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# Application of equilibrium theory to ternary moving bed configurations (four+four, five+four, eight and nine zones)

## I. Linear case

Alexandre Nicolaos<sup>a,\*</sup>, Laurence Muhr<sup>a</sup>, Patrice Gotteland<sup>b</sup>, Roger-Marc Nicoud<sup>c</sup>,  
Michel Bailly<sup>a</sup>

<sup>a</sup>Laboratoire des Sciences du Genie Chimique, CNRS-ENSIC, 1 Rue Grandville, B.P. 451, 54001 Nancy Cedex, France

<sup>b</sup>Rhône-Poulenc Industrialisation, 24 Avenue Jean Jaurès, 69153 Décines-Charpieu Cedex, France

<sup>c</sup>Novasep, 15 Rue du Bois de la Champelle, B.P. 50, 54502 Vandoeuvre-lès-Nancy Cedex, France

### Abstract

In this article, different ternary moving bed configurations are studied by determining the working flow-rates of the equivalent true moving bed at the low solvent consumption point using equilibrium theory. This method has been applied for linear adsorption isotherms. The simulated moving bed flow-rates can then be calculated and a final comparison between the performances of each process is given based upon two different objective functions. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Simulated moving bed chromatography; Low solvent consumption point; Equilibrium theory; Adsorption isotherms; Ternary moving bed configurations

### 1. Introduction

The separation of a mixture of chemical compounds by a classical chromatographic fixed bed is made possible by their difference of affinity for the stationary phase. This means that, if a mixture of several compounds is eluted throughout a chromatographic column and if these compounds show a difference of affinity for the stationary phase, these compounds will exit from the column at different times and can then be separated. The true moving bed (TMB) concept enhances the separation of a binary mixture, compared to a classical fixed bed, due to the addition of the counter-current motion of the solid phase in comparison to the liquid phase.

Moreover, this process can work continuously as can be seen from the theoretical working scheme shown in Fig. 1. In this figure, the TMB produces the less retained compound 1 in the raffinate stream and the more retained compound 2 in the extract stream, and consists of four different working zones delimited by two consecutive inlet and outlet streams of the process. The actual problem with this process is to handle the true recycling of the solid phase with reproducible conditions. As a consequence, the concept of “simulating” the solid-phase motion was introduced by Broughton in 1961 [1], which led to the process called simulated moving bed (SMB). The working principle is in fact the same as that introduced for the TMB, with one major difference: the mobile phase elutes through several fixed chromatographic columns while the inlet and outlet lines are periodically and simultaneously moved to simulate

\*Corresponding author.

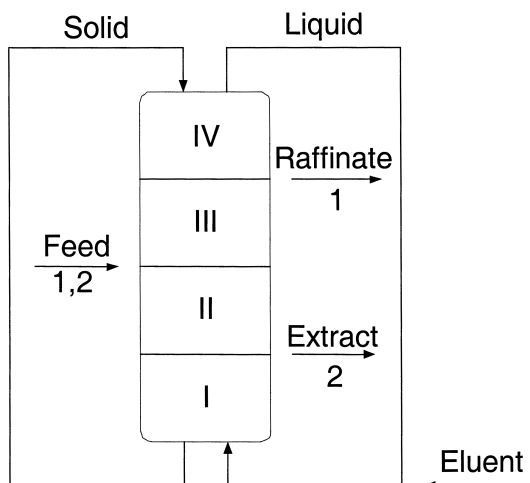


Fig. 1. Four zone true moving bed configuration.

the motion of the solid phase, as illustrated in Fig. 2. The SMB was initially used in the petrochemical and sugar industries on a very large scale [2]. At the beginning of the 1990s, the downsizing of the SMB was introduced for pharmaceutical and fine chemistry applications [3,4]. The studied chemical compounds may show either linear or non-linear adsorption isotherms. In order to obtain an efficient separation, the SMB working flow-rates have to be chosen properly in every zone. In order to do so, the flow-rate of the equivalent TMB can be determined using equilibrium theory. The SMB flow-rates are then determined from the equivalence between the TMB and SMB fluid velocity over one switching period. Equilibrium theory was originally introduced by Glueckauf [5] for two components characterized by Langmuirian isotherms. Rhee et al. developed the theory to predict the concentration profiles of a multicomponent mixture in a chromatographic column working either as a fixed bed [6] or as a counter-current bed [7,8]. The results of this theory have been used to determine the working flow-rates in every zone of the classical four zone TMB with linear or non-linear isotherms [9–15].

The classical four zone SMB shown in Fig. 2 has the following advantages: low solvent consumption, continuous feed, continuous production, high-purity products and high productivity [16,17]. Its major

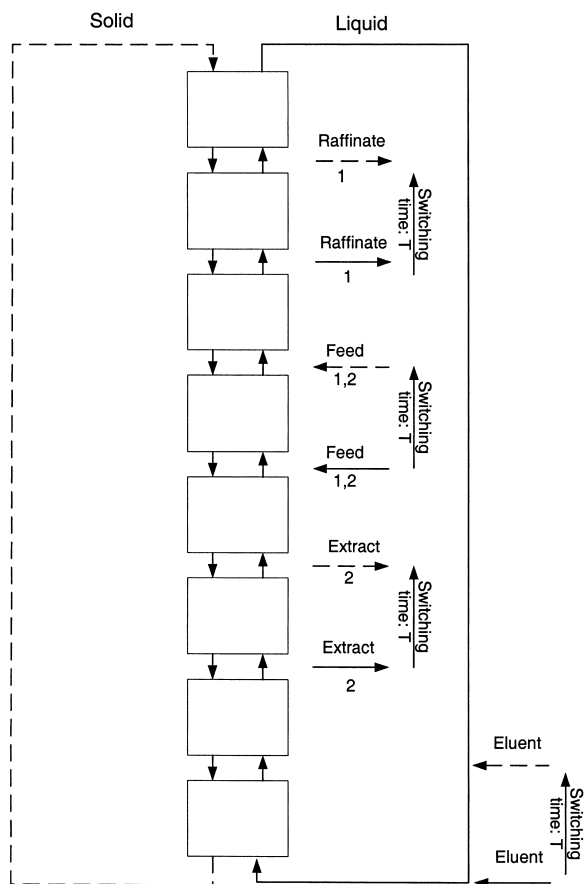


Fig. 2. Four zone simulated moving bed configuration.

drawback is the inability to purify a ternary mixture into three different pure fractions in a single pass. As a consequence, several concepts have been proposed to achieve this goal trying to keep the advantages of SMB. The first consist of keeping the four zones either by alternating two different adsorbents [18] or having a variation of the working flow-rates with respect to time within a switching period [19]. The second type of concept consists of adding a fifth zone and modifying the elution strength within the five zones [20–23], or keeping the same eluent within the entire configuration [24]. The third type of modification consists of having a feed discontinuity and switching columns adequately [25–27]. The last type consists of having two SMB in a row, which are either separated [28] or combined in a single device

[29–31]. The last configuration corresponds to the nine zone SMB [30].

