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Frontal analysis method to determine competitive adsorption isotherms

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Abstract

In order to design and to optimise preparative separations, the knowledge of the underlying thermodynamic functions, i.e., the adsorption isotherms, is the most essential information. Usually these functions cannot be predicted and various methods have been suggested to determine them experimentally. In particular, dynamic methods are attractive regarding time requirements and reliability. Frontal analysis (FA) is frequently applied to measure single solute isotherms. The theoretical background of this method is offered by the classical equilibrium theory of adsorption. Although this theory also explains the shape of multicomponent breakthrough curves, FA is only seldom applied to determine competitive isotherms. In this work FA was used to measure adsorption isotherms of three components as single solutes and in binary and ternary mixtures in a reversed-phase system. The obtained equilibrium data were correlated using the competitive Langmuir isotherm equation, a bi-Langmuir model, the ideal adsorbed solution theory and the real adsorbed solution theory. No substantial improvement of the predictions was achieved using the more complex models instead of the most simple Langmuir model. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Preparative chromatography has become a more and more important separation process for the purification of pharmaceuticals and other value added products. Higher requirements on product purities, growing importance of enantioseparations and im-

proved availability of highly selective stationary phases mainly promote this trend. However, chromatographic techniques are expensive and require on an industrial scale a careful optimisation of the operating conditions with respect to production rates, recoveries and separation costs. The most common technique used in preparative chromatography is still batch elution, however more sophisticated concepts such as recycling, displacement or the simulated moving bed process are increasingly applied to enhance yields and productivities [1]. The design of these processes is not an easy task. In different reviews devoted to theoretical aspects of non linear

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chromatography it was concluded, that an adequate simulation of a chromatographic separation process requires mainly reliable information on how the components of a mixture to be separated are distributed under equilibrium conditions between the mobile and stationary phases [2–5]. For a constant temperature this information is represented by adsorption isotherms. In general these functions can be determined only experimentally. Despite the fact that there are several experimental methods available, their application is still far away from being a routine job. In several papers different experimental methods have been compared and evaluated [6–12]. Often only the single solute isotherms are determined experimentally and the competitive isotherms are then predicted using isotherm models. However, often it was shown that the available theoretical concepts offer only limited accuracy and the experimental determination of at least a few multi-component equilibrium data is recommended. Unfortunately, in this area the number of reliable methods is smaller. Classical static methods have been frequently used [13] as well as perturbation methods [14,15]. Although frontal analysis (FA) can be considered to be a standard tool for measuring single solute isotherms and its potential to measure competitive isotherms has been known a long time [5] this method is only seldom applied to determine competitive isotherms.

In this paper the main equations needed to determine equilibrium data from multicomponent breakthrough curves are briefly revised in the frame of the classical equilibrium theory. Their application is demonstrated for the measurement of isotherms of three components as single solutes and in binary and ternary mixtures in a reversed-phase system. To follow the individual concentration fronts at the column outlet UV detection at different wavelengths was used.

In order to simulate chromatographic processes in fixed beds equilibrium data have to be represented by suitable isotherm models. There are several theoretical concepts available [6]. In this work the obtained data were correlated using the classical Langmuir equation and its extension assuming two different adsorption sites. Further, the ideal adsorbed solution theory (IAS [16,17]) and its extension taking into account the real behaviour of the adsorbed phase

(real adsorbed solution theory, RAS [18]) were applied.

2. Theory

2.1. Basics of equilibrium theory

Most of the dynamic experimental methods to determine adsorption isotherms rely on the analysis of the primary data on the classical equilibrium theory of chromatography. This powerful theory is explained in detail in a number of excellent papers [4,19–23] and monographs [5,24–26]. The general concept is based on considering just convection and equilibrium distribution between the two phases in a fixed bed. Kinetic effects causing band broadening are completely neglected. Thus, the concept is often also called the ideal model [5]. The shape of elution profiles and breakthrough curves predicted by the equilibrium theory is directly related to the course of the adsorption isotherms. This offers the key to also solve the inverse problem consisting in the determination of the isotherms from measured elution profiles or breakthrough curves. After briefly introducing the basic equations of the equilibrium theory this aspect will be considered below.

The basic equation of the equilibrium theory is the following mass balance for a component i and a volume element in a fixed bed:

$$\frac{\partial c_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial q_i(\bar{c})}{\partial t} + u \cdot \frac{\partial c_i}{\partial x} = 0; i = 1, N \quad (1)$$

In this equation c stands for the concentration in the fluid phase, q for the concentration in the solid phase, ε for the column porosity, u for the linear velocity and t and x are the time and space coordinates, respectively. In Eq. (1) it is assumed that the column efficiency is infinite and that the two phases are constantly in equilibrium expressed by the isotherm $q_i = q_i(\bar{c})$.

The solution of the system of partial differential Eq. (1) for different initial and boundary condition and for different adsorption isotherm models has been studied intensively in the last decades. In particular the method of characteristics has been applied successfully [25,26]. Thus, knowing the adsorption

isotherms elution profiles and breakthrough curves can be predicted. Often the classical Langmuir model (Eq. (2)) has been used offering the possibility to derive elegant analytical solutions based on appropriate transformations [24–26]:

$$q_i(\bar{c}) = q_{S,i} \cdot \frac{b_i c_i}{1 + \sum_{j=1}^N b_j c_j}; i = 1, N \quad (2)$$

The initial and boundary conditions characterising FA are specified by two different constant states:

Initial conditions:

$$c_i(t = 0, x) = c_i^{\text{Init}}; i = 1, N \quad (3)$$

Boundary conditions:

$$c_i(t, x = 0) = c_i^{\text{Feed}}; i = 1, N \quad (4)$$

The problem defined by Eqs. (1), (3) and (4) is a classical Riemann problem [25,26].

Figs. 1 and 2 illustrate typical effluent profiles for a ternary system ($N=3$) as predicted by the equilibrium theory. Fig. 1 shows the adsorption on an initially non preloaded column ($c_i^{\text{Feed}} > c_i^{\text{Init}}, c_i^{\text{Init}} = 0$) and Fig. 2 shows the process of total regeneration of an initially preloaded column ($c_i^{\text{Feed}} < c_i^{\text{Init}}, c_i^{\text{Feed}} = 0$). In both cases the initial and feed states are divided

by two ($N-1$) characteristic intermediate states (II and III). Due to the self-sharpening character of adsorption fronts for systems of the Langmuir type the transitions between the four states occur in Fig. 1 at three (N) characteristic retention times (t_R^1, t_R^2 and t_R^3) as shocks. The displacement effect triggers the typical overshooting of some effluent concentrations. The corresponding transition for the desorption process happens in a smoother manner. Equivalent averaged retention times of the simple waves can be calculated from mass balance considerations. Provided the adsorption isotherms are known the equilibrium theory (based on Eq. (1)) allows one to calculate the characteristic intermediate plateau concentrations ($c_i^{\text{II}}, c_i^{\text{III}}, \dots, c_i^N$), the retention times of the shocks ($t_{R,S}^1, t_{R,S}^2, \dots, t_{R,S}^N$), the shape of the waves and their averaged retention times ($t_{R,av}^1, t_{R,av}^2, \dots, t_{R,av}^N$). The latter mark the times where hypothetical shocks would fulfil the constraints set by the component mass balances. Well known equations describing the velocities of a shock and the velocity of a certain concentration in a wave can be derived from Eq. (1):

$$u_{i,S} = \frac{u}{1 + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\Delta q_i}{\Delta c_i}} \quad (5)$$

