Effect of mobile phase composition on the SMB processes efficiency Stochastic optimization of isocratic and gradient operation

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Abstract

The solvent composition was adjusted in a theoretical study in order to maximize the efficiency of a simulated moving bed (SMB) process. The isocratic realization of the process as well as the solvent gradient mode were considered. The solvent composition and the flow rates were used as decision variables in a random search optimization algorithm known to be a reliable tool for nonlinear programming problems. The results of the optimization indicate that the optimal composition of the mobile phase depends strongly on the feed concentration. The asymmetry of the internal concentration profiles, which has a negative effect on the separation efficiency, can be partly damped by an increase of the solvent strength. In the cases studied the optimal solvent strength determined for concentrated feed streams is higher than that for diluted ones. Moreover, the optimum is strongly influenced by the value of the selectivity factor and its dependency on the mobile phase composition. Different results were obtained for cases, in which the separation factor increases with increasing the modifier concentration, than for cases, in which the separation factor decreases with increasing the modifier concentration. A similar analysis was performed for a solvent gradient SMB process, in which different solvents are used at the two inlet ports: a weak solvent in the feed stream and a strong solvent in the desorbent stream. Again the optimal mobile phase composition was strongly affected by the type of the isotherms and their non-linearity. The potential of a gradient SMB process in terms of increasing the productivity and reducing the eluent consumption is exemplified.
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1. Introduction

The concept of affecting the adsorption behavior by a modulation of the solvent composition is frequently used in batch liquid chromatography for both analytical applications as well as for large-scale processes. Additives of the mobile phase (modifiers) influence the retention factors of the feed components. The concentration of each component in the adsorbed phase at equilibrium is then a function of the local concentration of all the sample components and of the modifier [1–3]. Hence, manipulation of solvent strength can

be utilized for optimization of the separation efficiency under either isocratic [4] or gradient conditions [5–7].

Recently, the idea of modulating the solvent strength in order to increase productivity was introduced to continuous chromatographic separations based on the simulated moving bed (SMB) process [8–13]. A SMB is a practical realization of a true moving bed (TMB) where solid and fluid phases move counter-currently. SMB units consist of several columns (fixed beds) arranged in series and connected through multifunctional valves with inlet and outlet ports. The movement of the solid phase is mimicked by periodical switching the positions of the ports or the columns at certain discrete time intervals [14–16].

For gradient SMB operations solvent strength can be modulated in two steps using different solvents at the two inlet

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ports. The feed is dosed continuously in a relatively weak solvent while a stronger solvent is used as the desorbent. Thus, in the classical four zones closed-loop SMB process two distinct levels of internal solvent composition exist which are separated by the two inlet positions. These two characteristic levels of solvent strength can be adjusted by using different amounts of a suitable modifier in the feed and desorbent streams.

Recent results of studying this type of two-step gradient SMB process demonstrated its potential to reduce significantly the solvent consumption and, thus, to increase product concentrations [8–13].

The influence of solvent composition on the performance of isocratic and gradient SMB processes under conditions of non-linear isotherm has been rarely analyzed systematically. The study on optimization of gradient SMB process performed by Houwing et al. [9] were limited to conditions of a linear isotherm and a true moving bed system with infinite efficiency. Such an approach allows only a rough prediction of operating parameters, however, it can be useful for initial guess of the process performance. In order to determine the optimal conditions of the separation accurately a more general mathematical model should be employed, which accounts for the dynamics of the process, the system efficiency, nonlinearity of the adsorption equilibria for the components to be separated as well as for the modifier. Such a model coupled with an adequate optimization procedure allows complete optimization of operating conditions.

In this work for optimization both the isocratic and the gradient SMB process a model of the process dynamics was coupled with a stochastic optimization algorithm.

Currently, an increasing interest in stochastic optimization approaches can be noticed. Of special interest are genetic algorithms, simulated annealing, random search, taboo search and ant colony approaches. They often offer a higher reliability in locating a global optimum compared to deterministic methods. An important advantage is that these methods provide an easy, direct way of handling discrete variables, discontinuous functions and logical conditions. Genetic algorithms are among the most popular stochastic optimization techniques at present. This strategy had been also recently applied for optimizing continuous chromatography processes, e.g., for the multiobjective optimization of a reactive SMB process [17], the classical isocratic SMB process and the Varicol process [18–20]. In these studies several decision variables have been considered (e.g., column configuration, switching time, fluid flow rates, diameter of the bed and of the particles), in combination with various objectives (e.g., product purity, throughput and eluent consumption).

However, according to literature information—e.g., [21] genetic algorithms suits well for combinatorial optimization problems but they are less efficient in case of typical nonlinear problems with continuous variables and, particularly, with non-equality constraints. The strategies of random search are considered as a robust and adequate techniques for nonlinear programming problems.

In this work for solving optimization problem the algorithm of Luus and Jaakola (LJ) [22] was selected. This algorithm appears to be particularly attractive due to its simplicity; it requires no more than 200 lines of numerical code. Various applications for general and process engineering problems presented in [23–27] proved its robustness and easiness of use. Moreover, it was also proved in [28] that some modifications of the LJ algorithm are more efficient and more robust for nonlinear problems than advanced genetic algorithms.

Nevertheless, a deep numerical analysis of numerical algorithms is outside the scope of this paper; the goal of the work is to study the effect of the mobile phase composition on the efficiency of SMB separations and the LJ algorithm was selected as a simple and robust numerical tool to accomplish this goal. It is possible that other stochastic approaches might allow solution of the problem with the same or similar efficiency.

As the objective function in the optimization procedure, the productivity or the eluent consumption were used subject to the purity constraints for the extract and raffinate streams. Five decision variables were considered: the four flowrates in the SMB zones and (a) the mobile phase composition for the isocratic process or (b) the modifier concentration in the desorbent port for the two-step gradient SMB process. The optimization procedure was repeated several times in order to investigate the influence of the feed concentration on the optimum of the mobile phase strength.

2. Simulated moving bed process

The general principle of a classical four-zone SMB unit is illustrated schematically in Fig. 1. There are two incoming
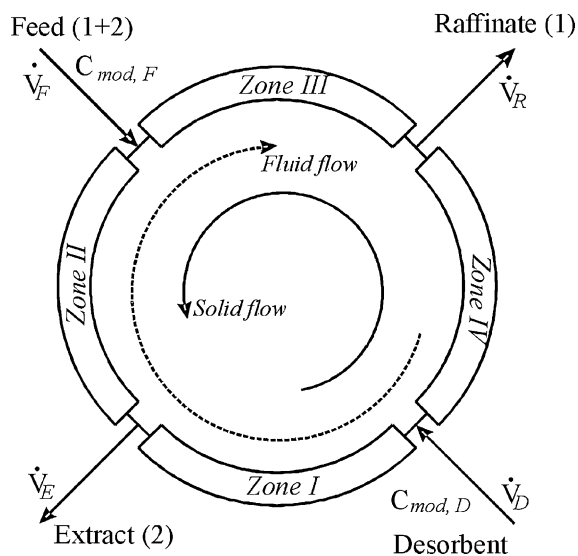

Fig. 1. Scheme of a four-zone SMB unit allowing the implementation of a gradient operation.

streams: the feed mixture to be separated, with flowrate ($\dot{V}_F$), and desorbent or eluent, ($\dot{V}_D$). Two streams leave the unit, one enriched with the less adsorbable component (raffinate, $\dot{V}_R$), and one enriched with the more adsorbable component (extract, $\dot{V}_E$). The four streams divide the unit into four zones (I–IV). Each of these zones has to fulfill distinct tasks and contains at least one fixed bed. By either fixing the fixed beds and shifting the in- and outlet positions co-currently with the fluid flow (moving port implementation) or fixing the in- and outlets and moving the fixed beds counter-currently against the fluid flow (moving column implementation) a counter-current between the fluid and the solid phases is simulated. The SMB switching time, t^*, corresponds to the solid phase flowrate of an equivalent true counter-current process, $\dot{V}_S$ [14–16].