## 2. General hypotheses

The goal of this work is to obtain information on the performances of ternary SMB processes working with a liquid mobile phase, which is assumed not to be retained by the solid phase. In order to study any kind of SMB process, it is more convenient to work on its equivalent TMB process. This is why we will base the following discussion on TMB processes. In the following study, we consider a mixture of three compounds, 1, 2 and 3. We consider that compound 1 is the less retained one, compound 2 the middle one and compound 3 is the more retained. The case considered in our study is the separation and recovery of pure fractions for each compound. In the case where compound 1 (or 3) is the only target compound, the separation can be processed by a single four zone TMB. In the case where compound 2 is the only target compound, it is then possible to use the configurations studied below. In order to fractionate this ternary mixture, four different configurations will be proposed. As a matter of fact, for each configuration, there exist two ways of processing the ternary mixture. If one takes the example of a classical four zone TMB processing of a multi-component mixture of  $M$  compounds, it is possible to define a KEY component as follows: all components going from 1 to KEY are produced in the raffinate and the remaining compounds going from KEY+1 to  $M$  are produced in the extract. If one applies this concept to a ternary mixture, then it will define two working cases. If KEY is respectively equal to 1 or 2, the remaining non-separated compounds 2 and 3 or 1 and 2 will have to be processed by a second TMB. In our study, the calculation of the working flow-rates will be detailed only for case KEY=1, and the results will be given for both cases in Table 10. As a matter of fact, the common concept for all the TMB configurations considered in this study is the use of two TMBs in a row, either in two different devices or combined in one single device. The first set of configurations consists of fractionating the ternary mixture in a first classical four zone TMB as

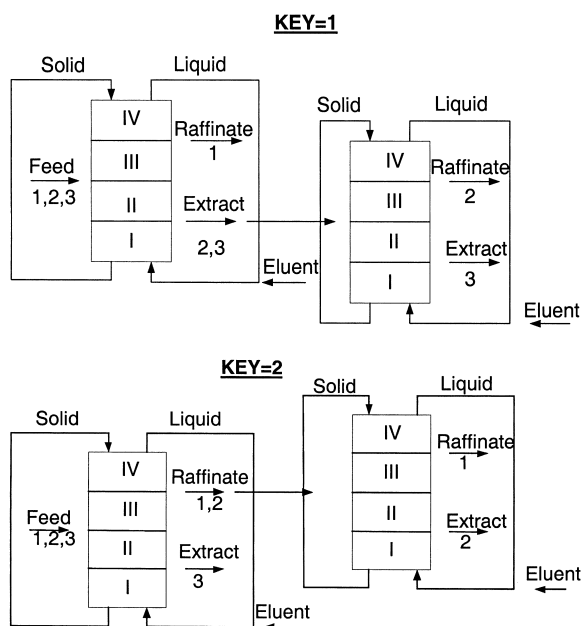


Fig. 3. Two four zone TMBs in a row.

a pseudo-binary mixture and sending the non-separated compounds to a second classical four zone TMB to obtain pure fractions of the two remaining compounds. Fig. 3 shows the two configurations resulting from the first concept.

As stated in the Introduction, a five zone SMB configuration has been proposed for the purification of a ternary mixture [24]. However, the proposed process and its equivalent five zone TMB cannot separate three compounds into three pure fractions because of the concentration profiles observed in this situation, as will be explained further. Consequently, the two non-separated compounds have to be sent to another four zone TMB and this gives the second set of configurations shown in Fig. 4. Instead of working with two different devices as shown in Figs. 3 and 4, it is possible either to join the two four zone TMB into an eight zone TMB, as shown in Fig. 5 [29], or to join the five zone TMB and the four zone TMB into a nine zone TMB, as shown in Fig. 6 [30]. All the configurations proposed above will be studied in the frame of equilibrium theory, which is based upon the ideal column concept. Initially, the following hypotheses were assumed [8]:

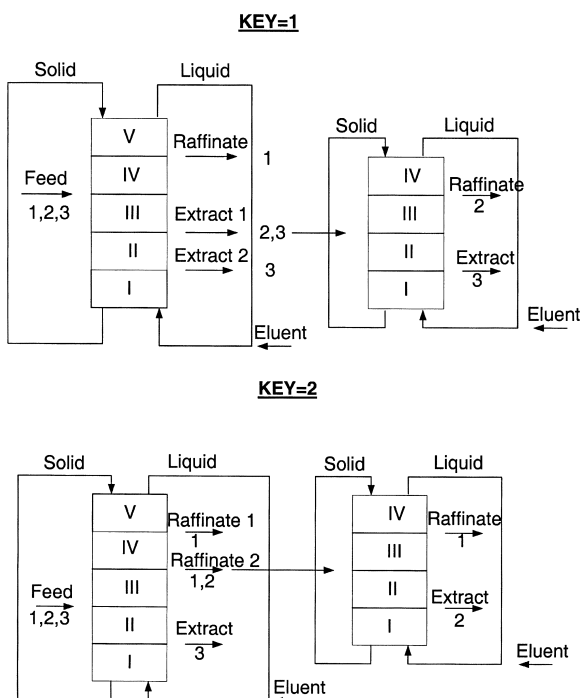


Fig. 4. One five zone TMB followed by a four zone TMB.

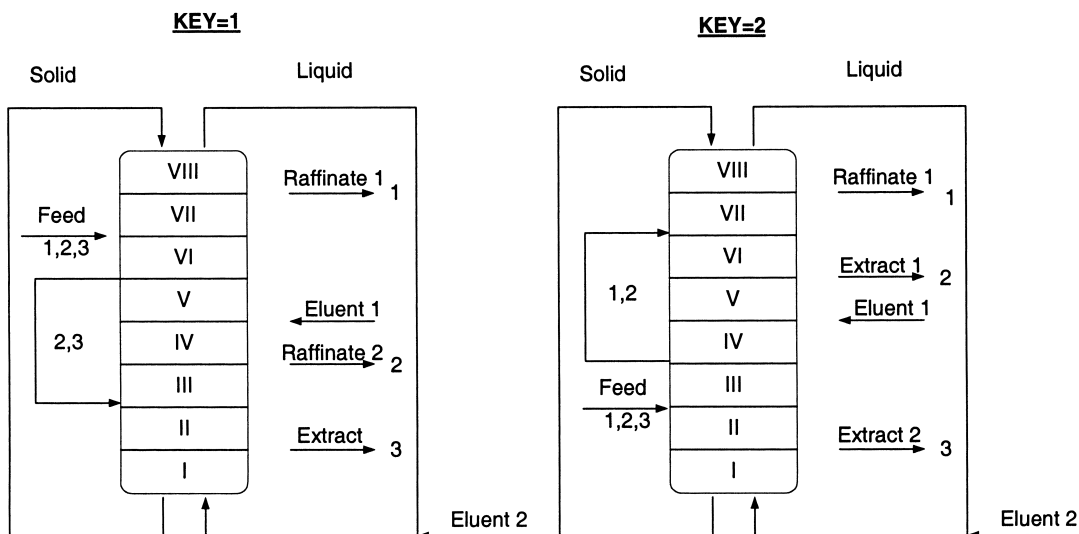


Fig. 5. Eight zone TMB.

- (i) isothermal and isochore,
- (ii) one directional flow,
- (iii) constant volumetric flow,
- (iv) constant porosity,
- (v) no channeling,
- (vi) no axial dispersion,
- (vii) no kinetic resistance, and
- (viii) local equilibrium established everywhere.

