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A pseudo three-zone simulated moving bed with solvent gradient for quaternary separations

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ABSTRACT

In a SMB with solvent gradient, as the eluotropic strength of the liquid in zone II (between the extract-port and feed-port) is higher than that in zone III (between the feed-port and the raffinate-port), the solute can move forward in zone II but backward in zone III to be trapped in the two zones consequently. On this basis, a pseudo-SMB was proposed to separate two medium retained solutes (B1 and B2) from a quaternary mixture by selectively trapping the two solutes. Once the columns in zones II and III are saturated with the target solutes, the solvent dissolving the feed is introduced at the feed-port to remove the least retained solute (A) from the raffinate-port and the most retained solute (C) from the extract-port. The two target components trapped in zones II and III are purified accordingly. At the same time, solute B1 would distribute in the columns of zone III whereas solute B2 spread in the columns of zone II if solute B2 had a stronger retention than solute B1. Thereby, the two medium retained solutes B1 and B2 could be recovered separately from the columns in zones II and III. This scheme was validated by the successful separation of capsaicin (B1) and dihydrocapsaicin (B2) from a crude capsaicinoids.

1. Introduction

The simulated moving bed (SMB) has been successfully applied in the petro-chemical food, and pharmaceuticals industries for binary separations [1–4]. A schematic diagram of the traditional SMB for binary separations is shown in Fig. 1. The four ports of the feed, raffinate, eluent and extract are switched periodically to give the apparent and counter-current movement of the solid against the liquid, making the SMB have advantages over the batch chromatography in terms of the productivity and solvent consumption. The design of SMB systems for binary separations has been extensively studied by many groups and is now well understood [5–9].

In many cases one or more medium retained products are required to be separated from a mixture, which cannot be resolved by the traditional SMB. Many modifications have been developed to tackle the problem [10–16]. Among them, nevertheless, major attention was paid to the ternary separations, in which only one medium retained product was separated. The use of SMB systems for quaternary [17,18] and other more complicated multicomponent systems has not been extensively studied. More efforts are required to improve the applicability of the SMB.

Wei et al. [19,20] have developed a pseudo SMB with solvent gradient to separate the medium retained solute in a ternary mixture. As the eluotropic strength of the liquid in zone II is higher than that in zone III, the solute can move in zone II more quickly than in zone III during each switch interval. Under suitable conditions, the medium retained solute B can move forward in zone II but backward in zone III to be selectively trapped in the two zones. Thereby, the medium retained solute B is separated from the least retained solute A and the most retained solute C.

We think the pseudo SMB can simultaneously trap two or more solutes in zones II and III as shown in Fig. 2. However, the solutes with different retentions should distribute in different columns in zones II and III. For example, solute B1 may occur in the columns close to the raffiante-port whereas solute B2 may spread in the columns adjacent to the extract-port if solute B2 has a stronger retention than solute B1. Accordingly, the two medium retained solutes B1 and B2 can be recovered separately from the columns in zones II and III. In the remainder of the paper, the idea of the separation of two medium retained solutes from a quaternary system will be verified.

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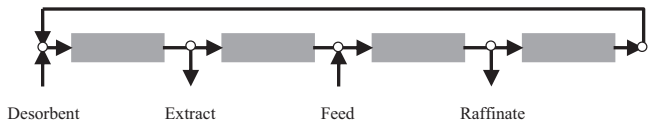

Fig. 1. Scheme of conventional four-zone SMB.

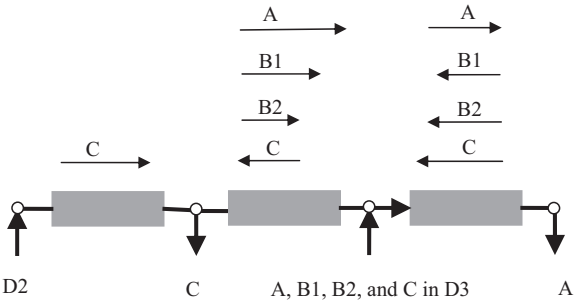

Fig. 2. Scheme of a three-zone SMB with solvent gradient for trapping the medium retained solutes B1 and B2 in different columns from a quaternary system.

Table 1
Compositions of the crude capsaicinoids.