The separation of a less retained component 1 and a more retained component 2 is supposed to occur in the two central zones II and III. Here the net flowrates must be set in such way that component 2 is carried in the direction of the extract outlet and component 1 in the direction of the raffinate outlet. The desorbent is fed to zone I in order to desorb component 2 and, thus, to regenerate the solid phase. Component 1 is adsorbed on the regenerated solid phase in zone IV in order to regenerate the desorbent.

Criteria to design the process for the classical isocratic mode have been elaborated in [29–33]. In this case the solvent strength is identical in all fixed beds (and zones).

The simple idea behind the two-step gradient mode is to set the solvent strength in the feed stream lower than that in the desorbent stream [34,35]. This is realized by using in the two inlet streams different concentrations of a stronger solvent (modifier $C_{mod,D}$ and $C_{mod,F}$, Fig. 1) in a mixture with a weaker solvent. Hereby the feed is dissolved in a stream with a lower concentration of the modifier compared to the concentration of the modifier in the desorbent stream (i.e., $C_{mod,D} > C_{mod,F}$). As a main result the concentration of the desorbent is higher in zone I and lower in zone IV and the SMB unit works more efficiently.

In an "open-loop" mode liquid stream leaving zone IV is discarded and a fresh desorbent is delivered to zone I, while in a "closed loop" mode total liquid stream is recycled to zone I allowing marked reduction of the solvent consumption and an increase the concentration in the product streams. If beside the component to be separated contaminants present in the feed stream the open-loop arrangement is preferable, otherwise closed-loop as an efficient mode can be suggested.

3. Design of the SMB process

For the ideal situation of the TMB process and an infinite number of equilibrium stages, regions of acceptable flowrates leading to pure raffinate and extract streams can be calculated analytically using the equilibrium theory (e.g., [33]). These regions are typically plotted in the (m^{II}–m^{III}) plane of the

following dimensionless flowrates m^K:

$$m^K = \frac{\dot{V}^K t^* - V\varepsilon_t}{V(1 - \varepsilon_t)}, \qquad K = I, \dots, IV \tag{1}$$

The switching time t^* in Eq. (1) is defined as:

$$t^* = \frac{V(1 - \varepsilon_t)}{\dot{V}_s} \tag{2}$$

where ε_t is the total column porosity, the $\dot{V}^K$ are the four volumetric flow rates in the zones, $\dot{V}_s$ is the solid flow rate in the equivalent TMB unit and V is the volume of one fixed bed.

For linear isotherm the region of complete separation has a triangular shape limited by the values of the two Henry constants [33]:

$$H_1 < m^{II} < H_2 \tag{3}$$

$$H_1 < m^{III} < H_2 \tag{4}$$

In addition the dimensionless flowrate in zone I has to fulfill a condition required for the complete regeneration of the solid phase:

$$H_2 < m^I \tag{5}$$

and the dimensionless flowrate in zone IV has to fulfill a condition required for the complete regeneration of the fluid phase:

$$m^{IV} < H_1 \tag{6}$$

The vertex of the triangle in the (m^{II}–m^{III}) plane corresponds to maximal throughput (i.e., maximal productivity) and minimum solvent consumption [31–33].

For nonlinear isotherms the shape of the triangle deforms with increasing feed concentration (increasing the effect of the nonlinearity of isotherm) as illustrated in Fig. 2.

The boundaries of the regions calculated using this theory correspond to 100% of purity of both the outlet streams. For a
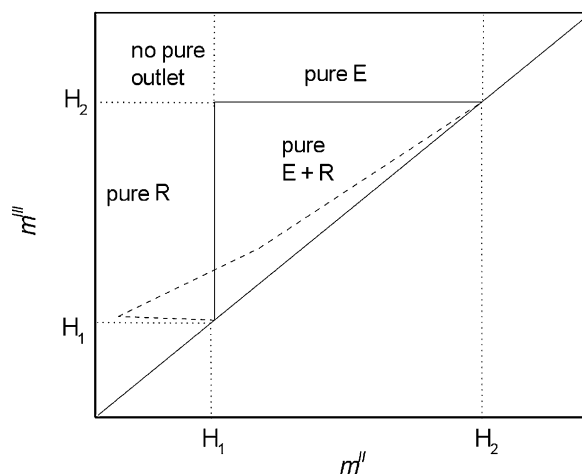

Fig. 2. Plane of m^{II}–m^{II}, typical shapes of separation regions for isocratic operation. Solid line: linear isotherm and dashed line: nonlinear isotherm.

real system with a finite column efficiency (or reduced purity demands) the equilibrium theory overestimates (or underestimates) the size of the separation region [36,37]. In more general cases the accurate position of the region boundaries is available only by numerical solution of a more detailed mathematical model of the process.

4. Kinetic stage model

For modeling the SMB process a kinetic stage model has been applied [38,10,39], which consist of the following mass balance equations for all N^C feed components and the modifier:

$$\frac{dC_{i,j}^K}{dt} + F\frac{dq_{i,j}^K}{dt} = \frac{C_{i,j-1}^K - C_{i,j}^K}{\tau^K} \qquad (7)$$

$$\frac{dq_{i,j}^K}{dt} = k_{mi}(\tilde{q}_{i,j}^K(\bar{C}_j^K) - q_{i,j}^K) \qquad (8)$$

$$i = 1, \dots, N^C, \text{mod}; \qquad j = 1, \dots, N^K; \qquad K = \text{I}, \dots, \text{IV}$$

where $C_{i,j}^K$ designates the fluid phase concentration of component i in cell j of zone K, $q_{i,j}^K$ is the solid phase concentration of component i, $\tilde{q}_{i,j}^K(\bar{C}_j^K)$ is the solid phase concentration at equilibrium with the corresponding overall liquid phase composition $\bar{C}_j^K$, K is the zone index, N^K is the number of cells in K-th zone of each fixed bed of volume V, k_{mi} is the lumped mass transport coefficient; $F = 1 - \varepsilon_t/\varepsilon_t$ is the phase ratio. τ^K stands for the liquid phase residence time in a cell:

$$\tau^K = \frac{\varepsilon_t V}{N^K \dot{V}^K} \qquad K = \text{I}, \dots, \text{IV} \qquad (9)$$

For solving the model equations the backward–forward finite difference algorithm was selected, which allows rapid calculations with acceptable accuracy for both the isocratic and gradient mode. Since the random search procedure described below requires to perform a number of repetitive simulations of the process the reduction of computation time is of major importance for solving optimization problems.

For $n = 1, \dots, N^{\text{end}}$ finite time steps the finite difference scheme can be expressed as follows:

$$\frac{C_{i,j}^{K,n+1} - C_{i,j}^{K,n}}{\Delta t}$$

$$+ \frac{1 - \varepsilon_t}{\varepsilon_t}\frac{(q_{i,j}^{K,n+1} - q_{i,j}^{K,n})}{\Delta t} + \frac{C_{i,j}^{K,n} - C_{i,j-1}^{K,n}}{\tau^K} = 0 \qquad (10)$$

$$\frac{q_{i,j}^{K,n+1} - q_{i,j}^{K,n}}{\Delta t} = k_{mi}(\tilde{q}_{i,j}^{K,n}(\bar{C}_j^{K,n}) - q_{i,j}^{K,n}) \qquad (11)$$

$$i = 1, \dots, N^C, \text{mod}; \qquad j = 1, \dots, N^K;$$

$$K = \text{I}, \dots, \text{IV}; \qquad n = 1, \dots, N^{\text{end}}$$

For each grid point n (in time) and j (in space) the solution $C_{i,j}^{K,n+1}$ is calculated for the components to be separated and the modifier until the end of switching time t^* is reached. The calculations are repeated until a cyclic steady state is achieved. The criterion applied to decide if this state is achieved was based on a check of the balance between the masses of component i collected in the outlet ports and the masses introduced with the feed during the switching period.

The time increment Δt should be chosen sufficiently small in order to reduce the influence of numerical dispersion on the accuracy of the solution.

For sufficiently high values of k_{mi} permanent equilibrium between the mobile and solid phases can be assumed and the model represented by Eqs. (7) and (8) is equivalent to the equilibrium stage model, which consist of single Eq. (7) with $q_{i,j}^K = \tilde{q}_{i,j}^K(\bar{C}_j^K)$. In such a case the kinetic stage and the equilibrium stage models can be used exchangeable. However, the backward–forward finite difference scheme ((10) and (11)) for solving the kinetic stage model allows calculation of the solution $C_{i,j}^{K,n+1}$ in successive points of the time and space grid explicitly, while for the equilibrium stage model this scheme is implicit and requires iterative, time consuming calculation (see analysis of the backward–forward scheme elsewhere, e.g., in [40]).