In our study, the same hypotheses will be considered. Let us consider an ideal counter-current chromatographic column (Fig. 7). Assuming an ideal column (no axial dispersion and no kinetic resistance) leads to the differential mass balance equation of compound  $i$ :

$$0 = u \cdot \frac{\partial C_i}{\partial x} - \frac{1 - \varepsilon}{\varepsilon} \cdot v \cdot \frac{\partial q_i}{\partial x} + \frac{\partial C_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial q_i}{\partial t}, \quad \forall i \in [1,3] \quad (1)$$

The local equilibrium hypothesis leads to the following expression:

$$0 = \left( \frac{\partial C_i}{\partial x} - \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{v}{u} \right) + \frac{1}{u} \left[ \frac{\partial C_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \sum_{j=1}^3 \left( \frac{\partial q_i}{\partial C_j} \cdot \frac{\partial C_j}{\partial t} \right) \right] \quad (2)$$

The resolution of this mass balance equation is the

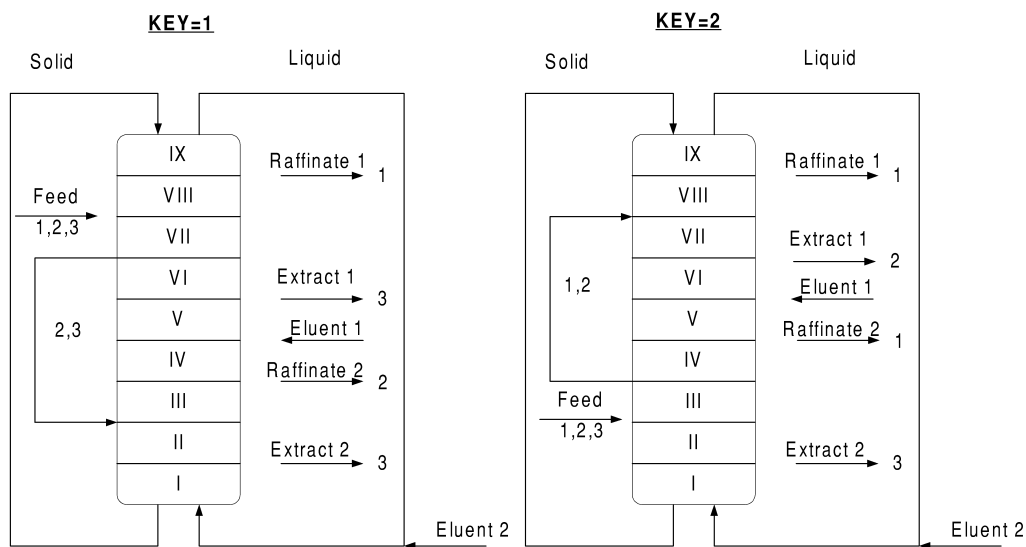


Fig. 6. Nine zone TMB.

basis of the upcoming discussion. After having stated all the general hypotheses used in this study, we will present a comparison of the configuration performances based on the separation of compounds characterized by linear adsorption isotherms.

### 3. Discussion

#### 3.1. Introduction

In this part, we assume that the adsorption isotherm of every compound is linear and expressed as follows:

$$q_i = K_i C_i \tag{3}$$

The application of equilibrium theory with linear

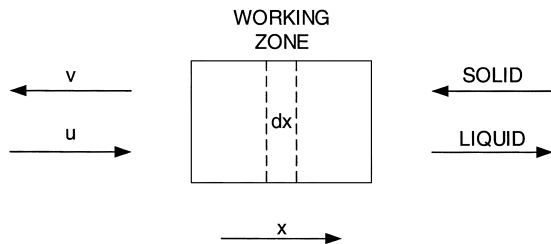


Fig. 7. Counter-current chromatographic zone.

isotherms was introduced by Ruthven [32]. The main purpose of this application is to determine the ratios of the liquid flow-rate over the solid flow-rate in every zone of a TMB.

#### 3.2. Flow-rate determination

In order to produce pure products with a TMB process, the compounds have to migrate either with the liquid phase or with the solid phase depending on the zone considered. This resulting set of rules, called migration directions, gives working flow-rate intervals in every single zone of a TMB. Then, to make a quantitative comparison of the configuration performances, a common working point has to be chosen. We decided to work at the low solvent consumption (LSC) point, which will be defined further.

##### 3.2.1. Migration directions

The TMB system must fulfill conditions on the migration directions of every compound to produce pure products. Let us consider one counter-current column and the corresponding mass balance equations (2). Substituting the expression of the linear adsorption isotherm (3) and introducing the adimensional variable  $m = [\varepsilon/(1 - \varepsilon)](u/v)$ , the following

equation is obtained:

$$0 = \frac{\partial C_i}{\partial x} \cdot \left(1 - \frac{K_i}{m}\right) + \frac{\partial C_i}{\partial t} \cdot \frac{1}{u} \cdot \left(1 + \frac{1 - \varepsilon}{\varepsilon} \cdot K_i\right) \quad (4)$$

Then, the velocity of concentration  $C_i$  is given by

$$\left(\frac{\partial x}{\partial t}\right)_{C_i} = \frac{u[1 - (K_i/m)]}{1 + [(1 - \varepsilon)/\varepsilon]K_i} \quad (5)$$

Two cases are now possible:

1. The compound  $i$  follows the liquid flow-rate:

$$\left(\frac{\partial x}{\partial t}\right)_{C_i} \geq 0 \Rightarrow m \geq K_i \quad (6)$$

2. The compound  $i$  follows the solid flow-rate:

$$\left(\frac{\partial x}{\partial t}\right)_{C_i} \leq 0 \Rightarrow m \leq K_i \quad (7)$$

These rules make it possible to determine the working intervals for the flow-rate ratio  $m$  in every zone by setting the migration direction of every compound. These intervals are given in Table 1 for the case of the classical four zone TMB illustrated in Fig. 1.

Moreover, mass balance equations can be written on the feed node and eluent nodes:

$$m_F = m_{III} - m_{II} \quad (8)$$

$$m_{EI} = m_I - m_{IV} \quad (9)$$

Eqs. (8) and (9) imply, respectively, that, for a given feed and eluent flow-rate, the following relationships must be fulfilled:  $m_{III} \geq m_{II}$  and  $m_I \geq m_{IV}$ . The application of these two conditions and of the intervals summarized in Table 1 in zones I to IV define, respectively, a working region with a triangular shape [12] in the plane  $(m_{II}, m_{III})$  and a semi-infinite rectangular shape in the plane  $(m_{IV}, m_I)$ , as

Table 1  
Flow-rate ratio intervals for a classical four zone TMB

Zone	Migration direction		$m$
	1	2	
IV	↓	↓	$\leq K_1$
III	↑	↓	$K_1 \leq m \leq K_2$
II	↑	↓	$K_1 \leq m \leq K_2$
I	↑	↑	$\geq K_2$

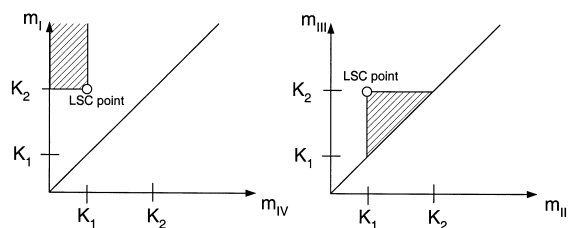


Fig. 8. Working regions of a four zone TMB (binary mixture).

seen in Fig. 8. It is important to remember here that all the flow-rate ratios are independent. After having defined the entire working region of a TMB process, it is interesting to define a specific working point.

