

# CONTINUOUS SEPARATION OF GLUCOSE-SALTS MIXTURE WITH NONLINEAR AND LINEAR ADSORPTION ISOTHERMS BY USING A SIMULATED MOVING-BED ADSORBER

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**Key Words:** Simulated Moving Bed, Nonlinear Adsorption Isotherm, Continuous Separation, Glucose, Ion Retardation, Chromatography, Desalination

Continuous glucose/NaCl separation was successfully performed by using a simulated moving-bed adsorber packed with ion-retardant resin. Two kinds of mathematical models, i.e. an intermittent moving-bed model and a continuous moving-bed model, were proposed to calculate concentration profiles in the adsorber where the adsorption isotherms of the first component (NaCl) and the second component (glucose) are represented respectively by the Langmuir equation and by a linear equation. The validity of the calculation methods proposed was experimentally confirmed.

## Introduction

Simulated moving-bed adsorbers have been successfully used to separate continuously two components with different adsorption selectivities, for example, in the recovery of *n*-paraffins from light naphthas,<sup>1)</sup> the separation of *p*-xylene from other *C*<sub>8</sub> hydrocarbons<sup>2)</sup> and glucose/fructose separation.<sup>4,7)</sup> The authors presented previously two mathematical models, an intermittent moving-bed model and a continuous moving-bed model, regarding the analysis of a simulated moving bed adsorber used for glucose/fructose separation in which the adsorption isotherms were expressed by two linear equations independent of each other.<sup>4)</sup>

In fermentation and food industries desalination is an important process. For example, molasses, which includes about 50% saccharides and 3–5% salts, is desalinated to prepare fermentation broth or to recover saccharides such as glucose. For this process, the chromatographic separation technique seems to be promising because of its low energy consumption and of its non-use of additives.

In this paper the glucose/NaCl separation process is described as an example of the desalting of saccharides by using a simulated moving-bed adsorber. The adsorption isotherm of NaCl is represented by the Langmuir equation, whereas the isotherm of glucose is expressed by a linear equation. Nonlinearity in the adsorption isotherms leads to mathematical difficulties in the development of the

models. Therefore, it is also the purpose of this paper to extend the authors' previous models to a system in which the adsorption isotherm of one component is described by a nonlinear equation.

## 1. Mathematical Models

### 1.1 An intermittent moving-bed model

The adsorption isotherm of one component is represented by a linear equation, that of the other component by the Langmuir equation. Assuming that the adsorption rate is represented by a linear driving force approximation<sup>3,6)</sup> for both components, and that axial dispersion can be ignored, we can write a mass balance equation referring to the concentration of a component *k* in the mobile phase, *C<sub>k</sub>*, as follows:

$$\varepsilon_b \frac{\partial C_k}{\partial t} = -v_n \frac{\partial C_k}{\partial z} - K_f a_v (C_k - C_k^*) \quad (k=1, 2) \quad (1)$$

where *C<sub>k</sub><sup>\*</sup>* is the concentration of the component *k* in the stationary phase. Other symbols are common and are summarized in the Nomenclature. The amount of the component adsorbed in the stationary phase, *q<sub>k</sub>*, is represented by

$$(1 - \varepsilon_b) \rho_p \frac{\partial q_k}{\partial t} = K_f a_v (C_k - C_k^*) \quad (k=1, 2) \quad (2)$$

Since *q<sub>k</sub>* is a function of *C<sub>k</sub><sup>\*</sup>*, Eq. (2) is rewritten as

$$(1 - \varepsilon_b) \rho_p \frac{\partial C_k^*}{\partial t} \frac{dq_k}{dC_k^*} = K_f a_v (C_k - C_k^*) \quad (k=1, 2) \quad (3)$$

The isotherms for two components are expressed as follows:

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$$q_1 = m_1 C_1^* / \rho_p \quad (4)$$

$$q_2 = \frac{K_2 C_2^*}{1 + K_1 C_2^*} \quad (5)$$

where  $m_1$  is the distribution coefficient, and  $K_1$  and  $K_2$  are constants in the Langmuir equation. Equation (3) then becomes

$$(1 - \varepsilon_b) \frac{\partial C_1^*}{\partial t} = \frac{K_f a_v}{m_1} (C_1 - C_1^*) \quad (6)$$

$$(1 - \varepsilon_b) \rho_p \frac{\partial C_2^*}{\partial t} = \frac{K_f a_v}{K_2} (1 + K_1 C_2^*)^2 (C_2 - C_2^*) \quad (7)$$