More details of the implementation of this algorithm for simulating gradients in SMB processes and concerning the required initial and boundary conditions can be found in [10].

5. Adsorption isotherms

The competitive adsorption between two components, 1 and 2, can be described by the competitive Langmuir model:

$$\tilde{q}_i(C_1, C_2) = \frac{H_i C_i}{1 + \sum_{l=1}^{2} K_{rl} C_l}, \qquad i = 1, 2 \qquad (12)$$

To account for the possible adsorption of the modifier the single component Langmuir model was used in this study:

$$\tilde{q}_{\text{mod}}(C_{\text{mod}}) = \frac{H_{\text{mod}} C_{\text{mod}}}{1 + K_{r\,\text{mod}} C_{\text{mod}}} \qquad (13)$$

Since typically the concentration of the modifier exceeds markedly the concentration of the components to be separated a competition between the sample and the modifier was neglected in Eq. (13).

To quantify the effect of the modifier concentration on the Henry coefficient, H_i, in Eq. (12) a power-law dependency (typical for a normal-phase system [41,42]) was applied:

$$H_i(C_{\text{mod}}) = (p_{H_i} C_{\text{mod}})^{-r_{H_i}}, \qquad i = 1, 2 \qquad (14)$$

The same type of dependency was also assumed to describe the effect of the modifier concentration on the equilibrium constant K_{ri}:

$$K_{ri}(C_{\text{mod}}) = (p_{K_{rii}} C_{\text{mod}})^{-r_{Kri}}, \qquad i = 1, 2 \qquad (15)$$

To quantify the equilibrium, the parameters H_{mod} and $K_{r\,mod}$ as well as the p_H, r_H, p_{Kr}, r_{Kr} have to be known. These coefficients are determined empirically by the measurement of adsorption isotherm of the components to be separated at various content of the modifier C_{mod} in the mobile phase and correlating the isotherm coefficients obtained in such way with the modifier concentration by Eqs. (14) and (15).

The separation factor $\alpha = H_2/H_1$, which is calculated on the basis of Eq. (14) is also a function of the modifier concentration. If the separation factor increases with the modifier concentration the efficiency of the separation improves for higher modifier content in the mobile phase. For an opposite dependency a relatively low modifier contents in the mobile phase is preferable. In the optimization study performed, isotherms exhibiting both types of dependency were considered.

6. Formulating of the optimization problem

6.1. Optimization problem

To optimize SMB processes typically two objective functions are used. One is related to the productivity of the process and the other is related to the solvent consumption.

If we consider both components leaving the unit at the raffinate and extract ports as target products, productivity I_P is defined as mass flowrate of the products normalized to the total volume of the stationary phase in the unit:

$$I_P = \frac{(C_{2,E}\dot{V}_E + C_{1,R}\dot{V}_R)}{(1-\varepsilon_t)VN^{\text{beds}}} \tag{16}$$

where N^{beds} is a number of beds (columns).

The second goal function I_{EC} corresponds to the eluent consumption and can be defined as volumetric flowrate of the eluent delivered into the unit in the feed and the desorbent ports per mass flowrate of the products collected:

$$I_{EC} = \frac{\dot{V}_D + \dot{V}_F}{C_{2,E}\dot{V}_E + C_{1,R}\dot{V}_R} \tag{17}$$

$C_{1,R}$, $C_{2,E}$ are the average product concentrations in the raffinate and extract ports calculated as:

$$C_{i,\text{port}} = \frac{\sum_{n=2}^{N^{\text{steps}}} C_{i,\text{port}}^n \Delta t}{t^*}, \qquad i = 1, 2, \quad \text{port} = E, R \tag{18}$$

where N^{steps} is defined as $N^{\text{steps}} = t^*/\Delta t$. The $C_{i,\text{port}}^n$ are calculated from the cell model Eqs. (10) and (11) at the positions corresponding to the extract and raffinate ports (the end of section I and the section III, respectively).

The following optimization problem has been considered:

The maximization of the productivity
- Max I_p

or alternative the minimization of the eluent consumption:
- Min I_{EC}

The Max I_p and Min I_{EC} for isocratic and gradient mode were optimized subject to constraints regarding the purity in the extract and raffinate ports:

$$\text{Pu}_E \geq \text{Pu}_{Emin} \text{ and } \text{Pu}_R \geq \text{Pu}_{Rmin} \tag{19}$$

The Pu_E and Pu_R are defined as follows:

$$\text{Pu}_E = \frac{C_{2E}}{C_{2E} + C_{1E}} \tag{20}$$

$$\text{Pu}_R = \frac{C_{1R}}{C_{1R} + C_{2R}} \tag{21}$$

In addition the following overall mass balances have to be respected:

$$m_D = m - m^{IV} > 0 \tag{22}$$

$$m_E = m - m^{II} > 0 \tag{23}$$

$$m_R = m^{III} - m^{IV} > 0 \tag{24}$$

$$m_F = m^{III} - m^{II} > 0 \tag{25}$$

where m_F, m_D and m_E, m_R correspond to the dimensionless flowrates of input (m_F and m_D) or output (m_E and m_R) streams (see Fig. 1, Eq. (1)).

For the sake of simplicity a typical separation system was considered, for which the pressure drop in the SMB unit was a limiting factor with respect to the process performance. In order to account for the pressure drop limitation the maximal volumetric flowrate $\max(\dot{V}^K)$ Eq. (1) was set equal to unity:

$$\max(\dot{V}^K) = 1 \tag{26}$$

The pressure drop constraint Eq. (26) can be considered as a scaling factor. It can be adjusted to the pressure constraints of a real system and all the dimensional streams can be recalculated maintaining the optimal dimensionless decision variables.

For the isocratic mode $\max(\dot{V}^K)$ always corresponds to the flowrate in the zone I, (wherein regeneration of the solid phase occurs). For the gradient mode the maximal flowrate may correspond to the zone I or III depending on the set of parameters.

If the four dimensionless flowrates m^K are specified, the constraint $\max(\dot{V}^K)$ determines the switching time in Eq. (1) and the solid phase flowrate in Eq. (2). Hence, the four dimensionless flowrates in combination with the pressure drop constraint determine completely all streams in the SMB unit.

6.2. Decision variables of the optimization procedure

6.2.1. Isocratic mode

In the optimization routine for the isocratic process five decision variables were considered: the dimensionless flowrates m^I, m^{II}, m^{III} and m^{IV} and the modifier concentration C_{mod}^{iso}. Any change of C_{mod}^{iso} alters the adsorption isotherms and all the four decision parameters (m^I, m^{II}, m^{III} and m^{IV}), which are required for a successful separation. In order to shorten

the computation time the modifier concentration $C_{\text{mod}}^{\text{iso}}$ was changed in a discrete manner and for each step just the four parameters (m^{I}, m^{II}, m^{III} and m^{IV}) were optimized.

6.2.2. Gradient mode

The essential difference to isocratic operation consists in the introduction of different modifier concentrations within the feed stream and desorbent streams ($C_{\text{mod,F}}$ and $C_{\text{mod,D}}$, with $C_{\text{mod,D}} > C_{\text{mod,F}}$). These concentrations form two new parameters to be optimized. It is obvious that in order to utilize efficiently the potential of gradient elution the modifier contents in the feed and in the desorbent should differ distinctly. This allows creating a difference between the concentrations of the modifier in the desorption zones I and II, (for which a high modifier content is preferable), and the in adsorption zones III and IV, (which work efficiently at low modifier concentrations) [10,11]. Both the $C_{\text{mod,F}}$ and $C_{\text{mod,D}}$ values affect strongly an average concentration of the modifier in the whole SMB unit $\bar{C}_{\text{mod}}$, which can be evaluated from the mass balance:

$$\bar{C}_{\text{mod}} = \frac{m_{\text{F}}C_{\text{mod,F}} + m_{\text{D}}C_{\text{mod,D}}}{m_{\text{F}} + m_{\text{D}}} \tag{27}$$

The average modifier concentration in SMB zones should correspond to the range of high sensitivity of the adsorption equilibria of the components to the mobile phase composition. In this case even a relatively small difference between the level of the modifier concentration in zones I and II ($\bar{C}_{\text{mod}}^{\text{I,II}}$) and zones III and IV ($\bar{C}_{\text{mod}}^{\text{III,IV}}$) results in significant differences in retention of the components in these zones. This allows exploiting the gradient potential effectively.

