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Thermal simulated moving bed concentrator

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ABSTRACT

The separation obtained in a simulated moving bed (SMB), which was developed for the separation of binary mixtures, can be improved by gradient techniques such as a thermal gradient. Modifying the SMB process with thermal gradient to produce one product concentrated in solutes and another product that is almost pure solvent results in the thermal SMB concentrator. This concentrator can continuously and efficiently concentrate dilute liquid systems with no addition of desorbent. Thermal SMB concentrators with two, three, and four zones are developed and a design method based on triangle theory is introduced to determine the operating conditions for maximum enrichment. The enriched concentration increases as the number of zones increases. Detailed Aspen Chromatography simulations including mass transfer resistances and axial dispersion were done for concentration of salicylic acid in water. The thermal energy consumed in this process was as low as 3% of thermal energy of an equivalent single-stage evaporator.

1. Introduction

The simulated moving bed (SMB) technique developed for continuous chromatographic separation of binary mixtures has been used in the separation of fine chemicals, enantiomers, and biological products [1–3]. This process is usually operated isothermally although some commercial operations are not isothermal. Many researchers have studied the operation of SMB processes under gradient conditions, such as pH, buffer, solvent, and temperature gradients [3–9] to improve performance by reducing desorbent consumption and increasing productivity. An advantage of gradient operation is that each zone can be operated under optimum conditions in accordance with its role (adsorption, separation, or desorption). Chemical gradients (pH, buffer, and solvent) require additional materials to change chemical concentrations. Energy driven gradient, usually a thermal gradient, does not need additional chemicals, but a thermal gradient will require additional heat exchangers. The advantages of thermal gradients in thermally stable dilute liquid systems are that the velocity of the thermal gradient is independent of the solutes, and the velocity of the thermal wave is usually much faster than the velocity of adsorbed solute wave [3,8,9]. Thus, the thermal gradient can be controlled and changed independently of the solutes.

Batch chromatography operation with reversible flow and temperature swings (parametric pumping) and operation with unidirectional flow and temperature swings (cycling zone adsorption), have been studied to separate binary liquid mixtures, remove pollutants from wastewater, and concentrate dilute solutions [3,10–14]. These techniques can separate liquid mixtures with moderate purity and can concentrate dilute solutes. Compared to these chromatographic processes a thermal SMB concentrator is expected to have the advantages of keeping the mass transfer zone inside the column and continuous operation. Conventional concentrating processes, such as batch distillation, evaporation, and freeze drying, rely on a phase change and thus consume a lot of energy. Alternative processes which use less energy are of considerable commercial interest. In this work, a modified SMB process is designed for concentration of dilute solutes, not for fractionation of the solutes. The preliminary design methods for the thermal SMB concentrator were developed from the equivalent true moving bed (TMB) process with the equilibrium theory [4,7,15]. Detailed simulations of the process are presented for the concentration of dilute salicylic acid, which is a problem of commercial interest.

2. Operation of thermal SMB concentrator

For continuous operation, a 2-zone thermal SMB can be arranged as a liquid concentrator as shown in Fig. 1. Dilute feed solution is fed into zone 2 and relatively large amounts of solute adsorb at the cold temperature. Port switching (going from step a to step b in Fig. 1) causes adsorbed solute to move towards zone 1 (hot zone). In hot zone 1, adsorbed solute desorbs and the enriched solute fluid moves towards zone 2 (cold zone) with the liquid phase flow. Consequently, after many port switches, a cyclic steady state is reached with solute focused between the hot and cold zones where it is collected from the Enrich port. Pure or almost pure solvent is col-

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Nomenclature

c	concentration of solute in the liquid phases (g/L)
c^0	equilibrium concentration of solute in the liquid phase (g/L)
c^∞	theoretical maximum enriched concentration (g/L)
c^{Max}	maximum concentration (g/L)
Cp	heat capacity (J/g/K)
D_{e}	axial dispersion coefficient (cm^2/min)
$E_{\mathrm{Evaporator}}$	energy consumption of the equivalent evaporator (kJ/(kg of pure solvent))
f_{h}	humidity factor of the solid phase
ΔH	heat of adsorption (J/mol)
ΔH_{V}	latent heat of boiling (J/g)
k_{e}	effective mass transfer coefficient (1/min)
K	equilibrium constant (L/g)
K_∞	pre-exponential factor of Eq. (2) (L/g)
m	ratio of net liquid flow-rate to net solid flow-rate
M	reduced mass flux of solute (g/L)
$\dot{M}$	mass flux of solute (g/min)
MW	molecular weight of solute (g/mol)
q	concentration of solute in the solid phases (g/L)
q_{Max}	maximum concentration of adsorbed solute in the solid phases (g/L)
q^0	equilibrium concentration of solute in the solid phase (g/L)
$\hat{q}$	mass base concentration of solute in the solid phase (mg/g)
$\hat{q}^*$	mass base equilibrium concentration at the solid film (mg/g)
Q	volumetric flow-rates of the liquid phase (ml/min)
R	ideal gas constant (J/K/mol)
t_{S}	port switching interval (min)
T_{Amb}	ambient temperature (K)
$T_{\mathrm{b.p.}}$	boiling point of solvent (K)
v	superficial velocity of the liquid phase (cm/min)
V_{C}	column volume (ml)
V_{Mixer}	volume of the mixer (ml)

Greek letters

β_{P}	ratio of the liquid volume to the solid volume in a porous particle ($=\varepsilon_{\mathrm{P}}/(1-\varepsilon_{\mathrm{P}})$)
ε	inter-particle void fraction
ε_{P}	intra-particle void fraction
ε_{T}	total void fraction ($=\varepsilon+(1-\varepsilon_{\mathrm{P}})\varepsilon$)
γ_{Mixer}	ratio of the mixer volume to the total outlet volume of the hot zone for one switching interval
ρ	density (g/mL)

Subscripts

1 to 4	zone 1 to 4
C	temperature of cold zone
Dilute	Dilute port
Enrich	Enrich port
Feed	Feed port
H	temperature of hot zone
L	Liquid phase
S	Solid phase
SMB	simulated moving bed system
Solvent	Solvent port
TMB	true moving bed system

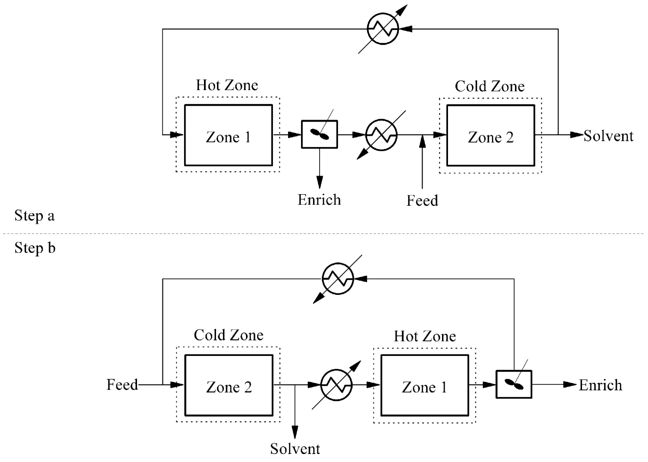

Fig. 1. Schematic illustration of the 2-zone thermal SMB concentrator. Step a is first step and step b is after valve switch.

lected at the Solvent port and a portion of this solvent is heated and recycled to the inlet of zone 1. Note that since no desorbent is added, desorbent recovery is unnecessary. In effect, the thermal SMB concentrator produces desorbent from the solvent in the feed stream.

When solute is desorbed by the thermal wave in zone 1, a high concentration solute band forms and rapidly propagates to the outlet of zone 1. Therefore, at the outlet of zone 1 high concentration solute elutes near the beginning of switching interval and this concentration decreases by the end of switching interval. If high concentration of solute enters into zone 2 at the beginning of switching interval, it is possible that this high concentration elution band will pass through zone 2 and contaminate the Solvent port even though the inlet concentration of zone 2 is diluted by mixing with the feed solution. To reduce the peak of inlet concentration to zone 2 a mixer can be connected at the Enriched port as shown in Fig. 1. Theory and simulations showed that use of a properly sized mixer is advantageous.

The system is easily constructed with 2-way on-off valves or with fewer, more complicated, multiple port valves. One construction approach is to switch the enriched product mixer with product line, cooler, and feed line as a single unit and to switch the solvent product line and heater as another single unit. This configuration has the advantage that the mixer always receives concentrated fluid and the heat exchangers do not switch between heating and cooling. Fig. 2 shows this construction with three-way valves and three pumps (one recycle pump and two product pumps). The disadvantage of this arrangement is the valve system is fairly complex. An alternative (not shown) is to permanently attach a mixer and heat exchanger to each column. At the same switch times feed is alternated between the two columns and the product lines are switched. The difficulties with this scheme are one of the mixers will initially contain the wrong product and the heat exchangers will periodically switch from cooling to heating and vice versa.