The following conditions are written for the introduction and withdrawal points located between two adjoining zones:

at the withdrawal point of the raffinate stream

$$C_{k,II,1} = C_{k,I,0} \quad (k=1, 2) \quad (8-a)$$

at the introduction point of the feed stream

$$v_f C_{k,f} + v_{III} C_{k,III,1} = v_{II} C_{k,II,0} \quad (k=1, 2) \quad (8-b)$$

at the withdrawal point of the extract stream

$$C_{k,IV,1} = C_{k,III,0} \quad (k=1, 2) \quad (8-c)$$

at the introduction point of the desorbent stream

$$v_I C_{k,I,1} = v_{IV} C_{k,IV,0} \quad (k=1, 2) \quad (8-d)$$

where the subscripts 0 and 1 denote the inlet and outlet of the liquid stream in each zone, respectively.

The partial differential equations (1), (6) and (7) are converted to finite difference equations and can be solved numerically. The partial derivative for time is converted to a finite difference equation of the forward type and the derivative for distance is replaced by that of the backward type. The nonlinear coefficient in Eq. (7) is represented approximately by use of the value of  $C_2^*$  at the previous time level, since the nonlinearity in the adsorption isotherm of NaCl is moderate.

## 1.2 A continuous moving-bed model

It is assumed in this model that the adsorbent particles move continuously at the rate of  $u_s = L_A/T$ , where  $L_A$  is the length of each column and  $T$  is the time interval of transportation of the introduction and withdrawal points of liquid streams. The mass balance equations at steady state are given by Eqs. (9), (10) and (11) in terms of  $C_k$  and  $q_k$ . The coordinate  $z$  is taken to be positive in the direction of the adsorbent movement.

$$u_n \frac{dC_k}{dz} = K_f a_v (C_k - C_k^*) \quad (k=1, 2) \quad (9)$$

$$(1 - \varepsilon_b) u_s m_1 \frac{dC_1^*}{dz} = K_f a_v (C_1 - C_1^*) \quad (10)$$

$$(1 - \varepsilon_b) u_s \rho_p \frac{K_2}{(1 + K_1 C_2^*)^2} \frac{dC_2^*}{dz} = K_f a_v (C_2 - C_2^*) \quad (11)$$

where  $u_n$  represents the superficial velocity of liquid flow in the zone  $n$  of the hypothetical moving-bed adsorber and is equal to  $v_n - \varepsilon_b L_A/T$ .

The concentration profiles of glucose in both fluid and solid phases are easily given since its isotherm is represented by a linear equation. Assuming that  $C_{1,n0}$  and  $C_{1,n0}^*$  at the inlet of zone  $n$  are known, Eqs. (9) and (10) are analytically solved and the following equations are obtained.

$$C_{1,n1} = \frac{\exp\{\alpha_n(1 - \beta_{n1})x\} - \beta_{n1}}{1 - \beta_{n1}} C_{1,n0} + \frac{1 - \exp\{\alpha_n(1 - \beta_{n1})x\}}{1 - \beta_{n1}} C_{1,n0}^* \quad (12)$$

$$C_{1,n1}^* = \frac{\beta_{n1}[\exp\{\alpha_n(1 - \beta_{n1})x\} - 1]}{1 - \beta_{n1}} C_{1,n0} + \frac{1 - \beta_{n1} \exp\{\alpha_n(1 - \beta_{n1})x\}}{1 - \beta_{n1}} C_{1,n0}^* \quad (13)$$

where

$$x = z/L_A \quad (14)$$

$$\alpha_n = K_f a_v L_A / u_n \quad (15)$$

$$\beta_{n1} = \beta_n \rho_p / m_1 = u_n / \{(1 - \varepsilon_b) u_s m_1\} \quad (16)$$

we can calculate the steady-state concentration profile of the component by solving a set of simultaneous algebraic equations obtained from Eqs. (12) and (13) with boundary conditions similar to Eqs. (8-a)–(8-d) in accordance with the method shown in the previous paper.

