

# THE EFFECT OF ADSORPTION ISOTHERMS AND FLOW RATES ON SEPARATION PERFORMANCE IN MULTICOMPONENT CONTINUOUS SEPARATION

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Adsorption isotherms of a ternary mixture containing dimethyl phthalate, diethyl phthalate and di-*n*-butyl phthalate were measured by the step-pulse method in a wide range of concentration. They were expressed by Langmuir-type equations with weak interaction between components. The applicability of the proposed process to multicomponent continuous separation was confirmed by coupling the results of single-column experiments and simulation of the total process based on the isotherms obtained. It was found that non-linearity in adsorption isotherms had a positive effect on the separation.

Separation performance depends significantly on the flow rates of desorbent fed to the columns in the refining zone and the shift time. Their effects on the separation were examined and the characteristic features of the proposed process were clarified. It was found for the ternary mixture tested that the middle component (i.e., diethyl phthalate) was quite sensitive to separation performance.

## Introduction

Continuous separation by liquid chromatography is promising for chemical industry. A simulated moving-bed adsorber has been applied commercially<sup>1)</sup> but it cannot be applied when the mixture contains more than three components. Hashimoto *et al.* have suggested a process for continuous separation of mixtures with three components by alternately arranging two types of columns packed with different adsorbents<sup>2)</sup>. Hence the object mixture was restricted by those columns in that process.

A new process for multicomponent continuous separation was proposed in a previous paper to utilize the advantage of high-performance liquid chromatography<sup>3)</sup>. The performance of the proposed system was confirmed partly by experiments with a single column for the main process and partly by simulation of the separation in the whole system for separation of a ternary mixture of dimethyl phthalate, diethyl phthalate and di-*n*-butyl phthalate.

In the previous paper, linear isotherms were assumed because the concentration of each component in the feed was low<sup>3)</sup>. The parameters of the linear isotherms were obtained by simulating the impulse response observed for the same column. The linearity held in that tested range. However, the process may often be applied in the range of higher concentration.

In the present study, the adsorption isotherms were measured over a wide range of concentration by the step-pulse method. The isotherms obtained appeared to be of a Langmuir type. The experiment and simulation

were done for multicomponent continuous separation with a feed mixture of higher concentration. The features of separation based on non-linear isotherms were also studied.

It is important in this process that the flow rates of desorbent and the shift time of column-groups are properly determined to achieve satisfactory separation performance. Hence these effects on separation performance were demonstrated by examining the concentration profile of each component in the columns.

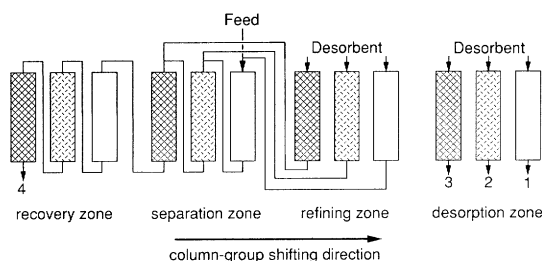
## 1. Separation Process

Figure 1 represents the basic configuration for three-component separation with recovery of desorbent. It is composed of four column-groups, each of which consists of three columns, namely the right-hand column, the middle column and the left-hand column. The feed solution is supplied to the right-hand column in the separation zone, and the desorbent is supplied to each column in both refining and desorption zones.

In the separation zone, the feed mixture is supplied to the right-hand column. The component with the smaller distribution coefficient in the feed flows faster and enters the adjacent middle column. After a certain period, all column-groups are shifted rightward. This shift time is determined in such a way that each intended component of the corresponding column in the column-group does not leak to the next column.

In the refining zone, the desorbent is supplied to each column and the components with distribution coefficients smaller than the intended one are forced to flow out of the column. The outlet flow from each column is

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**Fig. 1** Schematic representation of a multicomponent continuous separation process

refluxed to the corresponding column in the separation zone. Now each column has only the intended component at the next shift time when each column in the refining zone is moved to the desorption zone. Then each intended component is recovered from the corresponding column as product 1, 2 or 3 in Fig. 1. In this manner the feed mixture is separated into the pure components continuously.