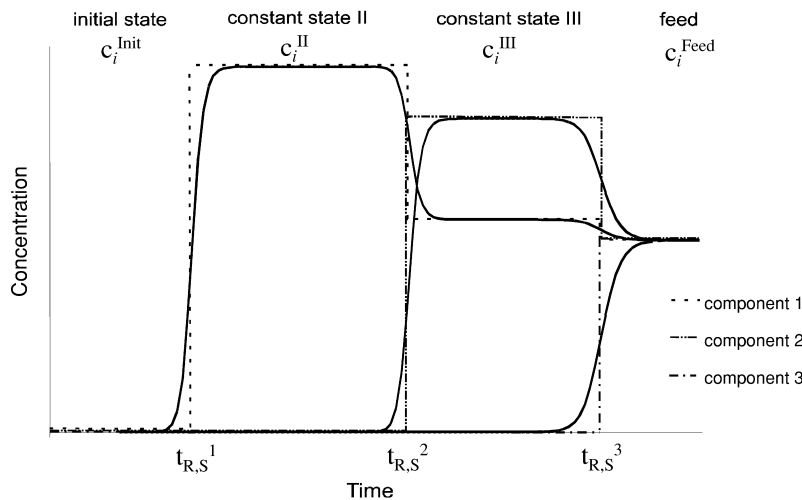


Fig. 1. Schematic representation of characteristic fronts for the adsorption on a non preloaded column ($c_i^{\text{Feed}} > c_i^{\text{Init}} = 0$). Ternary mixture ($i = 1, 2, 3$). Langmuir model (Eq. (2)). Dashed and dotted lines are predictions of equilibrium theory. Solid lines are the corresponding results of the equilibrium dispersive model (Eq. (7), D_{ap} corresponded to $N_p = 500$).

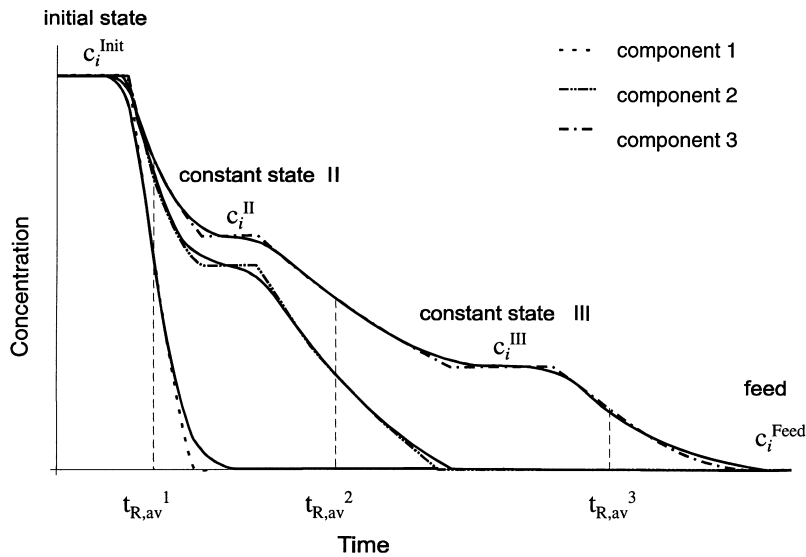


Fig. 2. Schematic representation of characteristic fronts for the desorption of a preloaded column ($c_i^{\text{Feed}} = 0 < c_i^{\text{Init}}$). Ternary mixture ($i = 1, 2, 3$). Langmuir model (Eq. (2)). Dashed and dotted lines are predictions of equilibrium theory. Solid lines are the corresponding results of the equilibrium dispersive model (Eq. (7), D_{ap} corresponded to $N_p = 500$).

$$u_i(\bar{c}) = \frac{u}{1 + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{dq_i(\bar{c})}{dc_i}} \quad (6)$$

2.2. Equilibrium dispersive model

The equilibrium model (Eq. (1)) was often found to be capable to predict overloaded elution in a very realistic manner. This holds, although an essential assumption of the equilibrium theory (i.e., the columns possess an infinite number of theoretical plates) is usually far too optimistic. The main reason for the success of the equilibrium model is the fact that in the non linear range of the isotherms the band shapes are determined mainly by thermodynamics. To include and evaluate the magnitude of additional kinetic effects the simple equilibrium dispersive model (Eq. (7)) was proven to be a useful tool [5]. In this model all contributions leading to band broadening (e.g., axial dispersion, finite rate of mass transfer processes) are lumped in a simplified manner into an apparent dispersion coefficient, D_{ap} :

$$\frac{\partial c_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial q_i(\bar{c})}{\partial t} + u \cdot \frac{\partial c_i}{\partial x} = D_{\text{ap}} \cdot \frac{\partial^2 c_i}{\partial x^2}, \quad (7)$$

$i = 1, N$

For efficient columns of length L the well known relation between D_{ap} and the number of theoretical plates N_p holds [5]:

$$N_p = \frac{uL}{2D_{\text{ap}}} \quad (8)$$

In addition to the predictions of the equilibrium theory Figs. 1 and 2 present also the numerically calculated predictions of the equilibrium dispersive model (Eq. (7)) for $N_p = 500$ (solid lines). Obviously, the deviations are not very big. In any case the typical features of the concentration–time profiles are already very well described by the much simpler equilibrium model (Eq. (1)).

2.3. Frontal analysis and equilibrium theory

The determination of adsorption isotherms from frontal analysis is just the inverse problem compared to the prediction of breakthrough curves from known isotherms. Since the equilibrium theory provides a convenient tool to predict characteristic features of such curves (intermediate plateau concentrations and retention times of shocks) only these data have to be determined experimentally to solve this inverse

problem. This concept is applied as a standard tool to determine single solute isotherms from the concentration dependence of the retention times of the breakthrough fronts. Less work was done to exploit the concept to determine competitive isotherms. One reason is obviously that in this case also the composition of intermediate plateaus has to be measured. Examples where the concept was applied have been published, e.g., by Jacobson and co-workers [9–11]. To determine whole isotherms (or isotherm branches) successive step changes at the column inlet (increasing and/or decreasing concentrations) have to be performed and the resulting breakthrough curves have to be analysed to determine the following characteristic features: (i) $N-1$ intermediate plateau concentrations: $c_i^{\text{II}}, c_i^{\text{III}}, \dots, c_i^{\text{N}}$; (ii) N retention times of shock fronts: $t_{\text{R,S}}^1, t_{\text{R,S}}^2, \dots, t_{\text{R,S}}^N$ or (iib) N averaged retention times of dispersed fronts (hypothetical shocks): $t_{\text{R,av}}^1, t_{\text{R,av}}^2, \dots, t_{\text{R,av}}^N$

The possibility that both shocks and dispersed fronts as composites appear [24–26] is not discussed here.

