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Non-equilibrium modelling of simulated moving bed processes for separation of Xylenes in petrochemical industry

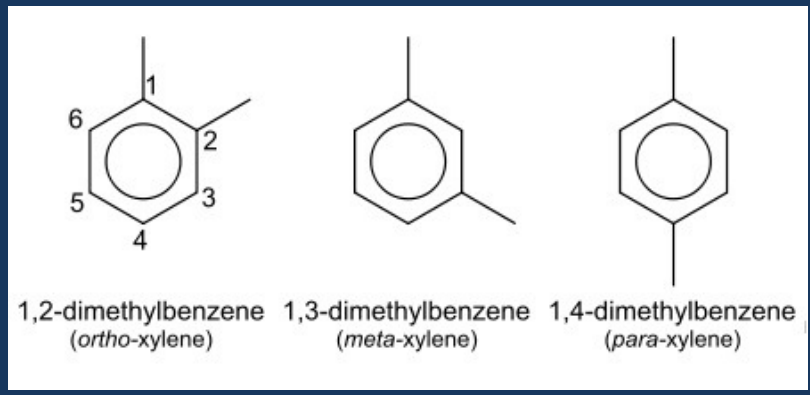
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- Xylene is an aromatic hydrocarbon with a single ring and two methyl groups attached to this ring in positions 1-2, 1-3 and 1-4, called *o-xylene*, *m-xylene*, and *p-xylene*.

- Xylenes are obtained as isomeric mixtures by repeated extractions or distillations of light petroleum fractions .

- o-Xylene and m-Xylenes are mainly used in the production of phthalic anhydride and isophthalic acid respectively.



- p-Xylene is the principal precursor to terephthalic acid and dimethyl terephthalate. PET (polyethylene terephthalate), is produced by the reaction of terephthalic acid and ethylene glycol. Amongst others, this specific example illustrates the importance of separation of pure p-Xylene from the remaining isomers.

- The separation of xylene isomers is one of the most difficult separations in petrochemistry. Literature reports numerous patents and articles on the use of several principles to separate xylene isomers.

- Nowadays adsorption processes are preferred because they achieve a significantly higher recovery of p-xylene.

- The state-of-the art processes for xylene separation were developed by UOP, Toray, and IFP group where Simulated Moving Bed (SMB) technology is employed.

- SMB processes for xylene separation systematically employ p-xylene selective adsorbents.

- **The simulated moving bed (SMB) technology is an important technique for large-scale continuous separation processes.**

- **This technology has been applied over four decades in the petrochemical industry.**

- **Currently enjoying separation of sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods and enantiomers.**

- The reference process for simulated moving bed (SMB) is true moving bed (TMB).

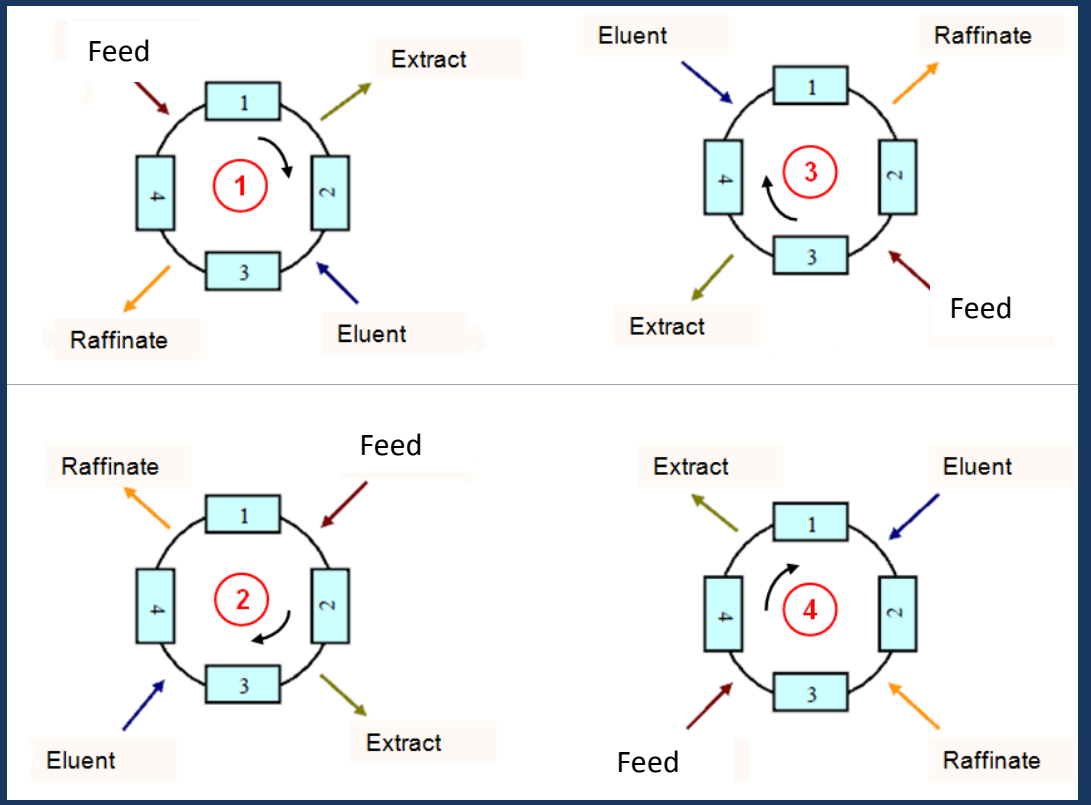
- Where, in a single column, counter-current flow between a solid and a liquid phase is imagined.

TMB operating principle (hypothetical)



- In the SMB system, the solid phase is not moving like in the hypothetical TMB.
- The simulation of solid phase movement is accomplished by switching the valves of inlet/outlet lines.

SMB operating principle



- Because of the complex nature of operation of SMB, generally a model-based control scheme is used for better understanding of the process.

- Thus a great deal of theoretical work* has been carried out for developing useful simulation procedures for design and process development purposes.