By installing a recovery zone where the component with the smallest distribution coefficient is adsorbed and prevented from flowing out of the bottom of the left-hand column, pure desorbent is recovered as product 4 in the figure.

## 2. Experimental and Method

Separation of a ternary mixture with recovery of desorbent supplied in the refining zone was examined. The column was packed with silica gel (mean diameter 60  $\mu\text{m}$ ) and was 20 mm in inside diameter and 100 mm long. A mixture of hexane and ethyl acetate in the volumetric ratio 3:2 was used as both desorbent and solvent in the feed solution. The feed mixture contained dimethyl phthalate (denoted as C1), diethyl phthalate (denoted as C2) and di-*n*-butyl phthalate (denoted as C4). Their concentrations in the feed mixture were 613 mol/m<sup>3</sup> for C1, 554 mol/m<sup>3</sup> for C2 and 501 mol/m<sup>3</sup> for C4.

### 2.1 Step-pulse method

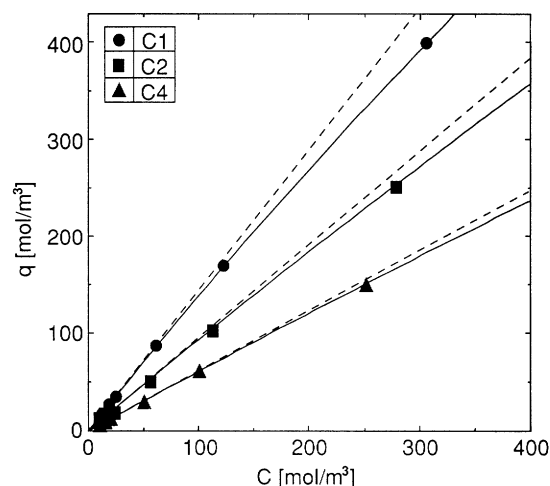
To measure the isotherms, the step-pulse method using the column that would be used in the subsequent experiment was applied. First, the column was equilibrated with a solution containing the object components at given concentrations. Then, a small amount (for example, 20 mm<sup>3</sup>) of sample containing the component at the same concentration as the feed was injected into the column. The derivative,  $dq/dC$ , was calculated from the elution time obtained by this impulse response.

### 2.2 Adsorption isotherms and adsorption rates

First, the isotherm for a single component, C1, C2 or C4, was examined. The closed keys in Fig. 2 represent the experimental data measured by the step-pulse method. These data are represented by the following Langmuir equation:

$$q_i = a_i C_i^* / (1 + b_i C_i^*) \quad (1)$$

The coefficients obtained for each component are shown in Table 1. The solid lines in Fig. 2 show the values cal-



**Fig. 2** Adsorption isotherms of dimethyl phthalate, diethyl phthalate and di-*n*-butyl phthalate

**Table 1.** Coefficients of Langmuir equation

Material	$a_i$ [-]	$b_i$ [m <sup>3</sup> /mol]
C1	1.44	$3.46 \times 10^{-4}$
C2	0.950	$1.58 \times 10^{-4}$
C4	0.612	$8.21 \times 10^{-5}$

culated by the above equation while the dashed lines show the values when  $b_i$  is assumed to be zero. The separation for the case at lower concentration, indicated by dashed lines, was discussed in the previous paper<sup>3)</sup>.

The distribution coefficient of each component in ternary mixtures was also measured by the step-pulse method. However, the observed values did not match those expected by the following multicomponent Langmuir Eq. (2) with the coefficients obtained by Eq. (1) for each component.