The theoretical analysis (see next section) showed that the separation can be increased with 3 zones (Fig. 3) by adding a zone between the cold heat exchanger and the feed addition point. Note that as zones are added, the functions of zones with the same number will change since the new zone will take the existing zone number. This extra zone allows for higher loading of solute in zone 2 because the flow rate into zone 2 in the 3-zone system is lower than in the 2-zone system. Further improvement can be obtained with 4 zones (Fig. 4). The addition of the dilute stream withdrawal allows one to reduce the flow rate in zone 2 of the hot section, which increases the solute concentration in the enriched product. The higher flow rate in zone 1 ensures that the column is completely

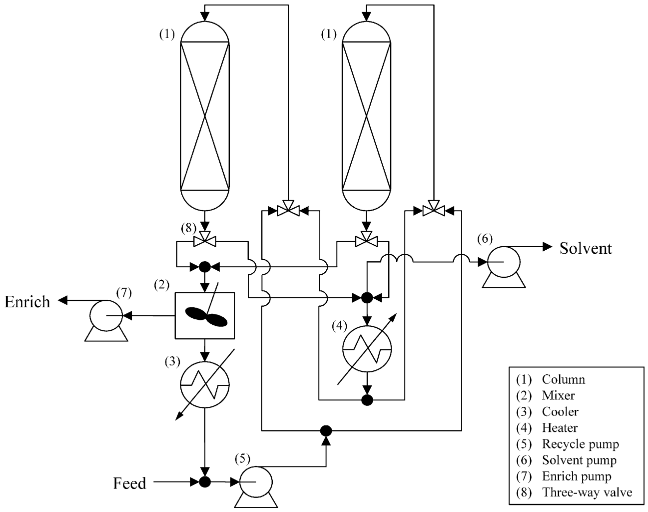

Fig. 2. Use of 3-way valves for 2-zone thermal SMB concentrator.

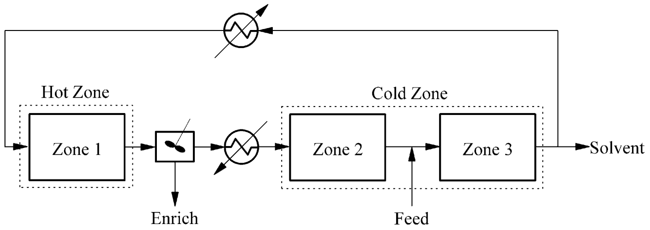

Fig. 3. Schematic illustration of the 3-zone thermal SMB concentrator. Valve switching is not illustrated.

regenerated. Since solute in the dilute stream reduces solute recovery in the enriched product, the dilute stream can be recycled to the feed.

To produce pure desorbent, adsorbent and desorbent have to be regenerated in the first and the last zones of the thermal SMB concentrator, respectively. The roles of these zones are equal to the corresponding zones in a standard 4-zone SMB. Since it is well known that the SMB process with multiple columns per zone more efficiently regenerates adsorbent and desorbent than single column per zone SMBs, we expect the thermal SMB concentrator with multiple columns in the first and the last zones will perform better than a thermal SMB concentrator with one column in these zones.

3. Design of thermal SMB concentrator with local equilibrium theory

3.1. Langmuir adsorption model

For the design of the thermal SMB concentrator, a single solute system which obeys Langmuir adsorption isotherm was considered,

$$q = \frac{q_{\mathrm{Max}} K(T) c}{1 + K(T) c} \tag{1}$$

where c and q are the concentration of solute in the liquid and solid phases, respectively, q_{Max} is the maximum concentration of adsorbed solute, and K is the equilibrium constant. The adsorption system is exothermic and the equilibrium constant follows the Arrhenius equation

$$K(T) = K_\infty \exp\left(-\frac{\Delta H}{RT}\right) \tag{2}$$

K_∞ is the pre-exponential factor, ΔH is the heat of adsorption, and R is the ideal gas constant. It was assumed that the maximum adsorption capacity (q_{Max}) is constant and the solute is thermally stable. For exothermic adsorption, ΔH is negative and the equilibrium constant (K) decreases as temperature increases.

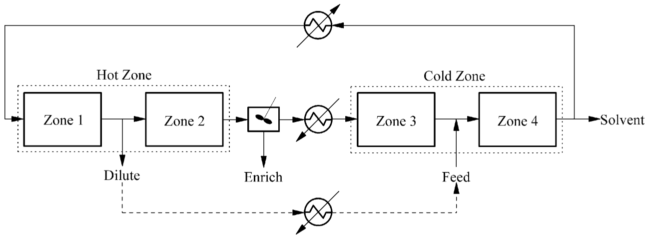

Fig. 4. Schematic illustration of the 4-zone thermal SMB concentrator. Valve switching is not illustrated. Dashed line from the Dilute port to Feed port illustrates an optional recycle line of dilute product.

3.2. Design parameters for thermal SMB concentrator

In the preliminary design of standard SMB processes, the most common method is to use the equivalent true moving bed (TMB) process that is easily solved with equilibrium theory (also known as triangle theory when applied to a SMB). Then detailed designs are done with a simulator. The operating conditions of a TMB can be converted to the operating conditions of a SMB by the following relationship of the volumetric zone flow-rate ratios [15].

$$m_{\mathrm{j}} = \frac{Q_{\mathrm{j}}^{\mathrm{TMB}} - \varepsilon_{\mathrm{P}} Q_{\mathrm{S}}}{(1-\varepsilon_{\mathrm{P}}) Q_{\mathrm{S}}} = \frac{Q_{\mathrm{j}}^{\mathrm{SMB}} t_{\mathrm{S}} - \varepsilon_{\mathrm{T}} V_{\mathrm{C}}}{(1-\varepsilon_{\mathrm{T}}) V_{\mathrm{C}}} \tag{3}$$

where $Q_{\mathrm{j}}^{\mathrm{TMB}}$ and $Q_{\mathrm{j}}^{\mathrm{SMB}}$ are the volumetric flow-rates of the liquid phase in zone j of TMB and SMB, respectively, ε_{P} and ε_{T} ($=\varepsilon + (1-\varepsilon_{\mathrm{P}})\varepsilon$) are the intra-particle and total void fractions, respectively, Q_{S} is the solid phase volumetric flow-rate of TMB, t_{S} is the switching interval of SMB, and V_{C} is the column volume of SMB.

Assuming that the system obeys equilibrium theory, the overall mass flux can be calculated from the mass balance in zone j,

$$\dot{M}_{\mathrm{j}} = \dot{M}_{j,L} - \dot{M}_{j,S} = (Q_{\mathrm{j}}^{\mathrm{TMB}} - \varepsilon_{\mathrm{P}} Q_{\mathrm{S}}) c_{\mathrm{j}} - (1-\varepsilon_{\mathrm{P}}) Q_{\mathrm{S}} q_{\mathrm{j}} \tag{4}$$

where $\dot{M}_{\mathrm{j}}$ is the overall mass flux of solute in zone j, and $\dot{M}_{\mathrm{j,L}}$ and $\dot{M}_{\mathrm{j,S}}$ are the mass fluxes of solute in the liquid and solid phases of zone j, respectively. Dividing Eq. (4) by $(1-\varepsilon_{\mathrm{P}})Q_{\mathrm{S}}$, the linear relationship between c and q is determined by the zone flow-rate ratio and reduced mass flux M_{j} and it can be drawn as a straight line on a c vs q plane.

$$q_{\mathrm{j}} = m_{\mathrm{j}} c_{\mathrm{j}} - M_{\mathrm{j}}, \qquad M_{\mathrm{j}} = \frac{\dot{M}_{\mathrm{j,L}} - \dot{M}_{\mathrm{j,S}}}{(1-\varepsilon_{\mathrm{P}}) Q_{\mathrm{S}}} \tag{5}$$

The slope of this operation line is the zone flow-rate ratio defined as Eq. (3) and the intercept is the reduced solute mass flux of zone j, M_{j}, defined analogously to the zone flow-rate ratio m_{j}. Thus, the equilibrium concentration of zone j can be obtained from the intersection points of the operation line and adsorption equilibrium curve.

If the direction of solute mass flux is the same as the liquid flow ($M_{\mathrm{j}} > 0$),

$$c_{\mathrm{j}}^{0} = \frac{K_{\mathrm{j}}(q_{\mathrm{Max}} + M_{\mathrm{j}}) - m_{\mathrm{j}} + \sqrt{\{K_{\mathrm{j}}(q_{\mathrm{Max}} + M_{\mathrm{j}}) - m_{\mathrm{j}}\}^2 + 4K_{\mathrm{j}} m_{\mathrm{j}} M_{\mathrm{j}}}}{2K_{\mathrm{j}} m_{\mathrm{j}}} \tag{6a}$$

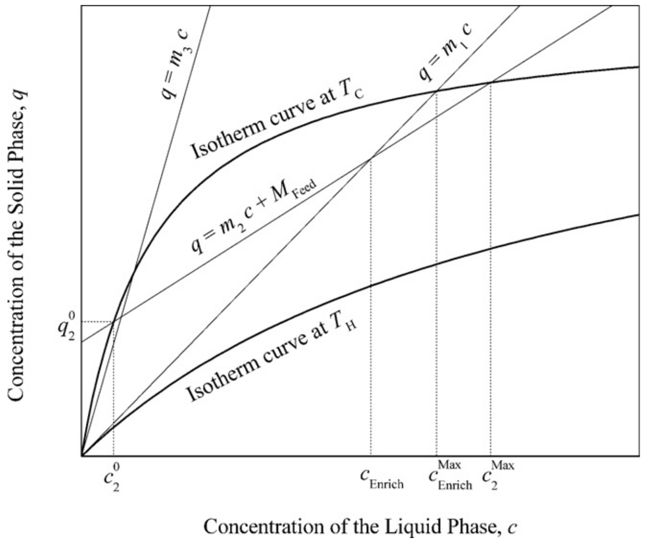

Fig. 5. Operation lines of 3-zone thermal SMB concentrator and isotherm curves on c vs. q plane. Solvent product concentration is assumed to be zero.