On the other hand, when an adsorption isotherm is expressed by the Langmuir equation, Eqs. (9) and (11) can be rewritten in semidimensionless forms as follows:

$$\frac{dC_2}{dx} = \alpha_n (C_2 - C_2^*) \quad (17)$$

$$\frac{dC_2^*}{dx} = \frac{\alpha_n \beta_n}{K_2} (1 + K_1 C_2^*)^2 (C_2 - C_2^*) \quad (18)$$

Numerical solutions of Eqs. (17) and (18) are obtained by using a finite difference method combined with the quasilinearization technique presented by Lee.<sup>5)</sup> Each column length is divided into  $N$  parts of equal width  $\Delta x$ .  $C_2$  and  $C_2^*$  at the  $i$ -th part are represented by  $y(2i-1)$  and  $y(2i)$ , respectively, to facilitate solving a set of simultaneous algebraic equations. The derivatives in Eqs. (17) and (18) are replaced by the following simple difference expressions:

$$\frac{dy_{j+1}(2i-1)}{dx} = \frac{y_{j+1}(2i+1) - y_{j+1}(2i-1)}{\Delta x} \quad (19)$$

$$\frac{dy_{j+1}(2i)}{dx} = \frac{y_{j+1}(2i+2) - y_{j+1}(2i)}{\Delta x} \quad (20)$$

where the subscript  $j+1$  represents the  $(j+1)$ th iteration. The right-hand sides of Eqs. (17) and (18) are expanded around  $y_j(2i-1)$  and  $y_j(2i)$  by use of the Taylor series with the second- and higher-order terms omitted.

Based on these treatments, the following algebraic equations are obtained:

$$\begin{aligned} &(-\alpha_n - 1/\Delta x)y_{j+1}(2i-1) + \alpha_n y_{j+1}(2i) \\ &+ (1/\Delta x)y_{j+1}(2i+1) = 0 \end{aligned} \quad (21)$$

$$\begin{aligned} &(\alpha_n \beta_n / K_2)(a_1 y_{j+1}(2i-1) + a_2 y_{j+1}(2i)) \\ &- (1/\Delta x)y_{j+1}(2i+2) \\ &= (\alpha_n \beta_n / K_2)(2K_1) a_1^{1/2} (y_j(2i-1) \\ &- y_j(2i)) y_j(2i) \end{aligned} \quad (22)$$

where

$$a_1 = (1 + K_1 y_j(2i))^2 \quad (23)$$

$$\begin{aligned} a_2 = & 2K_1(1 + K_1 y_j(2i)) y_j(2i-1) \\ & - 1 - K_1 y_j(2i)(4 + 3K_1 y_j(2i)) \\ & + (1/\Delta x)/(\alpha_n \beta_n / K_2) \end{aligned} \quad (24)$$

A set of simultaneous algebraic equations consisting of Eqs. (21) and (22) and the boundary conditions are solved to give the  $y_{j+1}$  values by assuming adequate  $y_j$  values. The calculation is iterated until the difference between  $y_{j+1}$  and  $y_j$  at each point becomes a value within a permissible error factor. The steady-state concentration profile can usually be obtained by this method with iteration less than 10 times when the permissible error factor  $|y_{j+1} - y_j|/y_j$  is set to be  $10^{-5}$  at each point.

The calculation method proposed is applicable to other systems containing nonlinear adsorption isotherms even when the amount adsorbed of a component is dependent on that of another component.

## 2. Experimental Apparatus

Figure 1(a) shows a schematic diagram of the simulated moving-bed adsorber used. A total of 12 columns packed with Retardion 11A-8 were connected to each other through a rotary valve. In glucose/NaCl separation, each of the four zones had three columns. Figure 1(b) shows details of the valve, which consisted of two stainless steel discs. The lower disc was stationary, whereas the upper disc could be rotated. The rotation of the upper disc was controlled by a beam switch.