$$q_i = a_i C_i^* / (1 + \sum b_j C_j^*) \quad (2)$$

It is supposed in the multicomponent Langmuir equation that all sites are energetically equivalent. However, it is reasonable to consider that a certain component is easily adsorbed around the sites where that component is adsorbed. This reasoning implies that the interaction, i.e., the effect of other components, is not so strong as expected from the above multicomponent Langmuir equation. Hence the following modification was proposed:

$$q_i = a_i C_i^* / (1 + \sum n_{ij} b_j C_j^*) \quad (3)$$

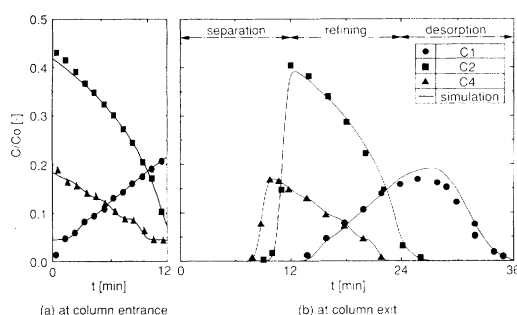
The modification coefficient  $n_{ij}$  may become more significant when the neighboring component  $j$  occupies a larger number of sites on the adsorbent, i.e., it has a larger distribution coefficient. Thus the following equation for  $n_{ij}$  was introduced for the adsorption isotherms:

$$j \neq i: n_{ij} = a_j / (1 + \sum a_k) \quad (4.a)$$

$$j = i: n_{ij} = 1 \quad (4.b)$$

By inserting the values in Table 1,  $n_{ij}$  for  $j \neq i$  becomes 0.18 to 0.42.

The overall mass transfer coefficient of each component is also required for predicting the separation.



**Fig. 3** Transient change in concentrations of realized result and that expected by simulation  
(a) at the entrance of the column  
(b) at the exit of the column

They were determined in such a manner that the shape of each peak observed by the impulse response could match that obtained by the simulation. They were  $8.0\text{s}^{-1}$  for C1,  $7.0\text{s}^{-1}$  for C2 and  $6.0\text{s}^{-1}$  for C4 respectively.

### 2.3 Experimental in the right-hand column

The experiment to examine the behavior of the right-hand column was performed. This column was selected because all three components were observed in it and its behavior was the most complicated in this process. First, the transient changes in the concentration at the entrance of this right-hand column in the separation zone at the steady state were calculated by a simulator developed for the simulation of pressure-swing adsorption<sup>4)</sup>. They are shown by the solid lines in **Fig. 3(a)**. The flow rates for this run are listed in **Table 2**. The period between the successive movements of column-groups was set as 12min. Second, the transient change in the concentration of each component at the entrance of this column at steady state predicted by the simulation of the separation in the whole system was realized experimentally by four computer-controlled pumps that supplied the three respective solutions of C1, C2 and C4 of the feed concentration and the desorbent. Those transient changes that were realized experimentally are shown by closed keys in **Fig. 3(a)**. It is found that the transient changes were realized satisfactorily. Third, the transient changes at the exit of this column by feeding the flow shown in **Fig. 3(a)** were analyzed and quantified by HPLC. This result was compared with that expected from the simulator. The experimental data for the transient changes at the exit of the column are shown by closed keys in **Fig. 3(b)**, while the simulation results are shown by curves.

The period up to 12min, which is the shift time, corresponds to the result for the above-mentioned experiment corresponding to the stage in the separation zone. The experiment and the simulation of the right-hand column for both refining and desorption zones were also performed. The period from 12min to 24min in **Fig. 3(b)** corresponds to the former and the period from 24min and 36min to the latter. During these periods, only desorbent was fed, at the flow rates shown in **Table 2**.

**Figure 3(b)** shows that the simulation results represent the experimental data satisfactorily. This confirms

**Table 2.** Flow rates

	Column 1 [mm <sup>3</sup> /s]	Column 2 [mm <sup>3</sup> /s]	Column 3 [mm <sup>3</sup> /s]
Feed	2.00		
Desorbent 1*	42.5	35.0	0.00
Desorbent 2**	19.0	12.3	36.3

\* Desorbent in refining zone

\*\* Desorbent in desorption zone

that the performance of the total process may be predicted by the simulation. The corresponding figures for the case at lower concentration were shown in **Figs. 5** and **6** in the previous paper<sup>3)</sup>.

