Autocatalytic reactions in a liquid chromatographic reactor

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Abstract

The possibility of extending the treatment of second-order on-column reactions with two different reactants by empirical peak shape equations to autocatalytic on-column reactions was investigated. An approximate analytical solution is presented, which for small to medium conversions agrees with the solution of the ideal non-equilibrium model of chromatography by a finite difference method.

Keywords: Autocatalytic on-column reactions; Kinetic parameters; Liquid chromatographic reactors

1. Introduction

Methods for the determination of rate constants from chromatograms, which are obtained with a reaction occurring on the chromatographic column, are often based on the investigation of the conversion as a function of certain chromatogram parameters (for general reviews, see Refs. [1] and [2]).

In simple irreversible first-order reactions, the knowledge of the dependence of the conversion on the reaction duration or retention time is sufficient for the evaluation of rate constants. However, in complex first-order reactions, it becomes necessary to approximate the product pulse shapes by suitable functions for the determination of the conversion [3,4], since it is not possible to separate all the reaction partners completely from each other.

Second-order reactions require consideration

of the amounts injected and the pulse shapes of the reactants [5]. Autocatalytic reactions of the type $R + C \rightarrow P + 2C$, which are complex second-order reactions, are rarely involved in discussions of chromatographic reactors, since these reactions are suppressed by the separation of the reactants.

In this paper, it is shown that autocatalytic reactions can be investigated by methods which are similar to those that we applied earlier to second-order reactions with two reactants. They can be carried out in a defined way if the slower reactant is injected first and the faster reactant is injected later. At first, a normal chromatographic process is in progress, but since the faster reactant overtakes the slower one, they are mixed at a certain zone on the column and the reaction occurs. After a certain time, the reactants are completely separated again, which will stop the reaction. Therefore, the products can, at least in principle, also be completely separated from the reactants.

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2. Mathematical modelling

All derivations are based on the model of linear non-equilibrium chromatography with an isothermal and homogeneous column and a constant flow-rate, and the additional assumption that the reaction rate is not limited by the mass transfer rate between the chromatographic phases:

$$-u\frac{\partial c_i}{\partial x} - k_{fi}q_ic_i + k_{fi}a_{1i} + r_i = \frac{\partial c_i}{\partial t}$$

$$k_{fi}q_ic_i - k_{fi}a_{1i} = \frac{\partial a_{1i}}{\partial t} \tag{1}$$

Especially in case of a non-linear reaction term, no analytical solution can be found. Unless no further simplification can be achieved, the determination of a rate constant would have to be based on a fitting algorithm including the time-consuming procedures for the numerical solution of the partial differential equation system.

However, the behaviour of the statistical moments can be studied by transforming the partial differential equation (PDE) system Eq. 1 into a system of ordinary differential equations (ODEs) of the statistical moments for each reactant, as shown previously [5] for simple second-order reactions:

$$u \cdot \frac{d\ln m_0}{dx} = m_{r0}$$

$$-u \cdot \frac{d\mu_1}{dx} + (q+1) = u \cdot \frac{d\ln m_0}{dx}(\mu_1 - \mu_{r1})$$

$$-u \cdot \frac{d\mu_2}{dx} + 2\left[\mu_1(q+1) + \frac{q}{k_f}\right]$$

$$= u \cdot \frac{d\ln m_0}{dx}(\mu_2 - \mu_{r2})$$

$$-u \cdot \frac{d\mu_3}{dx} + 3\left[\mu_2(q+1) + 2 \cdot \frac{q\mu_1}{k_f} + 2 \cdot \frac{q}{k_f^2}\right]$$

$$= u \cdot \frac{d\ln m_0}{dx}(\mu_3 - \mu_{r3})$$

$$-u \cdot \frac{d\mu_4}{dx}$$

$$+ 4\left[\mu_3(q+1) + 3 \cdot \frac{q\mu_2}{k_f} + 6 \cdot \frac{q\mu_1}{k_f^2} + 6 \cdot \frac{q}{k_f^3}\right]$$

