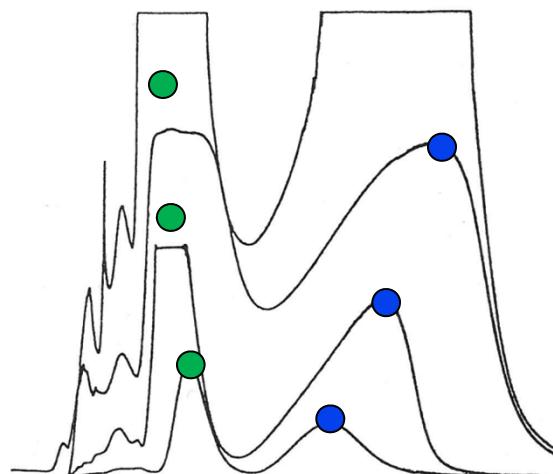


Structures of (-)-Tröger's base, (+)-Tröger's base

Hesse and Hagel

„Eine vollständige Racemattrennung durch
Elutions-Chromatographie an Cellulosetriacetat“
Chromatographia, 277-280, 1973

Unusual shapes in series of overloaded peaks (mobile phase: benzene)

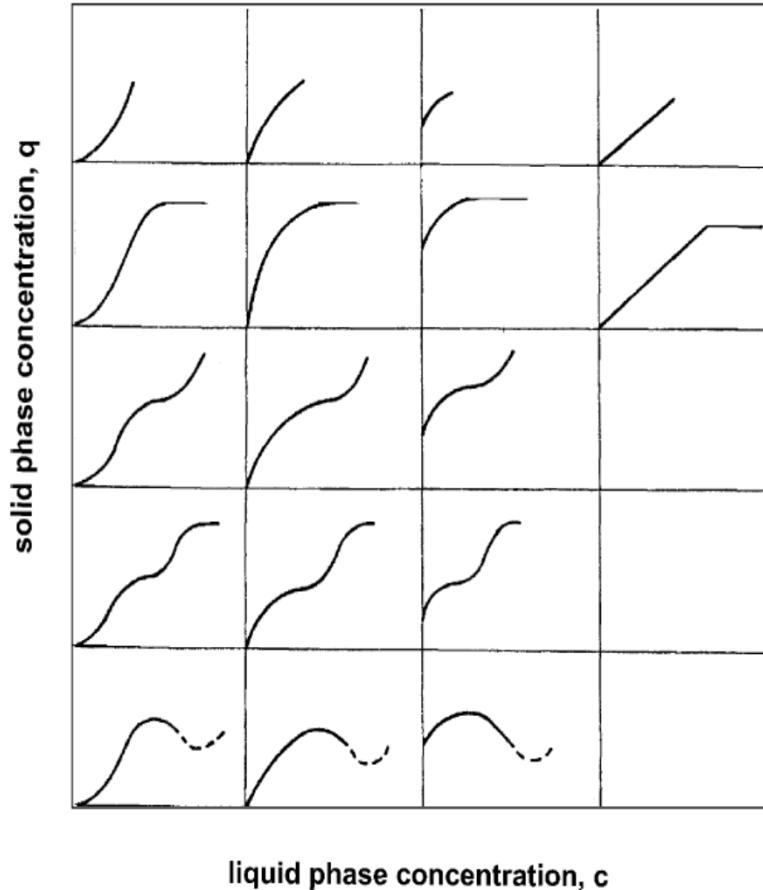
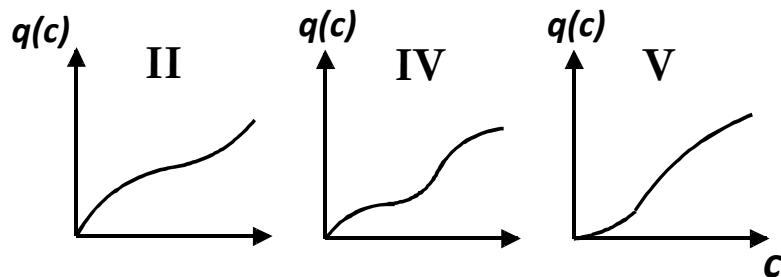
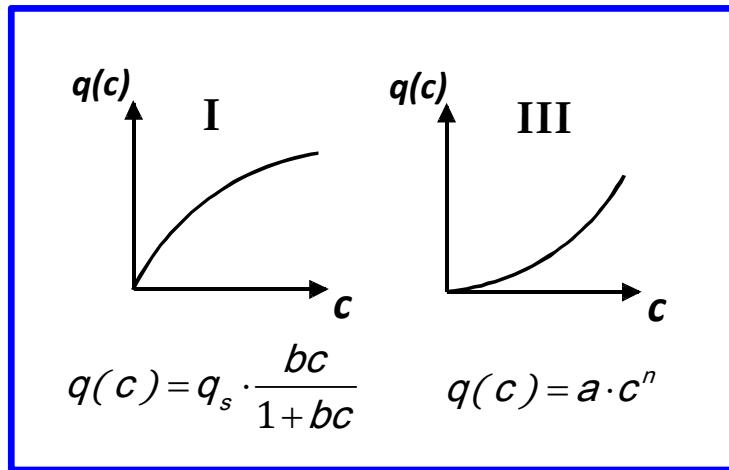


Kinkel, Reichert and Knöll,
“Präparative chromatographische Enantiomerentrennung”
GIT Verlag (Glas- und Instrumenten-Technik),
Supplement 3/89 – Chromatographie, 1989, 104, Wiley

Why?

Single component adsorption equilibria

$$q = q(c, T = \text{const.})$$



Brunauer
The Adsorption of Gases and Vapors
Princeton University Press, 1945

Giles et al.
J. Am. Chem. Soc., 1960, 3973

Column balance: Conserving total mass

Mass balance (convection dominated):

$$\frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q}{\partial t} + u_0 \frac{\partial c}{\partial x} = 0$$

If phases are permanently equilibrated:

$$\frac{\partial c}{\partial t} \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{dq}{dc} \right) + u_0 \frac{\partial c}{\partial x} = 0$$

Concentration dependent migration velocities and retention times

$$-\left. \frac{\frac{\partial c}{\partial t}}{\frac{\partial c}{\partial x}} \right|_{c_*} = \left. \frac{dx}{dt} \right|_{c_*} = u_c(c_*) = \frac{u_0}{\left(1 + \frac{1-\varepsilon}{\varepsilon} \left. \frac{dq}{dc} \right|_{c_*} \right)}$$

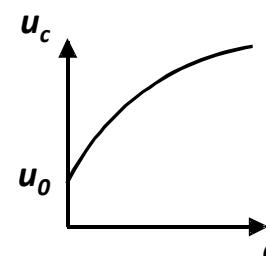
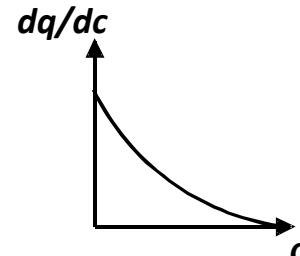
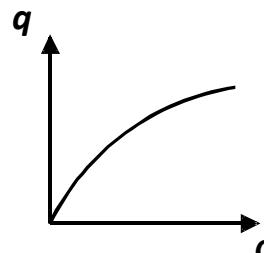
$$t_R(L, c_*) = \frac{L}{u_c(c_*)} = \frac{L}{u_0} \left(1 + \frac{1-\varepsilon}{\varepsilon} \left. \frac{dq}{dc} \right|_{c_*} \right)$$

Rhee, Aris and Amundson, On the Theory of Multi-Component Chromatography
 Philosophical Transactions of The Royal Society, A, 267, 1970, 419-455; A, 269, 1971, 187-215

Guiochon et al., Fundamentals of Preparative and Nonlinear Chromatography, Academic Press, 2006

Example

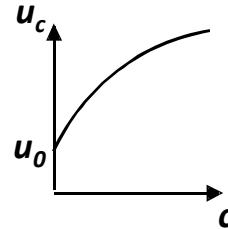
Type I isotherm
 (Langmuir type)



“larger concentrations move faster”

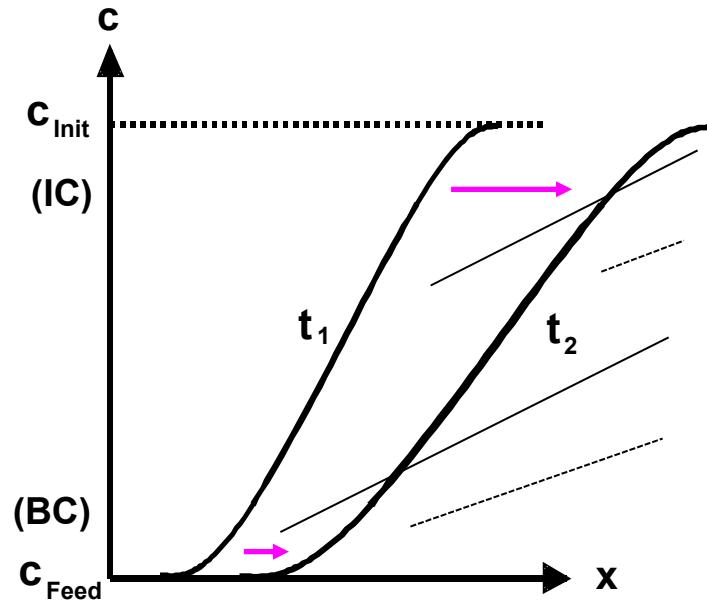
Adsorption vs. Desorption

Type I (Langmuir isotherms)



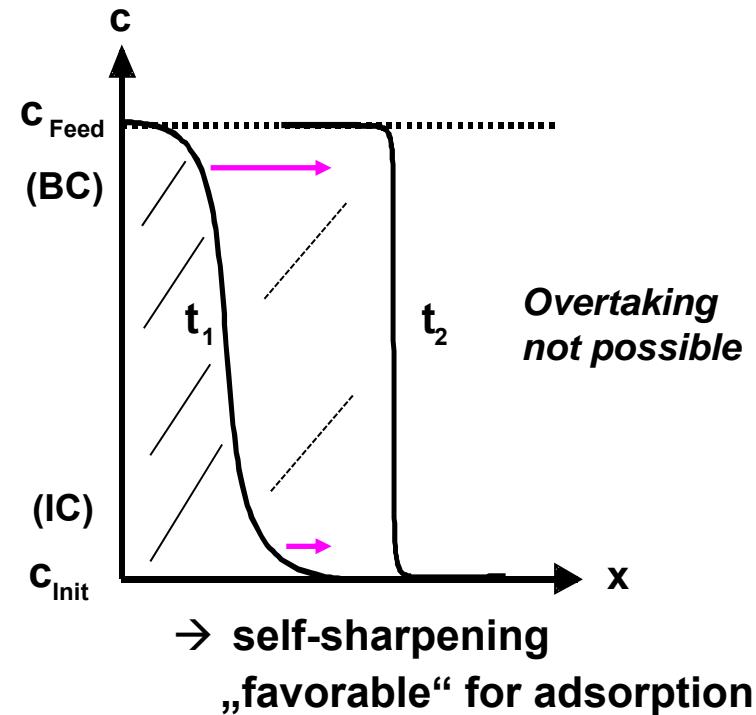
A) $c^{Feed} < c^{Init}$: Desorption → Waves

$$t_{R,i}(L, c_{i*}) = t_0 \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{dq_i}{dc_i} \Big|_{c_{i*}} \right)$$

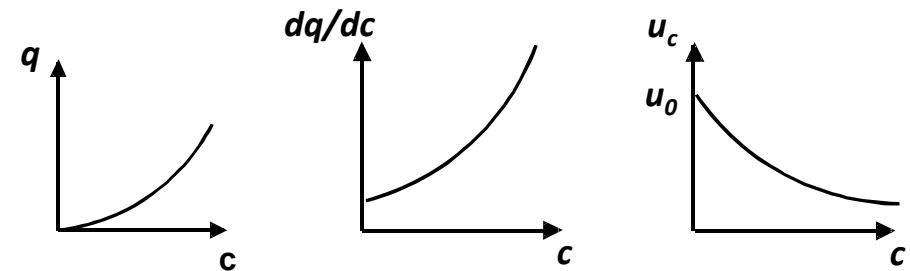


B) $c^{Feed} > c^{Init}$: Adsorption → Shocks

$$t_R = t_0 \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{\Delta q_i}{\Delta c_i} \right) = t_0 \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{q_i^{Feed} - q_i^{Init}}{c_i^{Feed} - c_i^{Init}} \right)$$

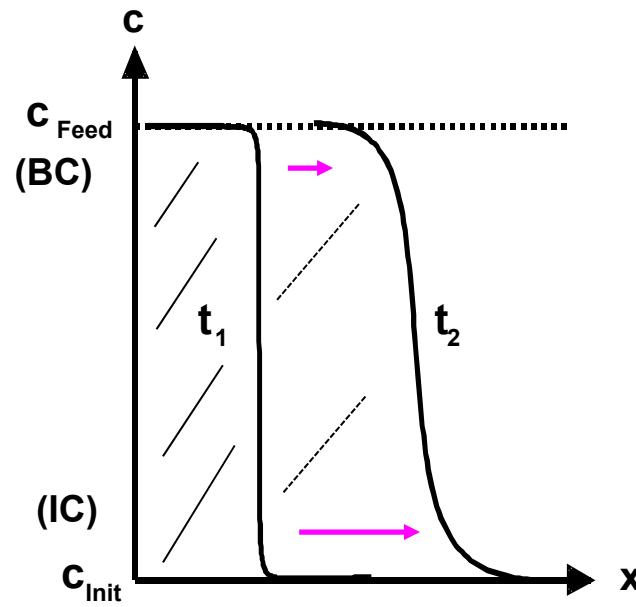


Type III ("Anti-Langmuir" isotherms)

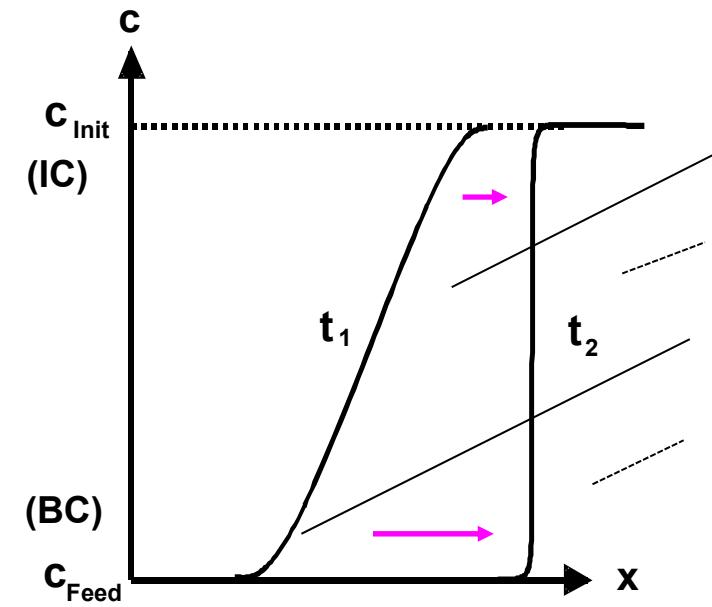


→ "larger concentrations move slower"