## 3. Separation Performance

### 3.1 Performance in the right-hand column

Let us examine the effect of non-linearity by comparing **Figs. 3(a)** and **(b)** in this paper with **Figs. 5** and **6** in the previous paper<sup>3)</sup>. Since the coefficient  $b_i$  of C4 is very small, no effect of non-linearity can be observed in this experiment. As for C1 and C2 in **Fig. 3(b)**, the peaks appear earlier and the rising parts of the peaks are sharper than those demonstrated in the previous paper<sup>3)</sup>. The simulation including the effect of  $b_i$  in the Langmuir-type isotherms can explain this fact.

For the head and tail of the peak, say the one at  $t = 13$  min in **Fig. 3(b)**, the concentration of some other component becomes large and the adsorbed amount of the specified component is decreased. At 22min, C1 and C2 have almost the same concentration. C1 has the largest distribution coefficient and hence has the strongest effect on the interaction among the three components, and it is more difficult for C2 to be adsorbed in the existence of C1. Consequently, C2 flows faster as compared to the case without interaction<sup>3)</sup>. Thus the separation of C1 and C2 becomes much easier. This means that the component that is adsorbed more strongly and is flowing more slowly is forced to sweep out the component that is adsorbed more weakly. This phenomenon is similar to displacement. Therefore, non-linearity in isotherms makes the separation easier and this may increase purity and recovery of the products.

### 3.2 Performance of the total system

The performance of the total system is simulated by using the above isotherms. The flow rates of desorbent for the other columns are also shown in **Table 2**.

**Figure 4** represents the concentration of each component in the four products. The three, 1, 2 and 3 in **Fig. 1**, flowed out of the columns in the desorption zone and the last one, 4 in **Fig. 1**, flowed out of the left-hand column in the recovery zone. Each key shows the average concentration over the shift time, 12 min. The purity and recovery of each component at the 40th final stage are shown in **Table 3**. **Figure 4** and **Table 3** show that each component is separated and refined satisfactorily and that pure desorbent is recovered from the left-hand column at position 4 in **Fig. 1**. This desorbent can

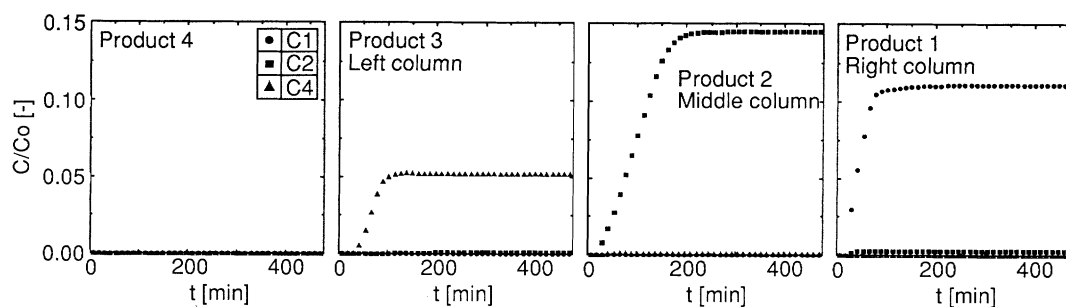


Fig. 4 Change in concentration of each component in the products

Table 3. Separation performance

	Product 1 (C1)	Product 2 (C2)	Product 3 (C4)
Purity [%]	98.1	99.6	97.6
Yield [%]	100.0	89.4	95.4

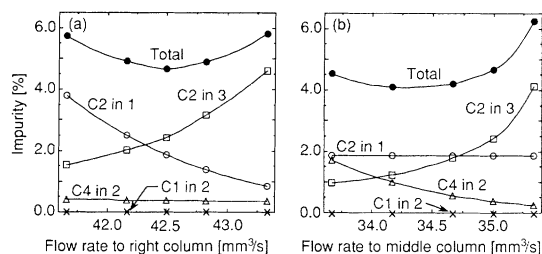


Fig. 5 Effects on impurities of flow rates of desorbent fed to columns in refining zone

be used as the desorbent in the refining and desorption zones.