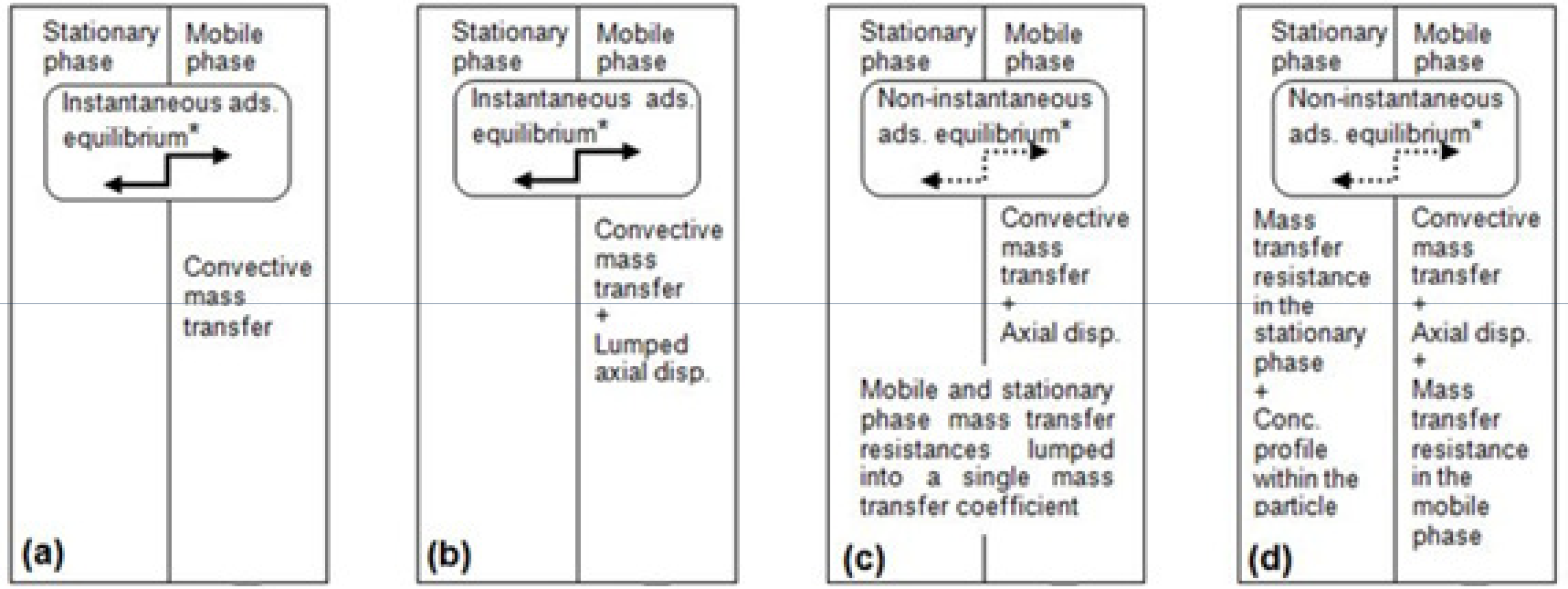
*Some examples:

T. Gu, Mathematical modelling and scale- up of liquid chromatography. Springer. New York. 1995.
G.M. Zhong, G. Guiochon , Chemical Engineering Science,52 (1997) 3117.
D.C.S. Azevedo, L.S. Pais, A.E. Rodrigues, Journal of Chromatography A, 865 (1999) 187.
G. Dünnebier, I. Weirich, K.-U. Klatt, Chemical Engineering Science, 53 (1998) 2537.
C. Migliorini, M. Mazzotti and M. Morbidelli, AIChE J., 46 (200) 1384.
A. Toumi, S. Engell, M. Diehl, H.G. Bock, J. Schlöder, Chemical Engineering and Processing 46 (2007) 1067.
K. B. Lee, R. Kasat, G. Cox, N.-H. L. Wang, AIChE J, 54(2008) 2852.
J. Wu, Q. Peng, W. Arlt, M. Minceva, Journal of Chromatography A, 1216 (2009) 8793.

There are several models to be used for chromatographic separations whether it is at the analytical scale or at the preparative/production scale, including:

- *the ideal model*
- *the equilibrium dispersive model*
- *the transport dispersive model*
- *the general rate model*

(a) the ideal model, (b) the equilibrium dispersive model, (c) the transport dispersive model, (d) the general rate model



*Linear or non-linear adsorption isotherm



Homogeneous Solid Diffusion

In homogeneous solid diffusion model, all solute within the particle, whether free or adsorbed, is lumped into a single quantity q.

particle phases →

$$\frac{\partial q}{\partial t} = \frac{D_{solid}\,\partial}{r^2\ \partial r}\left(r^2 \frac{\partial q}{\partial r}\right)$$