Provided the initial loadings (q_i^{Init}), the column porosity ε and the linear velocity u (or the dead time t_0) are known, Eq. (5) can be used to determine the unknown loadings q_i^{Feed} in equilibrium with all c_i^{Feed} according to the following relations:

$$q_i^{\text{Feed}}(\bar{c}^{\text{Feed}}) = q_i(\bar{c}^{\text{Init}}) + \frac{(t_{\text{R},i}^* - t_0)(c_i^{\text{Feed}} - c_i^{\text{Init}})}{\frac{1-\varepsilon}{\varepsilon} \cdot t_0}; i = 1, N \quad k = 2, N \quad (9)$$

with

$$t_{\text{R},i}^* = \frac{t_{\text{R}}^1(c_i^{\text{II}} - c_i^{\text{Init}}) + t_{\text{R}}^2(c_i^{\text{III}} - c_i^{\text{II}}) \dots + \dots + t_{\text{R}}^{k-1}(c_i^k - c_i^{k-1}) + t_{\text{R}}^k(c_i^{\text{Feed}} - c_i^k)}{c_i^{\text{Feed}} - c_i^{\text{Init}}},$$

$$t_0 = \frac{L}{u}, c_i^{k=1} = c_i^{\text{Init}}$$

At this point it should be mentioned that of course also the whole information of dispersed fronts can be analysed to determine adsorption isotherms using the equilibrium theory. This is the basis of the so called ECP method (elution by characteristic point) [5,7]. However, to apply this method very efficient columns are needed since kinetic effects also influence the shape of the profiles. An analysis based on Eq. (9) just using the retention times of shocks or

averaged retention times of dispersed fronts and intermediate plateau concentrations is not sensitive to kinetic effects as long as the required intermediate plateau concentrations can still be identified (i.e., the plateaus are not eroded completely by kinetic effects).

2.4. Adsorption isotherm models

Besides the classical Langmuir model given in Eq. (2) many other isotherm equations have been suggested, e.g., see Ref. [27]. To describe the separation of enantiomers frequently the following bi-Langmuir equation was found to be applicable [5,6]:

$$q_i = q_{\text{S},i}^a \cdot \frac{b_i^a c_i}{1 + \sum_{j=1}^N b_j^a c_j} + q_{\text{S},i}^b \cdot \frac{b_i^b c_i}{1 + \sum_{j=1}^N b_j^b c_j}; i = 1, N \quad (10)$$

A more general concept to describe competitive adsorption isotherms relying on the knowledge of the pure component isotherms is offered by the IAS theory [16,17]. This theory allows the calculation of competitive isotherms from single solute isotherms, $q_i^0 = q_i^0(c_i^0)$, without additional parameters. The usually implicit set of equations defining the isotherm model is shortly summarised below.

A modified spreading pressure Π_i is defined by:

$$\Pi_i(\tilde{c}_i^0) = \int_0^{\tilde{c}_i^0} \frac{q_i^0(c_i^0)}{c_i^0} \cdot dc_i^0; i = 1, N \quad (11)$$

The \tilde{c}_i^0 values are fictitious concentrations for the pure components at which these components would possess the same spreading pressure Π_{mix} alone as the mixture. Thus holds:

$$\Pi_{\text{mix}} = \Pi_i; i = 1, N \quad (12)$$

Raoult's law relates the molar fractions in the adsorbed phase z_i to the concentrations in solution:

$$c_i = z_i \tilde{c}_i^0(\Pi_{\text{mix}}); i = 1, N \quad (13)$$

As the sum of the molar fractions must be unity it further holds:

$$\sum_{i=1}^N \frac{c_i}{\tilde{c}_i^0} = 1 \quad (14)$$

For a given set of liquid phase concentrations c_i , $i=1, N$, Eqs. (11)–(14) can be solved (usually only numerically) in a first step to give the \tilde{c}_i^0 and z_i . The corresponding equilibrium concentrations of the solid phase, q_i , are then given by:

$$q_i = z_i q_{\text{tot}}; i = 1, N \quad (15)$$

with

$$\frac{1}{q_{\text{tot}}} = \sum_{j=1}^N \frac{z_j}{q_j^0(\tilde{c}_j^0)} \quad (16)$$

An advantage of the IAS theory is that no constraints concerning the structure of the single component isotherm equations exist. However, from a theoretical point of view its applicability is restricted to diluted solutions. The prediction of adsorption equilibria for concentrated solutions requires the consideration of possible solute–solute interactions and the formation of real adsorbed phases. The latter aspect can be treated by introducing into Eq. (13) adsorbed phase activity coefficients, γ_i , leading to the RAS theory [18]:

$$c_i = \gamma_i z_i \tilde{c}_i^0(\Pi_{\text{mix}}); i = 1, N \quad (17)$$

The activity coefficients, γ_i , are concentration dependent and have to fulfil consistency requirements set by the Gibbs–Duhems equation [18]:

$$\sum_{i=1}^N z_i d \ln \gamma_i = 0 \text{ for } \Pi_{\text{mix}} = \text{const. and } T = \text{const.} \quad (18)$$

For a binary system Eq. (18) can be formulated as follows:

$$\left. \frac{\partial \ln \gamma_1}{\partial z_1} z_1 = - \frac{\partial \ln \gamma_2}{\partial z_1} \right|_{z_2} \quad (19)$$

for $\Pi_{\text{mix}} = \text{const. and } T = \text{const.}$

Eq. (19) expresses the relation between the two adsorbed activity coefficients, γ_1 and γ_2 , for a binary mixture stating an opposite dependence on z_1 . For dilute solutions and for low spreading pressures the activity coefficients approach unity. Several models have been suggested (e.g., Margules and Wilson models [28,29]). In this work the following equation

proposed in Ref. [30] and based on regular solution theory [31] was applied:

$$\ln \gamma_i = \sum_j^N \sum_k^N (A_{ji}^1 - 1/2A_{jk}^1) \Phi_j \Phi_k$$

with

$$\Phi_i = \frac{z_i/q_i^0(c_i^0)}{\sum_j^N z_j/q_j^0(c_j^0)} \quad i = 1, N$$

$$A_{jk}^1 = \frac{1 - e^{C_{jk} \Pi_{\text{mix}}}}{q_i^0(c_i^0)} A_{jk}; A_{jk} = A_{kj}; A_{jj} = 0 \quad (20)$$

where A_{jk} and C_{jk} are adjustable parameters that have to be determined by matching theoretical and experimental binary equilibrium data. Numerical calculations revealed that Eq. (19) requires for a binary system $C_{12} = C_{21}$. For the total amount adsorbed holds according to the RAS theory (compare Eq. (16) for the IAS theory) [32]:

$$\frac{1}{q_{\text{tot}}} = \sum_{j=1}^N \frac{z_j}{q_j^0(\tilde{c}_j^0)} + \sum_{j=1}^N z_j \left(\frac{\partial \ln \gamma_j}{\partial \Pi_{\text{mix}}} \right)_{T,z} \quad (21)$$

The below measured equilibrium data were correlated with the Langmuir model (Eq. (2)), the bi-Langmuir model (Eq. (10)), the IAS theory (Eqs. (11)–(16)) and the RAS theory (Eqs. (11), (12), (14), (15), (17), (20), (21)).

3. Experimental

3.1. Chromatographic systems

The FA method was applied for the determination of equilibrium data and subsequently of isotherm model parameters for the three solutes phenol (PH) (Merck, Darmstadt, Germany), 2-phenylethanol (PE) and 3-phenyl-1-propanol (PP) (Fluka, Buchs, Switzerland). Experiments were carried out for all single solutes, for two binary mixtures (PH–PE and PE–PP) and for the ternary mixture. All solutes were applied as purchased. A reversed-phase material (Kromasil 100-5C₁₈, $d_p = 10 \mu\text{m}$, Eka Nobel, Sweden) was used as the stationary phase and methanol–water (50:50) mixtures as the mobile

phase. The column dimensions were 25 cm×0.46 cm. All measurements were performed at 21°C.