### 3.2.2. Low solvent consumption point

The LSC point is defined by the production of pure products with the highest value of the ratio of the feed flow-rate over the eluent flow-rate, which corresponds to the highest value of the feed flow-rate and the lowest value of the eluent flow-rate. In order to work at this specific point, we must choose the maximum (symbol +) or the minimum (symbol -) flow-rate in every flow-rate interval found with the migration directions. If one considers Eqs. (8) and (9), one can see that, in order to work with the highest feed flow-rate ratio, the highest flow-rate has to be chosen in zones III and IV and the lowest in zones I and II. In Fig. 12, this corresponds to the upper left point of the triangle in the diagram  $(m_{II}, m_{III})$  and to the lower right corner of the diagram  $(m_{IV}, m_I)$ . In the discussion below, the diagrams corresponding to the eluent flow-rate will be considered to be at the LSC point and will not be represented. All the reasoning can only be performed on the other zones because all the flow-rates are independent of each other due to the linear adsorption isotherm. The above rules will now be applied to the TMB configurations (case KEY=1) in order to calculate the working flow-rates at the LSC point. This will allow us to determine the performances of every configuration and compare them.

### 3.3. Two four zone TMB in a row

The application of the migration direction rules and the LSC point to two four zone TMB in a row is summarized in Table 2. The corresponding triangular

Table 2  
Flow-rates at the LSC point for a four zone TMB

Zone	Migration direction			$m$	LSC point	
	1	2	3		+ / -	$m$
<i>First TMB</i>						
IV	↓	↓	↓	$\leq K_1$	+	$K_1$
III	↑	↓	↓	$K_1 \leq \leq K_2$	+	$K_2$
II	↑	↓	↓	$K_1 \leq \leq K_2$	-	$K_1$
I	↑	↑	↑	$K_3 \leq$	-	$K_3$
<i>Second TMB</i>						
IV		↓	↓	$\leq K_2$	+	$K_2$
III		↑	↓	$K_2 \leq \leq K_3$	+	$K_3$
II		↑	↓	$K_2 \leq \leq K_3$	-	$K_2$
I		↑	↑	$K_3 \leq$	-	$K_3$

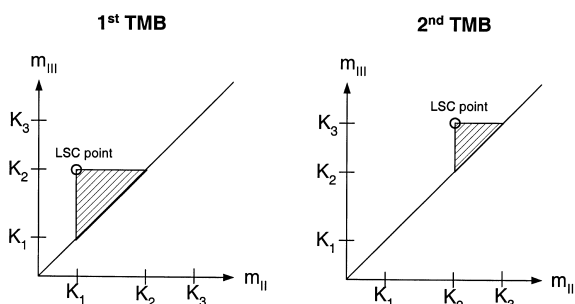


Fig. 9. Working region for two TMBs in a row (case KEY=1).

working region of the two TMBs is shown in Fig. 9. The relations between the zones flow-rate ratios and the inlet/outlet stream flow-rates are given by Eqs. (8)–(11):

$$m_E = m_I - m_{II} \tag{10}$$

$$m_R = m_{III} - m_{IV} \tag{11}$$

The stream flow-rate ratios are shown in Tables 3 and 4 for two four zone TMBs working in a row, each being at the LSC point. In our study, the extract stream of the first TMB is sent continuously to the second TMB. This means that, in order not to have

Table 3  
First four zone TMB flow-rate ratios

Stream	Flow rate ratio, $m$
Feed	$K_2 - K_1$
Raffinate	$K_2 - K_1$
Extract	$K_3 - K_1$
Eluent	$K_3 - K_1$

Table 4  
Second four zone TMB flow-rate ratios

Stream	Flow rate ratio, $m$
Feed	$K_3 - K_2$
Raffinate	$K_3 - K_2$
Extract	$K_3 - K_2$
Eluent	$K_3 - K_2$

any accumulation in the entire process, relationship (12) has to be fulfilled:

$$Q_E^{(1)} = Q_F^{(2)} \tag{12}$$

This condition leads to Eqs. (13) and (14):

$$Q_S^{(1)} m_E^{(1)} = Q_S^{(2)} m_F^{(2)} \tag{13}$$

$$\frac{Q_S^{(1)}}{Q_S^{(2)}} = \frac{K_3 - K_2}{K_3 - K_1} \tag{14}$$

Consequently, for a given value of the first TMB solid flow-rate, it is first possible to calculate the value of the second TMB solid flow-rate and then to determine all the working liquid flow-rates at the LSC point using the expressions given in Tables 3 and 4. The feed eluent flow-rates will be given in Table 10 as well as the flow-rates corresponding to the production of every compound.

### 3.4. One five zone TMB followed by a four zone TMB

The migration direction rules and the LSC point concepts were applied to the five zone configurations and the result is summarized in Table 5. The graphical working region of a five zone TMB

Table 5  
Flow-rates of the first five zone TMB

Zone	Migration direction			$m$	LSC point	
	1	2	3		+ / -	$m$
V	↓	↓	↓	$\leq K_1$	+	$K_1$
IV	↑	↓	↓	$K_1 \leq \leq K_2$	+	$K_2$
III	↑	↓	↓	$K_1 \leq \leq K_2$	-	$K_1$
II	↑	↑	↓	$K_2 \leq \leq K_3$	Independent <sup>a</sup>	
I	↑	↑	↑	$K_3 \leq$	-	$K_3$

<sup>a</sup> In the case considered, the LSC point rule does not allow the choice of any particular value for the flow-rate  $m_{II}$  inside the interval of values  $(K_2, K_3)$ .

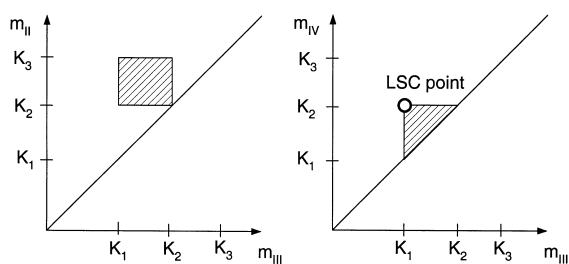


Fig. 10. Working region of a five zone TMB.

processing a ternary mixture is shown in Fig. 10, implying that the conditions on the flow-rate ratios in zones I and V are verified. We can clearly see the classical triangular shape [12] in the plane  $(m_{III}, m_{IV})$ , whereas a rectangular working region is defined in the plane  $(m_{II}, m_{III})$ . Considering the fractionation of a ternary mixture, these regions should correspond to production of the pure compounds 1, 2 and 3, respectively, in the Raffinate, Extract 1 and Extract 2 streams by the five zone TMB (case KEY=1). As stated above, the five zone TMB, as defined in our study, cannot produce pure compound 2 in Extract 1 at steady state because this stream lies between the Feed and Extract 2 streams, and the migration directions of compound 3 defined in Table 5 show that 3 enters the process in the feed stream and migrates all the way through zones III and II in order to reach Extract 2. This means that some product 3 will be produced in Extract 1 if Extract 2 has to be reached, and that the five zone TMB cannot be considered by itself if one wants to produce pure compound 2 in the case of a ternary mixture. The different inlet and outlet streams flow-rate ratios of the five zone TMB can be related to the flow-rate ratios of each zone by simple mass balances:

$$\begin{aligned}
 m_F &= m_{IV} - m_{III} \\
 m_R &= m_{IV} - m_V \\
 m_{E1} &= m_{II} - m_{III} \\
 m_{E2} &= m_I - m_{II} \\
 m_{El} &= m_I - m_V
 \end{aligned} \quad (15)$$

The resulting flow-rate ratios  $m$  of the inlet and outlet streams are shown in Table 6 at the LSC point. The five zone TMB (case KEY=1) is now fully characterized, and the Extract 1 stream is sent to a four zone TMB in order to process the two non-separated compounds 2 and 3. Application of the