If the direction of solute mass flux is the same as the solid flow ($M_j < 0$),

$$c_j^0 = \frac{K_j(q_{Max} + M_j) - m_j - \sqrt{\{K_j(q_{Max} + M_j) - m_j\}^2 + 4K_j m_j M_j}}{2K_j m_j} \tag{6b}$$

where c_j^0 and q_j^0 are the equilibrium concentration of solute in the liquid and solid phases of zone j, respectively, and K_j is the equilibrium constant at the corresponding temperature of zone j. Note that the design method based on equilibrium theory is developed from the equivalent TMB process assuming that temperature is constant in each zone.

The reduced mass flux of a port (M_{Port}) occurred by inflow or outflow of the external stream is,

$$M_{Port} = M_{Destination} - M_{Source} = c_{Port}(m_{Destination} - m_{Source}) \tag{7}$$

where c_{Port} is the concentration of the port, and subscripts, Destination and Source, represent the zones connected to the outlet and inlet of internal liquid flow at the port, respectively. If M_{Port} is positive, the external stream connected to the port is inflow. By defining the reduced mass fluxes of the zone and port, all design parameters (equilibrium concentrations of zones, concentrations of ports, reduced mass fluxes, and adsorption curves) can be drawn on the same c vs q plane. The concentration of a port can be easily obtained from the intersection point of neighboring zone operation lines.

3.3. Driving force of the thermal SMB concentrator

For isothermal and isocratic operation of a SMB process, the adsorption curve of a single solute is identical in every zone, so that it is impossible to obtain higher concentration product than the zone equilibrium concentration, which is lower than or equal to the feed concentration. To focus solutes at the designated port, the intersection point of neighboring zone operation lines has to be located below the adsorption curve of the destination zone and above the adsorption curve of the source zone as shown in Fig. 5 (the intersection point of zones 1 and 2 operation lines), so that the mass fluxes run into the enriched product port and the product concentration is enriched.

For Langmuir adsorption, the migration velocity of solute becomes faster as the solute concentration increases. The intersection point determining the concentration of the enriched product is easily located above the source zone adsorption curve. However, the enriched product concentration is limited by the concave adsorption curve of the destination zone, so that the maximum enriched concentration is determined by the intersection point of the source zone operation line and the adsorption curve of the destination zone as shown in Fig. 5.

In this work, the Feed port is located in the cold zone as shown in Figs. 1, 3 and 4 (called the standard formation). For Langmuir exothermic adsorption without internal feed recycling, the standard formation provides the best performance.

3.4. 2-Zone SMB concentrator

The simplest thermal SMB concentrator consists of two zones, one hot zone and one cold zone, as shown in Fig. 1. Fresh feed is fed into the cold zone with the outlet stream from the cooler (zone 2 in Fig. 1). Solutes are adsorbed at the cold temperature and pure solvent is collected at the Solvent port. Some of solvent is recycled to the inlet of zone 1 after being heated to the hot temperature. A large amount of solute is desorbed and enriched solution is collected at the Enrich port.

At the first and the last zones of the thermal SMB concentrator, there is no mass flux through the zone, so that the operation lines of zones 1 and 2 pass through the origin on c vs q plane (refer to the operation lines of zones 1 and 3 in Fig. 5). Therefore, the design criteria for the 2-zone thermal SMB concentrator to collect pure solvent at the Solvent port are,

$$q_{Max}K_H < m_1 < m_2 < \frac{q_{Max}K_C}{1 + K_C c_{Feed}} \tag{8}$$

where m_j is the flow-rate ratio of zone j, K_C and K_H are the equilibrium constants at cold and hot temperatures, respectively, and c_{Feed} is the concentration of the feed. To decide the operating condition of 2-zone SMB concentrator at the given flow-rate ratios and feed flow-rate, the flow-rate of the Enrich port should be fixed. From the mass balance of zone 2, inlet concentration of zone 2 has to be lower than the maximum concentration of zone 2 (c_2^{Max}) to prevent leakage of solute to the Solvent port. Thus, assuming there is no solute loss at the Solvent port ($c_{Solvent} = 0$), the maximum enriched concentration at the fixed m_1 and m_2 is,

$$\begin{aligned} c_{Enrich}^{Max} &= \frac{Q_2}{Q_1} c_2^{Max} = \left\{ \frac{m_2(1-\varepsilon_P)Q_S + \varepsilon_P Q_S}{m_1(1-\varepsilon_P)Q_S + \varepsilon_P Q_S} \right\} \left(\frac{q_{Max}K_C - m_2}{K_C m_2} \right) \\ &= \frac{m_2 + \beta_P}{m_1 + \beta_P} \frac{q_{Max}K_C - m_2}{K_C m_2} \end{aligned} \tag{9a}$$

where β_P ($= \varepsilon_P/(1-\varepsilon_P)$)is the ratio of the liquid volume to the solid volume in a porous particle. If β_P is zero ($\varepsilon_P = 0$), the maximum enriched concentration is,

$$c_{Enrich}^{Max} = \frac{q_{Max}K_C - m_2}{K_C m_1} \tag{9b}$$

The design criterion of the Enrich port flow-rate is,

$$Q_{Enrich} < \frac{c_{Feed}}{c_{Enrich}^{Max}} Q_{Feed} \tag{10}$$

where Q_{Port} is the volumetric flow-rate of the Port. According to Eqs. (8) and (9), the maximum enriched concentration of the 2-zone thermal SMB concentrator is the highest when the flow-rate ratio of zone 2 is infinitely close to the flow-rate ratio of zone 1. The theoretical maximum enriched concentration of the 2-zone thermal

SMB concentrator is,

$$c_{\mathrm{Enrich}}^{\infty}=\frac{q_{\mathrm{Max}}K_{\mathrm{C}}-m_1}{K_{\mathrm{C}}m_1} \tag{11}$$

To obtain this theoretical enriched concentration, the recycle flow-rate of the thermal SMB concentrator must be much greater than the feed flow rate. In practice the enriched concentration will be lower than $c_{\mathrm{Enrich}}^{\infty}$.

3.5. 3-Zone SMB concentrator

As shown in Fig. 1, in the 2-zone SMB concentrator the zone 2 flow-rate is faster than the zone 1 flow-rate and the inlet concentration of zone 2 is higher than the feed concentration because enriched solution is mixed with fresh feed at the Feed port. With a fast flow-rate and high inlet concentration to the cold zone the solute can pass through the cold zone and contaminate the Solute port. As a result, the maximum concentration of the 2-zone SMB concentrator is lower than its theoretical maximum concentration ($c_{\mathrm{Enrich}}^{\infty}$). The 3-zone thermal SMB concentrator, which has one more zone between the cooling heat exchanger and feed port, can operate one of the cold zones (zone 2 in Fig. 3) with slow flow-rate and prevent direct mixing of feed and enriched product.

Similar to the 2-zone SMB concentrator, the design criteria of zones 1 and 3 are,

$$q_{\mathrm{Max}}K_{\mathrm{H}}<m_1<m_3<\frac{q_{\mathrm{Max}}K_{\mathrm{C}}}{1+K_{\mathrm{C}}c_{\mathrm{Feed}}} \tag{12}$$

Assuming that the concentration of solute at the Solvent port is zero, the overall mass balance is,

$$M_{\mathrm{Feed}}+M_{\mathrm{Enrich}}=0 \tag{13}$$

and the local mass balances of the zones are,

$$M_3=0 \tag{14a}$$

$$M_{\mathrm{Feed}}+M_2=0 \tag{14b}$$

$$M_1=0 \tag{14c}$$

According to the local mass balance of each zone, the operation lines can be drawn on the c vs. q plane as shown in Fig. 5. Leakage of solute occurs in zone 2 if the concentration of the Enrich port calculated from the overall mass balance (c_{Enrich} in Fig. 5) is higher than the maximum concentration of zone 2 (c_2^{Max}). Therefore, the maximum enriched concentration can be obtained from the intersection point of the zone 1 operation line and the isotherm curve at cold temperature ($c_{\mathrm{Enrich}}^{\mathrm{Max}}$ in Fig. 5). The resulting design criteria for zone 2 is,

$$-\frac{\varepsilon_{\mathrm{P}}}{1-\varepsilon_{\mathrm{P}}}<m_2<\frac{m_1c_{\mathrm{Enrich}}^{\mathrm{Max}}-m_3c_{\mathrm{Feed}}}{c_{\mathrm{Enrich}}^{\mathrm{Max}}-c_{\mathrm{Feed}}} \tag{15}$$

and the maximum enriched concentration in the 3-zone thermal SMB concentrator is,

$$c_{\mathrm{Enrich}}^{\mathrm{Max}}=\frac{q_{\mathrm{Max}}K_{\mathrm{C}}-m_1}{K_{\mathrm{C}}m_1} \tag{16}$$

This maximum enriched concentration is the same as the theoretical maximum enriched concentration of the 2-zone thermal SMB concentrator, Eq. (11). However, Eq. (15) is much easier to satisfy than Eq. (10) and the 3-zone SMB concentrator can concentrate a solution more efficiently than a 2-zone SMB concentrator with the same temperature difference. For linear isotherms, if the flow-rate ratios of zones 1 and 3 are in-between the partition coefficients of hot and cold temperatures, the operation lines of the zones 1 and 3 do not intersect with the isotherm lines at hot and cold temperatures, respectively. Therefore, based on equilibrium theory, a 3-zone thermal SMB concentrator (and also 2-zone thermal SMB concentrator) can enrich the product concentration without limitation.