$$= u \cdot \frac{d\ln m_0}{dx}(\mu_4 - \mu_{r4}) \tag{2}$$

This system of ordinary differential equations is generally valid for linear liquid chromatographic reactors. Its usefulness, however, depends on the possibility of calculating the "moments of the reaction", μ_{ri}. These are formal applications of the definition of the moments to the reaction term, and in irreversible reactions they contain only the peak shape equations and reaction orders:

$$\mu_{ri} = \frac{\int_0^\infty \prod_{j=1}^l \Psi_j^{\alpha_j} t^i \, dt}{\int_0^\infty \prod_{j=1}^l \Psi_j^{\alpha_j} \, dt} \tag{3}$$

For an autocatalytic reaction:

$$\mu_{ri} = \frac{\int_0^\infty \Psi_C \Psi_R t^i \, dt}{\int_0^\infty \Psi_C \Psi_R \, dt} \tag{3a}$$

If the degradation of the peaks due to the reaction is not too large (as it might be with reversible reactions), then empirical pulse-shape equations can be applied to approximate these terms, and the ordinary differential equation system can be solved numerically, i.e., by the Runge–Kutta method.

Therefore, Eq. 1 was investigated by a finite difference method in order to estimate the distortion especially of the catalyst peak during the reaction. A Craig-like finite difference scheme [6] was used, where the step width in the time direction was evaluated from the spatial number of grid points and the void time: $\Delta t/t_0/n_x$. The spatial number of grid points was chosen in such a way that the peak with the narrowest variance was formed by the so-called numerical diffusion, i.e., the diffusion-like acting numerical error due to a limited number of grid points. The mass transfer coefficients of the other peaks were then adapted to meet their individual variances with the given spatial step width of the grid. Care has

to be taken that the mass transfer coefficients evaluated in this way do not interfere with the chemical reaction.

It was found (cf., Fig. 1) that there is a profound distortion of the catalyst peak during its overlay with the reactant; however, even this distorted peak can still be approximated by a monotonous empirical peak-shape equation [7], i.e., the Gram–Charlier series (GCS) can be used for the evaluation of the moments of the reaction in Eq. 2.

Further simplifications and even an analytical solution of Eq. 2 can be achieved if it is assumed that the influence of the third and fourth moments on the conversion can be neglected for sufficiently small conversions and, moreover, that also the deviation of the first moments and second central moments from linearity can be neglected, i.e., a Gaussian distribution with a linear dependence of its moments on the spatial coordinate is assumed for the pulse shape.

Then, the first equation of Eq. 2, together with the linear dependence of the first and the second central moments from the chromatographic process, can be used to derive an analytical function for the dependence of the zeroth moments on the inlet amounts and the reaction duration:

$$\ln\left(\frac{m_R}{m_{R0}}\right) - \ln\left(\frac{m_{R0} + m_{C0} - m_R}{m_{C0}}\right)$$
$$= \frac{k_a t_0}{|\mu_{R1} - \mu_{C1}|}(m_{R0} + m_{C0}) \qquad (4)$$

As in the case of a simple second-order reaction with two different reactants, there is no dependence of the conversion either on the difference in the injection times of both reaction partners or on their individual variances, as long as the faster reactant completely overtakes the slower one within the column. It should also be mentioned that there is a striking similarity to the analogous equation for an autocatalytic batch reaction (see textbooks of physical chemistry):

$$\ln\left(\frac{c_R}{c_{R0}}\right) - \ln\left(\frac{c_{R0} + c_{C0} - c_R}{c_{C0}}\right) = kt(c_{R0} + c_{C0})$$
$$(4a)$$

The concentrations in Eq. 4a correspond to the concentration–time areas or zeroth moments in Eq. 4, and the reaction duration t corresponds to the ratio of the void time to the difference of the retention times of the reactants, $t_0/|(\mu_{R1} - \mu_{C1})|$.