Table 6  
Flow-rate ratios  $m$  of a five zone TMB

Stream	Flow rate ratio, $m$
Feed	$K_2 - K_1$
Raffinate	$K_2 - K_1$
Extract 1	$m_{II} - K_1$
Extract 2	$K_3 - m_{II}$
Eluent	$K_3 - K_1$

migration direction and the LSC point rules lead to the flow-rate ratios already given in Table 4. The entire process presented in Fig. 4 has to work without any accumulation. This means that the Extract 1 liquid flow-rate of the five zone TMB has to be equal to the Feed flow-rate of the four zone TMB. This leads to a relationship between the solid flow-rates of the two TMBs. Eq. (13) can be used in that case by considering the Extract 1 stream of the five zone TMB, which leads, after simplification, to:

$$\frac{Q_S^{(1)}}{Q_S^{(2)}} = \frac{m_F^{(2)}}{m_{E1}^{(1)}} = \frac{K_3 - K_2}{m_{II} - K_1} \quad (16)$$

The application of the LSC point rule to the entire configuration allows the determination of the flow-rate ratio  $m_{II}$ . In fact, the total eluent liquid flow-rate can be expressed by Eq. (17) from Tables 4 and 6 and Eq. (16):

$$\begin{aligned}
 Q_{E1}^{(1)} + Q_{E1}^{(2)} &= Q_S^{(1)} \cdot \left( m_{E1}^{(1)} + m_{E1}^{(2)} \cdot \frac{Q_S^{(2)}}{Q_S^{(1)}} \right) \\
 &= Q_S^{(1)} \cdot (K_3 - K_1 + m_{II} - K_1)
 \end{aligned} \quad (17)$$

For a given solid flow-rate of the first TMB, the total eluent liquid flow-rate can be minimized if the smallest value of  $m_{II}$  is chosen, which corresponds to  $K_2$ , as seen from Table 5. Consequently, the solid flow-rate relationship is given by:

$$\frac{Q_S^{(1)}}{Q_S^{(2)}} = \frac{K_3 - K_2}{K_2 - K_1} \quad (18)$$

Once again, it is now possible to determine all the working flow-rates at the LSC point for a given solid flow-rate for the first TMB.

### 3.5. Eight zone TMB

The migration direction and the LSC point con-



Table 7  
Flow-rates of the eight zone TMB configuration (case KEY=1)

Zone	Migration direction			$m$	LSC point	
	1	2	3		+ / -	$m$
VIII	↓	↓	↓	$\leq K_1$	+	$K_1$
VII	↑	↓	↓	$K_1 \leq \leq K_2$	+	$K_2$
VI	↑	↓	↓	$K_1 \leq \leq K_2$	-	$K_1$
V	↑	↑	↑	$K_3 \leq$	-	$K_3$
IV		↓	↓	$\leq K_2$	+	$K_2$
III		↑	↓	$K_2 \leq \leq K_3$	+	$K_3$
II		↑	↓	$K_2 \leq \leq K_3$	-	$K_2$
I		↑	↑	$K_3 \leq$	-	$K_3$

cepts were applied to the eight zone TMB configuration (Case KEY=1), as shown in Table 7.

Comparing Figs. 3 and 5, the flow sent to the second TMB in the case of two TMBs in a row becomes internal in the case of the eight zone TMB. Moreover, a unique solid flow-rate is applied, which means that a degree of freedom is lost. The internal recycling flow-rate works continuously between zones (V,VI) and zones (II,III) in the case KEY=1 and this leads to mass balance equation (19) at steady state:

$$Q_{int} = Q_V - Q_{VI} = Q_{III} - Q_{II} \tag{19}$$

In order to see if this configuration is able to process a ternary mixture, the working regions in diagrams  $(m_{II}, m_{III})$ ,  $(m_{VI}, m_{VII})$  and  $(m_{VI}, m_V)$ , defined by the working intervals summarized in Table 7, have been plotted together in Fig. 11. In this figure, the internal recycling flow-rate line is represented by the dashed

line, which is parallel to the first diagonal line and may vary wherever decided in the diagram. This line is common to the two diagrams  $(m_{II}, m_{III})$  and  $(m_{VI}, m_V)$ . Moreover, if one wants to obtain a working point in these zones, as mass balance equation (19) has to be fulfilled continuously, the dashed line in Fig. 11 must simultaneously have an intersection with the triangular working of diagram  $(m_{II}, m_{III})$  and with the rectangular region  $(m_{VI}, m_V)$ . One can clearly see from Fig. 11 that there exists only one working point represented by P. Unfortunately, this point corresponds to  $m_{VI} = K_2$ , which leads to  $m_{VII} = K_2$  in the feed triangular working region. This corresponds, in fact, to a zero feed flow-rate, which shows that the eight zone TMB process cannot produce three pure compounds simultaneously in the case of linear isotherm compounds. This result shows that the loss of one degree of freedom between the eight zone TMB and the two four zone TMBs in a row has a major impact on the feasibility of the entire process. In fact, it was previously possible to make the two TMBs in a row each work at the LSC point, whereas Eq. (19) shows that it is not possible to do so for the eight zone TMB configuration. It is also possible to apply the same methodology to the eight zone TMB (case KEY=2), as seen in Fig. 12. This figure shows the possible working region implied by the application of the migration direction and the LSC point rules to an eight zone TMB (case KEY=2) fractionating a ternary mixture. The same conclusion as for the case of the KEY=1 configuration can be observed. In

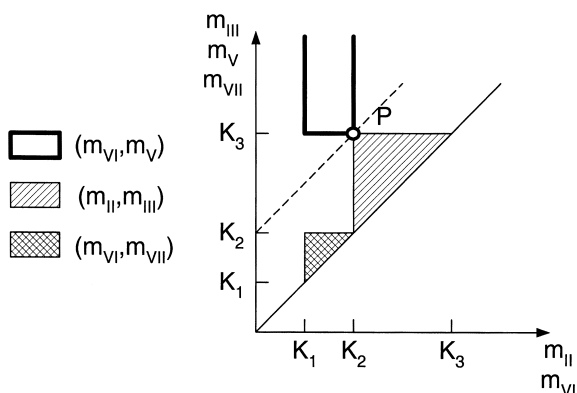


Fig. 11. Working diagrams for the eight zone TMB.

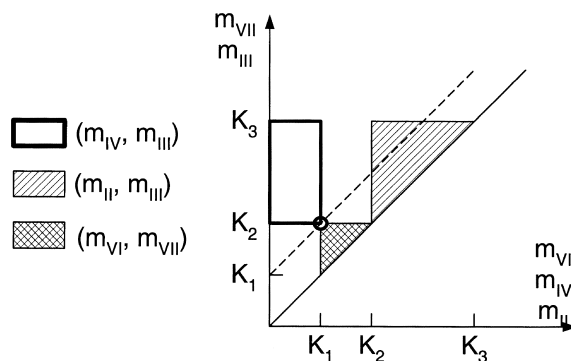


Fig. 12. Working diagrams for the eight zone TMB (case KEY=2).

fact, the only possible working point generates a zero feed flow-rate. In conclusion, we have shown that the eight zone TMB cannot produce three pure products simultaneously from a ternary mixture in our work frame.