bulk fluid ↓

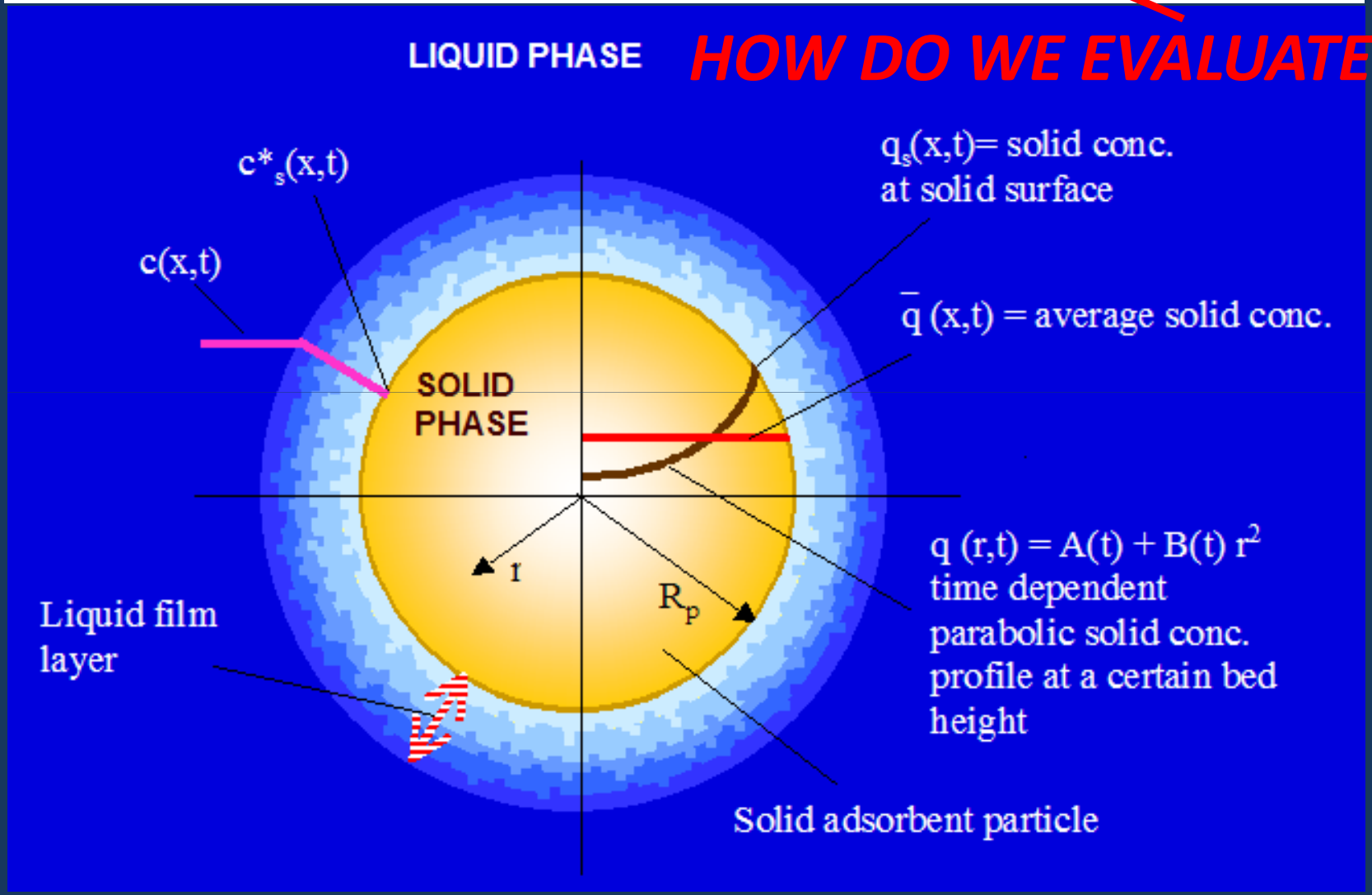
↕ **Adsorption Isotherm**

$$\frac{\partial c(x,t)}{\partial t} + v\frac{\partial c(x,t)}{\partial x} + \frac{3(1-\varepsilon)}{\varepsilon r_p} k_f \left[c(x,t) - c^*(x,t)\right] = D_a \frac{\partial^2 \left[c(x,t)\right]}{\partial x^2}$$

In the Column Governing Differential Equation, there are two independent variables (x & t) and two dependent variables (c & c*).

$$\frac{\partial c(x,t)}{\partial t} + v\frac{\partial c(x,t)}{\partial x} + \frac{3(1-\varepsilon)}{\varepsilon\, r_p} k_f \left[c(x,t) - c_s^*(x,t)\right] = D_a \frac{\partial^2 [c(x,t)]}{\partial x^2}$$

HOW DO WE EVALUATE ?



MAIN ASSUMPTIONS

- In order to represent the external and internal resistances, separate “film mass transfer coefficient” and “homogeneous solid diffusion coefficient” values are used for A and B components.

- Axial dispersion of components A and B can be represented with a single constant dispersion coefficient.

- Nonlinear isotherm (multicomponent Langmuir). Instant equilibrium is only attained at the solid-liquid interphase.

- Monosized spherical particles. Columns init. conc. (mobile and stationary phase) is zero.

$$q_{sA}^{*}(t) = \bar{q}_A(x,t) + \frac{Bi_A}{5}\left[c_A(x,t) - c_{sA}^{*}(x,t)\right] \quad (1)$$

$$q^{*}_{sA}(x,t) = \frac{a_A c^{*}_{sA}(x,t)}{1 + b_A c^{*}_{sA}(x,t) + b_B c^{*}_{sB}(x,t)} \quad (2)$$

$$q^{*}_{sB}(x,t) = \frac{a_B c^{*}_{sB}(x,t)}{1 + b_A c^{*}_{sA}(x,t) + b_B c^{*}_{sB}(x,t)} \quad (3)$$

In the numerical solution "one time step earlier" value this ratio will be used

$$c^{*}_{sB}(x,t) = \frac{a_A}{a_B}\frac{q^{*}_{sB}(x,t)}{q^{*}_{sA}(x,t)} c^{*}_{sA}(x,t) \quad (4)$$

From eqs. (1), (2) and (4)

$$\left(c^{*}_{sA}(x,t)\right)^{2}+\left[\frac{5}{Bi_A}\frac{q_{Am}}{\eta_A}-\frac{5}{Bi_A}\overline{q_A}(x,t)+\frac{K_A}{\eta_A}-c_A(x,t)\right]c^{*}_{sA}(x,t)-\frac{K_A}{\eta_A}\left[\frac{5}{Bi_A}\overline{q_A}(x,t)+c_A(x,t)\right]=0 \quad (6)$$

$$c_{sA}^{*}(x,t)=\frac{-M_A+\sqrt{M_A{}^{2}+4\frac{K_A}{\eta_A}\left[c_A(x,t)+\frac{5\overline{q}_A(x,t)}{Bi_A}\right]}}{2} \quad (7)$$

where

$$M_A=\left[\frac{5}{Bi_A}\frac{q_{mA}}{\eta_A}-\frac{5}{Bi_A}\overline{q_A}(x,t)+\frac{K_A}{\eta_A}-c_A(x,t)\right] \quad (8)$$

$$\eta_A=1+\frac{q^{*}_{sB}/q_{mB}}{q^{*}_{sA}/q_{mA}} \quad (9)$$

$$q_{mA}=a_A/b_A \quad (10)$$

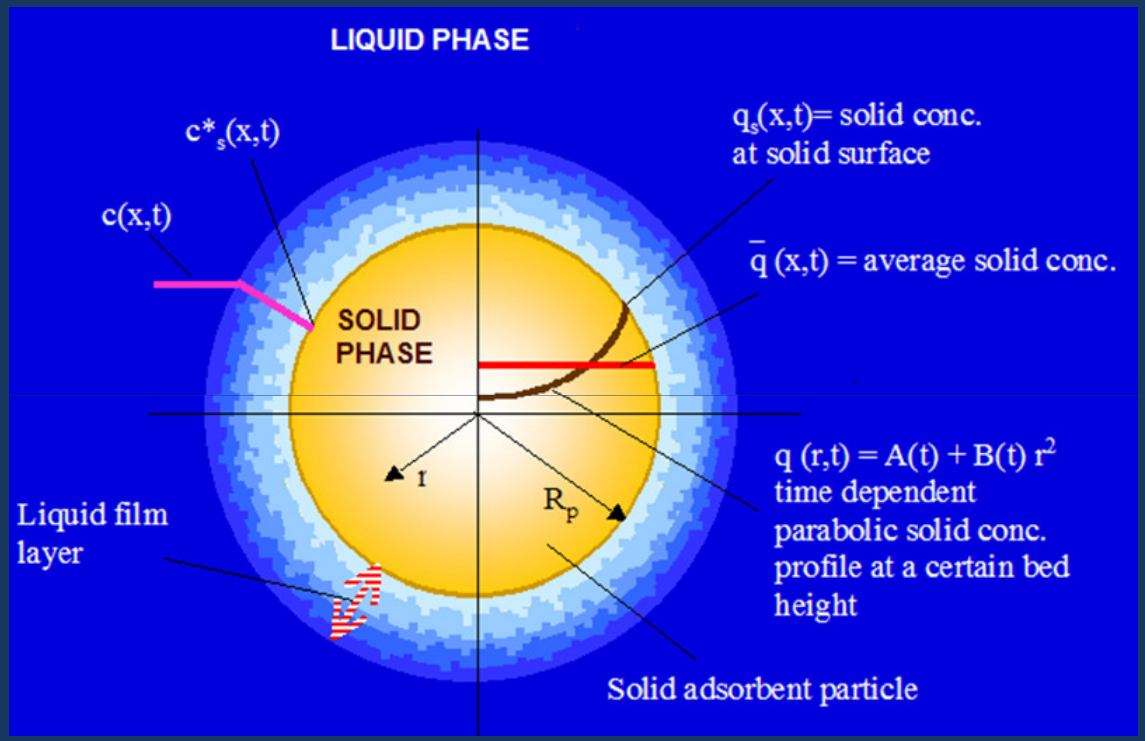
$$K_A=1/b_A \quad (11)$$

$$\frac{\partial c(x,t)}{\partial t} + v\frac{\partial c(x,t)}{\partial x} + \frac{3(1-\varepsilon)}{\varepsilon\, r_p} k_f \left[c(x,t) - c_s^*(x,t)\right] = D_a \frac{\partial^2 [c(x,t)]}{\partial x^2}$$