Feed, desorbent, raffinate and extract stream lines, were also connected to the columns through the valve (raffinate to No. 4 column, feed to No. 6 column,

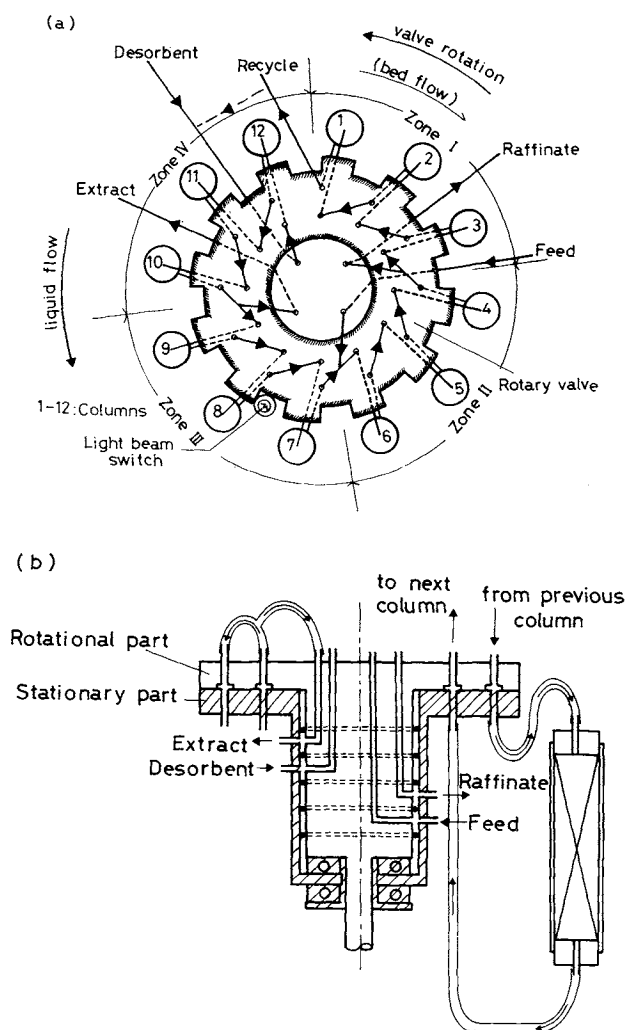


Fig. 1. Schematic diagram of experimental apparatus used (a), and details of rotary valve (b).

extract to No. 10 column and desorbent to No. 12 column in Fig. 1(a)). Without any movement of either the columns or the stream lines, the introduction and withdrawal points were switched at regular intervals in the direction of liquid flow by using the rotary valve. Since the feed, desorbent, raffinate and extract stream lines, respectively, were connected to the stationary part of the valve as shown in Fig. 1(b), each line was shifted to the adjoining column in the direction of liquid flow by rotation of the upper disc. Change of the introduction and withdrawal points caused countercurrent movement of the adsorbent particles in the liquid stream of the columns. Each column was 1.5 cm in inner diameter and approximately 18 cm in length. The apparatus was kept at 298 K by placing it in a thermostated chamber.

In the simulated moving-bed adsorber containing four zones, the liquid emerging from zone I is usually recycled to the desorbent stream since it contains a small amount of either of the two components. In this study, the liquid was not recycled in order to simplify

the operation. The boundary condition in Eq. (8-d) is obtainable since the two components were not contained in the liquid emerging from zone I. This was confirmed experimentally as shown in a later section.

### 3. Desalting of Glucose

Glucose and NaCl can be separated by one of two chromatographic methods. The first is ion-retardation chromatography using a snake cage resin. The other is ion-exclusion chromatography using a  $\text{Na}^+$  form of cation exchange resin. The adsorption isotherms of NaCl adsorbed onto Dowex Retardion 11A-8 and the  $\text{Na}^+$  form of Dowex 50WX2 were obtained at 298 K by integrating the breakthrough curve in a packed-bed column. Distilled water was used as the solvent for both the adsorbents. The physical properties of the adsorbents are presented in Table 1. The apparent density of each resin was measured by using a pycnometer. The mean diameters of resin particles were determined with a microscope. Being treated with 2 N NaCl, Dowex Retardion 11A-8 resin showed no further shrinkage.

Glucose was most frequently analyzed by the glucostat method.<sup>8)</sup> A high-performance liquid chromatograph equipped with a differential refractometer was also used to determine the concentration of glucose. The concentration of NaCl was determined by using a conductivity meter at 273 K. The bed voidage was estimated by measuring the response curve of a pulse input of pullulan p-800 ( $M_w = 8.5 \times 10^5$ ) solution.