### 3.6. Nine zone TMB configuration

The migration direction and LSC point rules were applied to the nine zone TMB (case KEY=1). The results are summarized in Table 8. In this configuration, the flow-rate ratio in zone VI has to be chosen considering the mass balance on the internal recycling flow-rate:

$$Q_{\text{int}} = Q_{\text{VI}} - Q_{\text{VII}} = Q_{\text{III}} - Q_{\text{II}} \quad (20)$$

In order to have a good understanding of the impact of this relation on the choice of the working flow-rates, the flow-rate constraints summarized in Table 8 for diagrams  $(m_{\text{II}}, m_{\text{III}})$ ,  $(m_{\text{VI}}, m_{\text{VII}})$  and  $(m_{\text{VII}}, m_{\text{VIII}})$  are shown in Fig. 13 for the case  $K_3 - K_2 \geq K_2 - K_1$ . The dashed line represents the internal recycling flow characterized by the relationship:  $m_{\text{III}} - m_{\text{II}} = m_{\text{VI}} - m_{\text{VII}}$ . This line may vary wherever decided depending on the values chosen for each flow-rate ratio. In diagram  $(m_{\text{II}}, m_{\text{III}})$ , the LSC point is chosen which corresponds to the upper left point of the triangle. We can observe in diagram  $(m_{\text{VI}}, m_{\text{VII}})$  that the corresponding line has an intersection with the rectangle and defines a working segment for the nine zone TMB. As the feed flow-rate has to be maximized, the

Table 8  
Nine zone TMB flow-rate configuration (case KEY=1)

Zone	Migration direction			$m$	LSC point	
	1	2	3		+ / -	$m$
IX	↓	↓	↓	$\leq K_1$	+	$K_1$
VIII	↑	↓	↓	$K_1 \leq \leq K_2$	+	$K_2$
VII	↑	↓	↓	$K_1 \leq \leq K_2$	-	$K_1^a$
VI	↑	↑	↓	$K_2 \leq \leq K_3$	Independent	
V	↑	↑	↑	$K_3 \leq$	-	$K_3$
IV		↓	↓	$\leq K_2$	+	$K_2$
III		↑	↓	$K_2 \leq \leq K_3$	+	$K_3$
II		↑	↓	$K_2 \leq \leq K_3$	-	$K_2$
I		↑	↑	$K_3 \leq$	-	$K_3$

<sup>a</sup> Depending on the configuration it is not always possible to choose this value, as will be explained further.

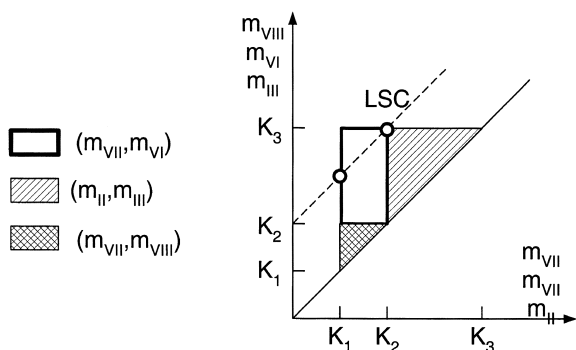


Fig. 13. Working diagrams for the nine zone TMB (KEY=1). Case:  $K_3 - K_2 \geq K_2 - K_1$ .

flow-rate ratio in zone VII has to be minimized because the following mass balance equation can be written:  $Q_F = m_F Q_S = (m_{\text{VIII}} - m_{\text{VII}}) Q_S$ . The minimal possible value of  $m_{\text{VII}}$  is given by  $K_1$ , as seen from Fig. 13. The obtained working point is thus characterized by:

$$m_{\text{VI}} = m_{\text{VII}} + m_{\text{III}} - m_{\text{II}} = K_1 + K_3 - K_2 \quad (21)$$

As a matter of fact, Fig. 13 shows that, in the frame of equilibrium theory, the nine zone TMB can produce pure compounds with the application of the LSC point conditions.

The same methodology can be applied to the nine zone TMB (case KEY=1) in the specific case  $K_3 - K_2 \leq K_2 - K_1$ , as seen in Fig. 14. In this particular case, the minimization of the flow-rate ratio in zone

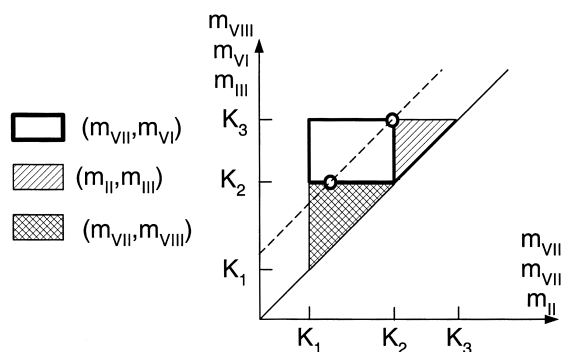


Fig. 14. Working diagrams for the nine zone TMB (case KEY=1). Case:  $K_3 - K_2 \leq K_2 - K_1$ .

Table 9  
Working flow-rates of the nine zone TMB (case KEY=1)

Stream	Flow rate ratio, $m$	
Case	$K_3 - K_2 \geq K_2 - K_1$	$K_3 - K_2 \leq K_2 - K_1$
Feed	$K_2 - K_1$	$K_3 - K_2$
Raffinate 1	$K_2 - K_1$	$K_2 - K_1$
Raffinate 2	$K_3 - K_2$	$K_3 - K_2$
Extract 1	$K_2 - K_1$	$K_3 - K_2$
Extract 2	$K_3 - K_2$	$K_3 - K_2$
Eluent 1	$K_3 - K_2$	$K_3 - K_2$
Eluent 2	$K_3 - K_1$	$K_3 - K_1$

VII cannot lead to the minimal value  $K_1$  of the working interval ( $K_1$ ;  $K_2$ ) defined in Table 8. In fact, the working segment defined by the intersection between the rectangle and the dashed line does not cross the left side of the rectangle corresponding to  $m_{\text{VII}} = K_1$ . However, the minimal possible value for  $m_{\text{VII}}$  is obtained when  $m_{\text{VI}} = K_2$ . Application of the mass balance equation on the internal recycling flow then leads to:

$$m_{\text{VII}} = m_{\text{VI}} - m_{\text{III}} + m_{\text{II}} = K_2 - K_3 + K_2 \quad (22)$$

Figs. 13 and 14 show that it is possible to find suitable working conditions for the nine zone TMB (case KEY=1), but the value given to  $m_{\text{VII}}$  will vary depending upon the values of the retention factors of the considered mixture. The obtained flow-rate ratios at the LSC point are summarized in Table 9 depending on the case studied. To conclude this part, the working flow-rates have been determined for all the ternary TMB configurations. It is now possible to

calculate their performance characteristics based upon the obtained results.