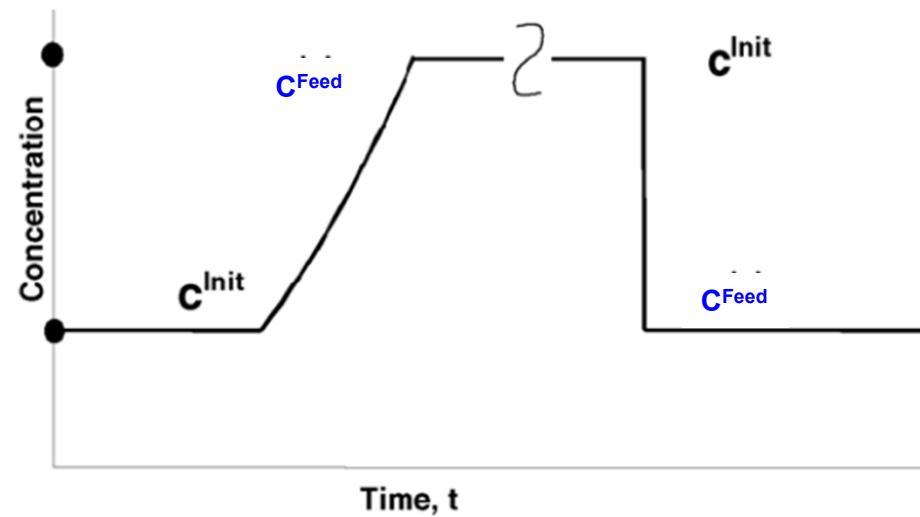
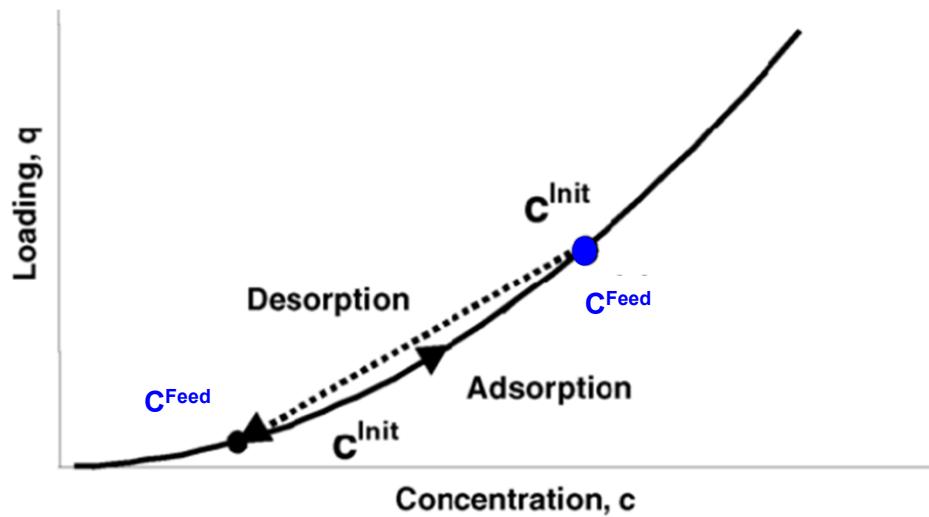
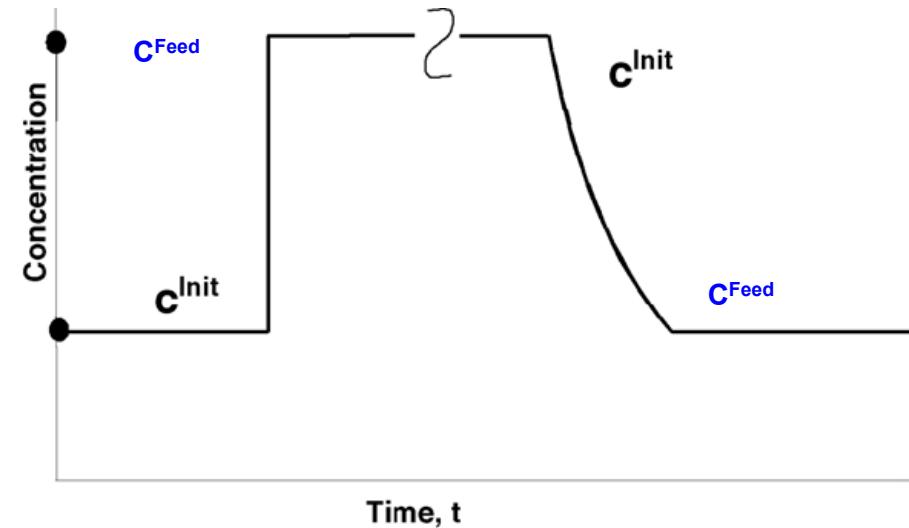
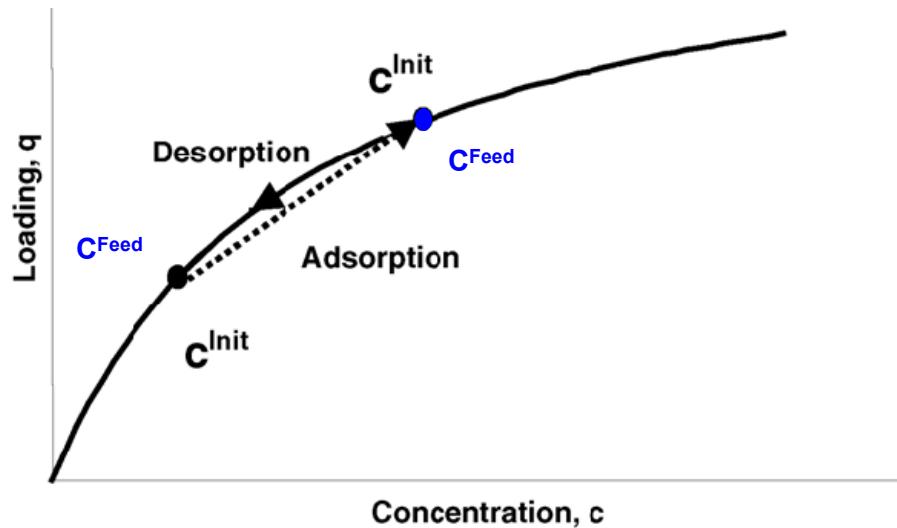
A) $c^{Feed} > c^{Init}$: Adsorption → Waves



B) $c^{Feed} < c^{Init}$: Desorption → Shocks



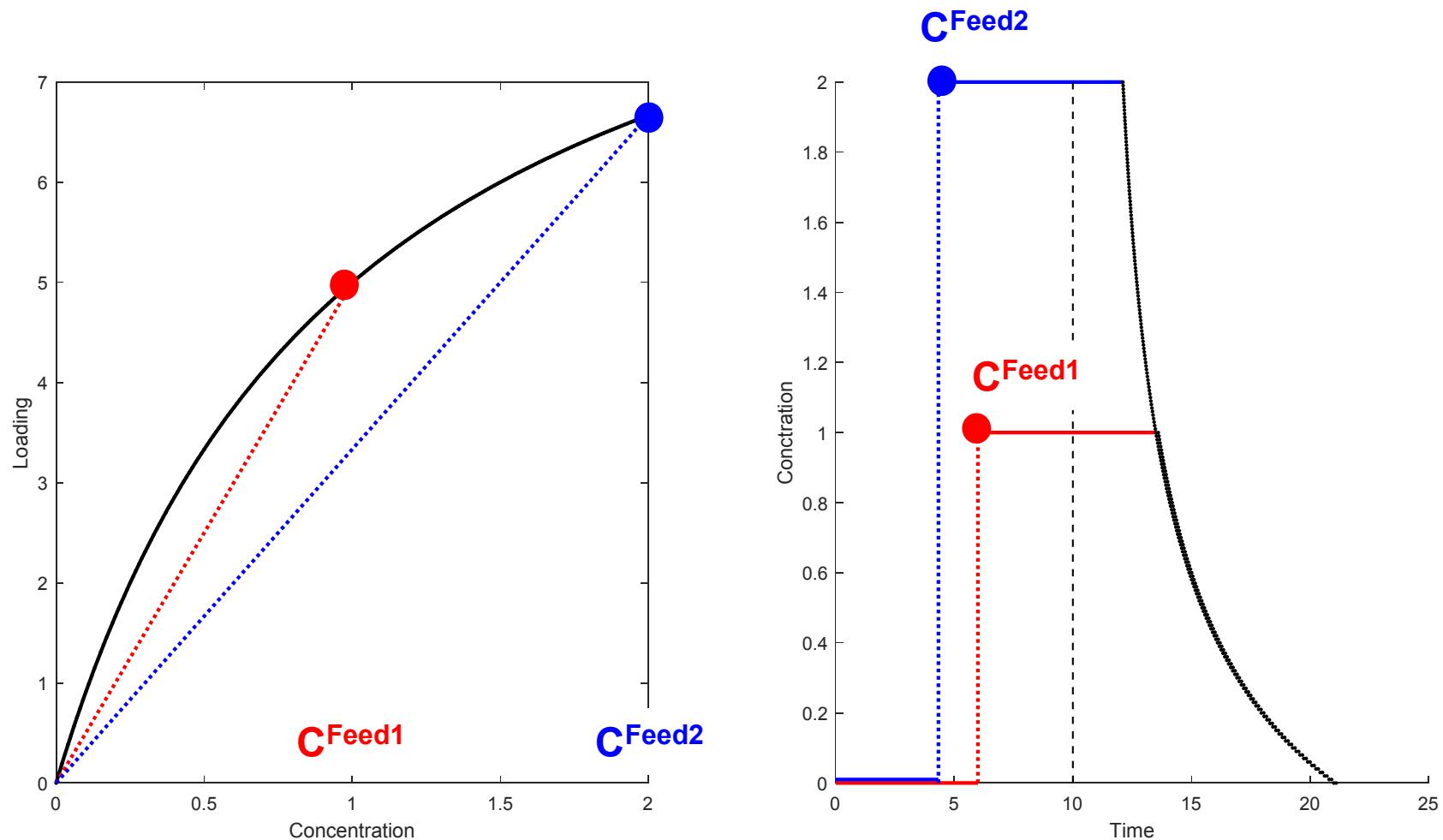
Chords vs. Tangents: „Rubber band rule“



Perry's Chemical Engineers' Handbook, 1984

Breakthrough curves for different feed concentrations

(Case: Langmuir type of isotherms)



Characteristics / Distance-Time-Diagram (Type I)

Shocks (Adsorption)

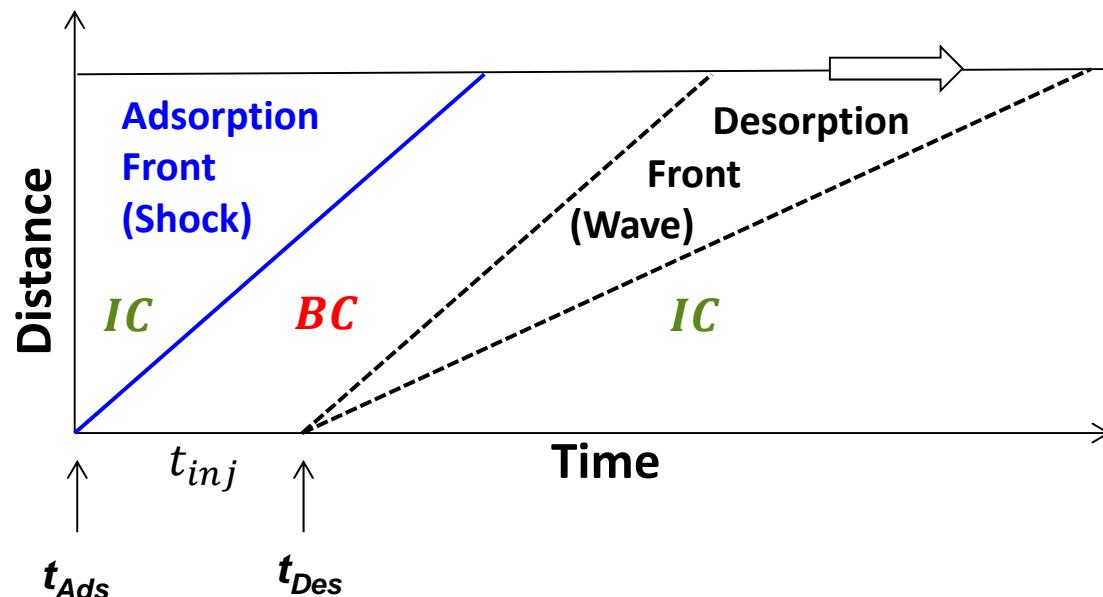
$$t_R = t_0 \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{q^{Feed} - q^{Init}}{c^{Feed} - c^{Init}} \right)$$

Waves (Desorption)

$$t_R(L, c_*) = t_0 \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{dq}{dc} \Big|_{c_*} \right)$$