3.6. 4-Zone SMB concentrator

The maximum enriched concentration is decided by the intersection point of the operation line of the hot zone connected to cooler and the isotherm curve at the cold temperature. To increase the maximum enriched concentration, the hot zone flow-rate ratio should be lower. However, the operation line of the hot zone in the 3-zone thermal SMB concentrator must be above the isotherm curve at the hot temperature and pass through the origin. If one more zone is added in the hot zone and dilute by-product is collected between the two hot zones (Fig. 4), the maximum enriched concentration is decided by the intersection point of the operation line of zone 2 and the cold temperature isotherm curve. In the 4-zone thermal SMB concentrator, the operation line of zone 2 has smaller slope than the zone 1 operation line and a positive intercept, so that the 4-zone concentrator is expected to produce more enriched product than the 3-zone thermal SMB concentrator.

The design criteria for zones 1 and 4 are equivalent to the design criteria for zones 1 and 3 of the 3-zone SMB concentrator:

$$q_{\mathrm{Max}}K_{\mathrm{H}}<m_1<m_4<\frac{q_{\mathrm{Max}}K_{\mathrm{C}}}{1+K_{\mathrm{C}}c_{\mathrm{Feed}}} \tag{17}$$

Assuming that the concentration of solute at the Solvent port is zero, the overall mass balance is written as,

$$M_{\mathrm{Feed}}+M_{\mathrm{Enrich}}+M_{\mathrm{Dilute}}=0 \tag{18}$$

and the local mass balances of the zones are,

$$M_4=0 \tag{19a}$$

$$M_{\mathrm{Feed}}+M_3=0 \tag{19b}$$

$$M_{\mathrm{Dilute}}=M_2 \tag{19c}$$

$$M_1=0 \tag{19d}$$

The Dilute outflow stream between zones 1 and 2 allows one to obtain an enriched concentration higher than the equilibrium concentration of zone 2 (c_2^0 in Fig. 6). The maximum enriched concentration is obtained when the operation line of zone 2 is tangent to the isotherm curve at the hot temperature as shown in Fig. 6. If the enriched product concentration is lower than the equilibrium concentration of zone 2 at the maximum mass flux of the Dilute port, there is no driving force to focus solutes between zones 2 and 3 and the enriched concentration theoretically will be the same as the equilibrium concentration of zone 2, although this was not confirmed with a simulation. Therefore, the maximized mass flux of the Dilute port is a necessary condition to collect enriched product higher than the equilibrium concentration of zone 2. At this condition, the reduced mass flux of the Dilute port is,

$$M_{\mathrm{Dilute}}=-\left(\frac{\sqrt{q_{\mathrm{Max}}K_{\mathrm{H}}}-\sqrt{m_2}}{\sqrt{K_{\mathrm{H}}}}\right)^2 \tag{20}$$

and the design criteria of m_2 is,

$$\left\{\frac{\sqrt{q_{\mathrm{Max}}K_{\mathrm{H}}}-\sqrt{q_{\mathrm{Max}}K_{\mathrm{H}}-(1+K_{\mathrm{H}}c_{\mathrm{Feed}})(q_{\mathrm{Max}}K_{\mathrm{H}}-K_{\mathrm{H}}c_{\mathrm{Feed}}m_4)}}{1+K_{\mathrm{H}}c_{\mathrm{Feed}}}\right\}^2<m_2<q_{\mathrm{Max}}K_{\mathrm{H}} \tag{21}$$

since $|M_{\mathrm{Dilute}}|$ has to be lower than $|M_{\mathrm{Feed}}|$ and higher than zero. The equilibrium concentration of zone 2 at this condition is,

$$c_2^0=\frac{K_{\mathrm{H}}(q_{\mathrm{Max}}+M_{\mathrm{Dilute}})-m_2}{2K_{\mathrm{H}}m_2} \tag{22}$$

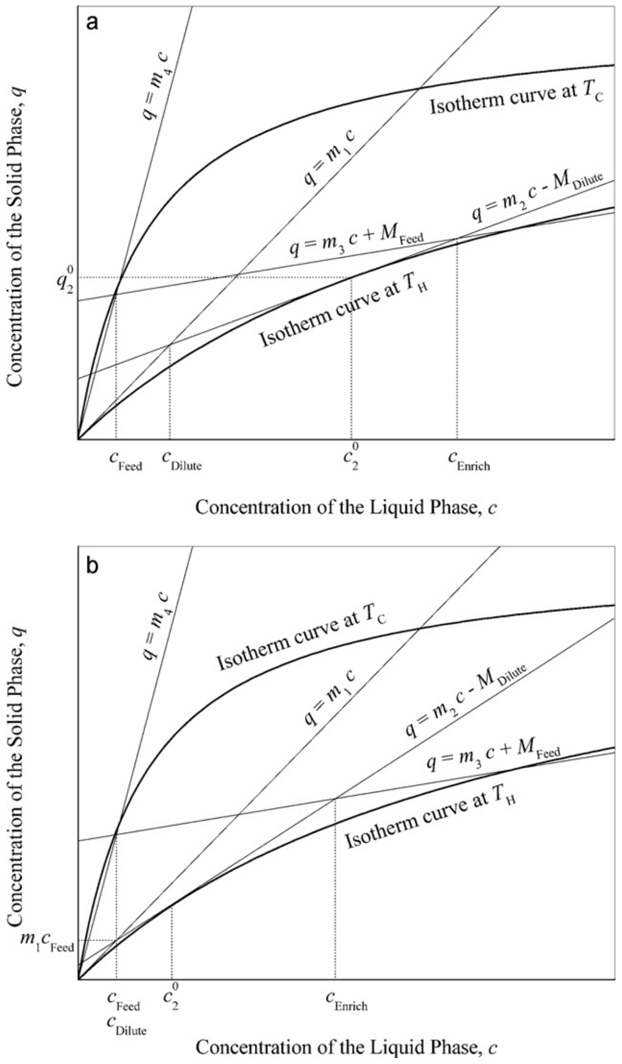

Fig. 6. Operation lines of 4-zone thermal SMB concentrator and isotherm curves on c vs. q plane. Solvent product concentration is assumed to be zero. (a) $c_{Dilute} \neq c_{Feed}$ and (b) $c_{Dilute} = c_{Feed}$.

The maximum enriched concentration, which can be obtained from the intersection point of the zone 2 operation line and the isotherm curve at cold temperature, is,

$$c_{Enrich}^{Max} = \frac{K_H(q_{Max} + M_{Dilute}) - m_2 + \sqrt{\{K_H(q_{Max} + M_{Dilute}) - m_2\}^2 + 4K_H m_2 M_{Dilute}}}{2K_H m_2} \tag{23}$$

The intersection point of zones 2 and 3 indicates the enriched concentration at the Enrich port and must be lower than the maximum enriched concentration obtained from Eq. (23). The resulting design criteria for zone 3 is,

$$-\frac{\varepsilon_P}{1-\varepsilon_P} \quad \text{or} \quad \frac{q_2^0 - m_4 c_{Feed}}{c_2^0 - c_{Feed}} < m_3 < \frac{m_2 c_{Enrich}^{Max} - M_{Dilute} - m_4 c_{Feed}}{c_{Enrich}^{Max} - c_{Feed}} \tag{24}$$

The concentrations of the Dilute and Enrich ports are obtained from the intersection points of operation lines of zones 1 and 2, and zones 2 and 3, respectively, as shown in Fig. 6a.

In most cases there will be no external use for the Dilute stream of intermediate concentration; thus, recycling the Dilute stream to the Feed port is an attractive option. If this stream is recycled, entropy production will be minimized if the dilute stream has the same concentration as the feed. To make the dilute stream the same concentration as the feed solution, the point $(c_{Feed}, m_1 c_{Feed})$ should be on the operation line of zone 2 as shown in Fig. 6b. To satisfy this condition, m_2 is,

$$m_2 = \left\{ \frac{\sqrt{q_{Max} K_H} - \sqrt{q_{Max} K_H - (1 + K_H c_{Feed})(q_{Max} K_H - K_H c_{Feed} m_1)}}{1 + K_H c_{Feed}} \right\}^2 \tag{25}$$

3.7. Role of the mixer connected between the cold and hot zones

Owing to the operation characteristics of the thermal SMB concentrator process, it is possible to have leakage of solute to the Solvent port if the peak of the concentration profile which enters the inlet of the cold zone is higher than the maximum concentration of the cold zone (c_2^{Max} in Fig. 5). This leakage can occur because with a Langmuir isotherm, the high concentration elution band moves faster than the low concentration elution band. Connecting a mixer between the hot zone outlet and the cold zone inlet reduces the size of the peak and can prevent this leakage. Because this peak in the inlet profile repeats with the same period as port switching, a constant inlet concentration can be obtained if two mixers are used to collect solution at the outlet of hot zone. While one mixer is filled with hot zone effluent, the other mixer feeds the cold zone. However, this method generates a stepwise constant inlet profile.