Changes in retention time of the components are the most pronounced at low modifier content in the mobile phase; illustration of this trend is presented in Figs. 3 and 4.

In order to operate within the range of high sensitivity of the adsorption equilibria to the modifier content and create a large "driving force" for the gradient the feed can be intro-
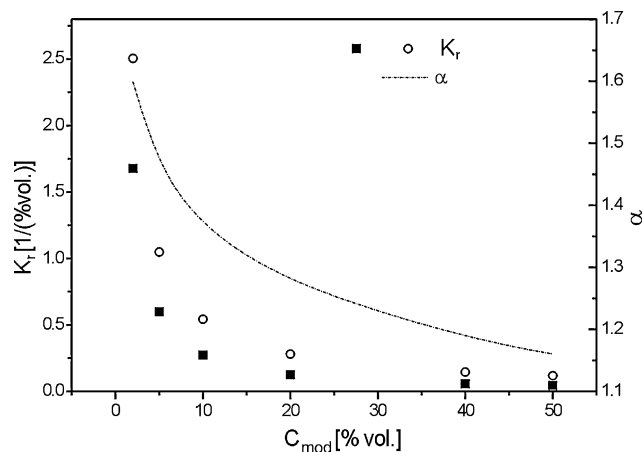
Fig. 4. Variation of the equilibrium constants of the components to be separated with the modifier content for both the isotherms I and II (symbols). Variation of the selectivity with the modifier content for the isotherm II (line).

duced in a pure weak solvent, i.e., $C_{\text{mod,F}}$ can be set to be zero or as low as possible respecting possible solubility limitations. Then, only the concentration in the desorbent port, $C_{\text{mod,D}}$, needs to be specified. The $C_{\text{mod,D}}$ influences the values of the isotherm equation parameters and the selectivity factor and determines the average concentration of the modifier in the whole SMB unit $\bar{C}_{\text{mod}}$:

$$\bar{C}_{\text{mod}} = \frac{m_{\text{D}}C_{\text{mod,D}}}{m_{\text{F}} + m_{\text{D}}} \tag{28}$$

Thus, in optimizing the gradient SMB process $C_{\text{mod,D}}$ was selected as an additional decision variable, which was changed in a discrete manner, similarly to the $C_{\text{mod}}^{\text{iso}}$ variable in the optimization of the isocratic mode. For several $C_{\text{mod,D}}$ values, the corresponding four dimensionless flow rate ratios m^{I}, m^{II}, m^{III} and m^{IV} were optimized.

7. Optimization procedure

7.1. Optimization algorithm

The LJ random search optimization procedure is organized in external loops where search regions for variables are gradually diminished. Trial points are generated randomly in internal loops executed several times within each external loop. It is important to note that a current best point is fixed in all internal loops within an external one, and, similarly, sizes of search regions are not changed in such internal loops. This is the crucial difference compared to other random search techniques, and, as shown in [26] this mechanism improves the efficiency of optimization.

The original LJ algorithm is briefly described in the following using the example under considerations, i.e., the determination of the four free parameters m^{I}, m^{II}, m^{III} and m^{IV}:
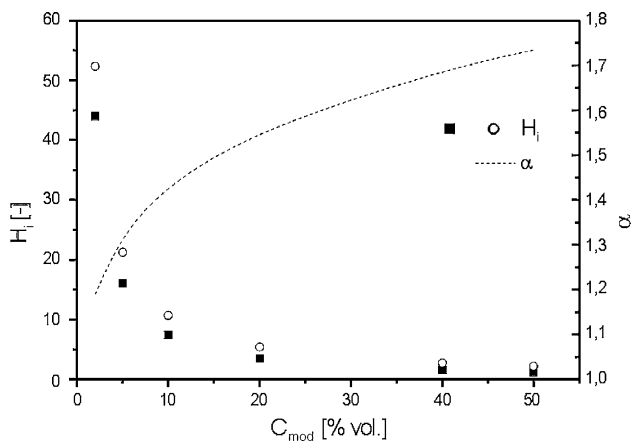

Fig. 3. Variation of the Henry coefficients of the components to be separated (symbols) and the selectivity (line) with the modifier content for the isotherm I.

Provided are:

(a) an initial vector $\bar{\boldsymbol{m}}^0 = [m^{K,0}; K = \text{I}, \ldots, \text{IV}]$, which becomes the best current solution $\bar{\boldsymbol{m}}^* = \bar{\boldsymbol{m}}^0$,
(b) initial search sizes $\bar{\boldsymbol{\delta}}^0 = [\delta^{K,0}; K = \text{I}, \ldots, \text{IV}]$,
(c) number of external loops (NEL),
(d) number of internal loops (NIL),
(e) a contraction coefficient $\mu (0 < \mu < 1)$,
(f) number of runs (NRUN).

The choice of the initial vector $\bar{\boldsymbol{m}}^0$ and the initial search sizes $\bar{\boldsymbol{\delta}}^0$ is based on the isotherm parameters (see Sections 7.2 and 7.3 in the following)

The procedure can be described as follows:

1. Set external loop counter $k_{\text{NEL}} = 1$.
2. Set internal loop counter $i_{\text{NIL}} = 1$.
3. Calculate $\bar{\boldsymbol{m}}^{i_{\text{NIL}}}$ from:

$$\bar{\boldsymbol{m}}^{i_{\text{NIL}}} = \bar{\boldsymbol{m}}^* + \bar{\boldsymbol{r}}^{i_{\text{NIL}}} \bar{\boldsymbol{\delta}}^{k_{\text{NEL}}-1} \qquad (29)$$

   where $\bar{\boldsymbol{r}}^{i_{\text{NIL}}}$ is a column vector of random numbers of uniform distribution and of range $\langle -0.5, 0.5 \rangle$.
4. Check constraints Eqs. (22)–(25), if they are fulfilled solve the model Eqs. (7) and (8) and check constraints Eq. (19), if these constraints are met; calculate the objective function Eqs. (16) and (17).
5. If $i_{\text{NIL}} < \text{NIL}$, $i_{\text{NIL}} = i_{\text{NIL}} + 1$, back to point 3, else go to 6.
6. Find the best point $\bar{\boldsymbol{m}}^{k_{\text{NEL}}}$ of all feasible points generated in the k_{NEL}th external loop, if the point is better than the existing best current point $\bar{\boldsymbol{m}}^*$ replace it with $\bar{\boldsymbol{m}}^{k_{\text{NEL}}}$, i.e., set $\bar{\boldsymbol{m}}^* = \bar{\boldsymbol{m}}^{k_{\text{NEL}}}$.
7. Update $\bar{\boldsymbol{\delta}}^{k_{\text{NEL}}}$ according to:

$$\bar{\boldsymbol{\delta}}^{k_{\text{NEL}}} = \mu \bar{\boldsymbol{\delta}}^{k_{\text{NEL}}-1}. \qquad (30)$$

8. If $k_{\text{NEL}} < \text{NEL}$, $k_{\text{NEL}} = k_{\text{NEL}} + 1$ and go back to 2, else stop calculations and accept $\bar{\boldsymbol{m}}^*$ as the final solution.
9. Repeat the whole procedure (1–8) NRUN times for the same $\bar{\boldsymbol{m}}^0$, NEL, NIL.
10. Accept the best $\bar{\boldsymbol{m}}^*$ of all the runs.

Some modifications of this basic LJ algorithm were proposed. Among them the modification called "final sizes" developed in [26] proved its robustness in many test problems. This modification was applied also in this work and it is briefly explained in the following.