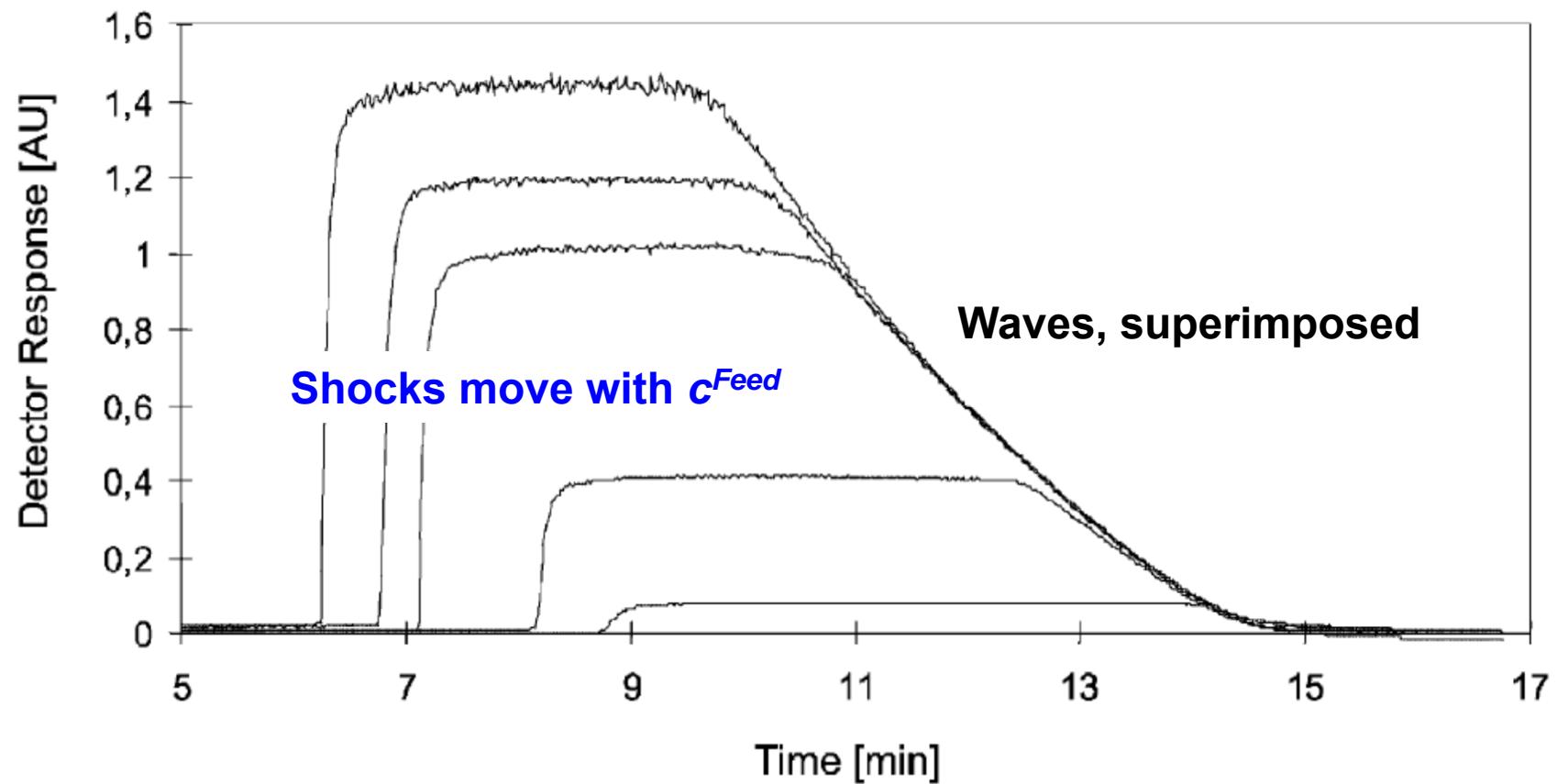
Distance-Time-Diagram

BC: $c(x = 0, t) = c^{Feed}$ **IC:** $c(x, t = 0) = c^{Init}$



Series of single component breakthrough curves (different c^{Feed} , same feed volume)

2-Phenyl-Ethanol / Octadecyl Silica
Methanol : Water = 1: 1 / ambient temperature

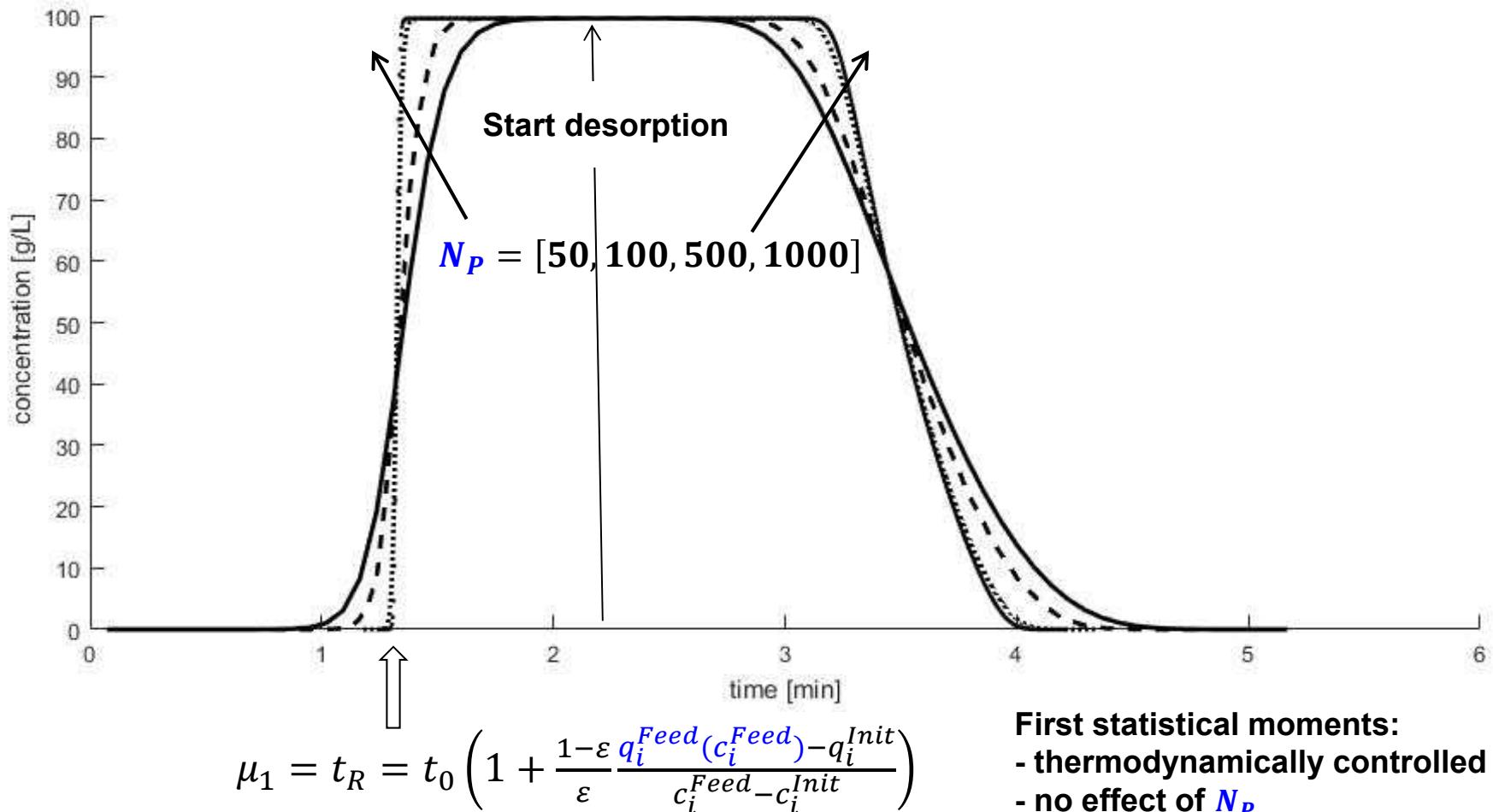


Seidel-Morgenstern, J. Chromat. A., 2004, 255

Influence of kinetics (e.g. back-mixing)

Equilibrium dispersion model

$$\frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q(c)}{\partial t} + u_o \frac{\partial c}{\partial x} = D_{ax} \frac{\partial^2 c}{\partial x^2} \quad \text{with } D_{ax} = \frac{u_0 L}{2N_P}$$



Measuring adsorption isotherms

Static methods

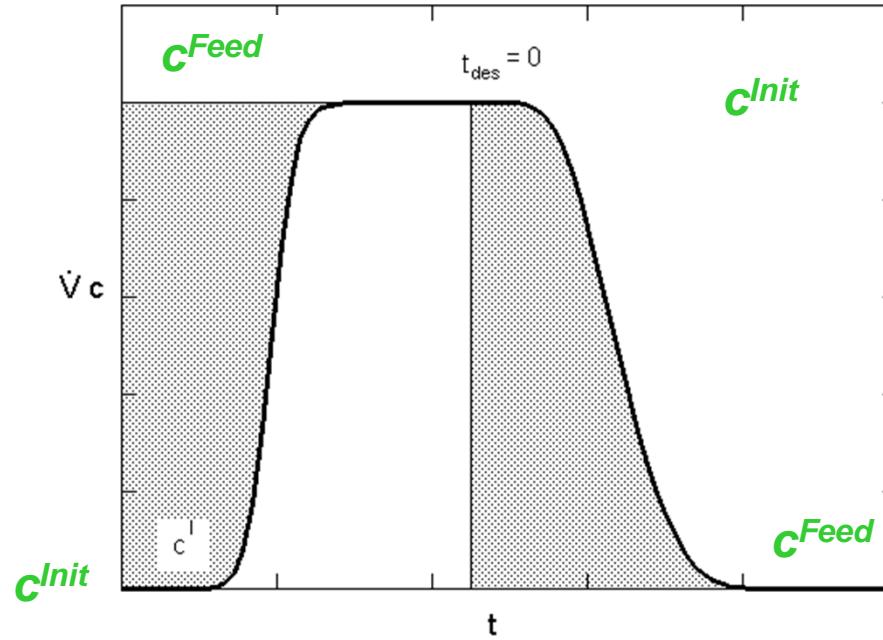
- no time dependences
 - gravimetric
 - shaking experiments
 - adsorption/desorption cycles
 - ...

Dynamic methods

- time dependent information recorded
 - „Perturbation Method“
 - elution by characteristic point (evaluation of waves)
 - peak fitting („Inverse Method“)
 - „Frontal Analysis (FA)“
 - ...

[Seidel-Morgenstern, J. Chromat. A, 2004, 255](#)

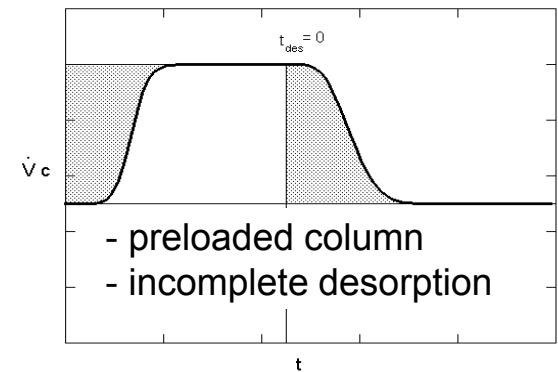
Connection between breakthrough curves and equilibrium data



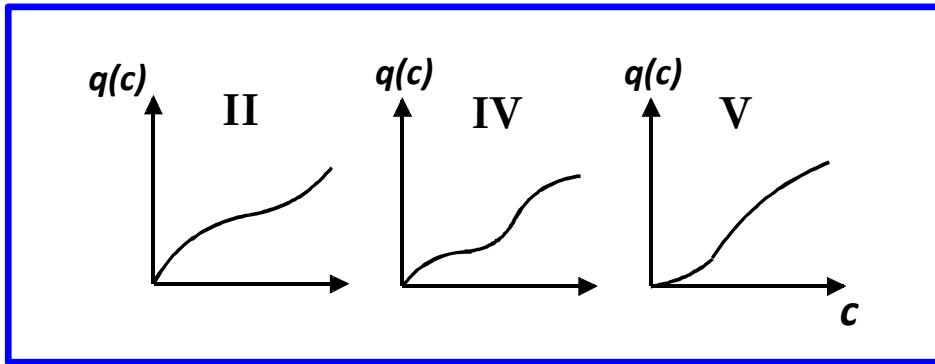
$$\varepsilon V(c_i^{Feed} - c_i^{Init}) + (1 - \varepsilon)V(q_i^{Feed}(c^{Feed}) - q_i^{Init}) = \dot{V} \int_0^{\infty} (c_i^{Feed} - c_i(t)) dt = \dot{V} * \boxed{\text{Area}}$$

→ Each front provides (only) one isotherm point

→ Variations via other c^{Init} and/or c^{Feed}



Other types of single component adsorption equilibria



Statistical thermodynamics

$$q = q_s \cdot c \frac{(P')^{N-1} (c^{N-1})}{P^N (c^N)}$$

$$e.g.: \quad q = q_s c \frac{b_1 + 2b_2 c}{1 + b_1 \cdot c + b_2 c^2} \quad (\text{quadratic isotherm model})$$

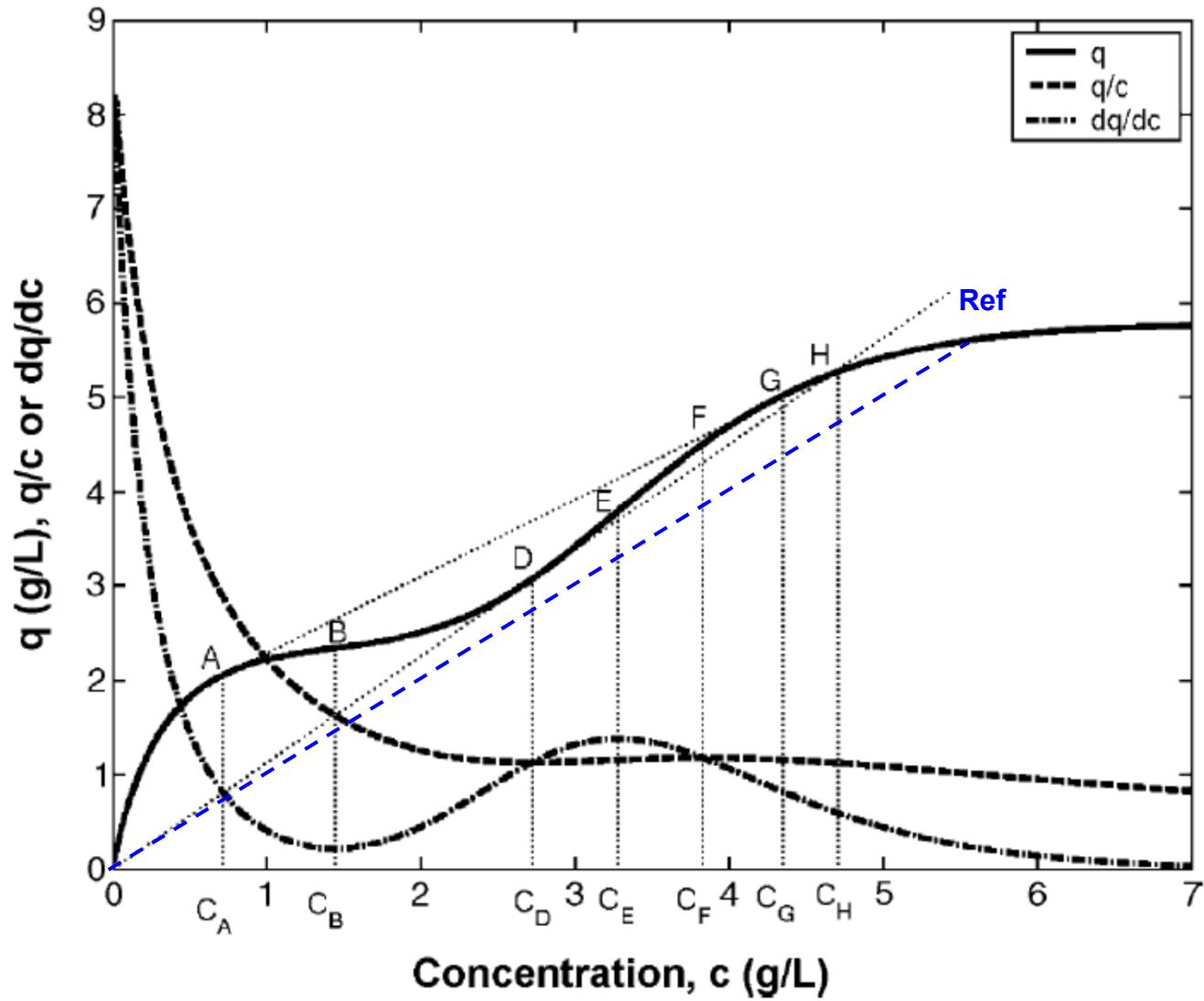
→ special case: BET equation

Hill, [Introduction to Statistical Thermodynamics, Addison-Wesley, Reading, 1960](#)

Corresponding breakthrough curves?