LIQUID PHASE

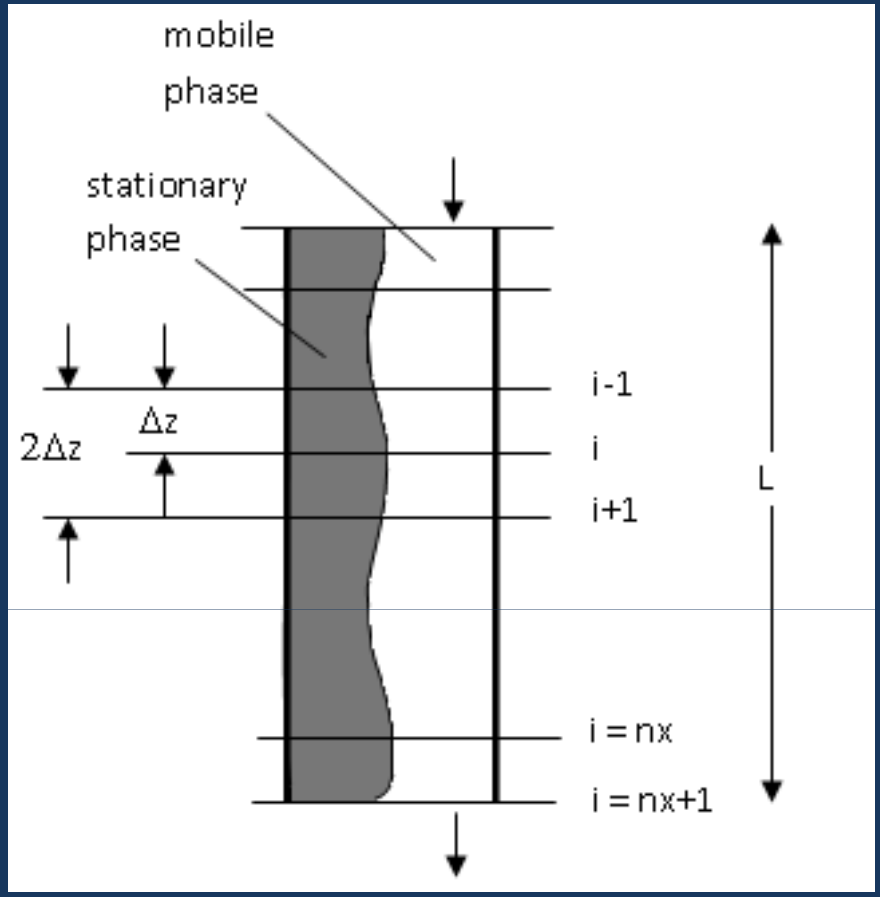
HOW DO WE EVALUATE ?

THIS IS HOW WE EVALUATE $c^*_{sA}(x,t)$

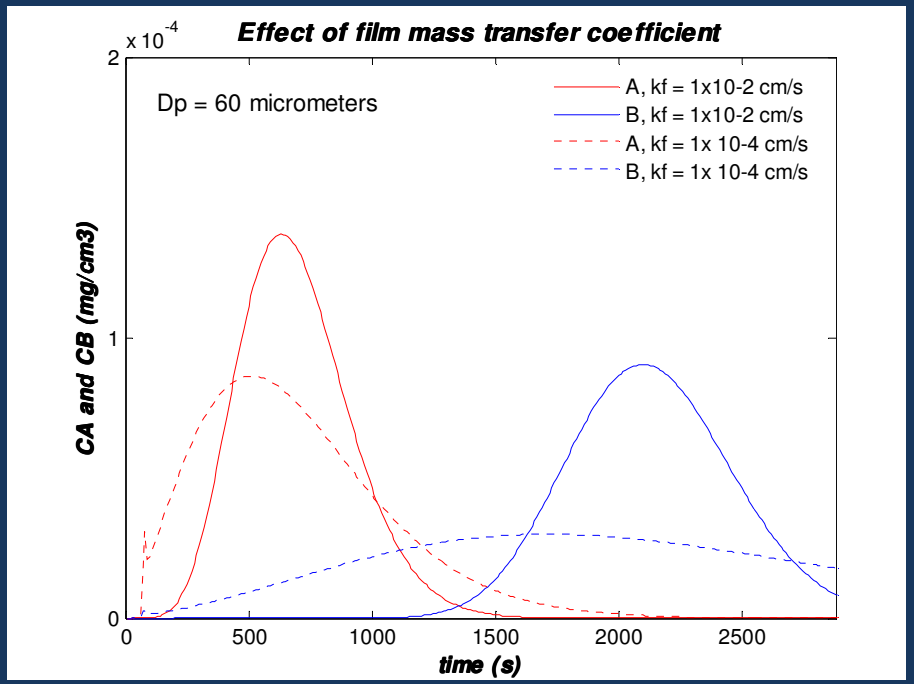


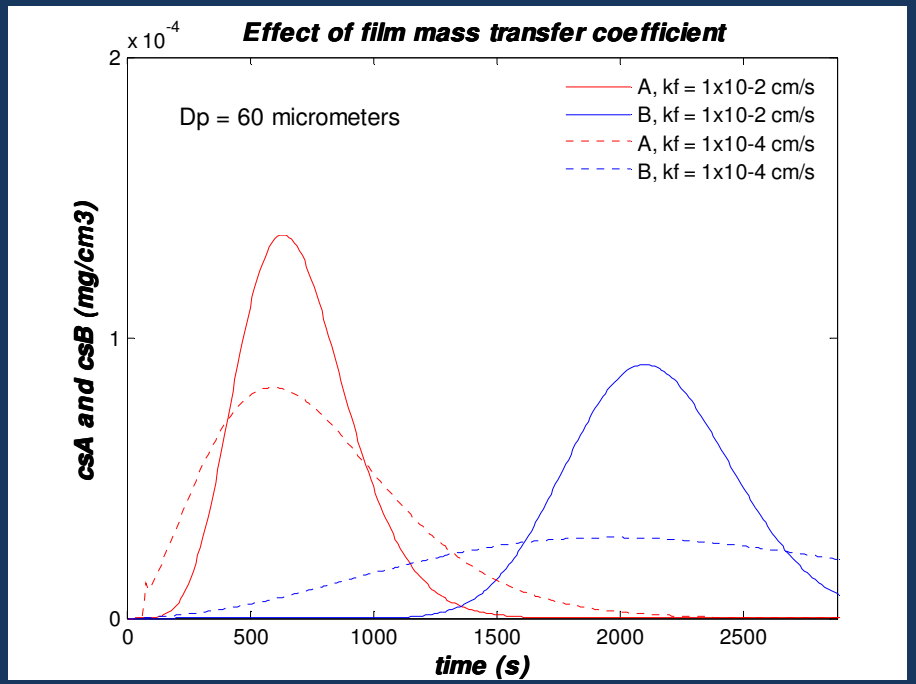
$$c_{sA}^*(x,t) = \frac{-M_A + \sqrt{M_A^2 + 4\dfrac{K_A}{\eta_A}\left[c_A(x,t) + \dfrac{5\bar{q}_A(x,t)}{Bi_A}\right]}}{2}$$