### 3.7. Configuration comparison

Application of the migration direction and the LSC point rules leads to different working flow-rate ratios for every configuration considered previously except for the eight zone TMB, which cannot produce three pure fractions simultaneously from any given ternary mixture (1, 2, 3) in our work frame. For these given conditions, Tables 10 and 11 summarize the following results: reduced feed flow-rate, total reduced eluent flow-rate and the reduced production flow-rate of each compound depending on parameter  $x$  defined by:

$$x = \frac{K_3 - K_2}{K_2 - K_1} \quad (23)$$

In order to choose a configuration for the separation of a given ternary mixture, it is compulsory to define a goal function. From an industrial point of view, the goal is the minimization of the cost function. In the frame of equilibrium theory, it is not possible to calculate this function. Instead, as the ratio  $R = Q_{\text{F}}/Q_{\text{El}}$  has been maximized for all the configurations at the LSC point, we will compare its value for all the configurations and see which one gives the highest value depending on the retention parameters characterized by the ratio  $x$  defined by Eq. (23). The value of criterion  $R$  expressed as a function of the ratio  $x$  is given in Tables 12 and 13 for all the configurations. In order to compare the configuration

Table 10  
Flow-rates for the two device configurations

KEY:	Four zones + four zones		Five zones + four zones	
	1	2	1	2
Feed flow-rate	$K_2 - K_1$	$K_3 - K_2$	$K_2 - K_1$	$K_3 - K_2$
Total eluent flow-rate	$2(K_3 - K_1)$	$2(K_3 - K_1)$	$K_3 + K_2 - 2K_1$	$2K_3 - K_1 - K_2$
Compound 1 flow-rate	$K_2 - K_1$	$K_3 - K_1$	$K_2 - K_1$	$K_3 - K_1$
Compound 2 flow-rate	$K_3 - K_1$	$K_3 - K_1$	$K_2 - K_1$	$K_3 - K_2$
Compound 3 flow-rate	$K_3 - K_1$	$K_3 - K_2$	$K_3 - K_1$	$K_3 - K_2$

Table 11  
Flow-rates of the single device configurations

KEY:	Nine zones			
	1		2	
Case	$x \geq 1$	$x \leq 1$	$x \geq 1$	$x \leq 1$
Feed flow-rate	$K_2 - K_1$	$K_3 - K_2$	$K_2 - K_1$	$K_3 - K_2$
Total eluent flow-rate	$2K_3 - K_2 - K_1$	$2K_3 - K_2 - K_1$	$K_3 + K_2 - 2K_1$	$K_3 + K_2 - 2K_1$
Compound 1 flow-rate	$K_2 - K_1$	$K_2 - K_1$	$2(K_2 - K_1)$	$K_3 - K_1$
Compound 2 flow-rate	$K_3 - K_2$	$K_3 - K_2$	$K_2 - K_1$	$K_2 - K_1$
Compound 3 flow-rate	$K_3 - K_1$	$2(K_3 - K_2)$	$K_3 - K_2$	$K_3 - K_2$

Table 12  
Performance comparison (two device configurations)

KEY:	Four zones + four zones		Five zones + four zones	
	1	2	1	2
$R$	$\frac{1}{2(1+x)}$	$\frac{1}{2[1+(1/x)]}$	$\frac{1}{2+x}$	$\frac{1}{2+(1/x)}$

performances in terms of  $R$ , it is convenient to plot its value as a function of  $x$ , as seen in Fig. 15. In this figure, it is possible to observe that the five+four zone TMB always gives the highest value in terms of  $R$ . This means that the five zone+four zone TMB in a row configuration characterized by two different solid flow-rates gives better results than the nine zone TMB configuration characterized by one solid flow-rate. Moreover, it is also possible to state that it is better to use a five zone TMB in the first pass instead of a four zone TMB. Consequently, if the choice of the best configuration is based upon the ratio  $R$ , in our work frame, the five zone TMB followed by a four zone TMB gives the best results.

Table 13  
Performance comparison (one device configuration)

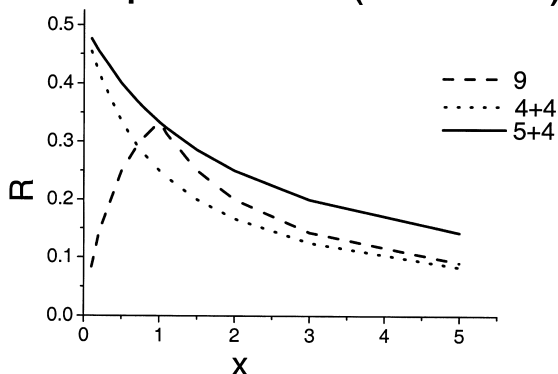
KEY:	Nine zones			
	1		2	
Case	$x \geq 1$	$x \leq 1$	$x \geq 1$	$x \leq 1$
$R$	$\frac{1}{1+2x}$	$\frac{1}{2+(1/x)}$	$\frac{1}{2+x}$	$\frac{1}{1+(2/x)}$

However, it is also important to know which KEY compound has to be used depending on the value of the retention parameters. In order to do so, we plot the value of the ratio  $R$  versus  $x$  for the two different five+four zone TMB configurations (Fig. 16). In this figure, one can observe that if the separation of 1 from 2 is more difficult than the separation of 2 from 3 ( $x > 1$ ), it is more suitable to use the five+four zone TMB process (case KEY=2). It is also possible to observe the opposite conclusion for  $x < 1$ . As a matter of fact, one can conclude that the difficult separation, 1 from 2 or 2 from 3 depending on the value of  $x$ , has to be performed by the second TMB in order to have the highest value of the ratio  $R$ . This conclusion remains the same for the four+four zone TMB configuration.

### 3.8. Practical considerations

The practical application of the TMB process is the SMB process. It is possible to determine the SMB working flow-rates by applying Eq. (24) obtained by considering the same amount of liquid

**TMB performances (case KEY=1)**



**TMB performances (case KEY=2)**

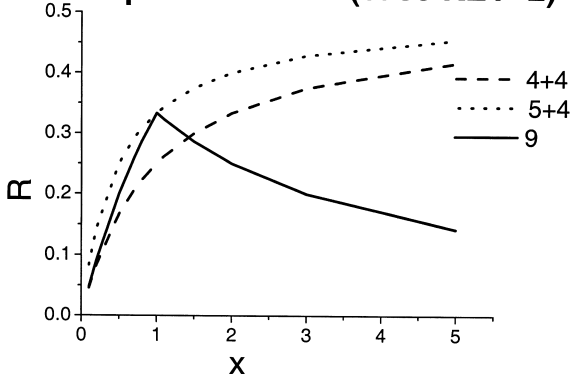


Fig. 15. TMB performance comparison in terms of *R*.

**5+4 zones TMB performances**

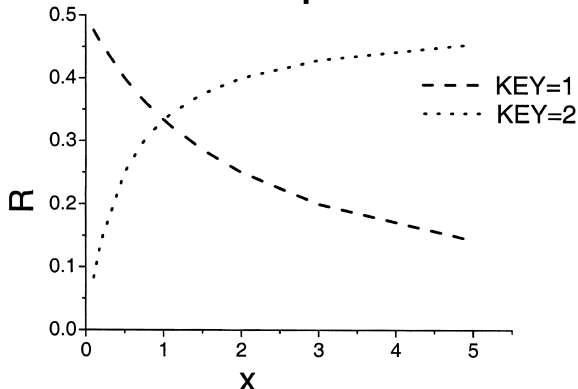


Fig. 16. Comparison of the five+four zone TMB performances.

and solid percolated inside a zone for the two processes over one switching period [33]:

$$Q^{\text{SMB}} = Q^{\text{TMB}} + \frac{\varepsilon}{1 - \varepsilon} \cdot Q_s \quad (24)$$

Eq. (24) can be applied to all the configurations considered in our study, and the former conclusions obtained for the TMB processes will remain exactly the same. The calculations presented previously were based only upon the assumptions linked to equilibrium theory. Some practical considerations will now be considered. As a matter of fact, the impact of the maximum pressure drop constraint will be studied, because in a real chromatographic process, this leads to limitations on the applied liquid flow-rates. In these new calculations, the following hypotheses will be assumed:

- (i) the two SMBs in a row work continuously,
- (ii) all the chromatographic columns are identical (same diameter, length and packing density), and
- (iii) no concentration step is performed between the two SMBs.