3. Results and conclusions

Summarizing the previous part of this paper, the following suggestions for the determination of the rate constant were introduced: numerical solution of the PDE Eq. 1; numerical solution of the ODE Eq. 2 with a GCS for the moments of the reaction; numerical solution of the ODE Eq. 2 with a Gaussian for the moments of the reaction; and analytical solution (Eq. 4) of Eq. 2, assuming a Gaussian with a linear dependence of its central moments on the spatial coordinate for the moments of the reaction.

Since the other equations originate from the PDE Eq. 1 by introducing simplifications of increasing degree, they can only be applied in a range where they are in agreement with the results of Eq. 1. Therefore, three essential cases were evaluated in investigating the possibilities of determining rate constants from autocatalytic reactions using liquid chromatographic equip-
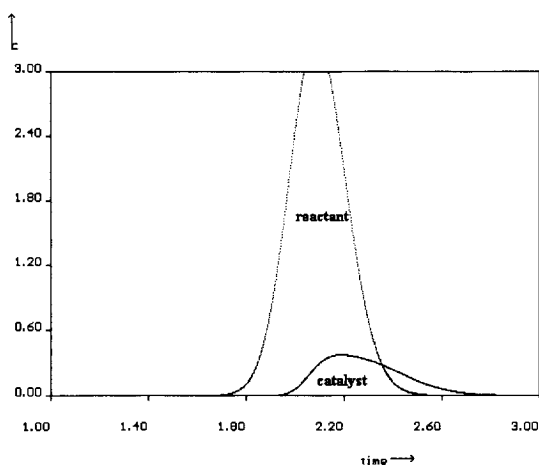

Fig. 1. Distortion of the catalyst peak during the overlay within the column [simulation for case (b): $m_{R0} = 1$, $m_{C0} = 0.1$, at $x/l = 0.4$ with the finite difference method].

ment: (a) moderate rate constants and comparable magnitudes of the molar inlet amounts of the reactant and the catalyst; (b) large rate constants and the reactant in large excess with respect to the catalyst; and (c) small rate constants and the catalyst in large excess with respect to the reactant. The resulting conversions from the different calculation methods are compared in Figs. 2–4.

It was found that there is in general a coincidence between the results from the finite difference method (PDE) and the solution of Eq. 2 using a GCS function as an approximation for the peak-shape equation. Using the Gaussian distribution as the approximate pulse-shape equation, there are no significant deviations from the PDE solution, except in case (b) and with high conversions.

In case (a), it seems that the deviations of the GCS and the Gaussian solution of Eq. 2 differ by the same amount, but in opposite directions, from the finite difference solution. Therefore, the calculations were repeated with a spatial grid point number of 10 000, because then the nu-
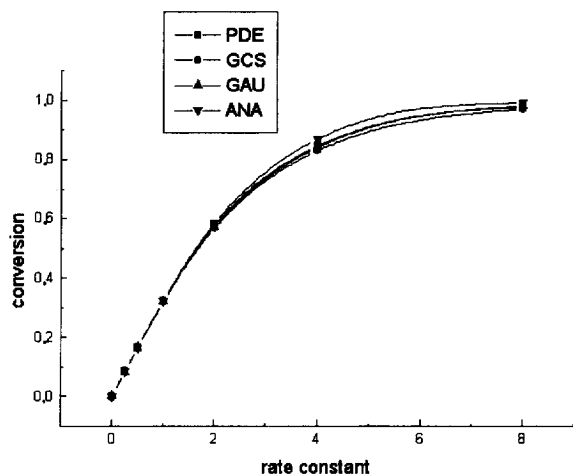

Fig. 3. Comparison of the dependence of the conversion with respect to the reactant on the rate constant [case (b): $m_{R0} = 1$, $m_{C0} = 0.1$]. Parameters as in Fig. 2.

merical diffusion can be neglected and the same mass transfer coefficients as in the GCS-solution are applied. As can be seen from Fig. 5, the differences between the conversions disappear almost completely.