Referring to the figure, mass balance for the control volume of 2Δz height gives stationary phase average concentration in discretization scheme as shown by Eq. (12), where h and k are the distance and time increments, respectively.



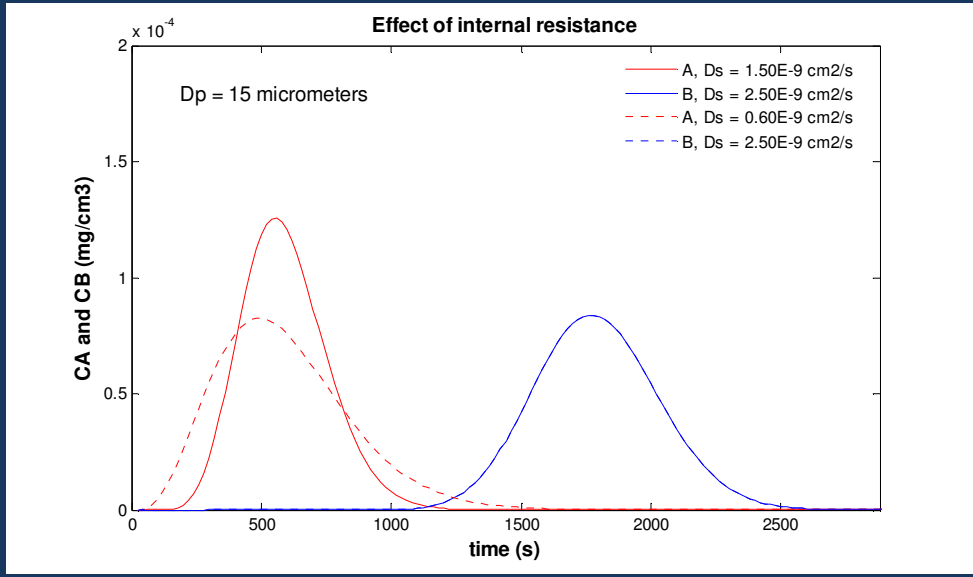
$$\bar{q}_{i,j} = \bar{q}_{i,j-1} + \frac{\varepsilon k}{2(1-\varepsilon)h}\left[v\left(c_{i-1,j} - c_{i+1,j}\right) - 2h\frac{\partial c(z,t)}{\partial t} + \frac{D_a\left(c_{i-1,j} - 2c_{i,j} + c_{i+1,j}\right)}{h}\right] \quad (12)$$

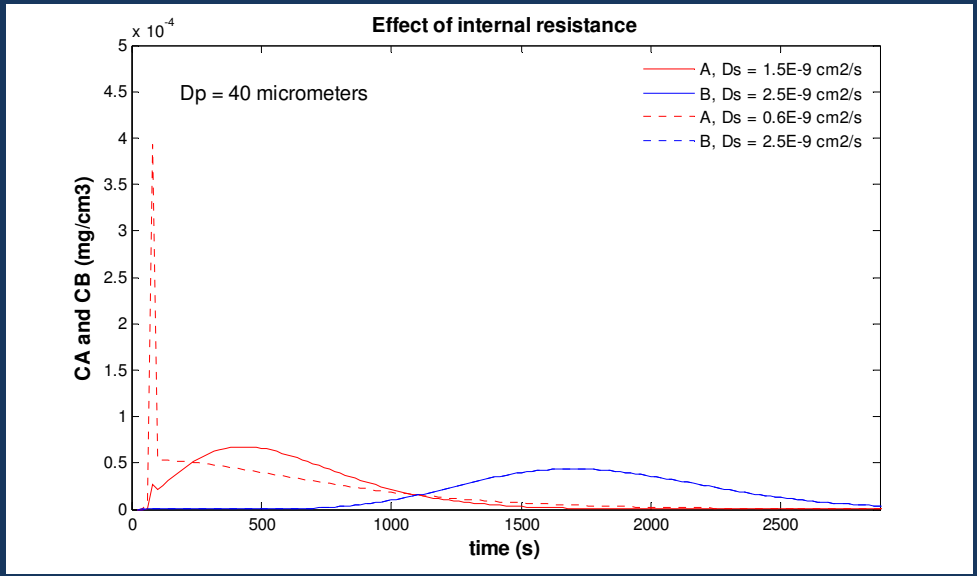




	Comp. A	Comp. B
q_m (mg/cm3 solid)	15	25
K (mg/cm3)	2	1
D_s (cm2/s)	1.50×10^{-8}	2.50×10^{-8}
D_a (cm2/s)	1.00×10^{-3}	1.00×10^{-3}
c_0 (mg/cm3)	50	50