Compound	Concentration (mg/mL)	Content (%)
Capsaicin (B1)	9.48	49.1
Dihydrocapsaicin (B2)	5.65	29.3

2. Experimental

2.1. Pretreatment of Capsicum oleoresin

Capsicum oleoresin (20% capsaicinoids, Guizhou Wubeizi, Guiyang, China) was dispersed in methanol/water (60/40, v/v). The insoluble impurities were removed by centrifugation to give a supernatant liquid. Then the supernatant liquid was fed into a column packed with ADS-8 macropore adsorption resin (Polystyrene, Naikai Hecheng, Tianjin, China) to discard the impurities with very strong retention, giving the crude capsaicinoids. As shown in Fig. 3, the crude capsaicinoids could be regarded as a quaternary system comprising solutes A, B1, B2 and C, in which solutes B1 and B2 denoted the two key components, capsaicin and dihydrocapsaicin, while solutes A and C denoted the compounds eluted before solute B1 and after solute B2, respectively. The compositions of the crude capsaicinoids were listed in Table 1. The next step of pseudo SMB would separate B1 and B2 from the quaternary system by trapping the two solutes in different columns in zones II and III.

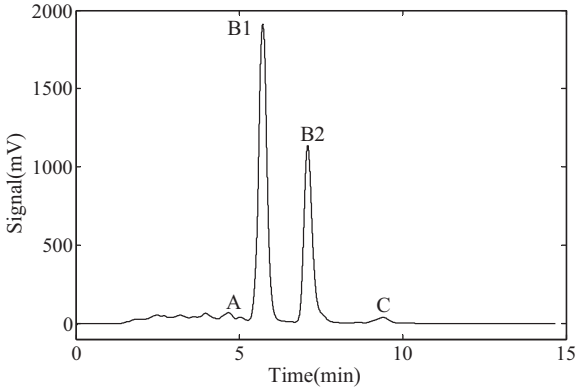

Fig. 3. Chromatogram of the crude capsaicinoids for feeding in pseudo SMB separation process.

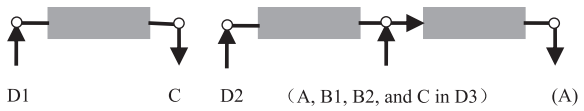

Fig. 4. Scheme of the three-zone SMB in this work.

2.2. Pseudo SMB separation process

The adopted pseudo SMB unit had been described in detail by Wei et al. However, there was a small modification as shown in Fig. 4, in which zone I was disconnected from zone II. This configuration made it easy to completely elute the unknown compounds eluted after solute C but not detected at 280 nm. The eight columns (100 mm × 10 mm) packed with ODS silica gel (diameter 10–20 μm, Fuji, Japan) were arranged in the 1-2-5 configuration. A mixture of methanol/water was used as the mobile phase in SMB.

The separation process consisted of three steps.

- Step 1: feeding—The crude capsaicinoids dissolved in solvent D3 (methanol/water = 60/40, v/v) was added at the node between zones II and III. Meanwhile, other solvent D2 (methanol/water = 85/15, v/v) was added to zone II. Obviously, the solvent strength of D2 was higher than that of D3 so that the eluotropic strength decreased from zone II to zone III. Accordingly, solutes B1 and B2 could move forward in zone II but backward in zone III, whilst solute A moved forward and solute C moved backward in zones II and III. Solute C moving back to zone I was eluted with solvent D1 (methanol). As shown in Fig. 2, solutes B1 and B2 were trapped and consequently accumulated in zones II and III. Thus, the columns in zones II and III would be saturated with solutes B1 and B2 finally so that the two solutes would leak from the raffinate-port. Henceforth, the feeding should be stopped.
- Step 2: purification—The feed solution was replaced with solvent D3 without changing the other operating conditions. Solutes A and C remaining in zones II and III were removed to purify solutes B1 and B2 trapped in zones II and III.
- Step 3: recovery—After solutes A and C were removed completely; solutes B1 and B2 trapped in different columns were recovered separately by stopping the pseudo SMB and eluting the columns in zones II and III offline.

Samples from the raffinate-port and the extract-port were analyzed with a HPLC system (P1201 pump, 1201 UV detector, Elite, Dalian, China) at 280 nm using an ODS column (150 mm × 4.6 mm, Elite, Dalian, China) with the mobile phase of methanol/water (70/30, v/v) and the flow rate was 1.0 mL/min.

3. Designing the pseudo SMB

Following the method developed by Wei et al. [19], the design criterions for operating conditions in steps 1 and 2 could be expressed as follows:

$$F_{\mathrm{I}} \cdot \Delta t > V_{\mathrm{R,C,I}} \quad (1)$$

$$F_{\mathrm{II}} \cdot \Delta t > V_{\mathrm{R,B2,II}} \quad (2)$$

$$F_{\mathrm{II}} \cdot \Delta t < V_{\mathrm{R,C,II}} \quad (3)$$

$$F_{\mathrm{III}} \cdot \Delta t < V_{\mathrm{R,B1,III}} \quad (4)$$

$$F_{\mathrm{III}} \cdot \Delta t > V_{\mathrm{R,A,III}} \quad (5)$$

where $V_{\mathrm{R,i,j}}$ was the retention volume of solute i on the column in zone j. As solute A was actually a group of compounds, instead of