In the LJ algorithm the sizes of search regions are diminished with the same rate for each variable according to Eq. (30). It might be advantageous if the reduction is performed for each variable separately. The idea of the modification is to use a final size of the search region for a decision variable instead of the parameter μ. For the given final sizes ($\bar{\boldsymbol{\delta}}^{\text{final}}$) the value of the vector $\bar{\boldsymbol{\mu}}$ for all variables is calculated in the optimization procedure from:

$$\mu^K = \left(\frac{\delta^{K,\text{final}}}{\delta^{K,0}} \right)^{1/\text{NEL}}; \qquad K = \text{I}, \ldots, \text{IV} \qquad (31)$$

The reason of applying final region sizes is that they are often easy to assess from "physical" interpretation of the optimization problem under consideration and the knowledge of initial region sizes [26].

The modification of the LJ algorithm with the "final sizes" option was implemented in the stochastic optimizer OPTI-STO together with other extensions that are elsewhere [24–26]. The algorithm is able to solve multi-modal nonlinear problems even with infeasible starting points. Additionally, the approach is relatively insensitive (in comparison with gradient-based deterministic optimization methods) with respect to the initialization scheme, i.e., the "goodness" of starting points and sizes of initial search regions. However, in order to find an optimum with "bad starting points" additional iterations have to be applied. Since the solution of the SMB model is time consuming the parameters NEL and NIL had to be diminished as far as possible. One way to achieve short CPU times is to apply a good initialization scheme, i.e., a good starting vector and narrow initial search regions. This approach was also applied in [18] where narrow search regions derived from the triangle theory were used in genetic algorithm optimizations. However, care should be taken since rigorous localization of an optimum region is not possible for relatively low system efficiency (small N^K), and hence, an optimum can be overlooked.

Apart from locating of a global optimum, other important aspect of optimization is determining of maintainability of the optimum, i.e., ability of the unit to be retained in the state, in which it can perform purity demand required. This problem is discussed in details in [39], wherein for evaluating maintainability of the optimal conditions for both the isocratic as well as the gradient SMB process the sensitivity functions were calculated.

7.2. Searching procedure (isocratic SMB mode)

The optimization was performed with a step increase of the modifier concentration $C_{\text{mod}}^{\text{iso}}$, which allowed locating the optimal value of $C_{\text{mod}}^{\text{iso}}$. Calculations were stopped when the value of the goal function I_{P} or I_{C} distinctly decreased after reaching maximum.

The searching was organized in two successive stages; solution of Stage I was used subsequently as a staring point in Stage II:

7.2.1. Stage I

1. To calculate the starting point for each discrete step the triangle theory was employed. The set of four starting dimensionless flowrates was calculated according to inequalities (3)–(6) (i.e., applying the separation criteria for linear isotherms) with a safety margin β ($\beta > 1$):

$$m^{\text{I},0} = H_2 \beta$$

$$m^{\text{IV},0} = \frac{H_1}{\beta}$$

$$m^{\mathrm{II},0} = \frac{H_1 + H_2}{2}$$

The starting point was selected to be very close to the diagonal, i.e.:

$$m^{\mathrm{III},0} = m^{\mathrm{II}} + 0.01$$

Thus, the starting point is always included in the region of points fulfilling the purity demands.

The actual H_1, H_2 for each discrete value of $C_{\mathrm{mod}}^{\mathrm{iso}}$ were calculated according to Eq. (14).

2. The obtained starting vector $\bar{\boldsymbol{m}}^0$ was used in the optimization run in the first stage. The search size $\delta^{K,0}$ was set to be $\delta_i^0 = m^{K,0} \pm 0.15 m^{K,0}$ for all m^K decision variables. Further was set:

$$\delta^{K,\mathrm{final}} = 0.01.$$

7.2.2. Stage II

1. The best solution obtained in Stage I became the starting point for Stage II.
2. The following vector was used in the optimization: $\delta_i^0 = m^{K,0} \pm 0.075 m^{K,0}$, $\delta^{K,\mathrm{final}} = 0.01$.

Both the stages were performed with NEL = NIL = 15, NRUN = 5. The purity constraint was assumed as $\mathrm{Pu_{Emin}} = \mathrm{Pu_{Rmin}} = 0.9$.

In preliminary calculations the procedure described was found to be very efficient in searching an optimum. It does not require a good starting point, which for limited column efficiency and a reduced purity demand cannot be evaluated accurately from the analytical solution provided by the equilibrium theory for linear as well as for nonlinear isotherms.

7.3. Searching procedure (gradient SMB mode)

7.3.1. Stage I

To find starting point, for which purity constrains are met, an auxiliary objective function I_{au} was used:

$$I_{\mathrm{au}} = \mathrm{Pu_E} + \mathrm{Pu_R} \tag{32}$$

Due to the variations of the isotherm parameters with the modifier concentration the plane of possible m^K can be very large and it is useful to limit the range of the search. The optimal modifier composition found for the isocratic mode $C_{\mathrm{mod}}^{\mathrm{iso}}$ offers a good hint for the optimization of the gradient mode. Hence, the starting interval of m^K was selected accordingly to the optimal concentration $C_{\mathrm{mod}}^{\mathrm{iso}}$ at $\delta_0^i = m^{K,0} \pm 0.2 m^{K,0}(C_{\mathrm{mod}}^{\mathrm{iso}})$. The optimization of the auxiliary objective function Eq. (32) was performed with step changes of $C_{\mathrm{mod,D}}$.

7.3.2. Stage II

The solution found from optimization of I_{au} was used as a starting point in the subsequent optimization of the I_{P} or I_{EC} objective functions (NEL = NIL = 15, NRUN = 5).

Table 1
Parameters of Eqs. (14) and (15) for the components 1 and 2

	(1)	(2)
p_{Kr}	0.316	0.1903
r_{Kr}	1.126	0.951
Isotherm I		
p_H	0.0161	0.009
r_H	1.102	0.985
Isotherm II		
p_H	0.0085	0.008
r_H	0.846	0.9457

For the modifier $H_{\mathrm{mod}} = 0.92$; $K_{r\,\mathrm{mod}} = 0.05$.

8. Results and discussion

8.1. Isocratic SMB mode

8.1.1. Isotherm equations and column efficiency

Two different types of the dependency of the separation factor on the modifier concentration have been analyzed—the isotherm I, for which the separation factor increases with elution strength and the isotherm II, for which the separation factor decreases with elution strength. The dependencies of the Henry constant, the equilibrium constant and the separation factor on the modifier concentration are illustrated in Figs. 3 and 4, the dependency coefficients are given in Table 1. The values of coefficients are selected to illustrate some typical behavior—the coefficients of the isotherm I were assumed the same as in [10,43] for a real separation on a normal phase system and then adjusted slightly to create the isotherm II. The same dependence of the equilibrium constant on the modifier content was used for both the isotherms I and II.

The simplest configuration of the unit was assumed: 1/1/1/1, i.e., one column per each K zone. The following column characteristics were assumed: length and column diameter—$L = 15$ cm and $d = 0.46$ cm, respectively, total void volume $\varepsilon_t = 0.75$. Since the analysis performed concerns dimensionless variables, the optimal decision variables do not depend on the column characteristics.

In all simulations a low system efficiency has been assumed; for each column $N^K = 50$. For the sake of simplicity all the contributions to band broadening such as axial dispersion and mass transport resistances were lumped and accounted for indirectly by the column efficiency N^K. The lumped mass transport coefficient k_{m} was chosen on the basis of numerical experiments sufficiently high to assure that the kinetic Eq. (8) did not influence the broadening of the concentration profiles simulated, i.e., in all simulations performed the value $k_{\mathrm{m}} = 200$ 1/min was assumed. In such way the permanent equilibrium between concentrations in the solid and mobile phases were mimicked and the kinetic stage model converged to the equilibrium stage model. Nevertheless, a more detailed analysis including mass transport kinetics for particular adsorption systems is obviously possible.