To generate a smooth, non-peaked inlet profile for the cold zone we can develop an "ideal" mixer. The outlet concentration of the ideal mixer ($c_{IdealMixer}$) is defined as,

$$c_{IdealMixer} = \frac{\int_{t-\Delta t}^{t} c_{HotZoneOutlet}\, dt}{\Delta t}, \qquad \Delta t = \begin{cases} t_S, & \text{if } t \geq t_S \\ t, & \text{if } t < t_S \end{cases} \tag{26}$$

where $c_{HotZoneOutlet}$ is the outlet concentration of the hot zone. This ideal mixer can be implemented by two mixers connected in series. The volume of the first mixer equals the elution volume of the hot zone for one port switch. The second mixer in series, which has a relatively very small volume compared to the first mixer, feeds directly into the cold zone. This ideal mixer can completely relieve oscillation of the cold zone inlet profile. In the 2- and 3-zone thermal SMB concentrators, one mixer is located at the Enrich port to relieve concentration oscillation at the outlet of the hot zone. In the 4-zone thermal SMB concentrator, two mixers are located at the Enrich and Dilute ports to relieve concentration oscillation at the outlets of two hot zones. Since the inlet profile of the cold zone oscillates with the same period as port switching, the size of mixer can be normalized by the total elution volume of hot zone per one port switch.

$$\gamma_{Mixer} = \frac{V_{Mixer}}{Q_{HotZoneOutlet} t_S} \tag{27a}$$

where $Q_{HotZoneOutlet}$ is the flow-rate of the outlet of the hot zone and V_{Mixer} is the volume of mixer. For an ideal mixer, we set this ratio to one.

$$\gamma_{IdealMixer} = 1.0 \tag{27b}$$

4. Detailed simulations

For the detailed simulations, 2-, 3-, and 4-zone thermal SMB concentrators were used to concentrate salicylic acid dissolved in water. Adsorbent was Sephabeads SP206 [16]. For the mass balance

Table 1
Parameters and properties used in the mass and energy balances of the system to concentrate salicylic acid in water with Sephabeads SP206 [16,17].

Column:	Length (cm)	20
	I.D. (cm)	9
	ε	0.4
	r_{p} (mm)	0.4
Liquid phase:	ρ_{L} (g/cm^3)	0.998
	μ_{L} (cP)	$2.866 \times 10^{-2} e^{515.93/(T-148.10)}$
	Cp_{L} (J/g/K)	4.184
	ΔH_{V} (J/g)	2260
Solid phase:	ρ_{S} (g/cm^3)	1.19
	Cp_{S} (J/g/K)	2.819
	f_{h}	0.5
Parameters:	K_{e} (J/cm/min/K)	$0.0522Lv$
	k_{e} (1/min)	$4.412 \times 10^{-6} e^{0.03012T}$
	q_{Max} (mg/g)	45.2
	K_{∞} (l/mg)	1.27×10^{-8}
	ΔH (J/mol)	−37,190

in the column, the equilibrium dispersive model with the linear lumped kinetic model were used [17]:

$$v\frac{\partial c}{\partial z} + \varepsilon\frac{\partial c}{\partial t} + (1-\varepsilon)\rho_{\mathrm{S}} f_{\mathrm{h}}\frac{\partial \hat{q}}{\partial t} = \varepsilon D_{\mathrm{e}}\frac{\partial^2 c}{\partial z^2} \tag{28a}$$

$$\frac{\partial \hat{q}}{\partial t} = k_{\mathrm{e}}(\hat{q}^* - \hat{q}) \tag{28b}$$

where v is the superficial velocity of the liquid phase, ε is the void fraction, ρ_{S} and f_{h} are the density and humidity factor (volume ratio of water in a particle of polymer resin) of the solid phase, respectively, D_{e} is the axial dispersion coefficient, $\hat{q}$ is the concentration of solute in the solid phase, $\hat{q}^*$ is the equilibrium concentration at the solid film, and k_{e} is the effective mass transfer coefficient. Axial dispersion coefficient was estimated from the Chung-Wen correlation [18]. Assuming that there is no heat loss at the column wall, the energy balance is,

$$v\frac{\partial \rho_{\mathrm{L}} Cp_{\mathrm{L}} T}{\partial z} + \varepsilon\frac{\partial \rho_{\mathrm{L}} Cp_{\mathrm{L}} T}{\partial t} + (1-\varepsilon)\frac{\partial \rho_{\mathrm{S}} Cp_{\mathrm{S}} T}{\partial t} + \frac{\Delta H}{MW}\frac{\partial q}{\partial t} = \frac{\varepsilon K_{\mathrm{e}}}{\rho_{\mathrm{L}} Cp_{\mathrm{L}}}\frac{\partial^2 \rho_{\mathrm{L}} Cp_{\mathrm{L}} T}{\partial z^2} \tag{29}$$

where ρ_{L} is the density of the liquid phase, Cp_{L} and Cp_{S} are the heat capacity of the liquid and solid phases, respectively, MW is the molecular weight of solute, and K_{e} is the axial thermal conductivity. All parameters used in the mass and energy balance are shown in Table 1 [16,17]. Since the heat capacity and density of the liquid and solid phases are constant, the velocity of thermal wave can be calculated as $(v\rho_{\mathrm{L}} Cp_{\mathrm{L}}/(\varepsilon\rho_{\mathrm{L}} Cp_{\mathrm{L}} + (1-\varepsilon)\rho_{\mathrm{S}} Cp_{\mathrm{S}}))$. Assuming that the column is adiabatic and that axial thermal conductivity is negligible, less than one column volume is large enough to change the column temperature since $\rho_{\mathrm{L}} Cp_{\mathrm{L}}$ (=4.18) > $\rho_{\mathrm{S}} Cp_{\mathrm{S}}$ (=3.35). In detailed simulations, the thermal wave velocity is much faster than the mass wave velocity, so that the transient for temperature change is quite small.

Table 2
Solubility of salicylic acid in water [19].

Temperature (K)	Solubility (g/L)[a]
293	1.76
313	3.93
333	8.74
353	19.45

[a] ln(solubility/1000) = 0.04(temperature) − 18.06.

To confirm the design method of thermal SMB concentrator, several simulations were carried out with Aspen Chromatography (Aspen Technology Inc., Burlington, MA, U.S.A., Ver. 2006.5). The finite element method with biased upwind scheme and the Gear method were used. For the simulation of the thermal SMB concentrator, two columns (9 cm I.D. × 20 cm length) were used in each zone. The feed conditions were fixed as 0.01 g salicylic acid/L at 100 mL/min. Table 2 shows the solubility of salicylic acid in water [19]. All feed and enriched concentrations obtained from the simulations were within the soluble range. To determine the cyclic steady state, each simulation was performed until the absolute ratio of total inlet to outlet mass was smaller than 5e−4. Ambient and cold zone temperatures were set to 293 K and runs with hot zone temperatures of 313 K, 333 K, and 353 K were used.

To compare energy consumption with a simple evaporation process, equivalent energy consumption for a single-stage evaporator doing the same concentration as the thermal SMB concentrator was calculated,

$$E_{\mathrm{Evaporator}} = \frac{Cp_{\mathrm{L}}(T_{\mathrm{b.p.}} - T_{\mathrm{Amb}}) + \Delta H_{\mathrm{V}}}{\rho_{\mathrm{L}} Q_{\mathrm{Solvent}}} \tag{30}$$

where $E_{\mathrm{Evaporator}}$ is energy consumption per unit mass of pure solvent of the equivalent single-stage evaporator, $T_{\mathrm{b.p.}}$ is the boiling point of solvent, T_{Amb} is the ambient temperature, and ΔH_{V} is the latent heat of boiling.

5. Results

In the 2-zone thermal SMB concentrator, the maximum enriched concentration is determined by the zone flow-rate ratios of zones 1 and 2. The purpose of the design method is to set initial values for these flow-rate ratios. To confirm the design method the simulation results with two different flow-rates of the Enrich port at the fixed flow-rate ratios of zones 1 and 2 were compared. One flow-rate was chosen so that based on Eq. (9a) the enriched product concentration would be 95% of the maximum enriched concentration. The other Enrich port flow-rate was set so that the enriched product concentration would have to be 105% of the maximum enriched concentration predicted by Eq. (9a) if the solvent product remained pure. If the local equilibrium design method is correct the first set of operating conditions will produce close to pure solvent (note that a higher mass transfer coefficient may be necessary), but the second set of operating conditions will be unable collect pure solvent regardless of the value of the mass transfer coefficient. Simulations of the 2-zone thermal SMB concentrator to collect 95% and 105% of the maximum enriched concentration were conducted with values of the flow-rate ratio of zone 2 (m_2) ranging from 895.44 to 445.44 at intervals of 50. The flow-rate ratio of zone 1 was fixed at 252.98, which is a safety margin of 20 compared to the minimum m_1 calculated from Eq. (8), ($q_{\mathrm{Max}}K$ at 333 K, is 232.98).