3.2. Set up

A conventional high-performance liquid chromatography (HPLC) system was used for the measurement of the breakthrough curves. The mobile phase was pumped by a HPLC pump (Knauer, 64.00, Berlin, Germany) through a six-port–three-way injection valve (Rheodyne, Berkeley, CA, USA) connected alternatively with different loops (0.1 ml, 0.3 ml or 1 ml) and the column. A second three-way valve placed before the HPLC pump permitted one to change between the mobile phase ($c_i^{\text{Init}}=0$) and the feed solution for the FA (c_i^{Feed}). The effluent from the analytical column was monitored by a UV diode-array detector (L3000, Merck–Hitachi, Darmstadt, Germany). More details concerning the set up including the determined and, in the data analysis, considered extracolumn volumes can be found elsewhere [33].

3.3. Procedures

In the first stage of the investigation the standard chromatographic parameters of the systems have been determined using conventional tracer experiments with the three solutes and the components of the binary mobile phase.

Subsequently, the detector was calibrated at 242.5 nm and at 292.5 nm. At 292.5 nm mainly PH and only slightly PP contribute to the spectrum. PE gives no signal at this wavelength.

Then the frontal analysis method was applied to determine the isotherms of the three single solutes. A sudden increase of the feed concentration was performed for an equilibrated unloaded column ($c_i^{\text{Feed}} > c_i^{\text{Init}}$, $c_i^{\text{Init}}=0$) by switching the three-way valve. After the breakthrough was recorded and the column was equilibrated with the feed solution the three-way valve was switched back to the pure mobile phase. Thus, the desorption fronts ($c_i^{\text{Feed}} < c_i^{\text{Init}}$, $c_i^{\text{Feed}}=0$) were also recorded. The same procedure was repeated for several feed concentrations. The maximum concentration studied was 40 g/l. About 30

breakthrough curves for each single solute were analysed in this concentration range. The characteristic retention times were calculated by integrating the breakthrough curves after the detector responses were transformed into concentrations.

Subsequently, systematic measurements of breakthrough curves for two binary systems (PH–PE and PE–PP, for each system 30 experiments for varying feed compositions: 9:1, 6:1, 3:1, 1:1; 1:3, 1:6, 1:9) and the ternary system (PH–PE–PP, 10 experiments with 1:1:1 mixtures) were performed. In the case of the binary systems the intermediate plateaus were formed just by one component. Thus, the concentrations could be determined from the corresponding calibration curves. For the ternary system intermediate plateaus form which contain two components. During the presence of these plateaus samples have been taken and their composition was analysed subsequently using the same column under analytical conditions.

After determining from Eq. (9) the equilibrium loadings of the single solutes a non linear regression based on Marquardt's method [34] was used to estimate the free parameters of Eqs. (2) and (10). Then, with the obtained parameters the corresponding loadings of the binary and ternary systems have been predicted using the IAS theory. Newton's method was applied to perform the iterations required to solve Eqs. (11)–(16) [33]. Subsequently, the set of RAS equations was used to describe the loadings for the two binary systems. The two free parameters, $A=A_{12}=A_{21}$ and $C_{12}=C_{21}$, describing the concentration dependence of the adsorbed phase activity coefficient (Eq. (20)) were estimated combining the iterative solution of the RAS Eqs. (11), (12), (14), (15), (17), (20) and (21)) with Marquardt's regression method. Details are given in Ref. [33].

Finally, a series of elution profiles was recorded using the injection valve. Several samples of different concentration and volume were injected. The purpose of these experiments was mainly to deliver a database to validate the determined isotherms and the fixed bed models (Eqs. (1) and (7)). For this, the theoretical chromatograms were transformed into theoretical detector response curves using the corresponding calibration factors. These curves were compared with the experimental response curves.

4. Results and discussion

4.1. Standard parameters

The determined total porosity of the column, ε , analytical retention volumes V_R^{analyt} , adsorption equilibrium constants, K , and the number of theoretical plates, N_p , are presented in Table 1. The elution order of the solutes is PH, PE and PP. The relative high number of theoretical plates (several thousand) indicates that the predictions of the equilibrium theory (assuming an infinite plate number) should be rather realistic.

4.2. Single solute isotherms

At first FA was performed for the single solutes. Typical breakthrough curves are given in Fig. 3 for PE. An increase of the feed concentration leads to earlier breakthroughs. The desorption fronts for this series of concentration overload coincide indicating

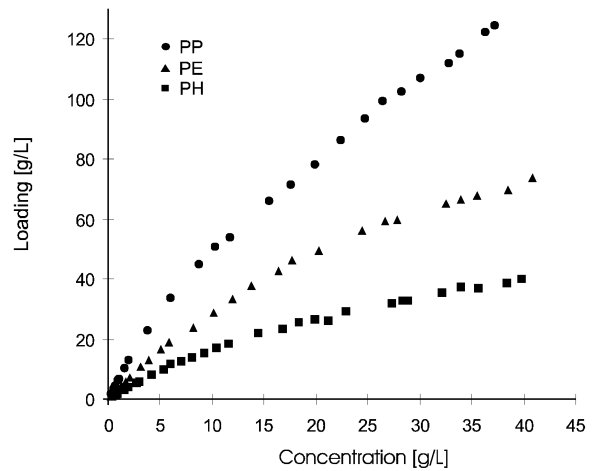


Fig. 4. Experimentally determined single solute adsorption isotherms of PH, PE and PP.

that the shape of the fronts is mainly determined by thermodynamics. The equilibrium loadings calculated from Eq. (9) are summarised in Fig. 4 for the

Table 1

Porosity ε , dead volume V_0 , plate number N_p , analytical retention volumes V_R^{analyt} , adsorption equilibrium constants K and retention factors k' of the single solutes

Single solute	ε	V_0	N_p	V_R^{analyt}	K	$k' = (V_R^{\text{analyt}} - V_0)/V_0$
PH	0.54 ^a	2.28 ^a	3500	6.51	2.15	1.76
PE			4000	9.20	3.61	2.96
PP			6000	15.25	6.85	5.62

^a From solvent peaks.

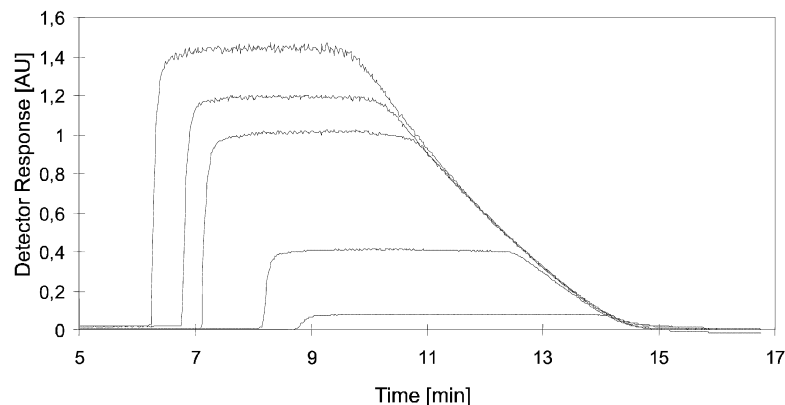


Fig. 3. Breakthrough curves of PE. $\dot{V} = 1$ ml/min, $c_{\text{PE}}^{\text{Feed}} = 1.06$ g/l, 5.87 g/l, 16.4 g/l, 20.3 g/l and 30.3 g/l (same injection volume).

three solutes. In agreement with the above mentioned elution order PP is best adsorbed and PH worst. The isotherms exhibit a significant deviation from linearity. The obtained data were correlated with the Langmuir model (Eq. (2)) and with the bi-Langmuir model (Eq. (10)). The parameters obtained from non linear regression based on Marquardt's method are summarised in Table 2. For the PH and PE isotherms there is no improvement in describing the experimental data using the more sophisticated bi-Langmuir model compared to the conventional Langmuir model. Only for the PP isotherm the expenditure of four compared to two parameters improved the fitting. However the reduction of the standard deviation was not very significant, thus the following analysis was performed exclusively on the basis of the Langmuir model.