More complex single component behaviour

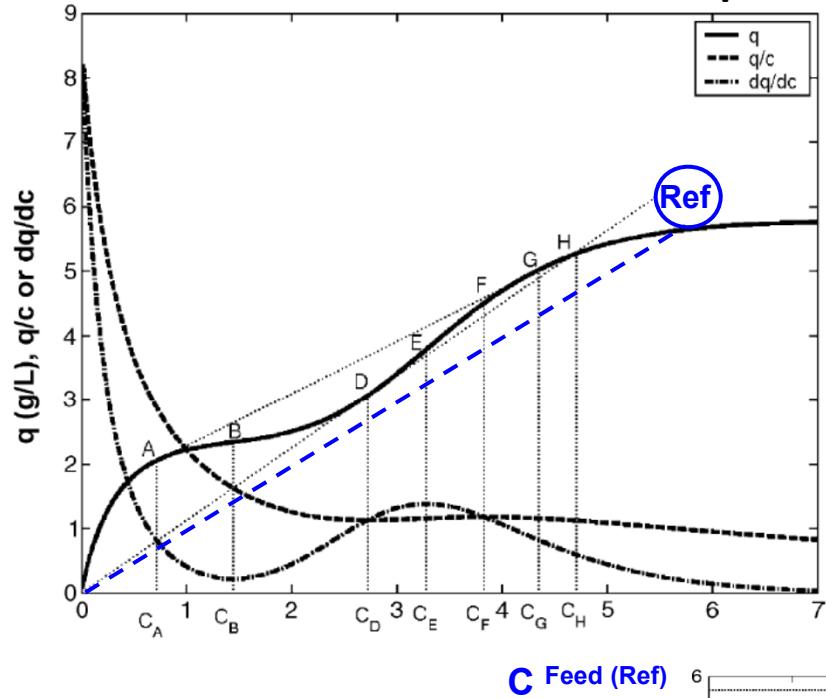
Type IV Isotherm with two inflection points (quadratic isotherm model)



Zhang, Shan and Seidel-Morgenstern, J. Chromat. A, 2006, 2016-225

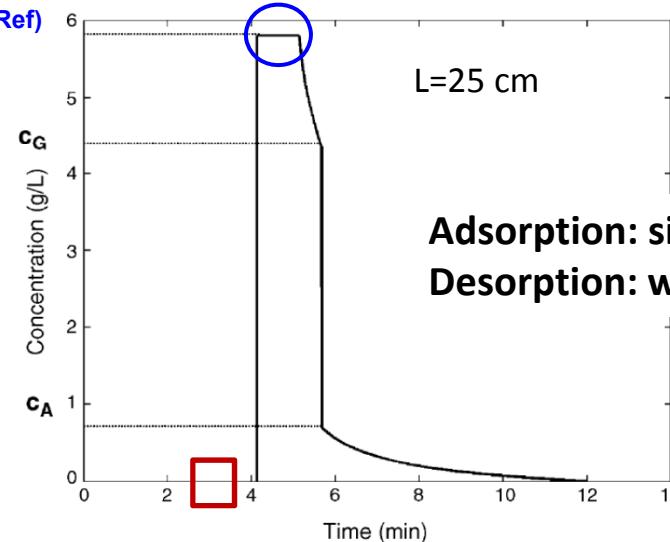
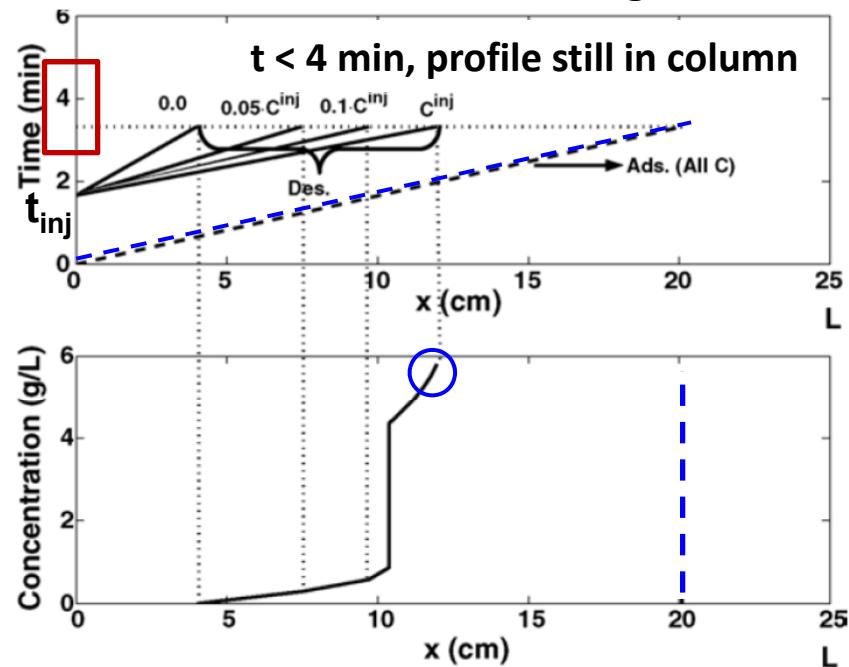
Method of characteristics and “Rubber band rule”

Isotherm with two inflection points



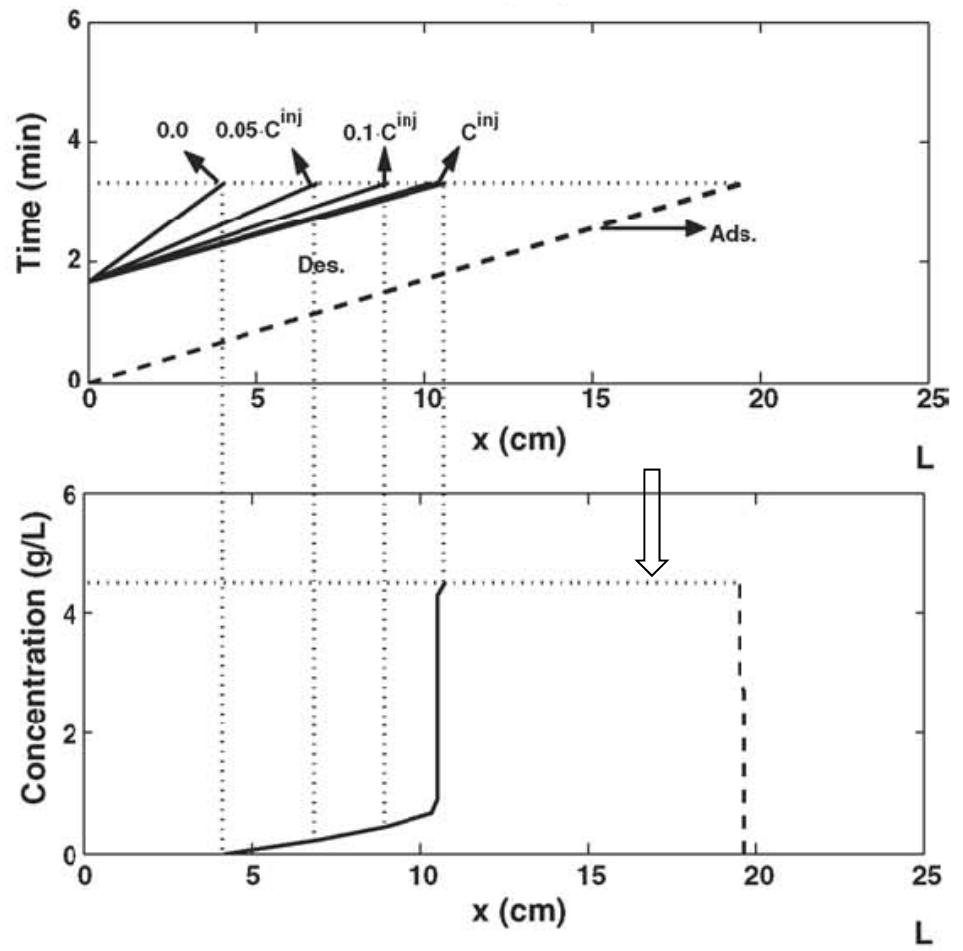
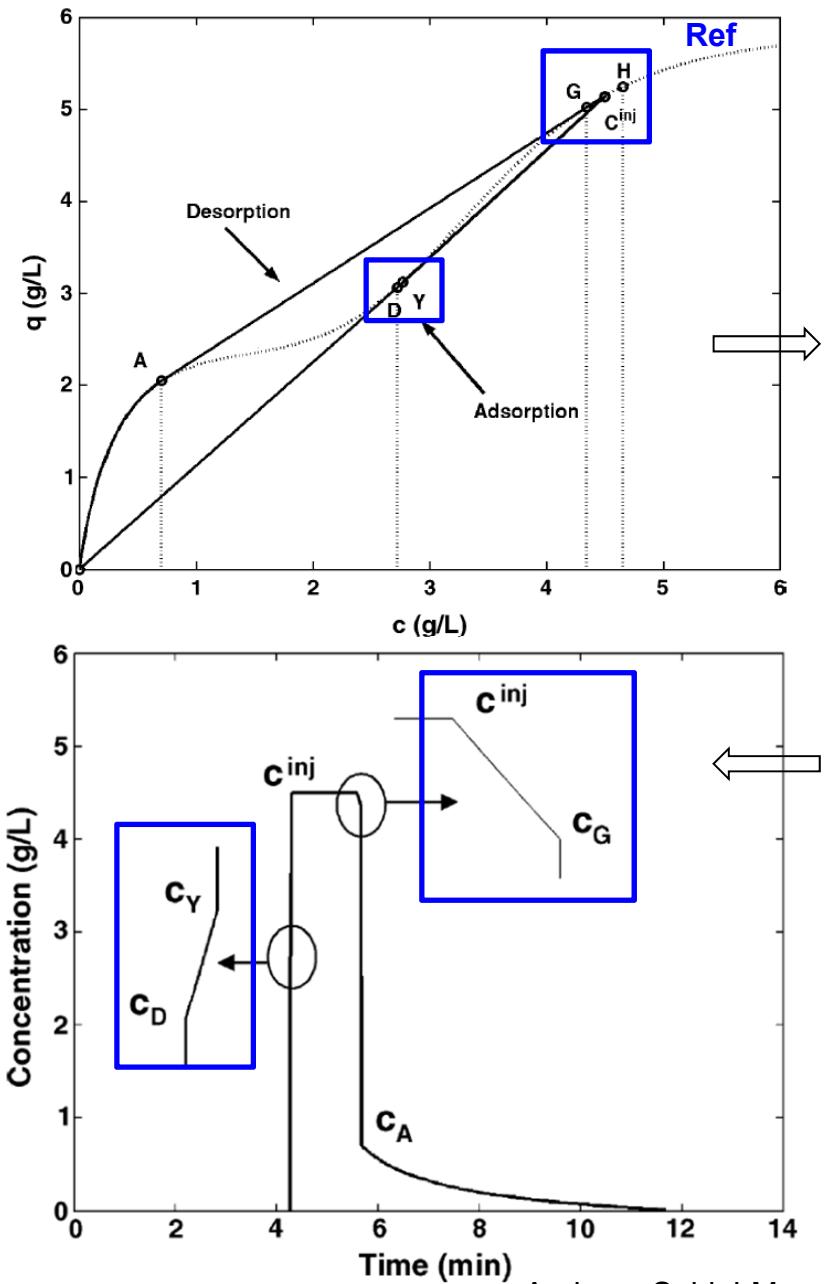
C Feed (Ref)

Time-Distance-Diagram



Adsorption: single shock
Desorption: wave → shock → wave

More complex situation



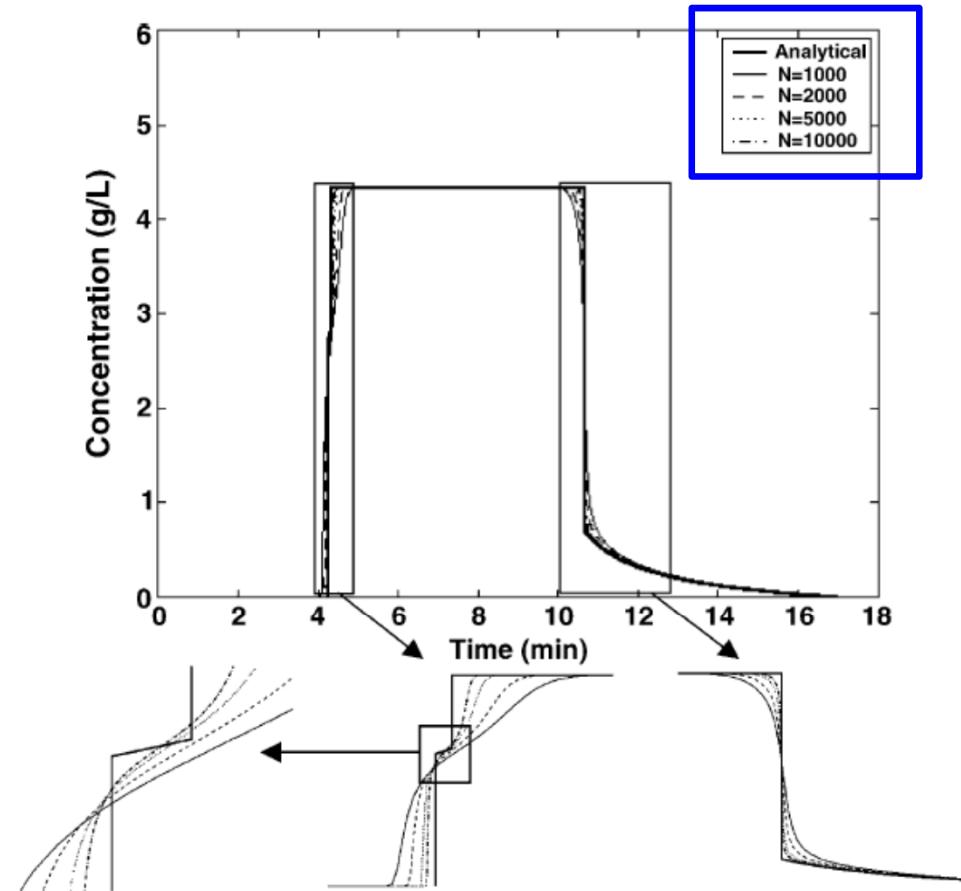
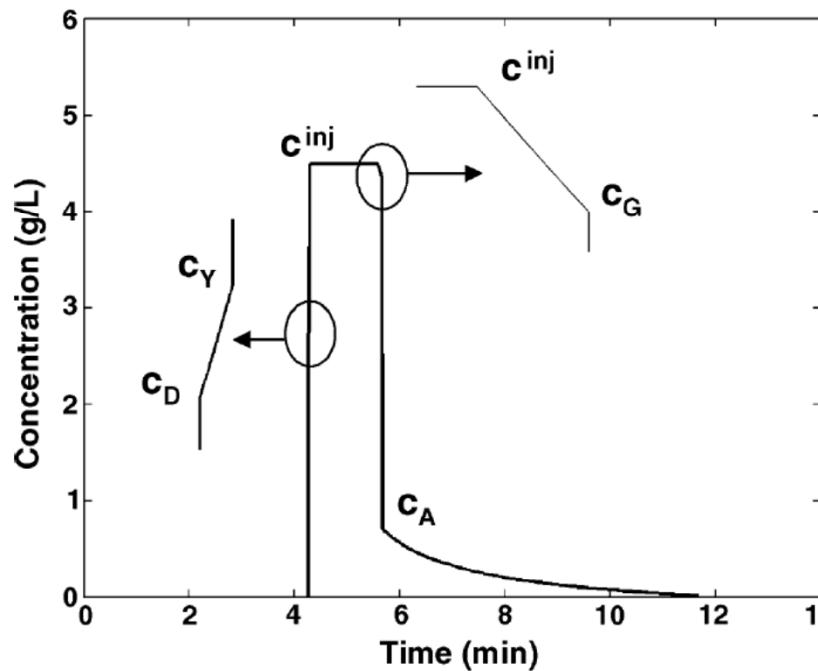
Adsorption: shock → small wave → shock
 Desorption: small wave → shock → wave