Fig. 7a shows the changes of the Enrich port concentration (c_{Enrich}) of the 2-zone thermal SMB concentrator as the flow-rate ratio of zone 2 (m_2) is changed. Solid and dash lines are calculated from the overall mass balance assuming that there is no solute loss at the Solvent port. To collect pure solvent, the enriched concentration has to be the same as the enriched concentration calculated from the overall mass balance without solute loss at the Solvent port. The simulated results of the operating condition to collect 105% of the maximum c_{Enrich} are lower than the values calculated from the mass balance. The simulation results to collect 95% of the maximum c_{Enrich} have a good agreement with the values calculated from the mass balance, so that there is no solute loss at the Solvent port as shown in Fig. 7b. As mentioned at Section 3.6, if there is no mixer between cold and hot zones, leakage of solute can be occur. To confirm the necessity of a mixer connected to the inlet of cold zone, systems with an ideal mixer and without a mixer were compared at the same operating conditions to collect 95% of the maximum c_{Enrich}. If no mixer is used between the hot and cold zones, some of solute passes through zone 2 and contaminates the Solvent port,

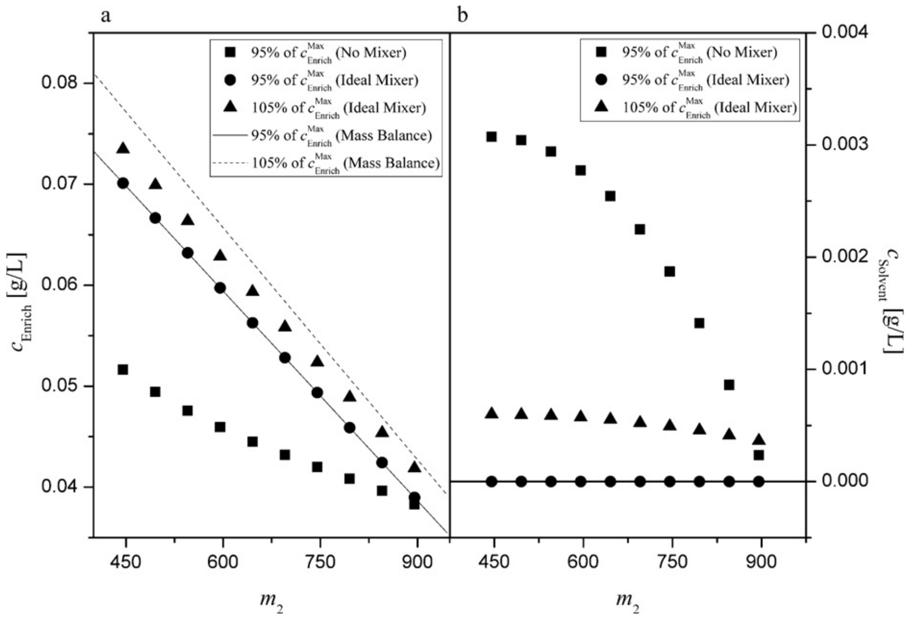

Fig. 7. Concentrations at the Enrich and Solvent ports of 2-zone thermal SMB concentrator for changes in the zone 2 flow-rate ratio ($Q_{\text{Feed}} = 100$ mL/min, $c_{\text{Feed}} = 0.01$ g/L, $m_1 = 252.98$). (a) The Enrich port and (b) the Solvent port.

so that the concentration of the Enrich port is much lower than the system with the ideal mixer. The concentration of the Solvent port increases as the Enrich port collects more enriched solution as shown in Fig. 7a and b.

The same comparisons were carried out for the 3-zone SMB concentrator as shown in Fig. 8. The maximum concentration of the Enrich port is decided by the flow-rate ratio of zone 1 (m_1) (Eq. (16)), so that the flow-rate ratio of zone 1 was varied from 252.98 to 452.98 at intervals of 20. The flow-rate ratio of zone 3 was fixed at 925.44 with 20 of safety margin (the maximum m_3 obtained from Eq. (12), $(q_{\text{Max}}K)/(1 + Kc_{\text{Feed}})$ at 293 K, is 945.44). As shown in Fig. 8a, the simulation results of the system with the ideal mixer can match the value obtained from the mass balance at the condition of 95% of the maximum c_{Enrich}. However, at the operating conditions to collect 105% of the maximum c_{Enrich} (5% excess of the design criteria), some solute was collected at the Solvent port since the maximum concentration of zone 2, c_2^{Max}, is lower than the designed concentration of enriched product. When the 3-zone thermal SMB concentrator was operated without a mixer at the inlet of the cold zone, it was impossible to collect pure solvent because of solute leakage.

According to the design method for the 4-zone thermal SMB concentrator, the maximum concentration of enriched product occurs when the absolute value of the Dilute port mass flux is the maximum (Eq. (20)), which is the necessary condition to collect an enriched product with a higher concentration than the equilibrium concentration of zone 2. Therefore, the maximum concentration of enriched product in the 4-zone thermal SMB concentrator is decided by the flow-rate ratio of zone 2. Fig. 9 shows the changes of the concentrations of the Enrich and Solvent ports for the 4-zone thermal SMB concentrator. The flow-rate ratios of zones 1 and 4 are fixed at 252.98 and 925.44 with the same safety margin used in the simulations of 2- and 3-zone thermal SMB concentrators. The flow-rate ratio of zone 2 was varied from 60 to 220 at intervals of 20. The flow-rate ratio of zone 3 was varied to collect enriched product at 95% and 105% of the maximum enriched concentration. As shown in Fig. 9a, the 4-zone thermal SMB concentrator cannot concentrate over the maximum concentration obtained from the local equilibrium design method while producing pure solvent. The 4-zone thermal SMB concentrator without a mixer cannot collect pure solvent at these operating conditions because of solute leakage.

The concentration of the Dilute port is limited by the maximized absolute mass flux of zone 2, which can be determined from the operation lines of zones 1 and 2 (Fig. 6a). The concentrations of the feed and the Dilute port should be almost same. Fig. 10 shows the changes of the Dilute port concentration and production yield. As shown in Fig. 9a, all enriched concentrations are higher than the equilibrium concentration of zone 2. The mass fluxes of Dilute port are the maximum and the dilute product concentrations do not depend upon the mixer; thus, the dilute product concentrations are in good agreement with the value obtained by the local equilibrium design method. To get higher enriched concentration than the 3-zone thermal SMB concentrator, m_2 has to be lower than the minimum m_1 calculated from Eq. (17), and some solute must be collected at the Dilute port at a relatively low concentration. As shown in Figs. 9a and 10, as m_2 decreases, the concentrations of Enrich and Dilute ports increase, but recovery decreases. Consequently, the 4-zone thermal SMB concentrator can produce highly enriched product compared to the 2- or 3-zone thermal SMB concentrators but with reduced yield.

6. Discussion

Because of the non-linearity of the isotherm very high peak outlet concentrations are predicted for the hot zone. Because mass transfer rates are finite, the thermal SMB concentrators were not able to obtain these predicted peak concentrations. The thermal SMB concentrator with an ideal mixer can produce enriched product with concentrations very close to those predicted by the local equilibrium design method. However, the ideal mixer will be difficult to implement. When a single mixer is used in the thermal SMB concentrator, the mixer size can be normalized by Eq. (27). Fig. 11 shows the ratio of Enrich port concentration with an actual mixer to the enriched concentration predicted with an ideal mixer and the concentration of the Solvent port as a function of the mixer ratio, γ_{Mixer}. Because the 2-zone thermal SMB concentrator operates with high flow-rate ratio of hot zone compared to zone 2 in 3-zone thermal SMB concentrator and zone 3 in 4-zone thermal SMB concentrator, operation without a mixer (Fig. 10a) results