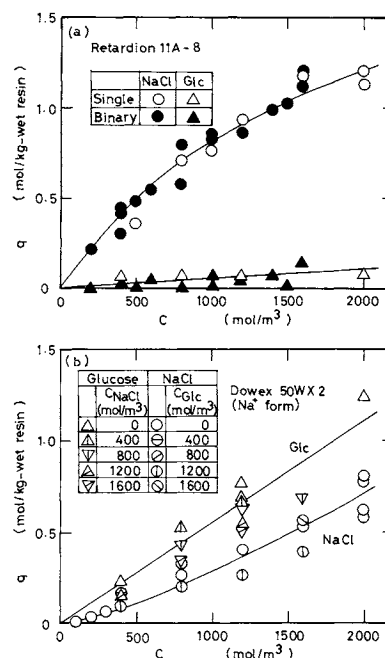
Figure 2(a) shows the adsorption isotherms of glucose and NaCl for Retardion 11A-8. The equilibrium relation for NaCl was expressed by the Langmuir equation. Glucose was very weakly adsorbed onto the resin, and its isotherm is linear. It is seen that the mechanisms of the respective adsorptions were different; i.e. NaCl was adsorbed over active sites on the resin, whereas glucose would only diffuse into pores in the resin. Therefore, the amount of NaCl adsorbed would be independent of that of glucose. The estimated adsorption isotherms are presented in Table 2.

Figure 2(b) illustrates the measured adsorption isotherms of glucose and NaCl for the  $\text{Na}^+$  form of Dowex 50WX2. A linear isotherm was obtained for glucose over a wide range of concentration.

From these results, Retardion 11A-8, although more expensive, was selected as adsorbent for the separation of glucose/NaCl mixture. The selection was based on the following reasons: Retardion 11A-8 shows a greater difference between the adsorption selectivity of NaCl and that of glucose than does Dowex 50WX2 ( $\text{Na}^+$  form). This difference appears over a wide range of concentration in each of the components, as shown in Fig. 2. Furthermore, the bed shrinkage of Retardion 11A-8 is less significant than

**Table 1.** Physical properties of Dowex Retardion 11A-8 and a  $\text{Na}^+$  form of Dowex 50WX2

Adsorbent	Apparent density [kg/m <sup>3</sup> ]	Mean diameter [μm]	Bed shrinkage in 2 N NaCl [%]
Dowex Retardion 11A-8	1164	$3.26 \times 10^{-4}$	94.5
Na form of Dowex 50WX2	1126	$3.48 \times 10^{-4}$	65.5



**Fig. 2.** Adsorption isotherms of glucose and NaCl on Dowex Retardion 11A-8 (a), and on Dowex 50WX2 ( $\text{Na}^+$  form) (b) at 298 K.

**Table 2.** Adsorption isotherms of glucose and NaCl for Dowex Retardion 11A-8

Adsorbate	Adsorption isotherms
Glucose	$q_{\text{glc}} = 5.71 \times 10^{-5} C_{\text{glc}}$
NaCl	$q_{\text{NaCl}} = \frac{1.24 \times 10^{-3} C_{\text{NaCl}}}{1 + 5.33 \times 10^{-4} C_{\text{NaCl}}}$

that of Dowex 50WX2. Therefore, glucose corresponds to component 1 and NaCl to component 2 of the previous section.

The overall volumetric mass transfer coefficient  $K_f a_v$  for glucose was determined by the pulse injection method. The  $K_f a_v$  values estimated were in the order of  $10^{-4} \text{ s}^{-1}$  under the experimental conditions. The  $K_f a_v$  for NaCl was estimated from the number of transfer units and the time difference between the exhaustion and break points. The estimated  $K_f a_v$  values were in a range from  $3 \times 10^{-3} \text{ s}^{-1}$  to  $1 \times 10^{-2} \text{ s}^{-1}$ .

Experimental runs of continuous desalting of glucose were performed by using a simulated moving-bed adsorber to examine the validity of the models. **Figure 3** shows typical transient changes in the concentrations of glucose and NaCl in the extract, raffinate and effluent streams. The extract stream contained only NaCl, and the amount of NaCl in the raffinate stream was very small. At steady state, the weight fraction of glucose to the total glucose and NaCl in the raffinate stream was more than 0.97. The liquid emerging from zone I (the effluent stream) contained minor amounts of either glucose or NaCl, so it was confirmed that the liquid can be reused as a make-up desorbent. Thus, the figure shows that continuous desalting of glucose can be accomplished by using a simulated moving-bed adsorber, based on ion retardation chromatography.