Surprisingly, the results of the approximate analytical solution in Eq. 4 are not significantly different from the other results for small to medium conversions, although there is the rigid additional assumption of linear variances, which

Fig. 2. Comparison of the dependence of the conversion with respect to the reactant on the rate constant [case (a): $m_{R0} = m_{C0} = 1$]. $\mu_{1R} = 5$, $\mu_{1C} = 2$, $\Delta t = 0.5$, $k_{fR} = k_{fC} = 0.015$ (in GCS calculations). PDE: solution of Eq. 1 by a variance-adapted finite difference method. GSC: solution of Eq. 2 with a Gram–Charlier series for the peak shape. GAU: solution of Eq. 2 with a Gaussian distribution for the peak shape. ANA: conversion as obtained by Eq. 4.
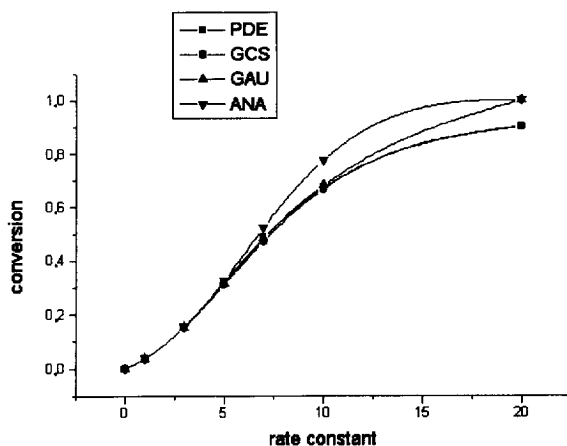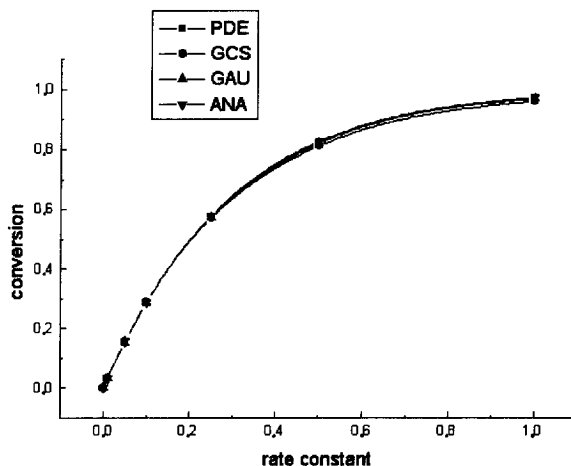

Fig. 4. Comparison of the dependence of the conversion with respect to the reactant on the rate constant for three different inlet amount ratios of catalyst and reactant [case (c): $m_{R0} = 1$, $m_{C0} = 10$]. Parameters as in Fig. 2.
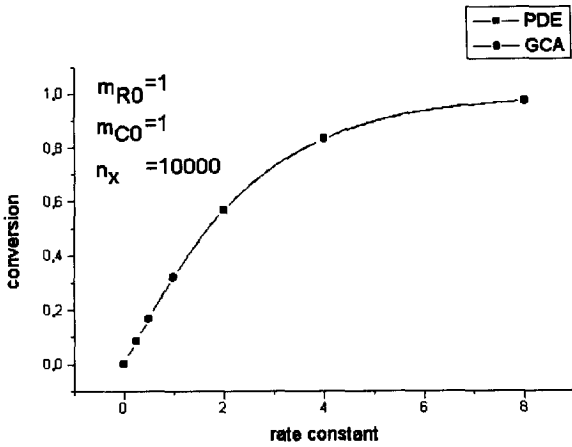
Fig. 5. Comparison of the dependence of the conversion with respect to the reactant on the rate constant [case (a)]. Parameters as in Fig. 2; PDE calculation with 10 000 steps in spatial direction.

is not valid at all with high conversions (Fig. 6). Consequently, it exhibits a marked deviation from the PDE result especially in case (b), but only a slight deviation in case (c).