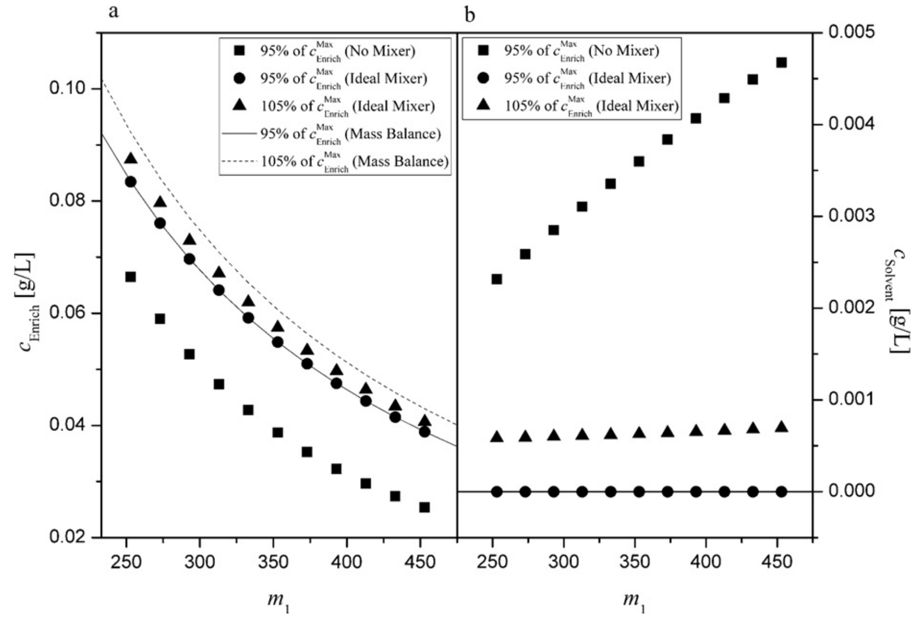

Fig. 8. Concentrations at the Enrich and Solvent ports of 3-zone thermal SMB concentrator for changes in the zone 1 flow-rate ratio (Q_{Feed} = 100 mL/min, c_{Feed} = 0.01 g/L, m_3 = 925.44). (a) The Enrich port and (b) the Solvent port.

in significant solute loss to the Solvent port. Thus, a relatively large mixer volume (~174 L, ~0.9 × 193.6 L) is required to obtain the designed enriched concentration. In addition, the designed enrichment concentration of the 2-zone thermal SMB concentrator (0.063) is lower than the 3-zone system (0.83) and the 4-zone concentrator (0.145 g/L). All designed enrichment concentrations are 95% of the maximum enriched concentration. Fig. 12 shows the start-up and cyclic steady state concentration profiles at the Enrich port of 2-zone SMB concentrator without a mixer ($\gamma_{Mixer} = 0$) and with a mixer ($\gamma_{Mixer} = 1$). Without a mixer (Fig. 12a), the high concentration profile elutes near the beginning of the switching interval and some solute passes through the cold zone to contaminate the Solvent product. Therefore, the average concentration is lower than the average concentration obtained from the system with a mixer ($\gamma_{Mixer} = 1$, Fig. 12b). When a mixer is connected in the Enrich port (Fig. 12b), the highest concentration of the hot zone elution profile occurs more towards the middle of switching interval and is much lower than that of the system without a mixer (Fig. 12a).

The total energy consumption of thermal SMB concentrator is much smaller than the thermal energy consumption in single-stage evaporation. Table 3 compares the thermal energy consumption for concentrating dilute aqueous solutions of salicylic acid with a thermal SMB concentrator and with the equivalent single-stage evaporator. In these comparisons, energy to condense evaporated solvent is not included. From Eq. (30), energy to produce pure solvent is equal to 2595 kJ/kg for all cases of equivalent evaporator. Except for the 2-zone thermal SMB concentrator with a small

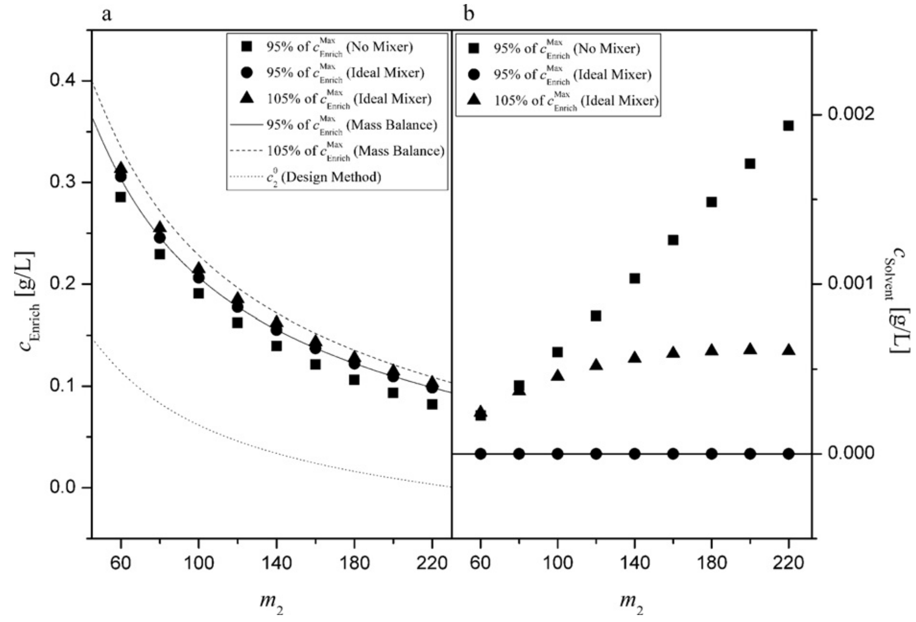

Fig. 9. Concentrations at the Enrich and Solvent ports of 4-zone thermal SMB concentrator for changes in the zone 2 flow-rate ratio (Q_{Feed} = 100 mL/min, c_{Feed} = 0.01 g/L, m_1 = 252.98, m_4 = 925.44). (a) The Enrich port and (b) the Solvent port.

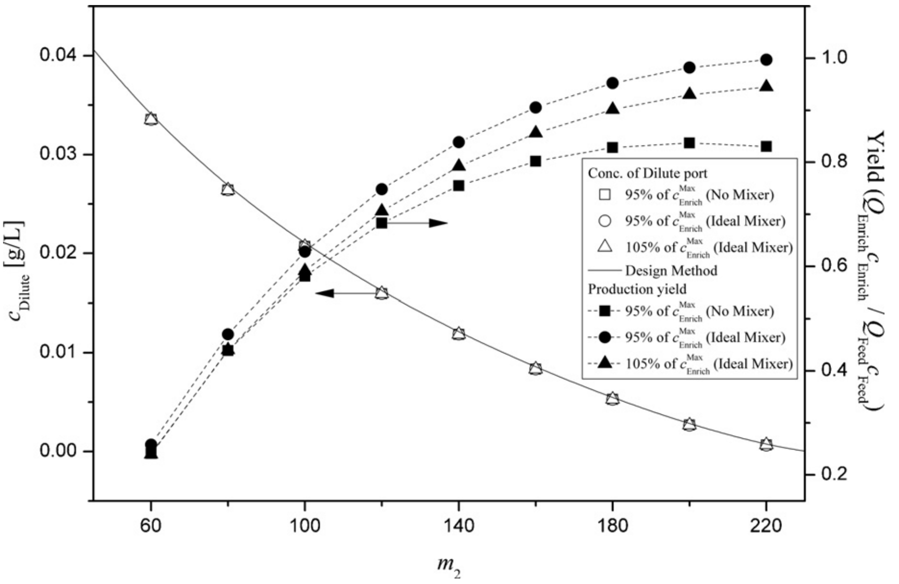

Fig. 10. Concentrations at the Dilute port and recovery yield of 4-zone thermal SMB concentrator by zone 2 flow-rate ratio ($Q_{Feed} = 100$ mL/min, $c_{Feed} = 0.01$ g/L, $m_1 = 252.98$, $m_4 = 925.44$).

temperature difference (313 K hot temperature), the thermal SMB concentrators consume less than 10% of the thermal energy consumed by the evaporator. As the hot temperature is increased, the energy consumption in the thermal SMB concentrators decreases and the enriched concentration increases. Energy consumption reported for the thermal SMB concentrator is the sum of energy for cooling hot liquid to cold temperature and for heating cold liquid to hot temperature. Obviously, this thermal energy consumption can be further decreased by heat exchange. All design parameters in Table 3 are calculated to collect 95% of the maximum enriched concentration at each temperature level. Therefore, the concentration of the Enrich port in Table 3 is the maximum concentrating capacity with a 5% safety margin. Mixer size ratio γ_{Mixer} was arbitrarily set to 1.