4.3. Binary mixtures

A typical binary breakthrough experiment is illustrated in Fig. 5 for the mixture PH(1)–PE(2). The obtained detector response curves are given for the two wavelengths 242.5 and 292.5 nm. At 292.5 nm only PH is visible. In the first part of the experiment (adsorption step) one can see two typical steep fronts appearing at $t_{R,S}^1$ and $t_{R,S}^2$. Also the intermediate plateau c_1^{II} where the concentration exceeds the feed concentration, c_1^{Feed} , can be clearly recognised. The desorption step possesses a characteristic plateau concentration of the second component, c_2^{II} . The retention times equivalent to hypothetical shocks, $t_{R,av}^1$ and $t_{R,av}^2$ were estimated from matching the marked areas ($A_1 = A_2$ and $A_3 = A_4$) by integration.

Equilibrium loadings for the binary system PH and

Table 2
Parameters of the single solute isotherms for PH, PE and PP and accuracy of predicting of the competitive isotherms for various models

Parameter	PH	PE	PP
Single solutes			
Langmuir isotherm (Eq. (2))			
q_s (–)	72.36	146.5	216.4
b (1/g)	0.030	0.025	0.036
Standard deviation, σ (%)	1.3	1.1	4.8
Bi-Langmuir isotherm (Eq. (10))			
q_s^a (–)	36.38	73.41	287.2
b^a (1/g)	0.03	0.025	0.016
q_s^b (–)	35.97	73.41	15.42
b^b (1/g)	0.03	0.025	0.144
Standard deviation, σ (%)	1.3	1.1	3.3
Binary mixtures, standard deviation, σ (%)			
Multi-Langmuir isotherm (Eq. (2))	6.3	5.4	
IAS theory (Langmuir isotherm for single solutes)	14.6	3.3	
RAS theory (Langmuir isotherm for single solutes; parameter for activity coefficients: $A=0.68$ g/l; $C_{12}=C_{21}=1.37 \cdot 10^{-5}$ 1/g)	14.6	3.3	
Multi-Langmuir isotherm (Eq. (2))		11.2	5.8
IAS theory (Langmuir isotherm for single solutes)		6.7	8.9
RAS theory (Langmuir isotherm for single solutes; parameter for activity coefficients: $A=80.7$ g/l; $C_{12}=C_{21}=7.6 \cdot 10^{-4}$ 1/g)		4.8	7.7
Ternary mixture, standard deviation, σ (%)			
Multi-Langmuir isotherm (Eq. (2))	7.3	8.2	3.6

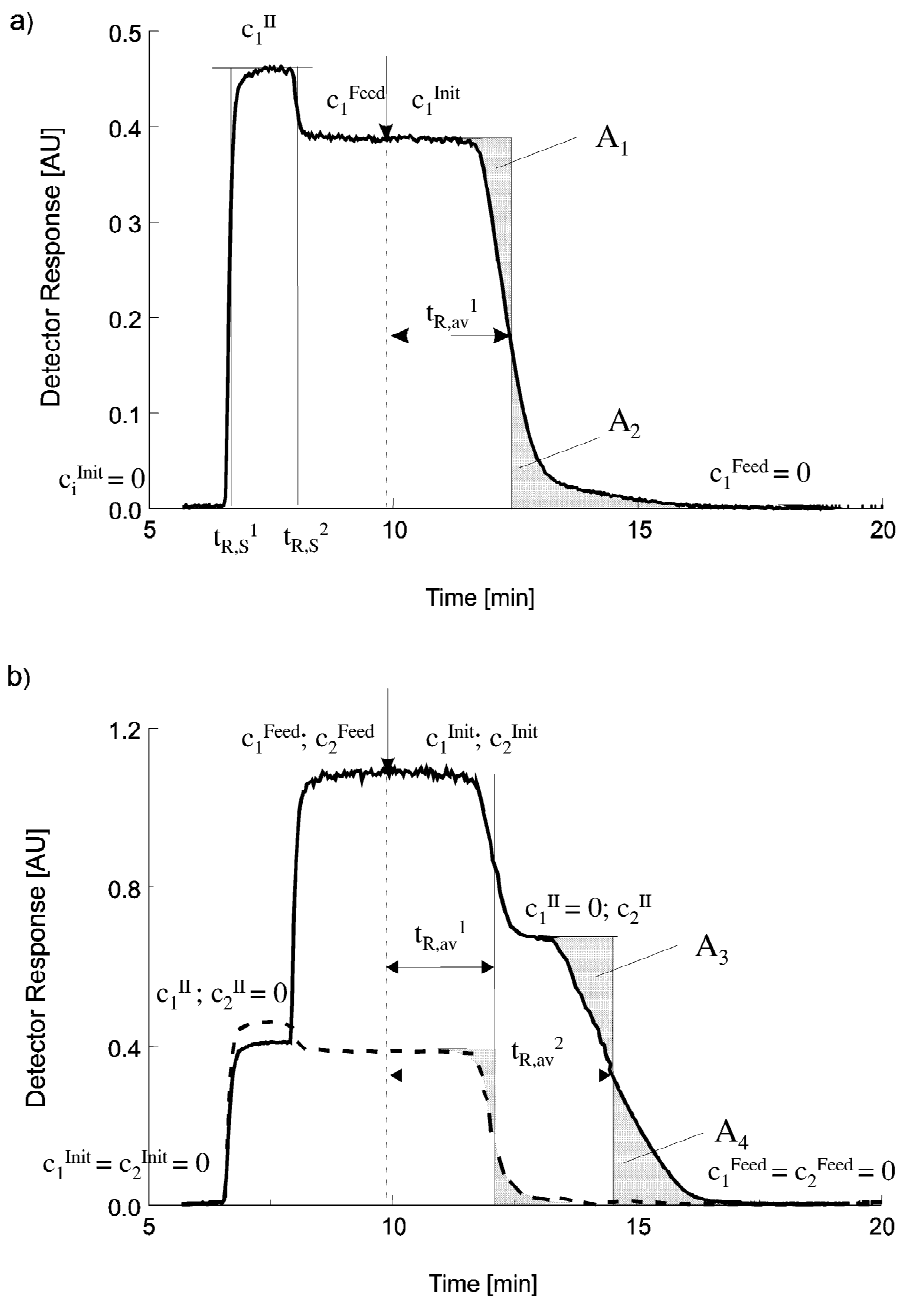


Fig. 5. Experimental breakthrough curves of a binary mixture PH(1)–PE(2). $c_{PH}^{Feed} = c_{PE}^{Feed} = 2$ g/l, $\dot{V} = 1$ ml/min. (a) Detector response at $\lambda = 292.5$ nm; (b) detector response at $\lambda = 292.5$ nm (only caused by PH, dotted line) and at $\lambda = 242.5$ nm (solid line).

PE obtained from frontal analysis experiments with 1:1 mixtures are shown in Fig. 6. A relatively good agreement was found comparing the loadings calculated from the adsorption and from the desorption

branches. The effect of competition is obvious when the results are compared with the also given corresponding single solute isotherms.