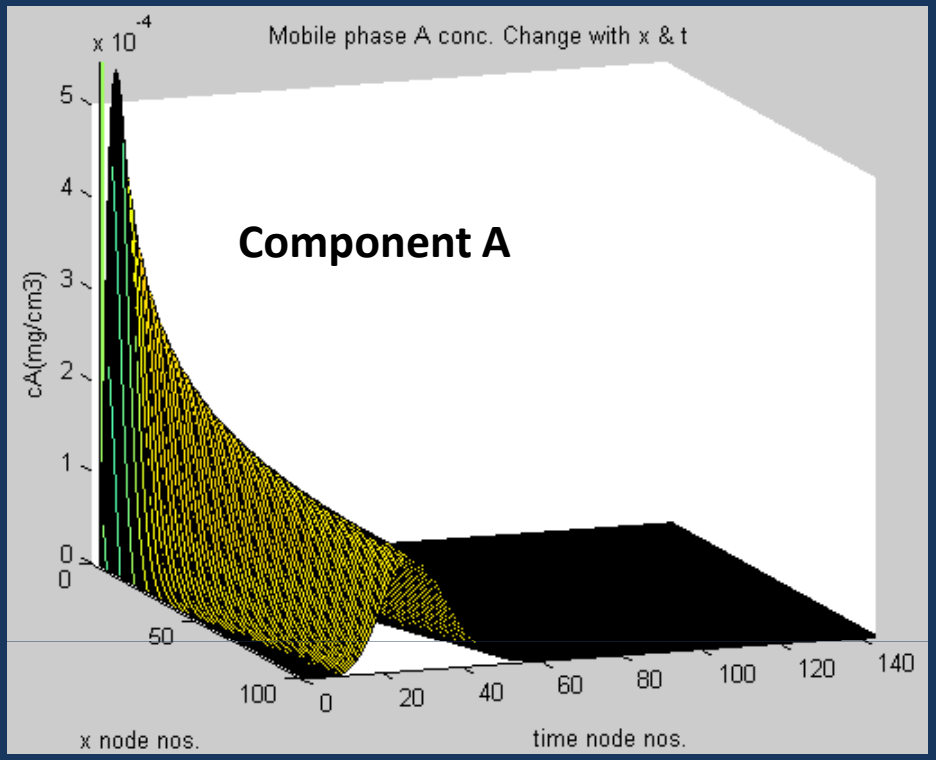
Common Parameters	
L (cm)	15
Vol_{Inject} (µL)	30
Q_{eluent} (cm3/min)	1.2
D_c (mm)	4.6
ε_c (-)	0.45

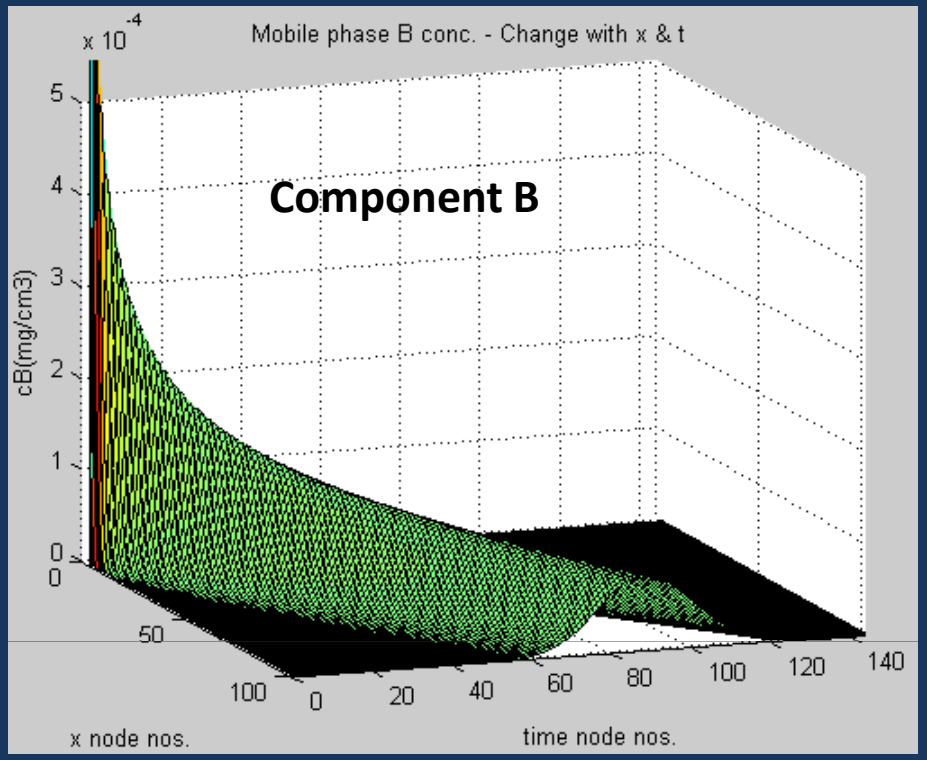




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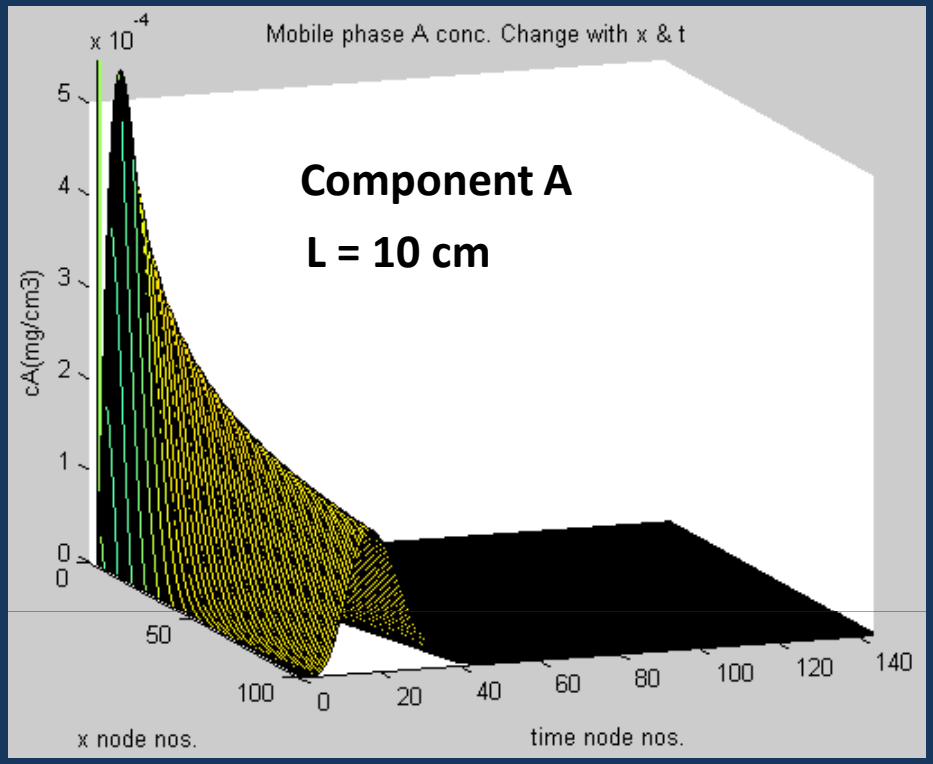
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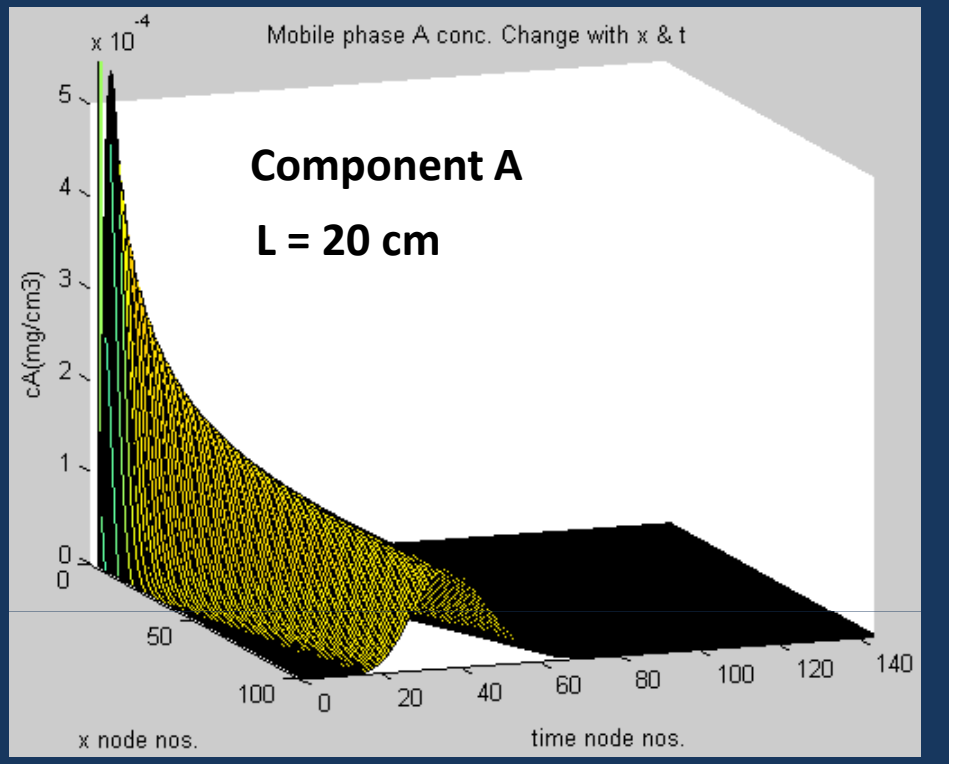