The simulations demonstrate that it is unnecessary to solve Eq. 1 numerically for the calculation of a rate constant for autocatalytic reactions running in a liquid chromatographic reactor. Even the GC solution of Eq. 2, although being most comparable to a finite difference solution of Eq. 1 with a large number of spatial grid points, is not required. The solution of Eq. 2 with a
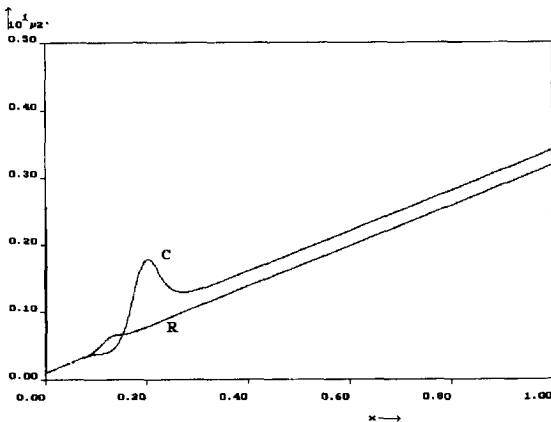

Fig. 6. Non-linearities in the dependence of the variances of the reactants on the column length during the overlay.

Gaussian for the calculation of the moment of the reaction will be sufficient in all practical cases.

However, the analytical solution Eq. 4 is able to substitute the numerical solutions for conversions ranging up to 30% in all cases, and almost completely in case (c). Additionally, in case (c) a further simplification of Eq. 4 becomes possible:

$$\ln\left(\frac{m_R}{m_{R0}}\right) = \frac{k_a t_0}{|\mu_{R1} - \mu_{C1}|} \cdot m_{C0} \qquad (5)$$

in which the ratio of the concentration–time areas on the left side can simply be substituted by the ratio of the reactant areas with a chemical reaction (overlaying the catalyst) and without a chemical reaction (not overlaying the catalyst). Measurements of this ratio with various catalyst amounts permit the determination of the rate constant from the slope of a plot of $\ln(m_R/m_{R0})$ vs. m_{C0}. Therefore, from the results of these simulations, it is recommended that one should choose the experimental conditions for the investigation of autocatalytic reactions in a liquid chromatographic reactor according to case (c).

Symbols

a_1	effective concentration in the stationary phase [mol/l]
c	concentration in the mobile phase [mol/l]
K	partition coefficient
k_f	mass transfer coefficient [1/s]
k_a	apparent rate constant, $k_a = k_m + k_s K_C q_R$ [1/mol · s]
k_s	rate constant (stationary phase) [1/mol · s]
k_m	rate constant (mobile phase) [1/mol · s]
l	length of the column [cm]
m_0	zeroth moment [mol/l s]
m_R	zeroth moment of the reactant (column end) [mmol/l s]
m_{R0}	zeroth moment of the reactant (column inlet) [mol/l s]
m_{C0}	zeroth moment of the catalyst (column inlet) [mol/l s]
m_{r0}	zeroth moment of the reaction [mol/l s]
n_x	number of spatial grid points

q	retention capacity
r	reaction terms
t	time [s]
v_0	void time [s]
u	linear flow rate [cm/s]
x	length coordinate [cm]
Δt	step width in time direction [s]
α_j	partial reaction order of the jth component
μ_i	absolute ith moments [s^i]
μ'_i	absolute ith central moments [s^i]
μ_{ri}	ith moment of the reaction [s^i]
Ψ_j	peak-shape equation of the jth component

GCS Gram–Charlier series
$$\Psi = 1/\sqrt{(2\pi\mu'_2)} \exp(-z^2/2)[1 + S/6(z^3 - z) + E/24(z^4 - 6z^2 + 3)]$$
$$S = \mu'_3/\sqrt{\mu'^3_2}$$
$$E = (\mu'_4 - 3\mu'^2_2)/\mu'^2_2$$

GAU Gaussian distribution
$$\Psi = 1/\sqrt{(2\pi\mu'_2)} \exp(-z^2/2)$$
$$z = (t - \mu_1)/\sqrt{\mu'_2}$$

Indices

C	catalyst
R	reactant
P	product

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