A typical comparison between the experimentally

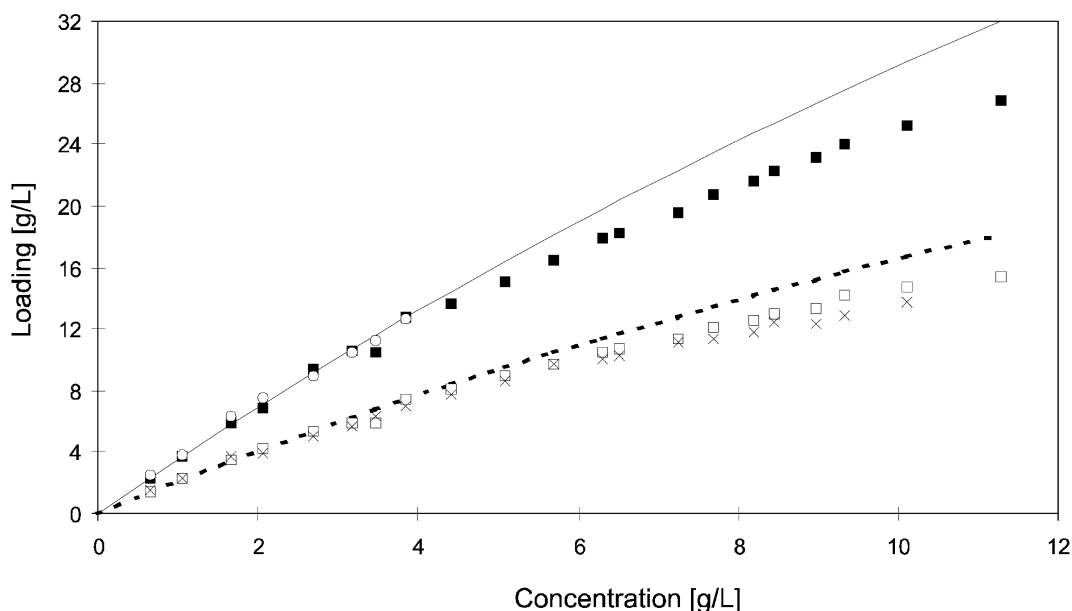


Fig. 6. Experimentally determined equilibrium loadings for binary systems of PH (■ = determined from adsorption fronts, ○ = determined from desorption fronts) and PE (□ = determined from adsorption fronts, × = determined from desorption fronts). The composition of the feed solutions was 1:1. Theoretical data of single solute isotherm as predicted by the Langmuir model (Eq. (2), parameters in Table 2) for PH (dotted line) and PE (solid line).

determined and theoretical loadings is shown in Fig. 7. Again the system PH–PE serves as the example. Simulations were done for the competitive Langmuir model, the IAS theory and the RAS theory. All theories were based on the same individual Langmuir parameters given in Table 2. Due to the different saturation capacities of the components there is a difference in the prediction of the competitive Langmuir model and the IAS theory. In principle due to the additional degrees of freedom the RAS theory always leads to improved results compared with the IAS theory. For the example shown in Fig. 7 the agreement with the measurements is best for the simple competitive Langmuir model. However, for other feed compositions the RAS theory was also found to be most superior. An overview of the standard deviations based on all experimentally determined and predicted loadings is given in Table 2. No general conclusion can be drawn. Just the surprising and encouraging fact can be noted that the most simple model is not inferior and leads for PH and PP to the best agreement. In Table 2 are also included the parameters A and C of the activity

coefficient model, Eq. (20), used in the RAS theory. The introduction of these parameters did not improve the predictions of the IAS for the PH–PE system. For the PE–PP system a slight improvement was achieved. The obtained parameters A and C correspond to activity coefficients located in the range between 1 and 1.06.

4.4. Ternary mixtures

The typical breakthrough behaviour of the ternary system is illustrated in Fig. 8. The characteristic fronts that have been predicted by the equilibrium theory (Figs. 1 and 2) can be identified. To ease the analysis of the experiments all breakthrough curves were recorded at both wavelengths. In this way the relevant retention times could be identified in a reliable manner. The concentrations of the intermediate plateaus have been determined from a separate analysis of samples that have been collected in the corresponding time interval.

The results of analysing 10 adsorption experiments with 1:1:1 mixtures are summarised in Table 3. Due

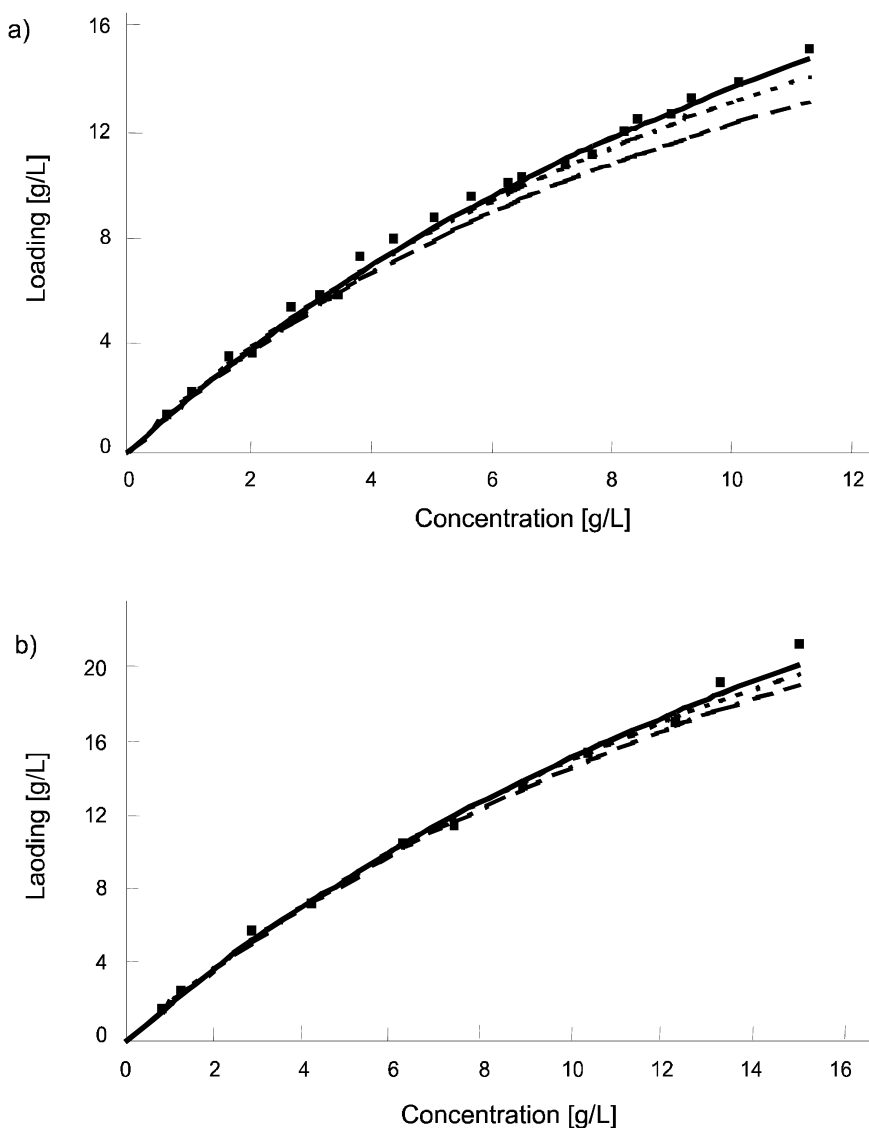


Fig. 7. Competitive isotherms for PH (a) and PE (b) in binary mixtures $c_{\text{PH}}^{\text{Feed}}:c_{\text{PE}}^{\text{Feed}} = 1:1$. Experimentally determined loadings (symbols) and theoretical data for the competitive Langmuir model (solid line), the IAS theory (dashed line) and the RAS theory (dotted line).

to the success of the simple competitive Langmuir equation only this model was used to predict the equilibrium loadings. The achieved agreement is visualised in Fig. 9. Obviously the results are not worse than the ones for the binary systems (e.g., Fig. 7). This is also confirmed by the standard deviations given in Table 2.