The curves in the figure are those calculated for glucose and NaCl, respectively, using the intermittent moving-bed model. The calculated curves satisfactorily express the experimental results, demonstrating the validity of the models.

**Figure 4** illustrates the steady-state concentration profiles of glucose and NaCl in the adsorber. The profiles were measured for the run shown in Fig. 3. The broken line in Fig. 4 was calculated for NaCl by the continuous moving-bed model described in this text. The experimental profile of NaCl coincides approximately with the calculated one. Any discrepancy between them may be due to the following reasons: experimental difficulty in adjusting bed voidage uniformly for each of the columns with the volume of the tubing, and inability of controlling the flow rate of the solution precisely.

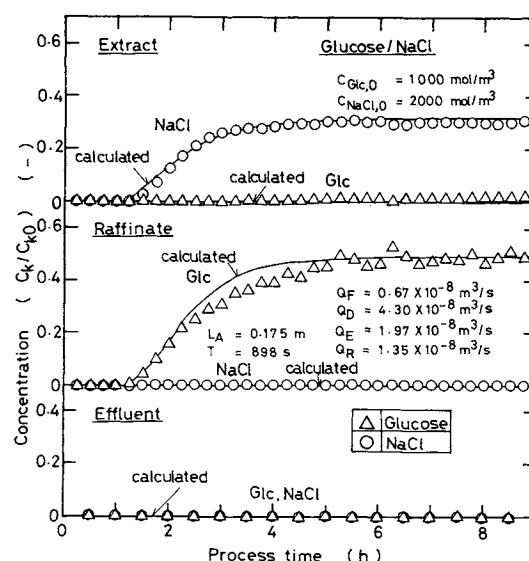
Since the intermittent moving-bed model was based on the actual behavior of the simulated moving-bed adsorber, concentration profiles in the adsorber under unsteady-state conditions as well as steady-state condition are predicted precisely by this model. On the other hand, the steady-state concentration profiles in the adsorber can be predicted easily by the continuous moving-bed model. Therefore, the continuous moving-bed model is useful in the quick calculation of approximate concentration profiles in the simulated moving-bed adsorber.

## Conclusion

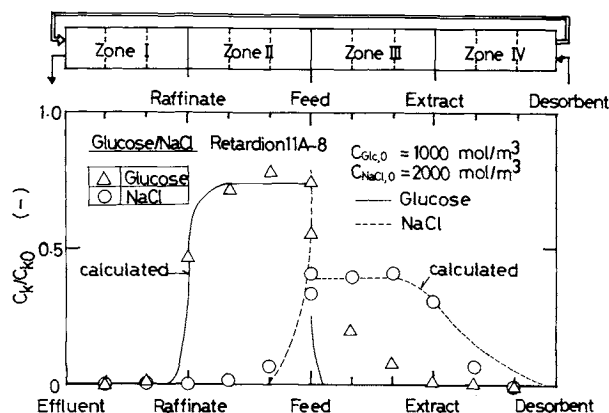
Two kinds of mathematical models are presented to calculate the concentration profile in a simulated moving-bed adsorber in a case where the adsorption isotherms are represented by either linear or nonlinear equations. The validity of the models was confirmed for the glucose/NaCl separation process.