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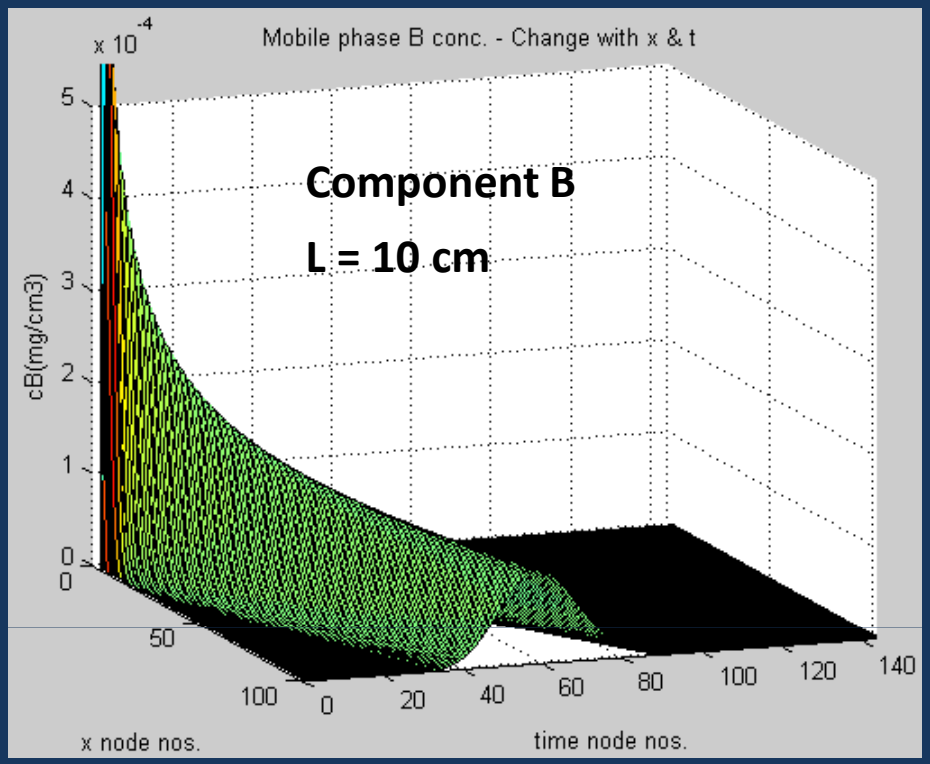
Common Parameters	
L (cm)	15
Vol_{Inject} (µL)	30
Q_{eluent} (cm3/min)	1.2
Dp (µm)	15
D_c (mm)	4.6
ε_c (-)	0.45