In the optimization routine various feed concentrations were considered covering a wide range of the isotherms—
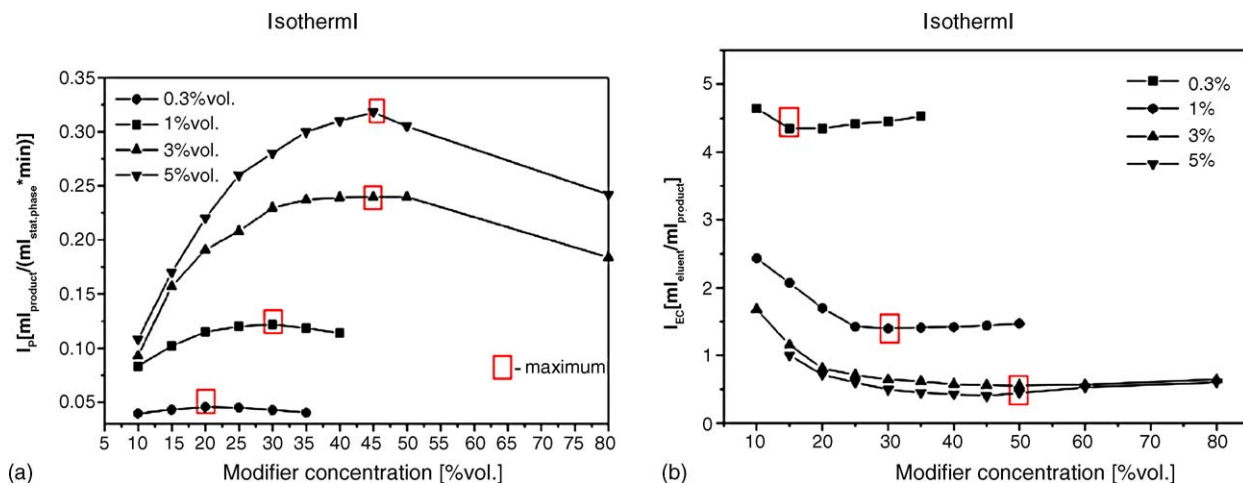
Fig. 5. Variation of (a) the productivity I_p and (b) eluent consumption I_{EC} for different C_F, with the stepwise increase of the modifier concentration for the isotherm I. Purities constraints set as $Pu_{R,E} \geq 90\%$. All the optima correspond to the bounds of the purity constraints in both the outlet streams i.e. $Pu_R \cong Pu_E \cong 90\%$, $N^K = 50$.

from a weak nonlinearity to a strong concentration overloading. Both the objective functions I_P and I_{EC} have been accounted for.

8.1.2. Effect of modifier concentration (C_{mod}^{iso})

Variations of the optimal productivity I_p versus the modifier concentration for isotherm I at different feed concentrations are presented in Fig. 5a. It is evident that the concentration range optimal for diluted streams ($C_F = 0.3$ vol.%) differs from that for concentrated streams. For a high modifier content the nonlinearity of the isotherm is reduced due to a decrease of the equilibrium constant, which improves the separation efficiency. Moreover, for highly concentrated feed streams the value of the productivity is very sensitive to the modifier content (Fig. 5a), therefore operating under not optimized conditions may lead to a loss of the process potential.

It is worth to note that the isotherm I, for which the separation factor increases with the modifier concentration, requires operation under high modifier contents.

The same trend is exhibited for the function I_{EC} as illustrated in Fig. 5b.

For both the objective function I_p and I_{EC} mass flowrate of the components collected is maximized (see Eqs. (16) and

(17)), which leads to similar results with respect to the optimal values of decision variables m^K.

However, the optimum of both the objectives can correspond to slightly different C_{mod}^{iso} (compare Fig. 5a and b and Table 2); the modifier concentration C_{mod}^{iso} corresponding to the optimum of I_{EC} is shifted towards higher values compared to those for I_p. Since the objective functions considered are not conflicting they could be observed in parallel provided that C_{mod}^{iso} is changed discretely. The optimum of the supplementary objective can be selected from among all feasible points generated randomly by the procedure. Thus, there is no necessity to employ a multiobjective optimization procedure.

The results of calculations for the isotherms II follow the similar trend: the maximum of productivity for concentrated feed streams corresponds to higher elution strength of the mobile phase compared to that for diluted ones (Fig. 6a and b, Table 3). Again the modifier concentration C_{mod}^{iso} corresponding to the optimum of I_{EC} is slightly shifted towards higher values compared to those for I_p (compare Fig. 6a and b and Table 3).

It is also evident that the optimal solvent strength decreases with an increase of the separation difficulty—for the isotherm I and high overloadings the optimum of I_p corresponds to

Table 2

Results of optimization for the isotherm I (isocratic mode)

C_F	Optimization of I_P		Optimization of I_{EC}	
	Optimal C_{mod} (vol.%)	Optimal I_P	Optimal C_{mod} (vol.%)	Optimal I_{EC}
0.3[*]	20	0.0456	20	4.45
1	30	0.1220	30	1.668
3	45/50	0.2398	50	0.6079
5[**]	45	0.318	50	0.403

All the optima correspond to the bounds of the purity constraints in both the outlet streams, i.e., $Pu_R \cong Pu_E \cong 90\%$. Illustrative set of the optimal m^K: for the objective I_P: [*]$m^I = 6.087$, $m^{II} = 3.063$, $m^{III} = 5.066$, $m^{IV} = 2.457$; [**]$m^I = 2.209$, $m^{II} = 1.002$, $m^{III} = 1.446$, $m^{IV} = 1.064$; for the objective I_{EC}: [*]$m^I = 5.408$, $m^{II} = 3.181$, $m^{III} = 4.834$, $m^{IV} = 3.182$; [**]$m^I = 2.042$, $m^{II} = 0.911$, $m^{III} = 1.351$, $m^{IV} = 0.893$.
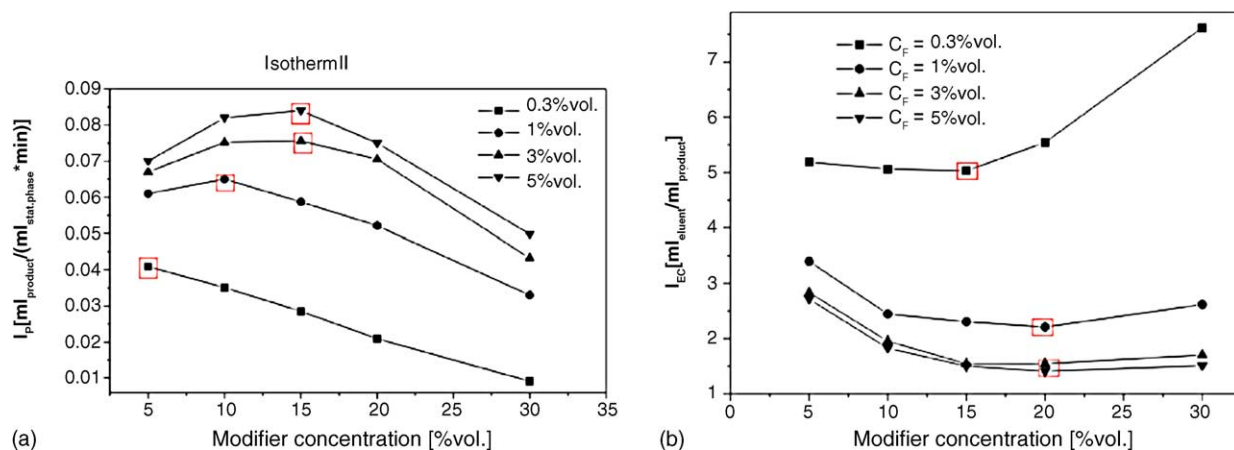
Fig. 6. Variation of (a) the productivity I_p and (b) eluent consumption I_{EC} with the stepwise increase of the modifier concentration for the isotherm II. Purities constraints set as $Pu_{E,R} \geq 90\%$. All the optima correspond to the bounds of the purity constraints in both the outlet streams, i.e. $Pu_R \cong Pu_E \cong 90\%$, $N^K = 50$.