Zhang, Shan and Seidel-Morgenstern
J. Chromat. A, 2006, 2016-225

Influence of mass transfer

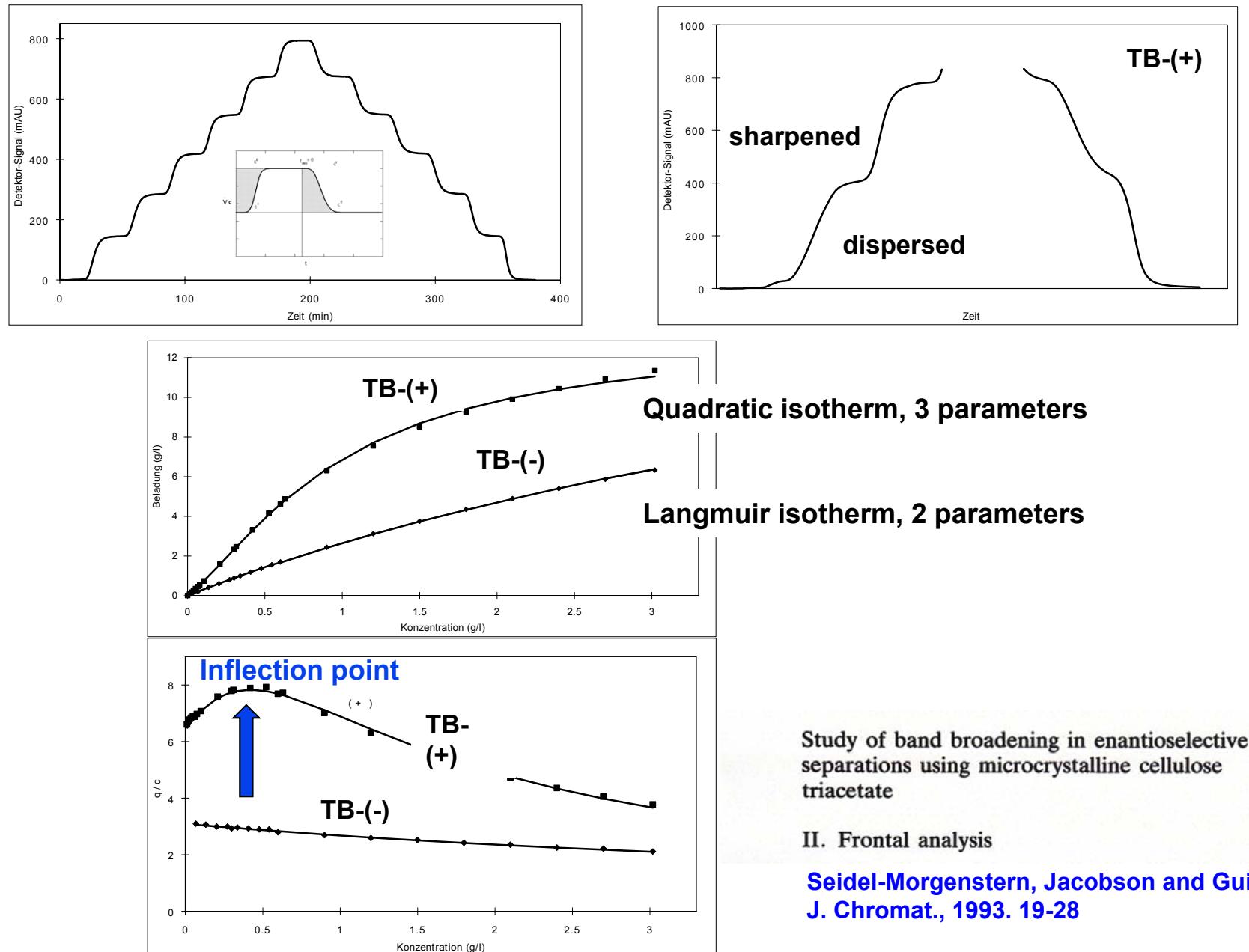
(again equilibrium dispersion model)

$$\frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q(c)}{\partial t} + u_o \frac{\partial c}{\partial x} = D_{ax} \frac{\partial^2 c}{\partial x^2} \quad D_{ax} = \frac{u_0 L}{2N_p}$$



Zhang, Shan and Seidel-Morgenstern, J. Chromat. A, 2006, 2016-225

Case study „TB and CTA“ (1): Frontal analysis and isotherms



Study of band broadening in enantioselective separations using microcrystalline cellulose triacetate

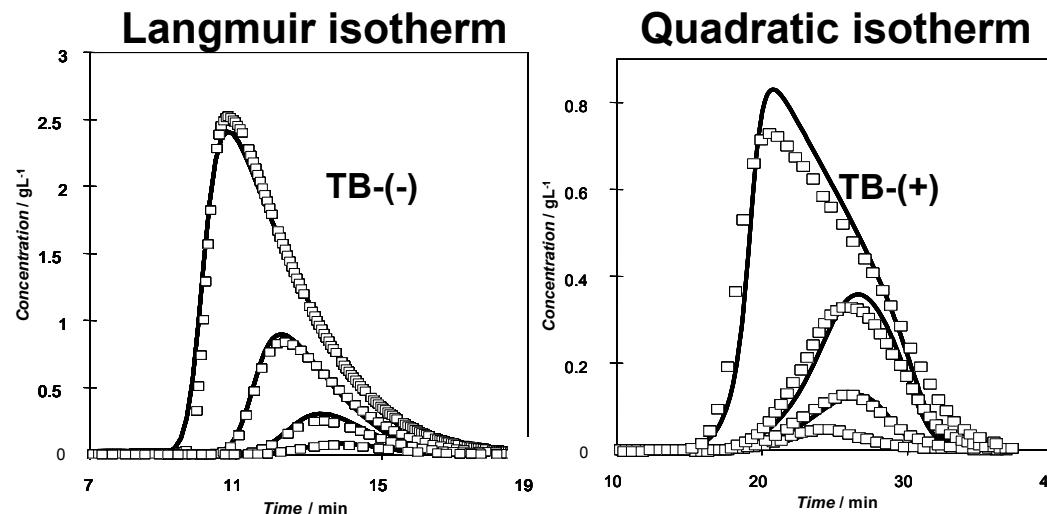
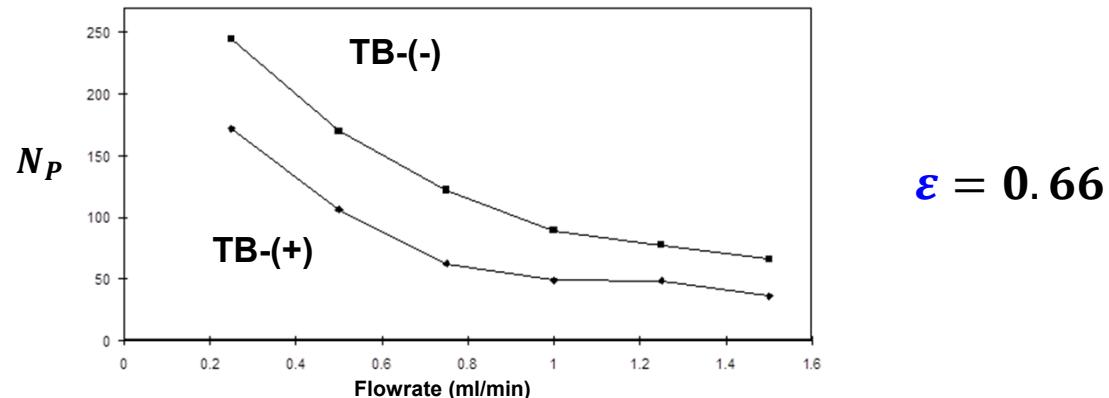
II. Frontal analysis

Seidel-Morgenstern, Jacobson and Guiochon
J. Chromat., 1993. 19-28

Case study „TB and CTA“ (2): Single component dynamics

Equilibrium dispersion model: $\frac{\partial c}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial q(c)}{\partial t} + u_o \frac{\partial c}{\partial x} = D_{app} \frac{\partial^2 c}{\partial x^2}$

$$D_{app} = \frac{u_0 L}{2 N_p}$$

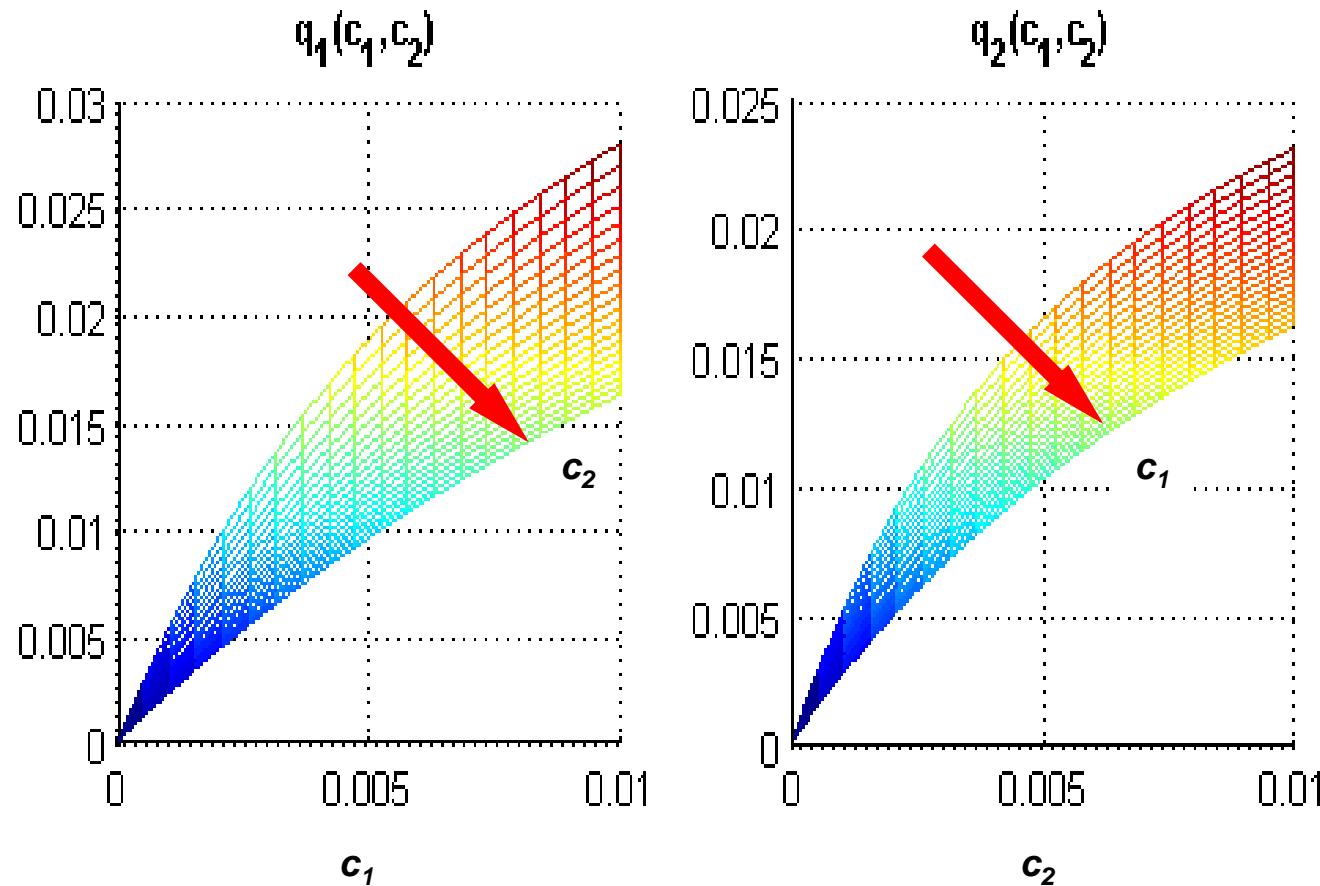


Seidel-Morgenstern and Guiochon, J. Chromat., 1993, 37-47

→ What about mixtures? Competitive isotherms needed.