Finally, selected breakthrough curves and elution profiles were measured for the ternary mixture and

simulated with the equilibrium dispersive model. The comparison was done based in measured and theoretical signals at two wavelengths using the corresponding calibration curves. In Fig. 10 a typical example is shown for a large injection volume and the situation of complete breakthrough. Obviously both the isotherm and the simple fixed bed model are capable of representing the essential part of the process dynamics properly. This general conclusion

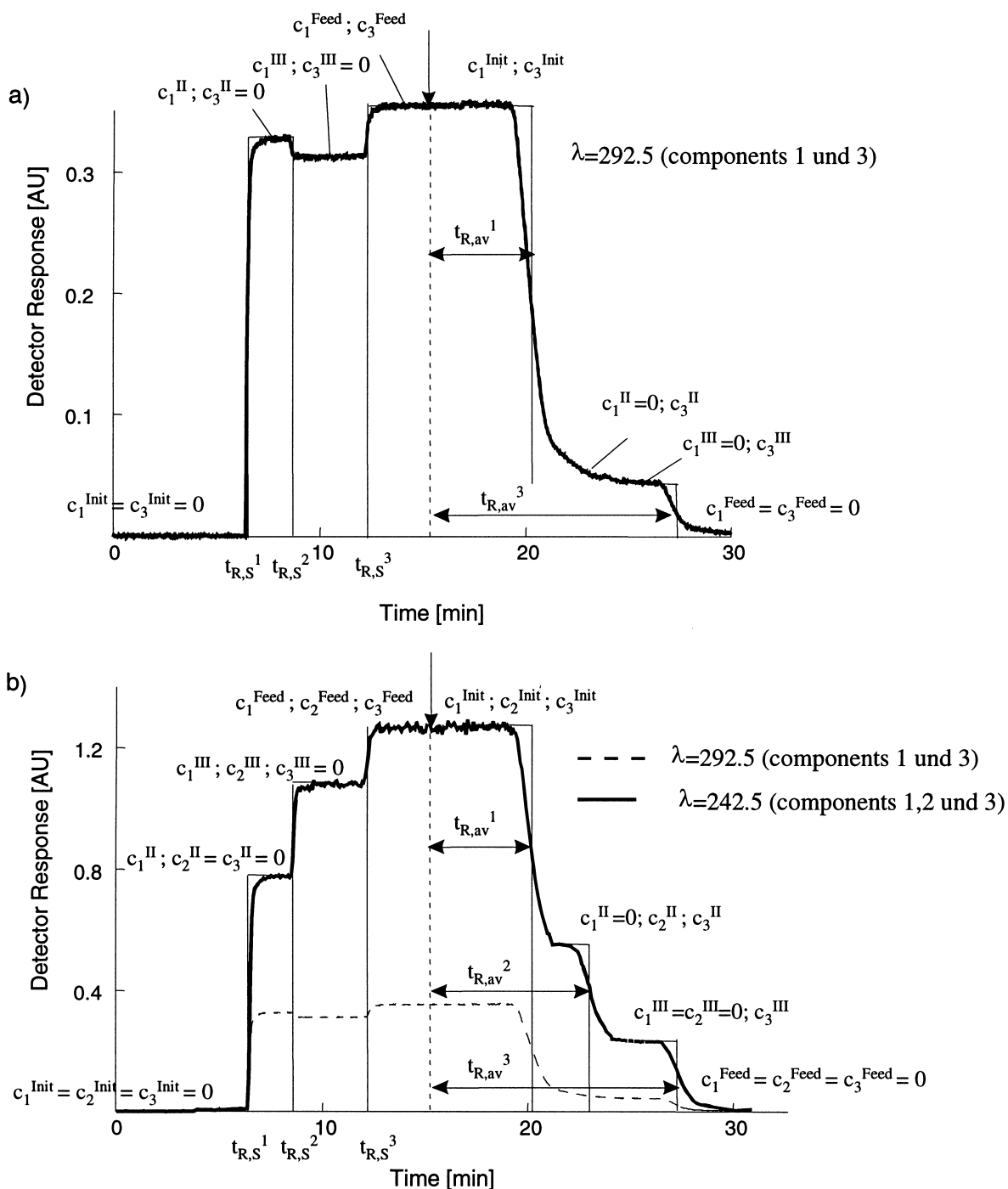


Fig. 8. Experimental breakthrough curves of a ternary mixture PH(1)–PE(2)–PP(3). $c_{PH}^{Feed} = c_{PE}^{Feed} = c_{PP}^{Feed} = 4.7$ g/l, $\dot{V} = 1$ ml/min. (a) Detector response at $\lambda = 292.5$ nm; (b) detector response at $\lambda = 292.5$ nm (dotted line) and at $\lambda = 242.5$ nm (solid line).

Table 3
Experimental data of the breakthrough experiments for the ternary system

Feed concentrations (g/l)			Plateau concentrations (g/l)			Retention times (min)			Loadings (Eq. (9)) (g/l)		
c_1^{Feed}	c_2^{Feed}	c_3^{Feed}	c_1^{II}	c_1^{III}	c_2^{III}	$t_{R,S}^1$	$t_{R,S}^2$	$t_{R,S}^3$	$q_1(\bar{c}^{\text{Feed}})$	$q_2(\bar{c}^{\text{Feed}})$	$q_3(\bar{c}^{\text{Feed}})$
0.58	0.58	0.60	0.58	0.58	0.60	6.36	8.95	14.81	1.20	1.91	3.85
0.98	0.98	1.00	1.00	0.99	1.00	6.17	8.63	14.18	1.93	3.20	6.24
1.98	1.98	2.04	2.00	1.99	2.10	6.05	8.42	13.30	3.84	6.05	11.79
3.24	3.24	3.33	3.40	3.30	3.50	5.91	8.11	12.25	5.71	9.17	17.19
4.27	4.27	4.40	4.40	4.20	4.80	5.89	7.85	11.7	7.91	11.17	21.61
4.68	4.68	4.82	4.90	4.70	6.03	5.78	7.98	11.75	7.82	10.83	23.06
6.06	6.06	6.25	6.50	6.20	7.90	5.49	7.37	10.28	9.47	13.30	26.19
7.00	7.00	7.60	7.50	7.30	9.02	5.26	6.92	9.98	9.92	13.74	30.65
8.07	8.07	8.32	9.00	8.50	11.01	5.26	6.88	9.92	11.21	14.92	33.70
8.97	8.97	9.24	10.00	9.50	12.27	5.15	6.69	9.87	11.86	15.37	37.18

was also confirmed for smaller injection volumes as shown in Fig. 11. However, in this case a considerable shift between the predicted and measured positions of the third shock front cannot be overlooked. A sensitivity analysis performed revealed the strong effect of small deviations in the isotherm parameters on the position of the shocks. Changes within the range of the standard deviations given in Table 2 caused considerable time shifts of the theoretical fronts (the effects were larger than the differences illustrated in Fig. 11). This emphasises

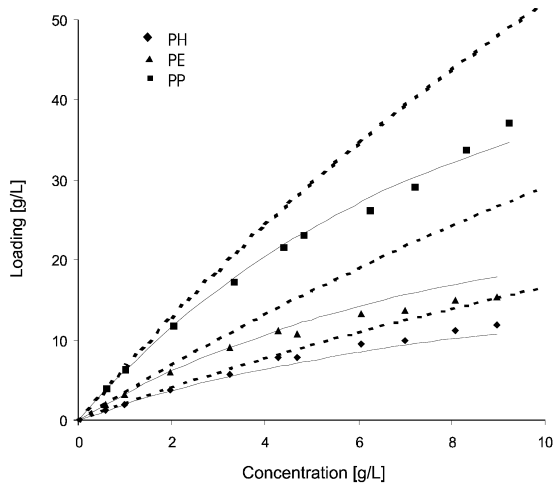


Fig. 9. Experimentally determined equilibrium data (symbols) for PH, PE and PP in ternary mixtures $c_{\text{PH}}^{\text{Feed}} : c_{\text{PE}}^{\text{Feed}} : c_{\text{PP}}^{\text{Feed}} = 1:1:1$, theoretical data of the competitive isotherms (solid lines) and single solute isotherms (dashed lines) calculated with the Langmuir model, Eq. (2).