Table 3
Results of optimization for the isotherm II (isocratic mode)

C_F	Optimization of I_P		Optimization of I_{EC}	
	Optimal C_{mod} (vol.%)	Optimal I_P	Optimal C_{mod} (vol.%)	Optimal I_{EC}
0.3[*]	5	0.0409 (5.27)[a]	15	5.03 (0.0364)[*]
1	10	0.0640 (2.84)[a]	20	2.82 (0.0521)[*]
3	15	0.0751 (1.97)[a]	20	1.90 (0.0638)[*]
5[**]	15	0.0831 (1.73)[a]	20	1.44 (0.070)[*]

All the optima correspond to the bounds of the purity constraints in both the outlet streams, i.e., $Pu_R \cong Pu_E \cong 90\%$. Illustrative set of the optimal m^K: for the objective I_P: [*]$m^I = 19.277$, $m^{II} = 10.693$, $m^{III} = 14.874$, $m^{IV} = 11.550$; [**]$m^I = 7.519$, $m^{II} = 4.251$, $m^{III} = 4.499$, $m^{IV} = 3.988$; for the objective I_{EC}: [*]$m^I = 7.402$, $m^{II} = 5.187$, $m^{III} = 6.501$, $m^{IV} = 5.154$; [**]$m^I = 5.343$, $m^{II} = 3.566$, $m^{III} = 3.744$, $m^{IV} = 3.399$.

[a] Parallel value of the second objective function: I_{EC} for the objective I_p or I_P for the objective I_{EC}.

ca. $C_{mod} = 45\%$ (Fig. 5a), while for the isotherm II to ca. $C_{mod} = 15\%$ (Fig. 6a). For very difficult separations and an unfavorable dependency of the separation factor, a low modifier content is preferred corresponding to very large retention of components accompanied often with a strong modifier adsorption and thus problems with the system equilibration. Hence, a low bound for the modifier concentration should be set. Here 5% was assumed as a limit for C_{mod}.

Note that because of conflicting character of productivity (or eluent consumption) and the purity the optimum of productivity always corresponds to the lowest acceptable limit of purity (here optimum always corresponds to Pu = 90% for both the streams).

8.1.3. Effect of feed concentration (C_F)

The optimization was performed for four different feed concentrations, and the typical results are depicted in the plane of (m^{III}–m^{II}) in Fig. 7. With an increase of feed concentration the optimal points change their position in direction to the left corner of the plane, which is in agreement with results of the equilibrium theory [30–33]. Such a change of the optimum position on the (m^{III}–m^{II}) plane is additionally enhanced by the shift of the mobile phase composition toward higher modifier content. For a high feed concentration high modifier content is preferable.

Fig. 7. Location of optimal points with respect to I_p obtained for different feed concentration ($C_F = 0.3$, 1, 3 and 5 vol.%) in the plane of m^{III}–m^{II} parameters for isotherm I. Squares: results for the objective I_{EC} and crosses: for the I_p. $N^K = 50$. Purities constraints set as $Pu_{E,R} \geq 90\%$. All the optima correspond to the bounds of the purity constraints in both the outlet streams, i.e. $Pu_R \cong Pu_E \cong 90\%$.
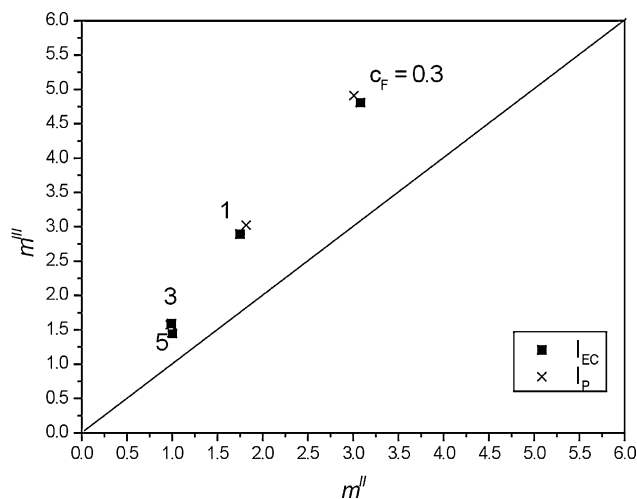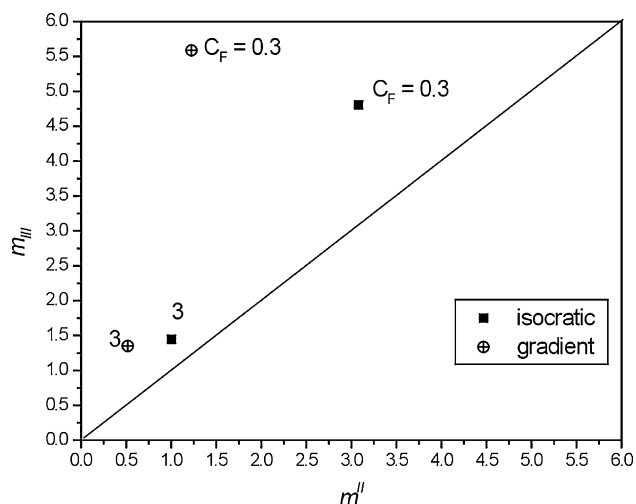
Fig. 8. Location of optimal points with respect to I_P obtained for different feed concentration ($C_F = 0.3$ and 3 vol.%) in the plane of m^{III}–m^{II} parameters for isotherm I. Solid squares: the optimum for the isocratic mode and circles: optimum for the gradient mode. Purities constraints set as $Pu_{E,R} \geq 90\%$. $N^K = 50\%$.

The values of objective functions corresponding to the optima for both the isotherms are presented in Tables 2 and 3. In both cases increasing of feed concentration results in reducing of eluent consumption.

8.2. Gradient elution

8.2.1. Effect of modifier concentration (C_{mod})

As mentioned above for diluted streams ($C_F = 0.3\%$ vol.) or easy separations a high modifier concentration in the desorbent port is preferable and $C_{mod,D} = 100\%$ allows one to achieve successful separation with the highest driving force for the gradient, i.e., $C_{mod,F} = 0\%$ and $C_{mod,D} = 100\%$.

For larger concentrations and difficult separations the amount of feed, which is possible to separate decreases. In this case the feed flowrate is markedly exceeded by the desorbent flowrate and is not sufficient to create a proper driving force for the gradient. Since the desorbent stream dominates, the value of $C_{mod,D}$ determines the average composition in the SMB unit. In order to achieve the required purity of the products the concentration of $C_{mod,D}$ has to be set relatively close to the C_{mod}^{iso}. This obviously reduces the driving force of the gradient. The range of the step searching of $C_{mod,D}$ ($C_{mod}^{iso} \leq C_{mod,D} \leq 100\%$) may be reduced by performing prior to the optimization the numeric searching of the separation region according to the strategy described in [10].

The results of optimization of I_P for the isotherm I are plotted in Fig. 8, where the operating points corresponding to the optimum under isocratic and gradient conditions are depicted on the plane of (m^{III}–m^{II}) parameters. The optimal decision variables and the goal functions are summarized in Table 4a and b. It is evident that optimization of

Table 4
Results of optimization for the isotherm I (gradient mode)

C_F (vol.%)	Optimal $C_{mod,D}$ (vol.%)	m^I	m^{II}	m^{III}	m^{IV}	Optimal I_P	I_{EC} for the optimal I_P	$\bar{C}_{mod}^{I,II}$ (vol.%)	$\bar{C}_{mod}^{III,IV}$ (vol.%)	Pu_E (%)	Pu_R (%)
(a) Optimization of I_P											
0.3	100	4.20	1.32	6.15	2.65	0.123	2.27	13.4	36.7	96	97
3	100	1.44	0.48	1.51	0.28	0.502	0.39	35.5	81.3	90	91
C_F (vol.%)	Optimal $C_{mod,D}$ (vol.%)	m^I	m^{II}	m^{III}	m^{IV}	Optimal I_{EC}	I_P for the optimal I_{EC}	$\bar{C}_{mod}^{I,II}$ (vol.%)	$\bar{C}_{mod}^{III,IV}$ (vol.%)	Pu_E (%)	Pu_R (%)
(b) Optimization of I_{EC}											
0.3	100	5.19	2.75	7.71	4.48	1.98	0.107	8.83	17.3	96	96
3	100	1.23	0.54	1.50	0.43	0.340	0.461	33.6	69.5	90	90

$\bar{C}_{mod}^{I,II}$ and $\bar{C}_{mod}^{III,IV}$ are the average modifier concentrations in zones I, II and III, IV calculated by integrating concentration profile of the modifier.

both the objectives I_p and I_{EC} leads to slightly different results; the optimum of I_{EC} corresponds to slightly lower modifier content compared to that for I_p. In general, the superiority of the gradient process in terms of productivity and eluent consumption compared to the isocratic mode is significant. Due to differences in the modifier distribution and the retention properties of the component to be separated in zones II and III, the optimal values of m^{II} are lower and the optimal values of m^{III} higher compared to the isocratic mode. Hence, much higher feed flowrates can be introduced at the same purity demand. High elution strength of the desorbent stream improves regeneration and allows reduction of the eluent consumption. These advantages are pronounced for diluted feed solutions, for which large flowrates can be treated and a large driving force for the gradient can be imposed.