Competitive adsorption isotherms

$$q_i = q_i(c_1, c_2, \dots, c_N, T=const.) \quad i=1, N$$



Examples of competitive adsorption isotherm models

Classical competitive Langmuir model

$$q_i = q_{s,i} \frac{b_i c_i}{1 + b_1 \cdot c_1 + b_2 \cdot c_2} = \frac{H_i c_i}{1 + b_1 \cdot c_1 + b_2 \cdot c_2} \quad i=1,2$$

Multi-Bi-Langmuir model

$$q_i = q_{s,1} \frac{b_{1i} c_i}{1 + b_{11} \cdot c_1 + b_{12} \cdot c_2} + q_{s,2} \frac{b_{2i} c_i}{1 + b_{21} \cdot c_1 + b_{22} \cdot c_2} \quad i=1,2$$

Statistical thermodynamics

$$q_1 = q_{sat} c_1 \frac{b_1 + b_{12} c_2 + 2b_{11} c_1}{1 + b_1 c_1 + b_2 c_2 + b_{12} c_1 c_2 + b_{11} c_1^2 + b_{22} c_2^2}$$

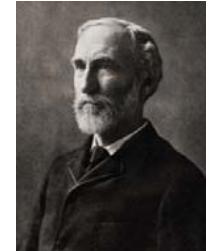
Ideal Adsorbed Solution Theory (IAST)

- very general
- based on arbitrary single component isotherm models
- thermodynamically consistent

Myers and Prausnitz, AIChE Journal, 1965, 121

Andreas Seidel-Morgenstern, Leipzig, 14.5.2019

Ideal Adsorbed Solution Theory



$$q_i = q_i(c_1, c_2, \dots, c_N, T=const.) \quad i=1, N$$

Gibbs' fundamental equation for adsorbed phase

$$dG = V \cdot dP - S \cdot dT + \mu \cdot dn$$

$$dG^{ads} = A \cdot d\pi - S^{ads} \cdot dT + \mu^{ads} \cdot dq$$

$$\mu^{ads} \cdot dq + q \cdot d\mu^{ads} = 0$$

Equilibrium at constant temperature

$$0 = A \cdot d\pi - q \cdot d\mu^{ads}$$

Chemical potentials

$$\mu^{ads} = \mu^\ell = \mu^{\ell,ref} + RT \ln \frac{c}{c^{ref}}$$

or

$$d\mu^{ads} = RT d\ln c$$

Differential Gibbs' adsorption isotherm

$$A \cdot d\pi = R \cdot T \cdot \frac{q}{c} \cdot dc$$

Integrated Gibbs' adsorption isotherm generates **Spreading Pressure π**

$$\pi^{(mod)}(c^*) = \frac{A}{RT} \pi(c^*) = \int_0^{c^*} \frac{q(\xi)}{\xi} d\xi$$

Ideal Adsorbed Solution Theory

Identical reduced component specific spreading pressures

$$\pi_i(c_i^0) = \pi_{i+1}(c_{i+1}^0), \quad i=1, \dots, N-1,$$

$$\boxed{\pi} = \pi_i(c_i^0) = \int_0^{c_i^0} \frac{q_i^0(\xi)}{\xi} d\xi \quad i=1, N$$

Ideal phases

$$c_i = z_i \cdot c_i^0(\pi) \quad i=1, N$$

Closure condition

$$\sum_{i=1}^N \frac{c_i}{c_i^0} = \sum_{i=1}^N z_i = 1$$

Sub-set II

Required loadings q_i follow **explicitly**



Sub-set I

- **Implicit** nonlinear problem
- unknowns: π , c_i^0 and z_i



Total concentration in the solid phase

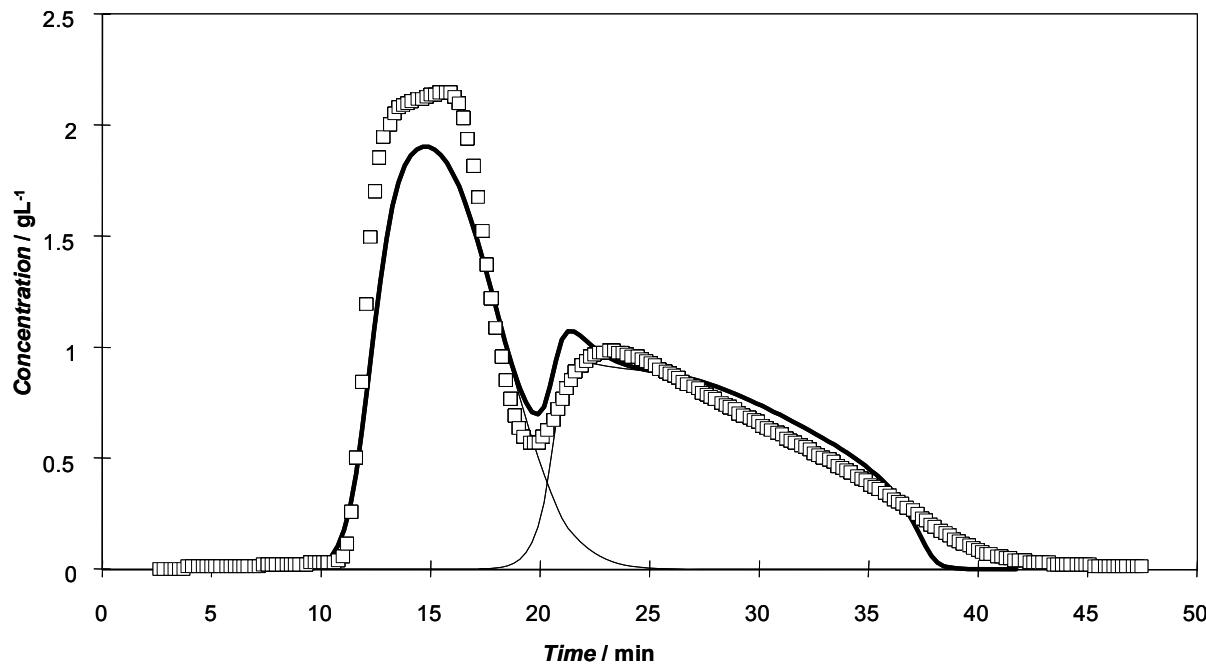
$$q_{tot} = \left[\sum_{i=1}^N \frac{c_i(c_i^0)}{c_i^0 \cdot q_i^0(c_i^0)} \right]^{-1}$$

Solid phase concentration, loading of i

$$\boxed{q_i} = q_{tot} \cdot \frac{c_i}{c_i^0}, \quad i=1, N$$

Myers and Prausnitz, AIChE J., 1965, 121

Case study „TB and CTA“ (3): Model validation for mixtures



MODELLING OF THE COMPETITIVE ISOTHERMS AND THE CHROMATOGRAPHIC SEPARATION OF TWO ENANTIOMERS

→ validates both isotherm (IAS) and simple column model (equilibrium dispersion)

[Seidel-Morgenstern and Guiochon, Chem. Eng. Sci., 1993, 2787-2797](#)

→ Problem: time consuming numerical solution required

Rapid analytical solution of IAST for quadratic single component isotherm model

Quadratic isotherm equation

$$q_i^0(c_i^0) = q_s \cdot \frac{c_i^0 \cdot (b_{i1} + 2 \cdot b_{i2} \cdot c_i^0)}{1 + b_{i1} \cdot c_i^0 + b_{i2} \cdot c_i^{02}} \quad i=1,2$$

$$\pi_1(c_1^0) = \pi_2(c_2^0)$$

$$\int_0^{c_1^0} \frac{(b_{11} + 2 \cdot b_{12} \cdot \xi)}{1 + b_{11} \cdot \xi + b_{12} \cdot \xi^2} d\xi = \int_0^{c_2^0} \frac{(b_{21} + 2 \cdot b_{22} \cdot \xi)}{1 + b_{21} \cdot \xi + b_{22} \cdot \xi^2} d\xi \quad \rightarrow \quad 1 + b_{11} \cdot \frac{c_1}{z_1} + b_{12} \cdot \left[\frac{c_1}{z_1} \right]^2 = 1 + b_{21} \cdot \frac{c_2}{1-z_1} + b_{22} \cdot \left[\frac{c_2}{1-z_1} \right]^2$$

Incorporation of closure condition: → cubic equation

Explicit competitive isotherm model

$$a_1(c_1, c_2) \cdot z_1^3 + a_2(c_1, c_2) \cdot z_1^2 + a_3(c_1, c_2) \cdot z_1 + a_4 = 0$$

$$q_i(c_1, c_2) = \left[\frac{z_1}{q_1^0(c_1^0)} + \frac{z_2}{q_2^0(c_2^0)} \right]^{-1} \cdot z_i \quad i=1,2$$

→ unique root z_1 in $[0,1]$, explicit analytical expression

$$z_2 = 1 - z_1, \quad c_i^0 = \frac{c_i}{z_i}$$

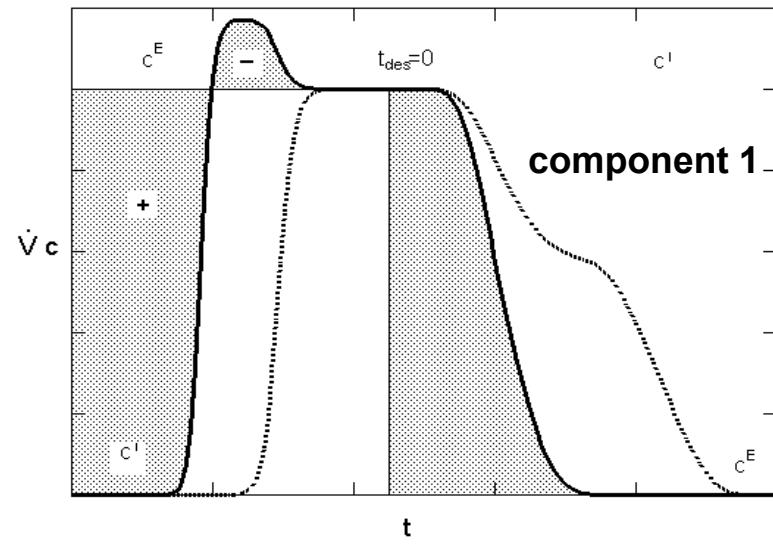


→ allows rapid calculation, frequently applicable

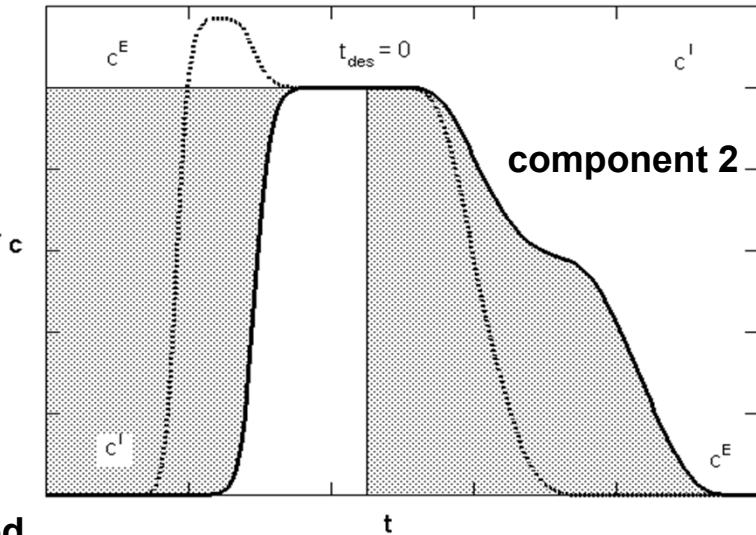
Ilić, Flockerzi and Seidel-Morgenstern, J. of Chromat. A, 2010, 2132

Frontal Analysis (FA) with binary mixtures ("point-wise" determination of loadings)

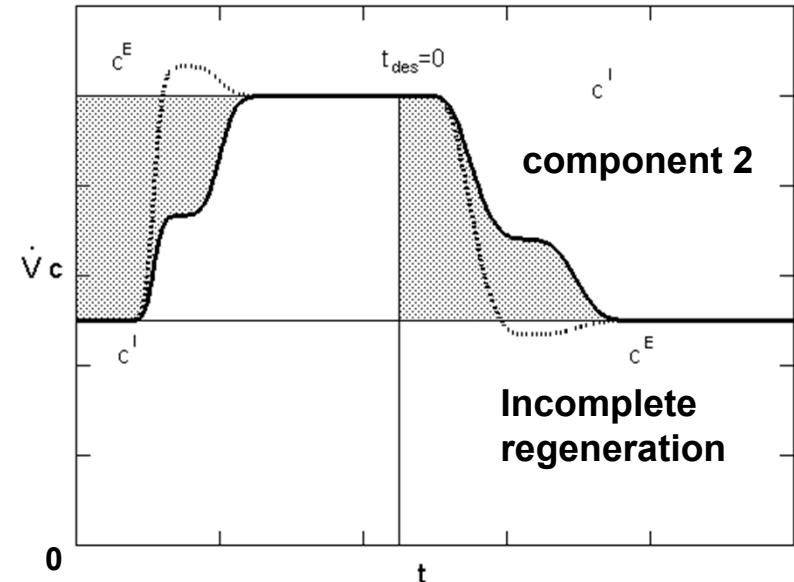
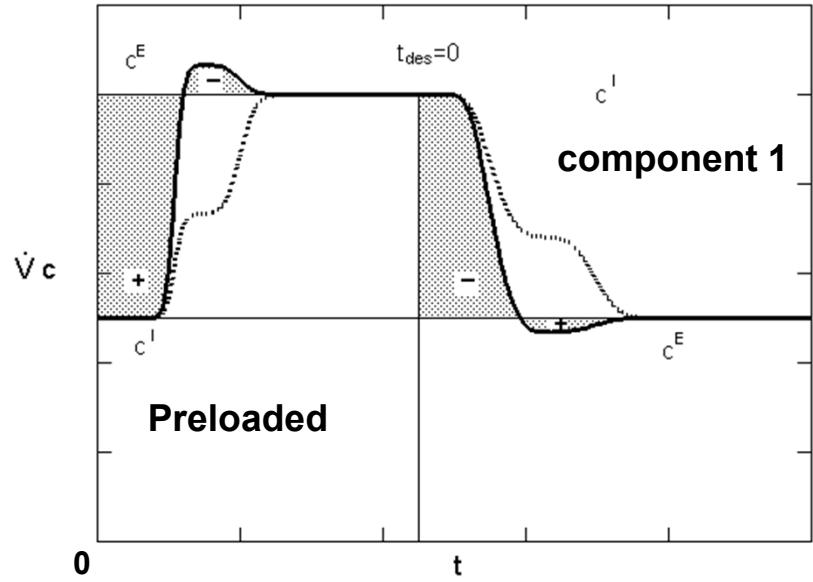
$$\varepsilon V(c_i^{Feed} - c_i^{Init}) + (1 - \varepsilon)V(q_i^{Feed} - q_i^{Init}) = \dot{V} \int_0^{\infty} (c_i^{Feed} - c_i(t))dt \quad i = 1,2$$



Initially
empty bed



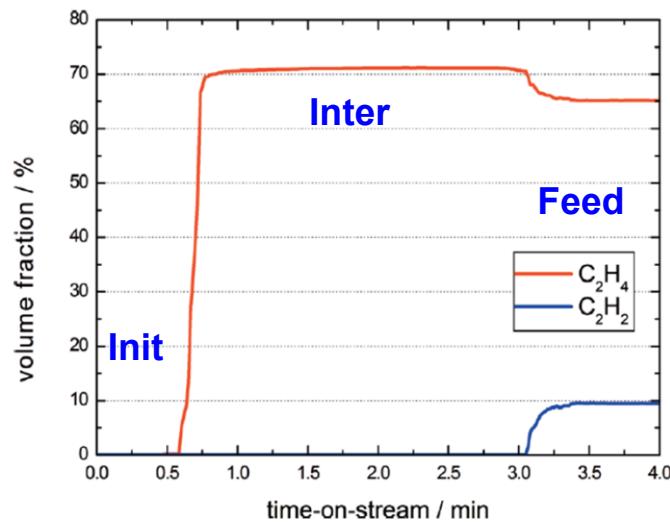
FA: Preloading and incomplete regeneration (binary system)