Compared with the separation performance shown in Fig. 7 in the previous paper<sup>3)</sup>, 25 to 40% higher normalized concentration was obtained for C1 and C2. Furthermore, the steady state can be reached earlier. This indicates that the separation performance in the range of high concentration is better than in the range of low concentration. Since such advantages are caused by the effect of non-linearity of the isotherms, selection of the feed concentration is important.

#### 4. Effects of Desorbent Flow Rates and Shift Time

The desorbent flow rates in the refining zone affect purity and recovery significantly and hence their optimization is very important. They have been determined by examining the concentration profiles in the columns so far, but systematic examination is required.

The effect of the flow rates of desorbent fed to the right-hand and middle columns in the refining zone on the products from the three columns in the desorption zone is examined by simulation of the case when the feed rate is fixed as described in Table 2. Also, the effect of the shift time is discussed. In this study, desorbent is not supplied to the left-hand column in the refining zone.

##### 4.1 Effect of the flow rate of desorbent fed to the right-hand column

The effect of the flow rate of desorbent to the right-

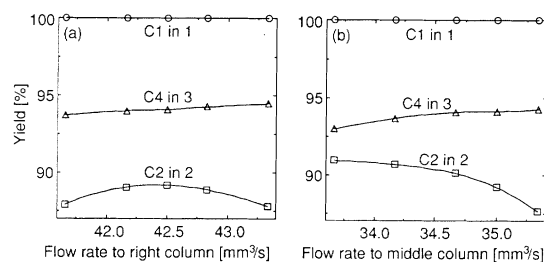


Fig. 6 Effects on yields of flow rates of desorbent fed to columns in refining zone

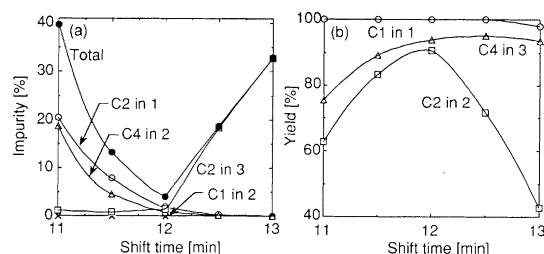


Fig. 7 Effects of shift time on impurities and yields

hand column in the refining zone is examined by setting the shift time at 12 min and the flow rate of feed and that of desorbent to the middle column in the refining zone at the values shown in Table 2.

Figure 5(a) shows the relation between the flow rate of desorbent to the right-hand column in the refining zone and the percentage of impurities in product, 1, 2 or 3 in Fig. 1, from each column in the desorption zone. Their total values are also shown by closed keys. Since the larger flow rate of desorbent to the right-hand column in the refining zone sweeps more impurities (i.e., C2 and C4) out of this column, impurities (mostly C2) in product 1 decrease. On the other hand, the increase in this desorbent flow rate makes the flow rate in the middle column in the separation zone larger and more impurities (mostly C2) tend to leak from the middle column to the left-hand column in the separation zone, resulting in an increase of impurities in product 3.

The impurities C1 and C4 in product 2 are affected much less significantly than C2 in 1 or C2 in 3, where C2 is the middle-distribution-coefficient component. C4 in 2 decreases slightly with increasing desorbent flow rate in the right-hand column. C1 in 2 is negligibly small since the yield of C1 in 1 is almost 100%, as shown later.

#### 4.2 Effect of the flow rate of desorbent fed to the middle column

The effect of the flow rate of desorbent to the middle column in the refining zone is shown in Fig. 5(b), where the shift time is fixed at 12 min and the flow rate of desorbent to the right-hand column in the refining zone is  $42.5 \text{ mm}^3/\text{s}$ . The latter is the value to make the total impurity minimal in Fig. 5(a).

The effect of the desorbent flow rate is basically similar to that described in Fig. 5(a). As the flow rate of desorbent to the middle column in the refining zone increases, the flow rate in the middle column in the separation zone also increases and more impurities (i.e., mostly C2) leak to the left-hand column in the separation zone. Thus the impurities in product 3 increase. On the other hand, more impurity (i.e., C4) is swept out of the middle column in the refining zone and the impurity in product 2 decreases.