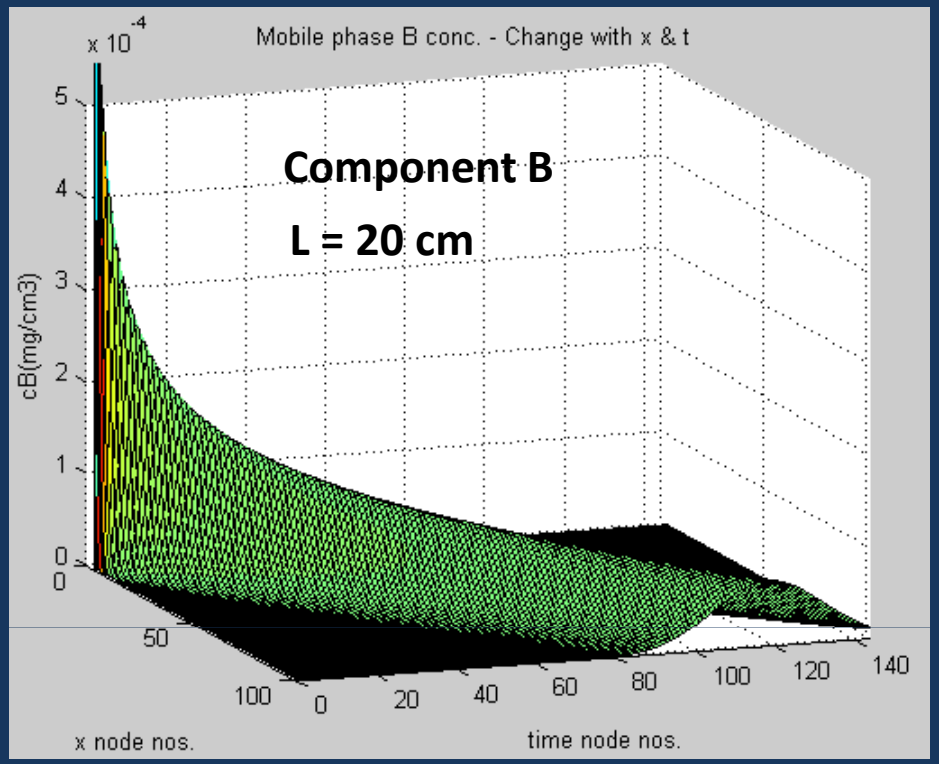




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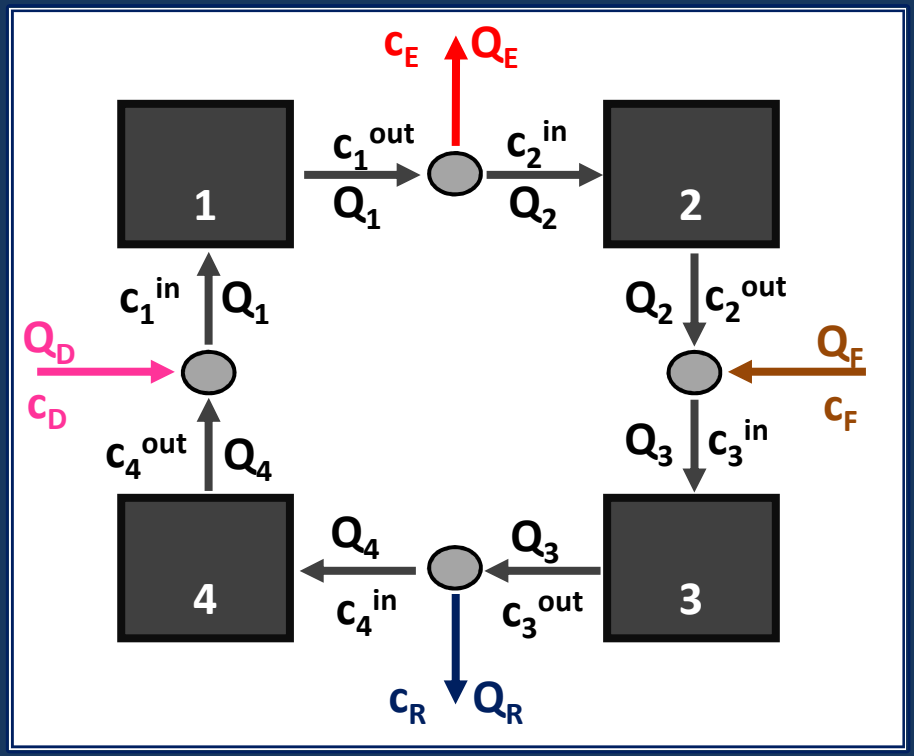




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Dp (µm)	15
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The node model



$$Desorbent\ Node: \quad Q_1 = Q_D + Q_4$$

$$c_1^{in} = (c_D Q_D + c_4^{out} Q_4)/(Q_D + Q_4)$$

$$Extract\ Node: \quad Q_2 = Q_1 - Q_E$$

$$c_E = c_1^{out} = c_2^{in}$$

$$Feed\ Node: \quad Q_3 = Q_2 + Q_F$$

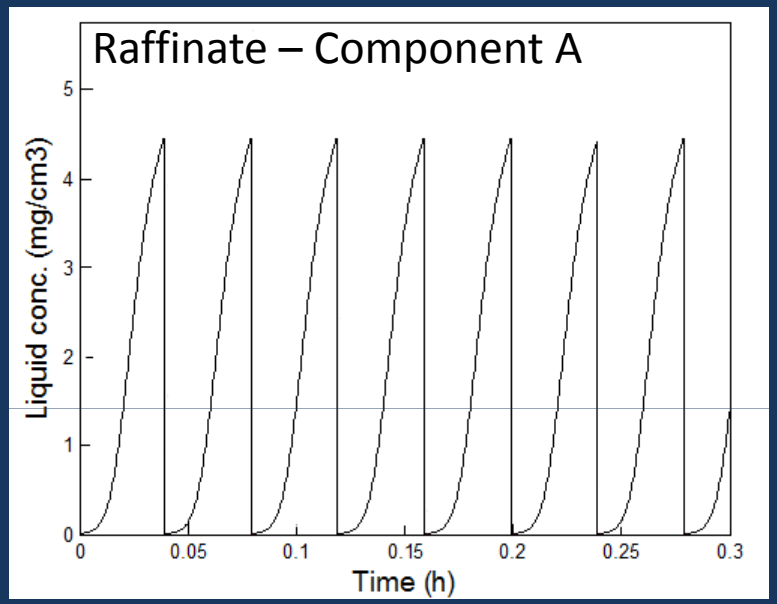
$$c_3^{in} = (c_F Q_F + c_2^{out} Q_2)/(Q_F + Q_2)$$

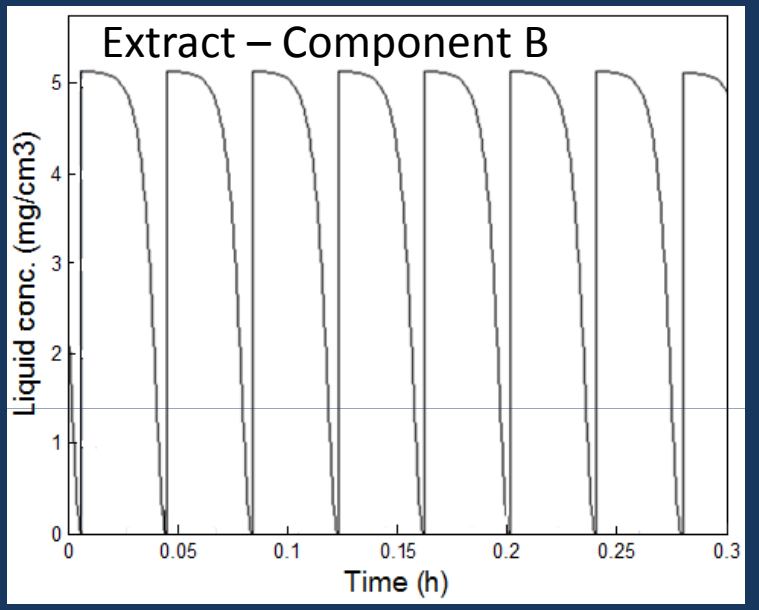
$$Raffinate\ Node: \quad Q_4 = Q_3 - Q_R$$

$$c_R = c_3^{out} = c_4^{in}$$

$$Overall: \quad Q_E + Q_R = Q_F + Q_D$$

- Node model - Cyclic port switching - Assigning new values for column inlet flow rates and inlet concentrations at each switch.
- The General Rate Model
- Non-linear adsorption isotherm (multicomponent Langmuir)





Switching time: 4 minutes

Time = 12 switching time + the time shown on the x axis

Q_{Des} = 5.30 mL/min; Q_F = 1.20 mL/min; Q_{Ext} = 3.00 mL/min; Q_{Raf} = 3.50 mL/min;

q_{mA} = 15 mg/cm^3 $_{solid}$; q_{mB} = 25 mg/cm^3 $_{solid}$; K_A = 2mg/cm^3 ; K_B = 1mg/cm^3;

D_{Aa}= D_{Ba} = 1 x 10^{-3} cm^2/s; k_{fA}=k_{fB} = 5 x 10^{-3} cm/s; D_{sA}=1.5 x 10^{-3} cm^2/s; D_{sB}=2.5 x 10^{-3} cm^2/s;

L = 15 cm D_c = 4.6 mm D_p = 15µm

Thank you
for
your attention.