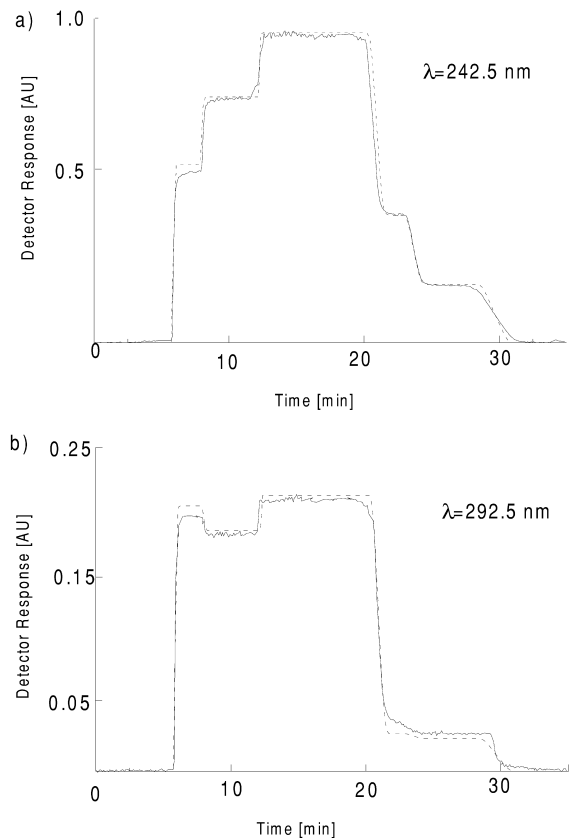


Fig. 10. Comparison of breakthrough curves for a ternary mixture of PH-PE-PP (1:1:1). $c_{\text{PH}}^{\text{Feed}} = c_{\text{PE}}^{\text{Feed}} = 3.24$ g/l, $c_{\text{PP}}^{\text{Feed}} = 3.33$ g/l, $\dot{V} = 1$ ml/min, $V_{\text{inj}} = 10$ ml, $N_{\text{p}} = 3000$. The predictions (dotted lines) were obtained using the equilibrium dispersive model (Eq. (7)) with the Langmuir model (Eq. (2)) using the calibration factors at two different wavelengths. (a) $\lambda = 242.5$ nm (where all three components contribute to the overall signal), (b) $\lambda = 292.5$ nm (where only PH and PP contribute).

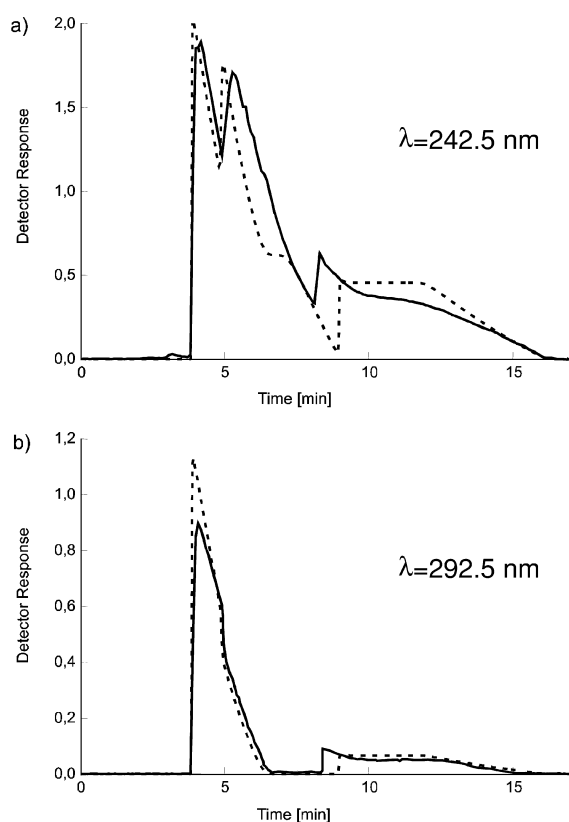


Fig. 11. Comparison of elution profiles for a ternary mixture of PH-PE-PP (1:1:3). $c_{\text{PH}}^{\text{Feed}} = c_{\text{PE}}^{\text{Feed}} = 20$ g/l, $c_{\text{PP}}^{\text{Feed}} = 60$ g/l, $\dot{V} = 1$ ml/min, $V_{\text{inj}} = 0.1$ ml, $N_{\text{p}} = 3000$. The predictions (dotted lines) were obtained using the equilibrium dispersive model (Eq. (1)) with the Langmuir model (Eq. (2)) using the calibration factors at two different wavelengths. (a) $\lambda = 242.5$ nm (where all three components contribute to the overall signal), (b) $\lambda = 292.5$ nm (where only PH and PP contribute).

the high requirements on the accuracy of isotherm measurements in order to achieve reliable band profile simulations.

5. Conclusions

Frontal analysis (FA) was found to be a useful method to quantify multicomponent adsorption equilibria. An essential supposition for an application of the method is that the intermediate plateaus can be identified and are not eroded by kinetic effects. Thus, efficient chromatographic columns are required. Since the compositions of the intermediate plateaus

have to be determined experimentally the availability of selective detectors would be most helpful.

The equilibrium data determined in this study could be described successfully using the simple competitive Langmuir model. Neither the IAS theory nor the RAS theory led to significant improvements. In particular the considerable efforts needed to apply the RAS theory with thermodynamically consistent activity coefficients did not pay off. However, this might be different for other systems.

6. Nomenclature

A	Parameter in Eq. (20)
b	Isotherm equation parameter (Eqs. (2) and (10))
c	Concentration
\tilde{c}	Fictitious concentration (IAS theory)
C	Parameter in Eq. (20)
D_{ap}	Apparent dispersion coefficient
K	Adsorption equilibrium constant
k'	Capacity factor, $k' = K(1 - \varepsilon)/\varepsilon$
L	Column length
N	Number of components
N_{p}	Number of theoretical plates
q	Loading
q_{s}	Saturation loading (Eqs. (2) and (10))
t	Time
u	Linear velocity
V	Volume
\dot{V}	Volumetric flow-rate
x	Space coordinate
z	Fraction in adsorbed phase

Greek symbols

ε	Porosity
Φ	Parameter in Eqs. (20) and (21) (RAS theory)
γ	Adsorbed phase activity coefficient
λ	Wavelength
Π	Modified spreading pressure

Subscripts

0	Value for a non retained component
av	Averaged value
mix	Mixture value
R	Retention

S Shock
tot Total value

Superscripts

o Single component value
analyt Analytical (diluted) conditions
av Averaged value
a, b Surface sites in Eq. (10)
Feed Feed state
Init Initial state
II, III Constant intermediate states

Acknowledgements

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