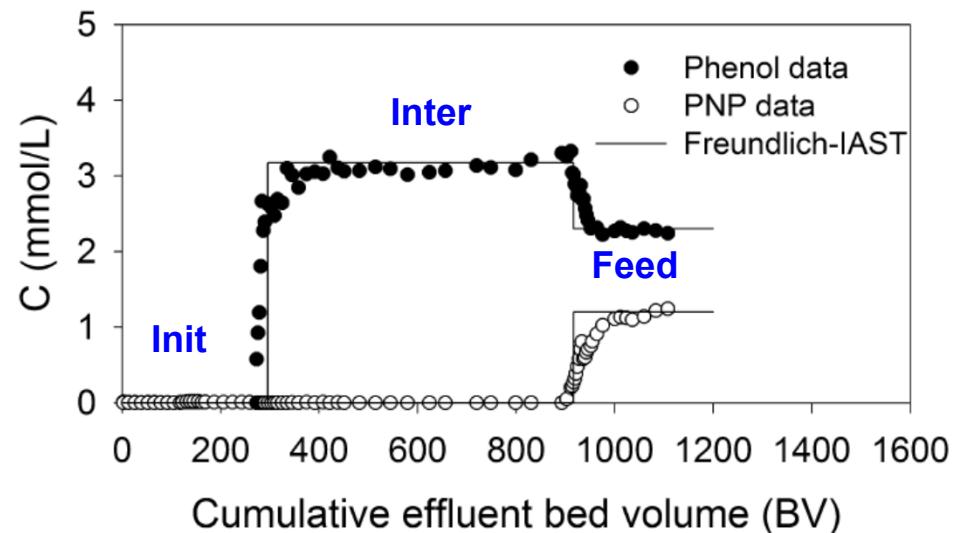
$$\varepsilon V(c_i^{Feed} - c_i^{Init}) + (1 - \varepsilon)V(q_i^{Feed} - q_i^{Init}) = \dot{V} \int_0^\infty (c_i^{Feed} - c_i(t)) dt \quad i=1,2$$

Measured breakthrough curves for binary systems

Acetylene (1) and Ethylene (2)
SIFSIX-2-Cu-I (MOF) / Helium
3P INSTRUMENTS GmbH & Co. KG
Chem. Ing. Techn., 90, 2018, 1640-1641



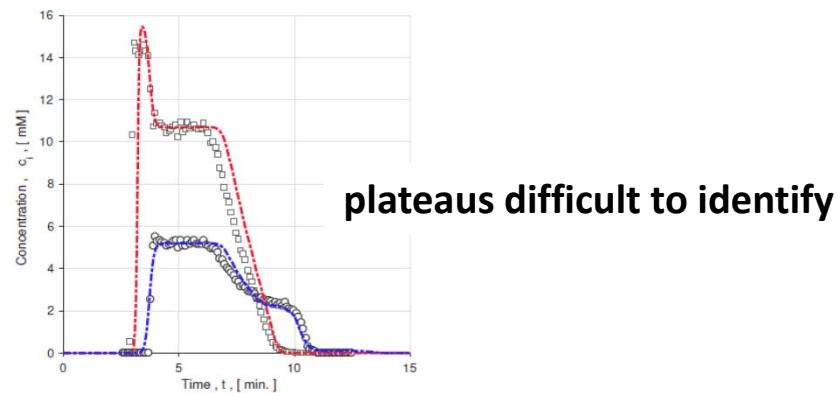
Phenol (1) and p-Nitrophenol (2)
Activated carbon / Water
Lu, Chang, Chern
Journal of the Taiwan Institute of Chemical Engineers
45, 2014, 1608–1617



→ single transition: two fronts and one intermediate state

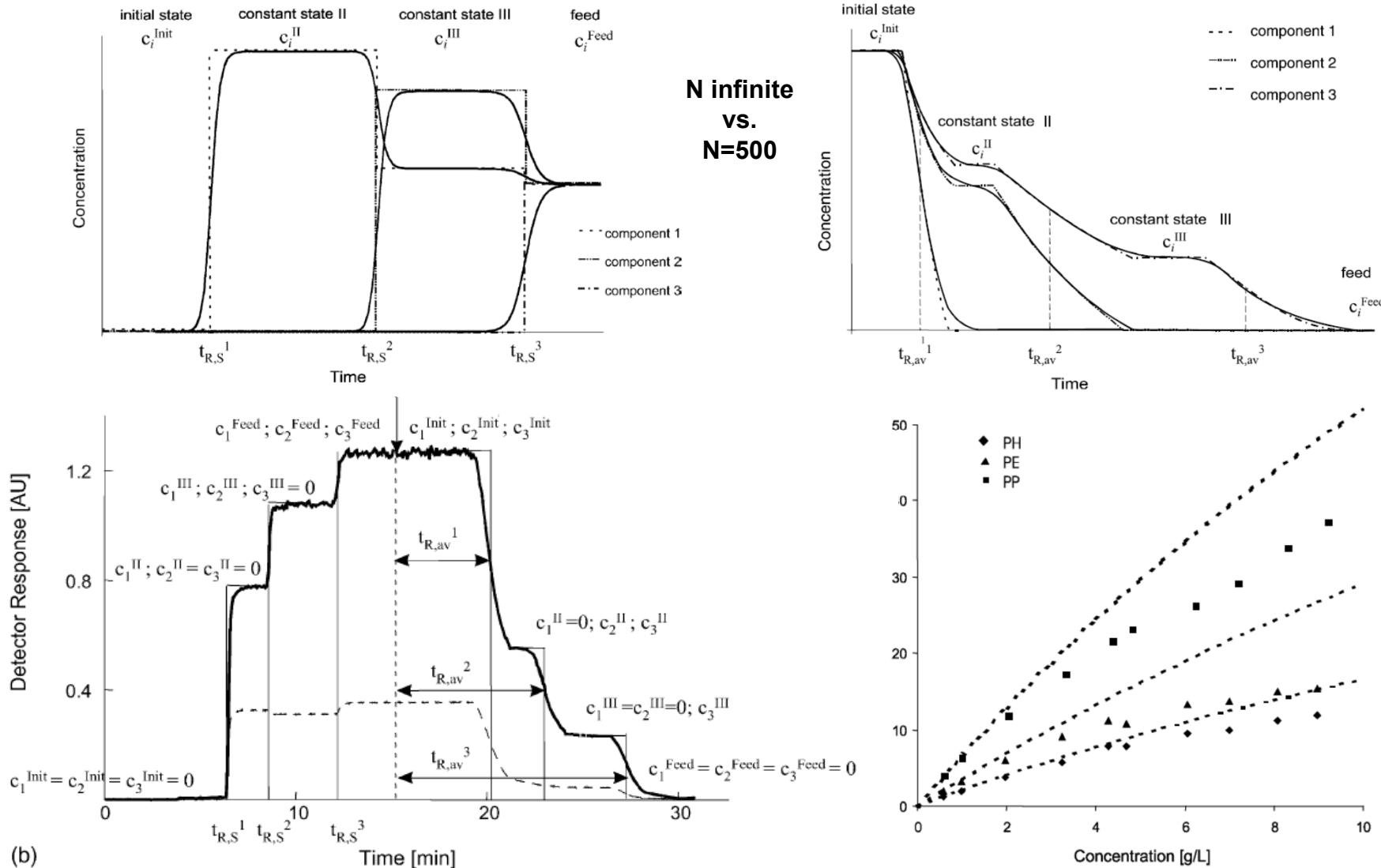
Decylbenzene (1) and undecylbenzene (2)
Porous graphitic carbon / Acetonitrile

→ adsorption desorption cycle
Rubiera-Landa, Dissertation, Magdeburg, 2017



FA: Extension to ternary mixtures (and beyond)

$N=3$: three fronts and two intermediate states (in general: $N, N-1$)



Seidel-Morgenstern, J. Chromat. A., 2004, 255

Andreas Seidel-Morgenstern, Leipzig, 14.5.2019

Equilibrium theory for binary mixtures

$$\frac{\partial c_i}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i(c_1, c_2, \dots, c_N)}{\partial t} + u_0 \frac{\partial c_i}{\partial x} = 0 \quad i = 1, 2$$

with $dq_i = \sum_j^2 \frac{\partial q_i}{\partial c_j} dc_j \rightarrow \frac{dq_i}{dt} = \sum_j^2 \frac{\partial q_i}{\partial c_j} \frac{dc_j}{dt}$ or $\frac{dq_i}{dc_i} = \sum_j^2 \frac{\partial q_i}{\partial c_j} \frac{dc_j}{dc_i}$

$$\frac{\partial c_i}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \sum_j^2 \frac{\partial q_i}{\partial c_j} \frac{dc_j}{dt} + u_0 \frac{\partial c_i}{\partial x} = 0 \quad \text{or} \quad \frac{\partial c_i}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \sum_j^2 \frac{\partial q_i}{\partial c_j} \frac{dc_j}{dc_i} \frac{dc_i}{dt} + u_0 \frac{\partial c_i}{\partial x} = 0$$

$$\frac{\partial c_i}{\partial t} \left(1 + \frac{1-\varepsilon}{\varepsilon} \frac{dq_i}{dc_i}\right) + u_0 \frac{\partial c_i}{\partial x} = 0$$

Coherence condition: $\frac{dq_1}{dc_1} = \frac{dq_2}{dc_2}$

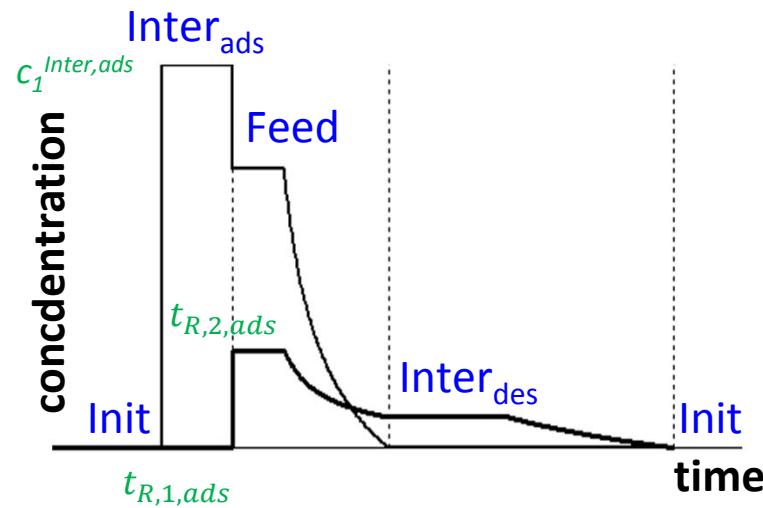
$$\left(\frac{dc_1}{dc_2}\right)^2 + \frac{\left(\frac{\partial q_2}{\partial c_2} - \frac{dq_1}{dc_1}\right)}{\frac{\partial q_2}{\partial c_1}} \frac{dc_1}{dc_2} - \frac{\left(\frac{\partial q_1}{\partial c_2}\right)}{\frac{\partial q_2}{\partial c_1}} = 0$$

→ 2 specific roots for each pair $[c_1^*, c_2^*]$: $\frac{dc_1}{dc_2 pos}$, $\frac{dc_1}{dc_2 neg}$

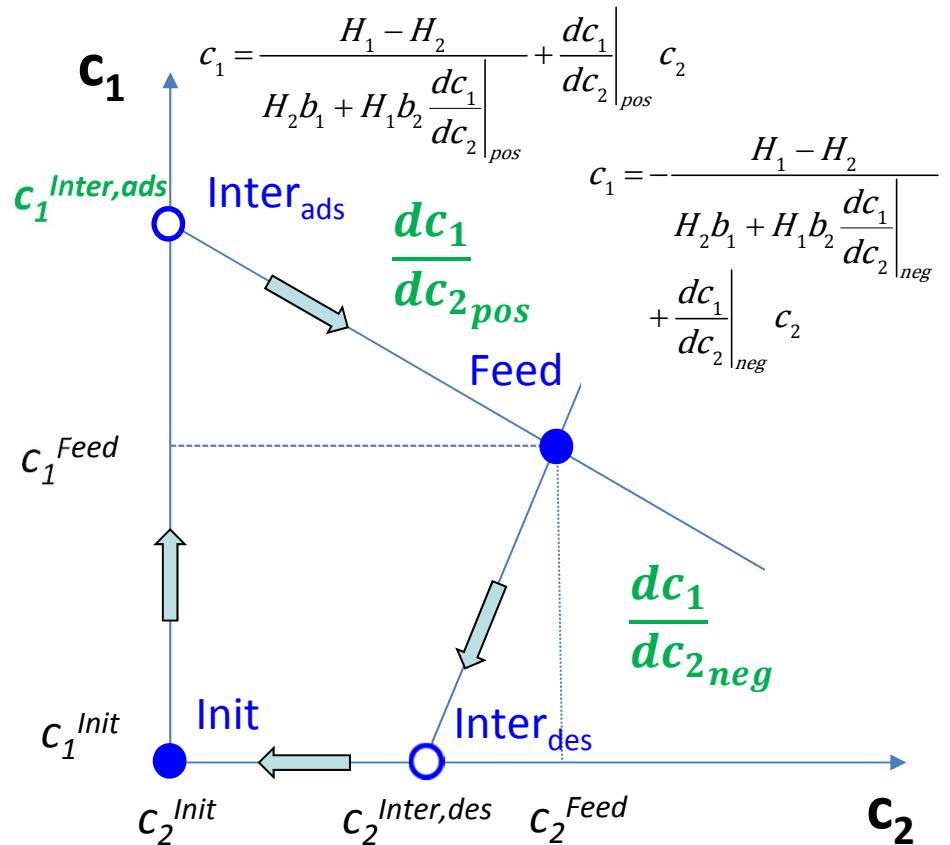
Equilibrium theory: Langmuir isotherms:

$$q_i = \frac{H_i c_i}{1 + b_1 \cdot c_1 + b_2 \cdot c_2}$$

3 unknowns A: $q_{S,1} = q_{S,2} \Rightarrow H_2 = \frac{b_2}{b_1} H_1$



Hodograph Plane: \rightarrow 2 straight lines



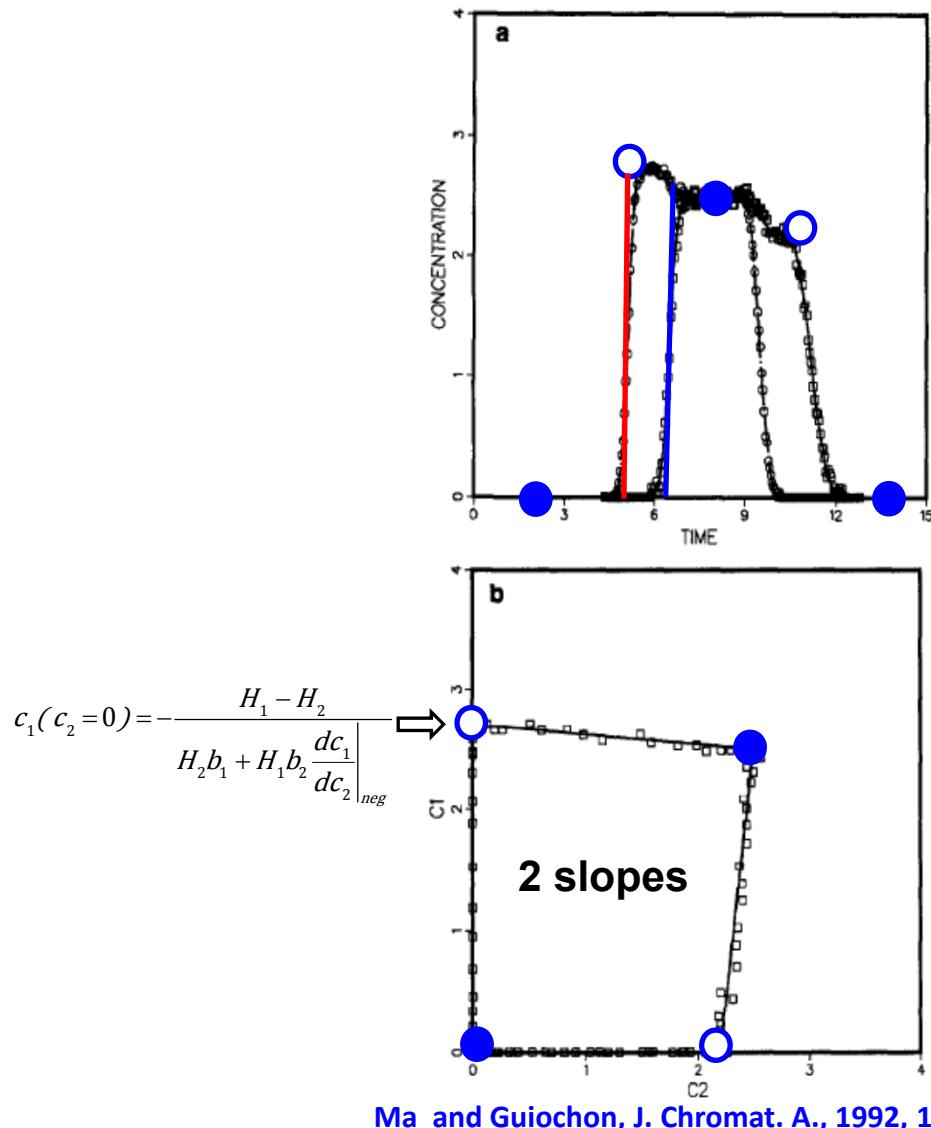
3 unknowns B: e.g. for adsorption front

$$t_{R,1,ads} = t_0 \left(1 + F \frac{q_1^0(c_1^{Inter,ads}) - 0}{c_1^{Inter,ads} - 0} \right)$$

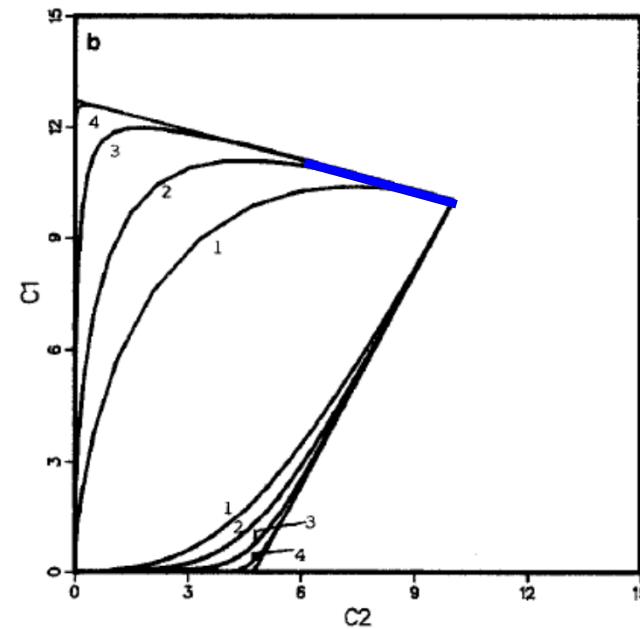
$$t_{R,2,ads} = t_0 \left(1 + F \frac{q_2(c_1, c_2, Feed) - 0}{c_2, Feed - 0} \right)$$

Illustration of hodograph plots

2-Phenyl-Ethanol / 3-Phenyl-Propanol / Octadecyl Silica / Methanol:Water=1:1

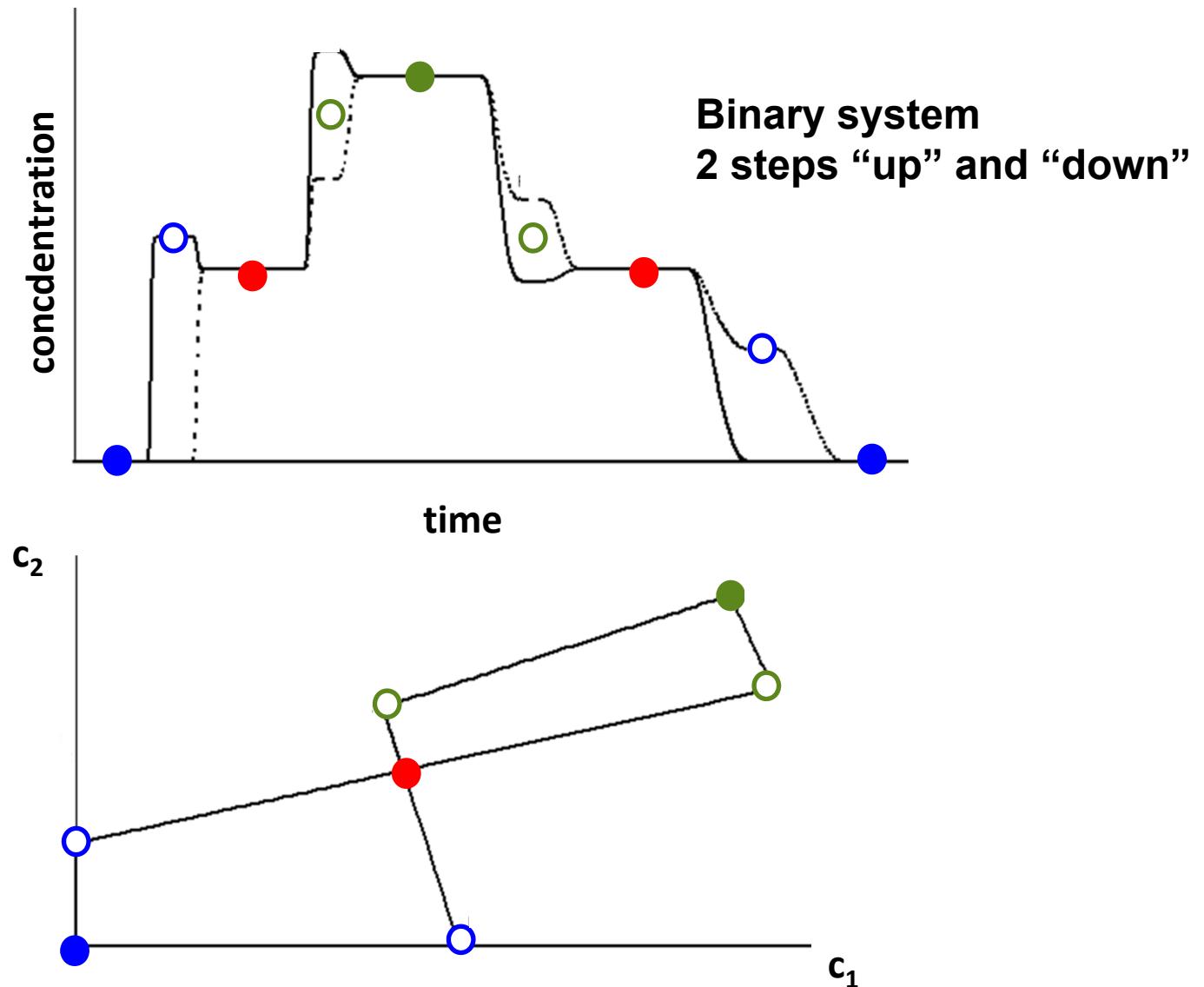


Hodograph plots for reduced rates



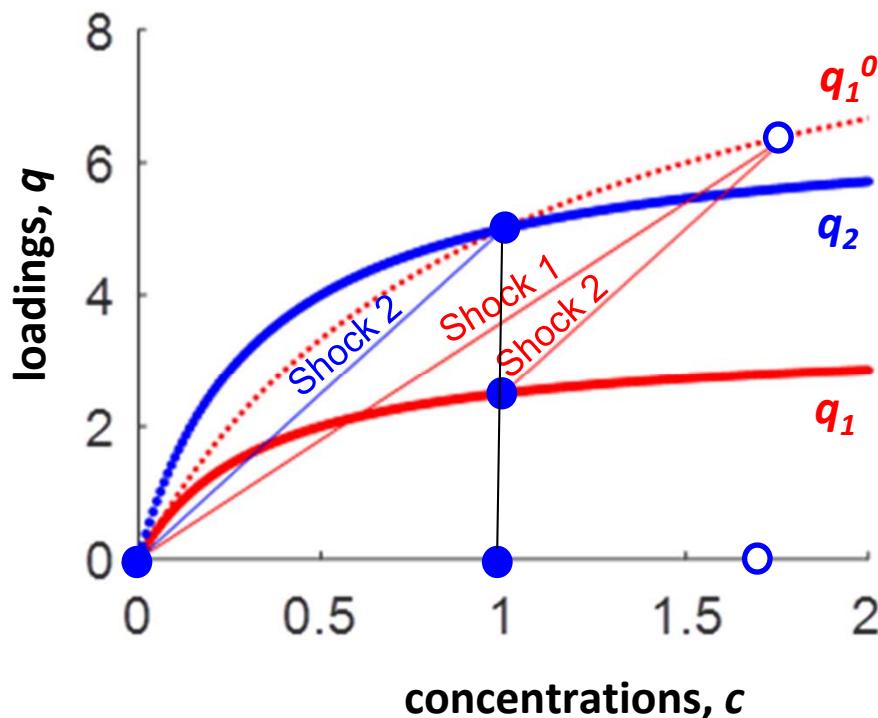
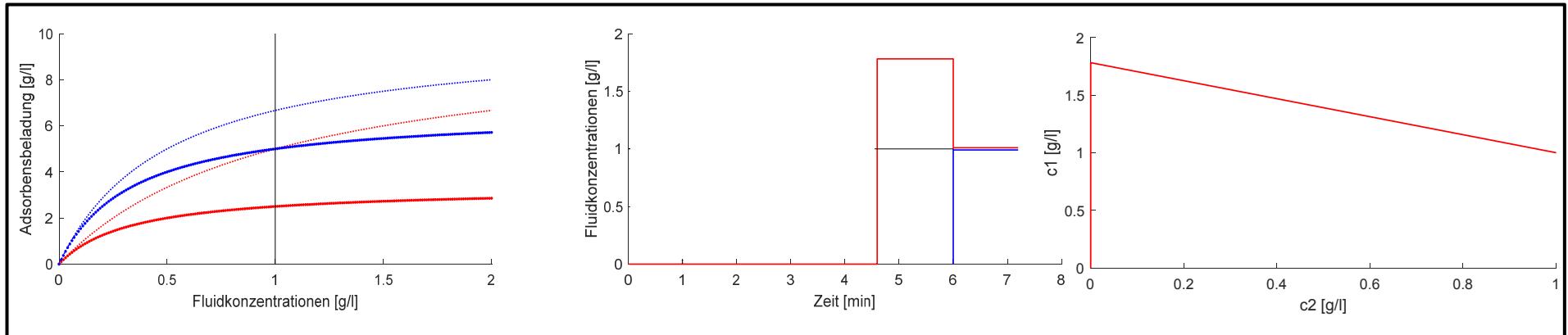
Ma and Guiochon, J. Chromat. A., 1992, 13-25

Stair case breakthrough curves and corresponding hodograph plot



Graphical solution for binary breakthrough

(connection between isotherms, two retention times and one plateau concentration)

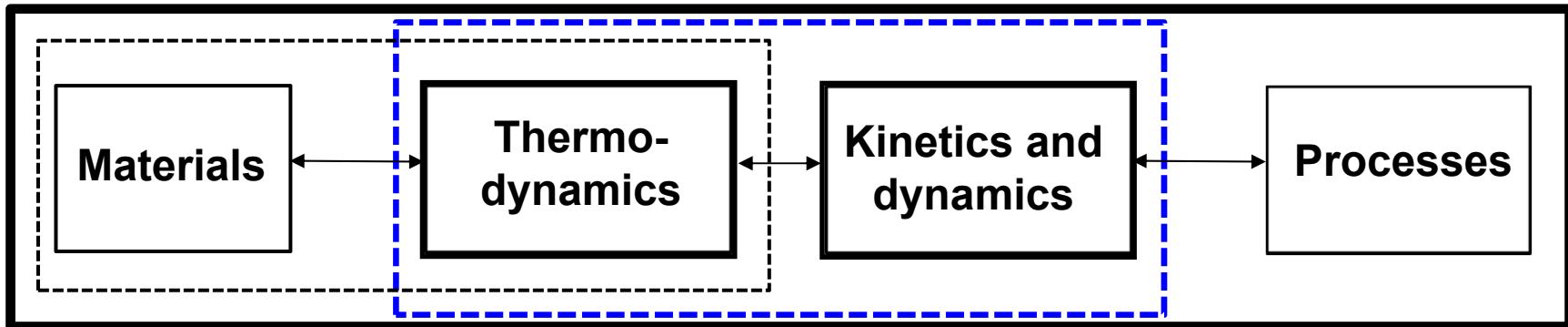


If isotherms provided:

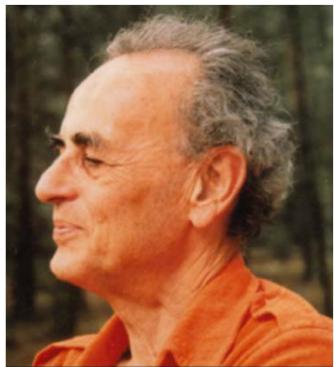
→ 3 unknowns

- 1) $t_{R,2,ads}$ (from Shock 2)
- 2) $c_1^{Inter,ads}$ (also Shock 2)
- 3) $t_{R,1,ads}$ (from Shock 1)

Conclusions and Acknowledgement



- Knowledge regarding adsorption isotherms is essential to characterize adsorbents and to design adsorption processes
- To determine isotherms it is attractive to exploit dynamic experiments (e.g. FA)
- The determination of competitive adsorption isotherms is a difficult task



David Gelbin, East Berlin
(1925-1986)



Jochen Kinkel, Darmstadt
(1953-2016)



Georges Guiochon, Knoxville
(1931-2014)



Klaus Unger, Mainz