Let us now consider the four+four zone SMB (case KEY=1). In the first place, the highest flow-rate applied in the system has to be found, because it will be the one considered to be fixed as a function of the maximum pressure drop thanks to the Kozeny–Karman equation. In a classical four zone SMB process the highest flow-rate is reached in zone I. In some cases, the flow-rate can be as high in zone III, but is never higher. Consequently, one has to find which zone I flow-rate is the highest between the two SMB processes used:

$$Q_1^{(i)} = m_1^{(i)} Q_s^{(i)} = \left( K_3 + \frac{\varepsilon}{1 - \varepsilon} \right) \cdot Q_s^{(i)}, \quad i = 1, 2 \quad (25)$$

Their ratio leads to  $Q_1^{(1)}/Q_1^{(2)} = Q_s^{(1)}/Q_s^{(2)}$ , however the second SMB is fed continuously by the first SMB process, which results in Eq. (26) using Eq. (14):

$$\frac{Q_1^{(2)}}{Q_1^{(1)}} = \frac{Q_s^{(2)}}{Q_s^{(1)}} = 1 + \frac{K_2 - K_1}{K_3 - K_2} \quad (26)$$

Eq. (26) shows that, for the considered hypotheses, the liquid flow-rate in zone I of the second SMB is the highest and will have to be fixed as a function of the maximum possible pressure drop in the system. Let us express the feed flow-rate as a function of the maximum liquid flow-rate applied in the system:

$Q_{\max} = Q_1^{(2)}$ . The expression of the feed flow-rate is  $Q_F = m_F Q_S^{(1)}$ . The expression of the solid flow-rate of the first SMB is obtained from Eqs. (14) and (24):

$$Q_S^{(1)} = \frac{K_3 - K_2}{K_3 - K_1} \cdot \frac{Q_1^{(2)}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$$

and this leads to Eq. (27) by replacing  $m_F$  by the expression  $m_F = K_2 - K_1$ :

$$Q_F = (K_2 - K_1) \cdot \frac{K_3 - K_2}{K_3 - K_1} \cdot \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]} \quad (27)$$

The same methodology is applied to all the other configurations and the expressions of the feed flow-rate are summarized in Table 14. These expressions depend on the parameter  $y$  defined by:

$$y = \frac{K_2 + [\varepsilon/(1 - \varepsilon)]}{K_3 + [\varepsilon/(1 - \varepsilon)]} \quad (28)$$

After having determined the feed flow-rate for all the different configurations, the values obtained may be compared. Table 15 shows the best configuration as

Table 15  
SMB feed flow-rates (best configuration)

Case	Best configuration
$x \leq 1$	Four + four (KEY = 2)
$x \geq 1$	Five + four (KEY = 2)

a function of the retention parameter cases (Table 14). These results show that the new assumptions considered with the application of the maximum pressure drop constraint may lead to different conclusions about the best configuration to be used in order to process a ternary mixture (1, 2, 3) depending on their retention parameters. In fact, the initial assumptions stated in this part are very restrictive and the choice of the goal function is very important because, in one case, the five+four zone TMB process performances were the best and, in the other case, the conclusion was different. Consequently, the equilibrium theory frame is a good tool to be used as a first guess to obtain information on the working behavior of the TMB processes, but as far as the real

Table 14  
SMB feed flow-rates for a given maximum pressure drop

SMB	KEY	Case	$Q_{\max} = Q_1$	$Q_1^{(2)}/Q_1^{(1)}$	$Q_F$	
Four + four	1		Second SMB	$\frac{K_3 - K_1}{K_3 - K_2}$	$\frac{(K_2 - K_1) \cdot (K_3 - K_2)}{K_3 - K_1} \cdot \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
			Second SMB	$\frac{K_3 - K_1}{K_2 - K_1}$	$\frac{(K_2 - K_1) \cdot (K_3 - K_2)}{K_3 - K_1} \cdot \frac{Q_{\max}}{K_2 + [\varepsilon/(1 - \varepsilon)]}$	
Five + four	1	$x \geq 1$	First SMB	$\frac{K_2 - K_1}{K_3 - K_2}$	$(K_2 - K_1) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
		$x \leq 1$	Second SMB	$\frac{K_2 - K_1}{K_3 - K_2}$	$(K_3 - K_2) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
	2	$x \geq 1$	$x \geq 1/y$	Second SMB	$\frac{K_3 - K_2}{K_2 - K_1}$	$(K_2 - K_1) \frac{Q_{\max}}{K_2 + [\varepsilon/(1 - \varepsilon)]}$
		$x \geq 1$	$1/y \geq x \geq 1$	First SMB	$\frac{K_3 - K_2}{K_2 - K_1}$	$(K_3 - K_2) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$
		$x \leq 1$	First SMB	$\frac{K_3 - K_2}{K_2 - K_1}$	$(K_3 - K_2) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
Nine	1	$x \geq 1$	–	–	$(K_2 - K_1) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
		$x \leq 1$	–	–	$(K_3 - K_2) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
	2	$x \geq 1$	–	–	$(K_2 - K_1) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	
		$x \leq 1$	–	–	$(K_3 - K_2) \frac{Q_{\max}}{K_3 + [\varepsilon/(1 - \varepsilon)]}$	

SMB process is concerned, practical considerations have to be taken into account and the calculation of a cost function is compulsory in order to choose the best configuration for the fractionation of a given ternary mixture.

#### 4. Conclusion

The study of several ternary SMB configurations has been performed in the frame of equilibrium theory based upon their equivalent TMB processing ternary mixtures of compounds characterized by linear adsorption isotherms. The application of this theory at the LSC point allowed the determination of explicit expressions of the different working flow-rates and a comparison of the configuration performances. Two different objective functions were used. The first is the ratio  $R$  maximized at the LSC point, which corresponds to the reverse of a specific solvent consumption. The second is the feed flow-rate applied for a given maximum pressure drop constraint in one section, which is qualitatively linked to the productivity of the processes.

In this work frame, we have been able to show that the five zone TMB alone and the eight zone TMB configurations cannot produce three pure compounds simultaneously from a given ternary mixture. Moreover, we have shown that it is more suitable to use a five+four zone TMB configuration and that the most difficult separation has to be performed by the second TMB. However, this conclusion may change depending on the working assumptions and the considered goal function, which means that a cost function has to be considered for real SMB processes. Besides, it seems that, with the considered assumptions, the second SMB limits the performance of the entire configuration. This problem could be solved either by changing the design of the limiting SMB by changing its geometry or by applying a concentration step between the two.

#### 5. Nomenclature

1	less retained compound (binary and ternary mixtures)
2	intermediary compound (ternary mixture)

3	more retained compound (ternary mixture)
$C$ (g/L)	concentration in the liquid phase
$K$	retention factor
$m$	flow-rate ratio (liquid over solid)
$P$	arbitrary working point
$q$ (g/L)	concentration in the solid phase
$Q$ (mL/min)	flow-rate
$R$	difference of retention parameter ratio $R = (K_3 - K_2)/(K_2 - K_1)$
$t$ (s)	time variable
$T$ (s)	switching time
$u$ (m/s)	interstitial velocity of the liquid phase
$v$ (m/s)	interstitial velocity of the solid phase
$x$ (m)	space variable
$\varepsilon$	total porosity

#### Subscripts

El	eluent
E	extract
F	feed
R	raffinate
S	solid
I to IX	zone

#### Superscripts

(1)	first TMB
(2)	second TMB

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