The zone 2 flow-rate ratio of 4-zone thermal SMB concentrator is calculated to set the concentration of the Dilute port to the same concentration as the feed solution, so that this dilute port product can be recycled to the feed directly after cooling down to feed temperature. As shown in Table 3, at 313 K of hot zone temperature, 45.57 mL/min of dilute product recycles to the Feed port, so that fresh feed flow-rate decreases to 54.43 mL/min and additional energy is required to cool the hot recycle stream. Because of this additional energy, energy consumption of the 4-zone thermal SMB concentrators is similar to that of the 3-zone thermal SMB concentrators. However, the 4-zone thermal SMB concentrators can produce much more enriched product than the 3-zone thermal SMB concentrators, and feed throughput increases as a larger temperature difference is used. Because hotter solvent can flush out more

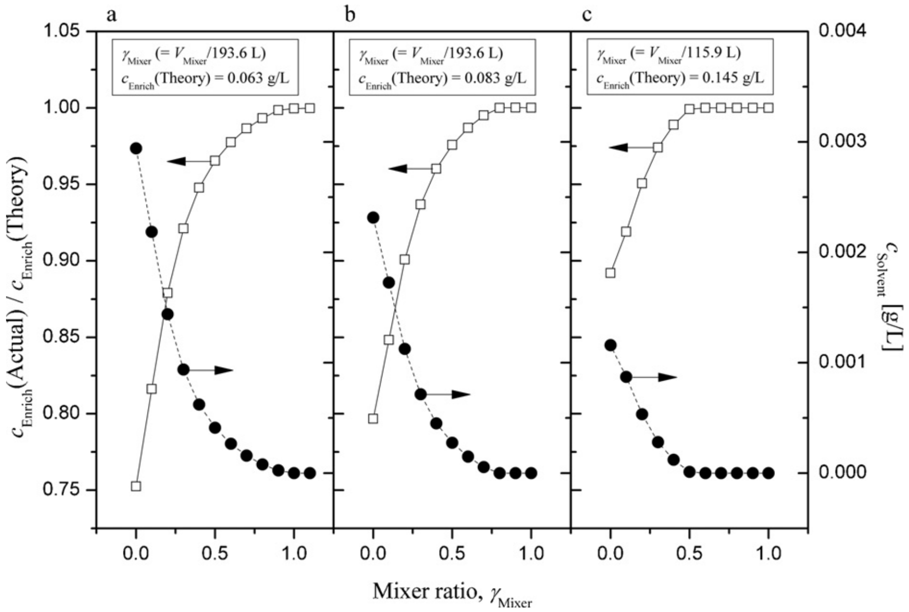

Fig. 11. Enriched port concentration ratio and the Solvent port concentration of the system as γ_{Mixer} is increased. (a) 2-Zone thermal SMB concentrator ($Q_{Feed} = 100$ mL/min, $c_{Feed} = 0.01$ g/L, $m_1 = 252.98$, $m_2 = 645.44$, $Q_E = 17.77$ mL/min, $T_C = 293$K, $T_H = 333$K). (b) 3-Zone thermal SMB concentrator ($Q_{Feed} = 100$ mL/min, $c_{Feed} = 0.01$ g/L, $m_1 = 252.98$, $m_2 = 161.45$, $m_3 = 925.44$, $T_C = 293$K, $T_H = 333$K). (c) 4-Zone thermal SMB concentrator ($Q_{Feed} = 100$ mL/min, $c_{Feed} = 0.01$ g/L, $m_1 = 252.98$, $m_2 = 151.12$, $m_3 = 101.07$, $m_4 = 925.44$, $T_C = 293$K, $T_H = 333$ K).

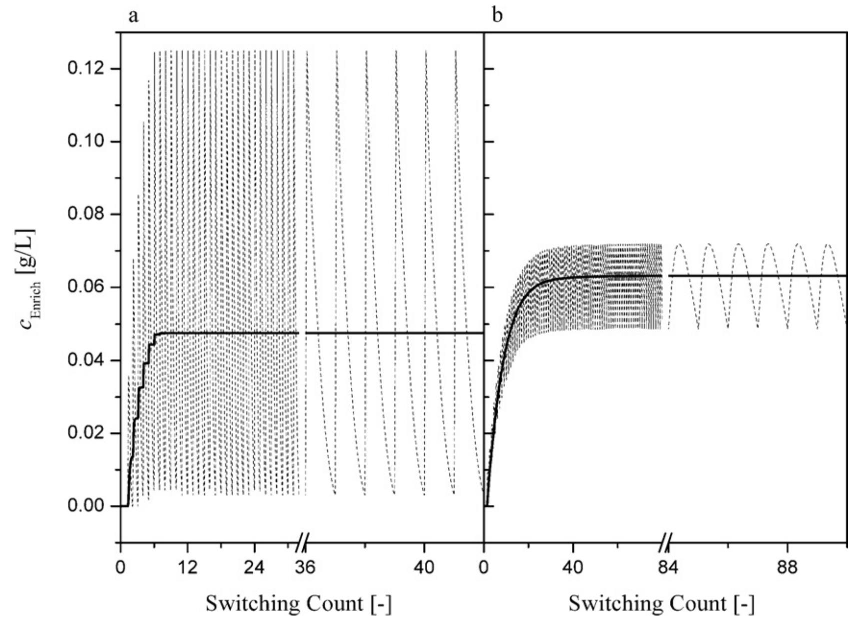

Fig. 12. Elution profiles at the outlet of hot zone of 2-zone thermal SMB concentrator (Q_{Feed} = 100 mL/min, c_{Feed} = 0.01 g/L, m_1 = 252.98, m_2 = 545.44, and Q_{Enrich} = 15.82 mL/min). (a) γ_{Mixer} = 0 (V_{Mixer} = 0 L), (b) γ_{Mixer} = 1 (V_{Mixer} = 193.6 L).

solute in zone 1, less solvent is recycled and the total amount to be cooled down at the inlet of the hot zone also decreases. Furthermore, a larger difference of the adsorption characteristics by temperature swing allows production of a highly enriched product.

The thermal SMB concentrator was compared with a single-stage evaporator, and obviously the energy consumption in the evaporator can be decreased by adding additional stages. However, even with a large number of evaporation stages, the energy consump-

Table 3
Energy consumption of thermal SMB concentrator and equivalent single-stage evaporator.

2-Zone thermal SMB concentrator

Operating conditions ($m_1/m_2/Q_E$ (ml/min))	Temperature (K) (Ambient/Cold/Hot)	Outlet conc. (g/L) (Enrich/Solvent)	Flow-rate (ml/min) (Feed/Solvent)	Energy consumption (kJ/kg)	
				Thermal SMB	Evaporator[a]
569.66/645.44/40.01	293/293/313	0.025/2.4e−5	100/59.99	1213 (578/635)[b]	
252.98/645.44/17.77	293/293/333	0.056/1.8e−10	100/82.23	181 (72/109)[b]	2595 (335/2260)[c]
128.84/645.44/9.05	293/293/353	0.110/1.2e−18	100/90.95	101 (38/63)[b]	

3-Zone thermal SMB concentrator

Operating conditions ($m_1/m_2/m_3$)	Temperature (K) (Ambient/Cold/Hot)	Outlet conc. (g/L) (Enrich/Solvent)	Flow-rate (ml/min) (Feed/Solvent)	Energy consumption (kJ/kg)	
				Thermal SMB	Evaporator[a]
569.66/364.32/925.44	293/293/313	0.027/3.3e−7	100/63.41	222 (87/135)[b]	
252.98/161.45/925.44	293/293/333	0.083/1.1e−11	100/88.02	104 (40/64)[b]	2595 (335/2260)[c]
128.84/82.19/925.44	293/293/353	0.181/7.3e−20	100/94.47	67 (26/41)[b]	

4-Zone thermal SMB concentrator

Operating conditions ($m_1/m_2/m_3/m_4$)	Temperature (K) (Ambient/Cold/Hot)	Outlet conc. (g/L) (Enrich/Dilute/Solvent)	Flow-rate (ml/min) (Feed/FF[d]/Solvent)	Energy consumption (kJ/kg)	
				Thermal SMB	Evaporator[a]
569.66/227.46/174.57/925.44	293/293/313	0.078/0.0099/7.4e−8	100/54.43/47.38	257 (41/81/135)[e]	
252.98/151.12/101.07/925.44	293/293/333	0.145/0.0099/4.4e−13	100/87.64/81.57	114 (25/25/64)[e]	2595 (335/2260)[c]
128.84/82.01/53.38/925.44	293/293/353	0.289/0.0097/4.7e−22	100/94.63/91.35	73 (17/15/41)[e]	

[a] Energy consumption calculated from Eq. (30).
[b] (Energy consumption for cooling/Energy consumption for heating).
[c] (Energy consumption for heating liquid/Energy consumption caused by latent heat of boiling).
[d] Flow-rate of fresh feed when dilute product is recycled to the Feed port (=$Q_{\mathrm{Feed}} - Q_{\mathrm{Dilute}}$).
[e] (Energy consumption for cooling between zones 2 and 3/Energy consumption for cooling recycle/Energy consumption for heating).

tion of the 4-zone thermal SMB concentrators will be significantly less than the evaporators.

7. Conclusions

The SMB process, which was originally developed as a fractionator to separate components using a desorbent, was modified to concentrate a solution with a thermal gradient and no added desorbent. Two, three, and four zone configurations of thermal SMB concentrators were designed to concentrate salicylic acid in water. A design method for thermal SMB concentrators based on local equilibrium theory was introduced to calculate the maximum enriched concentration, and the predictions were compared to detailed Aspen Chromatography simulations. The maximum enriched concentrations of the thermal SMB concentrators increase as more zones are added. However, in the 4-zone thermal SMB concentrator, enriched product solute recovery decreases unless the dilute product is recycled to the feed. Due to the behavior of SMB operation and the temperature swing, the elution profile of the hot zone periodically fluctuated and a high solute concentration is eluted near the beginning of the switching interval. Adding a mixer prevents leakage of solute through the cold zone caused by the high velocity of the high concentration peaks. Properly designed thermal SMB concentrators consume remarkably little energy compared to the equivalent single-stage evaporation. Thermal energy consumption is decreased as more zones are used and with larger temperature differences producing highly enriched product. Of course, energy costs are only part of the picture, and capital costs need to be determined to compare thermal SMB concentrators to the alternatives. Further research is required to develop optimum concentration processes, which may well be a hybrid of a thermal SMB concentrator with another process.

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