The same trend as for the isotherm I can be observed for the isotherm II, for which the $C_{mod,D} = 100\%$ was found to be optimal only for diluted streams (see Table 5a and b), while for concentrated streams the optimal $C_{mod,D}$ value was markedly reduced (i.e., for $C_F = 1\%$ the optimal $C_{mod,D} = 25\%$; for $C_F = 3\%$ $C_{mod,D} = 20\%$).

For both types of isotherm, the productivity achieved even for diluted streams exceeds productivities in the isocratic mode. However, effectiveness of the gradient mode depends strongly on type and scale of the variation of the isotherm parameters with changes of the mobile phase composition and should be analyzed for each particular system separately.

Analogously as for the isocratic mode the optimum of productivity corresponds to a reduced purity, however, since the shape of the operating regions for the gradient mode is no longer triangle [8–13], the lowest bound of Pu = 90% is not always achieved for both the streams.

8.2.2. Effect of feed concentration (C_F)

As it is shown in Table 4a and b for the isotherm I with an increase of feed concentration the optimal average modifier concentration in the zones I, II and III, IV is also increasing. These changes are more pronounced for the gradient mode compared to that for isocratic (compare Tables 2 and 4). The optimal average concentration in the unit (see average of $\bar{C}_{mod}^{I,II}$ and $\bar{C}_{mod}^{III,IV}$) for the given feed concentration is only slightly higher than the optimal C_{mod}^{iso} for the isocratic mode. Hence, as it was mentioned above, on the basis of the optimum of the modifier concentration found in the isocratic mode the average optimal concentration under gradient conditions can be evaluated.

The results for the isotherm II are presented in Table 5a and b. As one can observe also for this case the optimal average modifier concentration in the zones I, II and III, IV increases with increasing concentration of the feed stream. It is worth to note that this improvement happens in costs of "driving force", i.e., optimal concentration in desorbent stream decreases. In both cases (isotherms I and II) increasing of feed concentration results in lower eluent consumption.

Table 5
Results of the optimization for the isotherm II (gradient mode)

C_F (vol.%)	Optimal $C_{mod,D}$ (vol.%)	m^I	m^{II}	m^{III}	m^{IV}	Optimal I_P	I_{EC} for the optimal I_P	$\bar{C}_{mod}^{I,II}$ (vol.%)	$\bar{C}_{mod}^{III,IV}$ (vol.%)	Pu$_E$ (%)	Pu$_R$ (%)
(a) Optimization of I_P											
0.3	100	8.16	4.09	8.83	7.53	0.090	2.03	8.04	11.7	90	98
1	25	6.06	3.62	4.77	3.75	0.092	1.66	14.4	17.2	90	90
3	20	5.77	3.73	4.08	3.53	0.086	1.38	16.4	17.3	90	90

C_F (vol.%)	Optimal $C_{mod,D}$ (vol.%)	m^I	m^{II}	m^{III}	m^{IV}	Optimal I_{EC}	I_P for the optimal I_{EC}	$\bar{C}_{mod}^{I,II}$ (vol.%)	$\bar{C}_{mod}^{III,IV}$ (vol.%)	Pu$_E$ (%)	Pu$_R$ (%)
(b) Optimization of I_{EC}											
0.3	100	8.22	4.93	8.90	7.76	1.99	0.075	7.97	10.5	92	96
1	25	5.92	4.05	5.04	4.42	1.42	0.079	13.4	15.3	90	90
3	20	5.81	3.77	4.12	3.56	1.41	0.084	16.5	17.4	90	90

9. Conclusions

In this work the effect of mobile phase composition on the efficiency of the SMB process was investigated. The optimal mobile phase composition was determined by the use of a random search routine, namely the Luus–Jaakola algorithm. This algorithm is considered as an efficient and robust tool in solution of nonlinear problems in chemical engineering.

The optimization was performed for isocratic mode with the same composition of the mobile phase in the feed and the desorbent stream and for gradient mode, for which different compositions of the mobile phase for two inlet streams were used. Optimization of the isocratic process was performed in a discrete manner: the mobile phase concentration was changed stepwise; for each step the four dimensionless flowrates in the four SMB zones were optimized. For optimization two objective functions have been used, i.e., productivity and eluent consumption.

The results indicate that for concentrated feed streams higher solvent strength is preferable compared to that for diluted feed streams. The optimal strength was found to be also dependent on the difficulty of the separation, i.e., on the value of the separation factor and its dependency on the modifier content in the mobile phase. For a favorable dependency (when the selectivity factor increases with the solvent strength) a mobile phase with relative high modifier content is preferable. If the selectivity factor decreases with the solvent strength a low content of the modifier allows achieving higher productivity. Results of optimization of the objective functions considered (productivity and eluent consumption) exhibit similar trend. Since both the objectives are not conflicting the optimum for the supplementary function can be found in parallel in a single-objective optimization.

It is evident that in order to use the process potential completely the optimization of the mobile phase composition is indispensable for each specific case.

For the gradient elution the optimization becomes crucial for the process design; the space of the free operating parameters is large.

The results of the optimization for the gradient SMB process indicate the same trend as for the isocratic mode—the optimal conditions were affected by the feed concentration and the dependency of the separation factor on the mobile phase composition. The most important conclusion is that the potential of the gradient SMB process can be utilized most efficiently for relatively diluted streams, for which larger feed flowrates can be used. However, the scale of advantages depends strongly on the adsorption equilibria of the system investigated and, particularly, on the sensitivity of the isotherm parameters on the mobile phase composition.

10. Nomenclature

C	concentration in mobile phase (vol.%)
$F = (1 - \varepsilon_t)/\varepsilon_t$	phase ratio
H	Henry constant
I_{EC}	eluent consumption ($ml_{eluent}/ml_{product}$)
I_P	productivity ($ml_{product}/ml_{stat.phase}$ min)
k_m	lumped mass transport coefficient (1/min)
K_r	equilibrium constant (1/vol.%)
m	flow rate ratio
$\bar{m}$	vector of continuous decision variables
N	number of theoretical plates
N^{beds}	number of beds (columns) in the unit
N^C	number of components
N^{end}	number of points in the time grid
NEL	total number of external loops in the optimization algorithm
NIL	total number of internal loops in the optimization algorithm
p_H	parameters in Eqs. (14) and (15)
Pu	purity (vol.%)
P_{Kr}	parameters in Eqs. (14) and (15)
q	stationary phase concentration (vol.%)
$\tilde{q}_i$	stationary phase concentration in equilibrium with the local stagnant mobile phase concentrations (vol.%)
r_H	parameters in Eqs. (14) and (15)
r_i	ith random variable from uniform distribution and from the range $\langle -0.5, 0.5 \rangle$
r_{Kr}	parameters in Eqs. (14) and (15)
S	column cross area
t	time (min)
t^*	switching time (min)
u	superficial velocity (m/s)
V	column volume (ml)
V_S	volume of the stationary phase (ml)
$\dot{V}$	volumetric flow rate (ml/min)
x	axial coordinate (m)

Greek letters

α	selectivity $\alpha = H_2/H_1$
δ_I	parameter defining search region for variable m^K
ε_t	total void fraction
μ	safety coefficient control parameter for reducing the search region

Subscripts

D	desorbent
E	extract
F	feed
i	component index
j	space interval index
mod	modifier
R	raffinate

Superscripts

f	refers to final search region
i_{NIL}	refers to i_{NIL}th iteration of optimization algorithm
K	zone index
k_{NEL}	refers to k_{NEL}th iteration of optimization algorithm

* refers to current best value
0 refers to initial values
n time interval index
s refers to solid phase

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