Impurity C1 in product 2 is of negligibly small amount by the same reason as for Fig. 5(a), while C2 in 1 is unchanged because the middle column is not affected by the desorbent flow fed to the right-hand column. It is seen that the effect of the adsorption in the recovery zone is insignificant.

It is found in Figs. 5(a) and (b) that summation of impurities becomes minimal at proper flow rates of desorbent in the refining zone and that the increase in flow rate of desorbent fed to a given column in the refining zone makes the impurities in the product from that column decrease, but those in the product from the downward columns increase.

#### 4.3 Effect of desorbent flow rates on yield

In Fig. 6, the yield of each intended component in the corresponding product is plotted against the flow rates of desorbent to the right-hand and middle columns in the refining zone.

The yield of C2 in product 2 in Fig. 6(a) is found to have maximum value when the flow rate of desorbent to the right-hand column in the refining zone is  $42.5 \text{ mm}^3/\text{s}$ . This curve can be anticipated from the curves C2 in 1 and C2 in 3 in Fig. 5(a). Similarly, the yield of C2 in 2 in Fig. 6(b) can be anticipated from the curves C2 in 1 and C2 in 3 in Fig. 5(b). This feature can be seen also for C4 in product 3. That feature is characteristic for this process because the object component for a certain column becomes an impurity for the other column.

#### 4.4 Effect of shift time

The shift time also affects the impurities and the yields of the products in the desorption zone as shown in Fig. 7, where the flow rate of desorbent fed to the right-hand column in the refining zone is fixed at  $42.5 \text{ mm}^3/\text{s}$  and that to the middle column at  $34.3 \text{ mm}^3/\text{s}$ . Each of them is selected so that summation of percentage of impurities reaches minimum in Figs. 5(a) or (b).

Generally, at the fixed desorbent flow rates, more impurities are swept out of a certain column in the refining zone as the shift time becomes longer, resulting in a decrease in impurities in the product from the

column. But more impurities leak into the next downward column, resulting in an increase in impurities in that column. This indicates that the effects of longer shift time are quite similar to those observed for larger desorbent flow rates. This is seen in Fig. 7(a). As the shift time increases, impurities (mostly C2) in product 3 increase, and impurities (mostly C2) in product 1 and impurity (C4) in product 2 decrease. These trends are closely related to those in Figs. 5(a) and (b). Thus the shift time is also one of the key parameters in optimizing the separation performance.

It is found in Figs. 5 through 7 that the yield of the middle-distribution-coefficient component C2 is the lowest and that it exhibits the most complicated behavior in this example process. The examination of other feed mixtures by simulation gave similar results. Hence the focus on the middle-distribution-coefficient component is quite important in this process.

#### Conclusion

The proposed continuous multicomponent separation by a set of liquid chromatography column-groups was applied to feed mixture of dimethyl phthalate, diethyl phthalate and di-*n*-butyl phthalate at high concentration and the following conclusions were obtained.

- 1) The adsorption isotherms were measured by the step-pulse method and correlated by a Langmuir-type equation.
- 2) The experiment on the right-hand column which played the most significant role in the proposed process was performed. The experimental result agreed with that expected by simulation based on the isotherms obtained.
- 3) The performance of the separation at higher feed concentration was better than that at lower concentration because of the non-linearity of isotherms.
- 4) The effects of both the flow rates of desorbent fed to the columns in the refining zone and the shift time on separation performance features such as impurities and yields were examined in detail.

#### Acknowledgment

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#### Nomenclature

$a_i$	=	coefficient of a Langmuir equation of $i$ component	[-]
$b_i$	=	coefficient of a Langmuir equation of $i$ component	$[\text{m}^3/\text{mol}]$
$C$	=	concentration in the mobile phase	$[\text{mol}/\text{m}^3]$
$C^*$	=	concentration in equilibrium with the stationary phase	$[\text{mol}/\text{m}^3]$
$q$	=	amount adsorbed	$[\text{mol}/\text{m}^3\text{-adsorbent}]$
$t$	=	time	$[\text{s}]$

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