## Nomenclature

$a_v$  = specific surface area  $[\text{m}^2/\text{m}^3\text{-bed}]$



**Fig. 3.** Typical transient change in concentration of glucose and NaCl in extract, raffinate and recycle streams.



**Fig. 4.** Concentration profiles of glucose and NaCl in adsorber at steady state.

$C$	= concentration in the mobile phase	$[\text{mol}/\text{m}^3]$
$C^*$	= concentration in the stationary phase	$[\text{mol}/\text{m}^3]$
$K_f$	= overall mass transfer coefficient	$[\text{m}/\text{s}]$
$K_1$	= coefficient in the Langmuir equation	$[\text{m}^3/\text{mol}]$
$K_2$	= coefficient in the Langmuir equation	$[\text{m}^3/\text{kg}]$
$L_A$	= length of each adsorption column	$[\text{m}]$
$m_1$	= distribution coefficient	$[-]$
$q$	= amount adsorbed	$[\text{mol}/\text{kg}]$
$T$	= time interval of transposition of introduction and withdrawal points	$[\text{s}]$
$t$	= time	$[\text{s}]$
$u$	= superficial velocity of liquid flow in hypothetical moving bed	$[\text{m}/\text{s}]$
$u_s$	= velocity of adsorbent flow	$[\text{m}/\text{s}]$
$v$	= superficial velocity of liquid flow in fixed bed	$[\text{m}/\text{s}]$
$x$	= $z/L_A$	$[-]$
$y$	= $C$ or $C^*$	$[\text{mol}/\text{m}^3]$
$z$	= axial distance	$[\text{m}]$
$\alpha_n$	= $K_f a_v L_A / u_n$	$[-]$
$\beta_n$	= $u_n / ((1 - \epsilon_b) u_s \rho_p)$	$[\text{m}^3/\text{kg}]$
$\epsilon_b$	= bed voidage	$[-]$
$\rho_p$	= apparent density of adsorbent	$[\text{kg}/\text{m}^3]$

#### <Subscripts>

d	= desorbent
f	= feed
j	= iteration times
k	= components
n	= zone number (=I to IV)
0	= inlet
1	= outlet

#### Literature Cited

- 1) Broughton, D. B.: *Chem. Eng. Prog.*, **64**(8), 60 (1968).
- 2) Broughton, D. B., R. W. Neuzil, J. M. Pharis and C. S. Brearly: *Chem. Eng. Prog.*, **66**(9), 70 (1970).
- 3) Glueckauf, E.: *Trans. Faraday Soc.*, **51**, 1540 (1955).
- 4) Hashimoto, K., S. Adachi, H. Noujima and H. Maruyama: *J. Chem. Eng. Japan*, **16**, 400 (1983).
- 5) Lee, E. S.: *AIChE J.*, **14**, 490 (1968).
- 6) Miura, K. and K. Hashimoto: *J. Chem. Eng. Japan*, **10**, 490 (1977).
- 7) Neuzil, R. W. and R. H. Jensen: 85th National AIChE Meeting, Philadelphia, Pa., June 4-8 (1978).
- 8) Toren, E. C. Jr.: *J. Chem. Educ.*, **41**, 172 (1967).

## A SIMULATION FOR LIQUID SURFACTANT MEMBRANE PERMEATION IN A CONTINUOUS COUNTERCURRENT COLUMN

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**Key Words:** Extraction, Liquid Surfactant Membrane, Column Operation, Simulation, Permeation Process, Metal Ion

The continuous permeation of metal ions in a countercurrent column was simulated in order to develop a continuous separation process with the liquid surfactant membrane technique. In the simulation, an axial dispersion model was applied for a continuous phase. For the permeation of metal ion in a dispersed phase, an approximate model was adopted in which the external diffusion around the dispersed phase, the diffusion through a peripheral thin oil layer in the dispersed phase and the extraction reaction at the interface between the continuous and dispersed phases were taken into account. The observed concentration distributions of metal ions in the column reported by Marr *et al.* were satisfactorily simulated by the models applied and by use of the conventional relations for liquid-liquid extraction.

### Introduction

The liquid surfactant membrane technique has been noted as a novel separation and concentration method. In the industrial application of this technique, a continuous operation using a mixer-settler or a column is required. A column operation is preferable for treating a large amount of feed solution. However, only one study has been reported, in which continuous permeation tests of some metals were carried out in a countercurrent column by Marr *et al.*<sup>6)</sup>

The purpose of our work is to develop a continuous

separation process with the liquid surfactant membrane technique. In the present paper, simulation results for a continuous permeation of metal ions when a countercurrent column is used as liquid membrane contact equipment are presented. The simulation was made on the basis of the column and the experimental results reported by Marr *et al.*<sup>6)</sup> The column has only a stirrer and does not have baffle plates or staters.

### 1. Simulation Model

Figure 1 shows a model of a continuous countercurrent column operation. The feed, an aqueous phase containing a metal ion, is supplied at a top of column as a continuous phase. The dispersed phase is a (W/O)

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