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Separation of Electrolyte and Nonelectrolyte by an Ion Retardation Resin

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Abstract

The separation of electrolyte and nonelectrolyte by an ion retardation resin is studied by the impulse response method. Mass transfer parameters are evaluated by the moment method. The contributions of each mass transfer process to the total resistance are indicated. Experimental chromatographic curves are compared with calculated ones.

INTRODUCTION

Chromatographic separation of multicomponents solutions has been developed as analytical techniques. This method may also be applied to industrial separation processes.

Ion retardation resin (snake-cage resin) is one of adsorbents for the separation of electrolyte and nonelectrolyte. Ion retardation is caused by the differences of adsorption ability to resins containing anion and cation sites. It has the advantage that the adsorbed material can be desorbed by washing with water without using chemical agents.

Ion retardation resin was prepared for desalting of nonelectrolyte solutions and separation of ionic species by Hatch et al. (*1*). It was applied to separate sodium chloride from glycerine, and more than 90% of the sodium chloride was removed (*2*). Rollins et al. (*3*) applied it in desalting amino acid solutions. Wolf et al. (*4*) prepared resins of divinylbenzene and studied the influence of structure on the separation of electrolyte and nonelectrolyte mixtures. Bogoczek (*5*) synthesized the resins, cross-linking the acrylic acid

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polymer to prevent a decrease in chemical stability followed by a loss of separation ability. Sweed et al. (*6*) applied it to parametric pumping, and Rice and Foo (*7, 8*) investigated the equilibrium and kinetics by batch and column methods.

In this paper the separation of sodium chloride (electrolyte) and sucrose (nonelectrolyte) is investigated by the column method and is analyzed kinetically by the moment method.

THEORY

Mass transfer steps such as axial dispersion, film diffusion, and intraparticle diffusion are important factors in a fixed-bed operation. The following equations can be derived from mass balance equations.

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Mass balance of the adsorbable component in the flowing phase:

$$D_L \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{3\bar{D}}{R}\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)\left(\frac{\partial \bar{C}}{\partial r}\right)_{r=R} - \frac{\partial C}{\partial t} = 0 \quad (1)$$

Mass balance in the particle:

$$\bar{D}\left(\frac{\partial^2 \bar{C}}{\partial r^2} + \frac{2}{r}\frac{\partial \bar{C}}{\partial r}\right) - \frac{\partial \bar{C}}{\partial t} = 0 \quad (2)$$

The boundary conditions:

$$\bar{D}(\partial \bar{C}/\partial r)_{r=R} = k_f(C - C^*) \qquad \text{at } r = R,\ t > 0 \quad (3)$$

$$\partial \bar{C}/\partial r = 0 \qquad \text{at } r = 0,\ t > 0 \quad (4)$$

The following initial boundary conditions may be taken for a bed which is initially free of adsorbed materials and a finite step function in the influent concentration.

$$C = C_0, \qquad z = 0,\ 0 \le t \le t_0 \quad (5)$$

$$C = 0, \qquad z = 0,\ t > t_0;\ z > 0,\ t = 0 \quad (6)$$

$$\bar{C} = 0, \qquad z \ge 0,\ t = 0 \quad (7)$$

If the adsorption equilibrium relationship is assumed to be linear

($\bar{C} = KC^*$), the moment method based on the theory of Kubin (*9, 10*) can be employed to analyze the chromatogram obtained experimentally. The first absolute and the second central moment can be expressed as follows:

$$\mu_1' = (z/\varepsilon_B)\{\varepsilon_B + (1 - \varepsilon_B)K\}/v + t_0/2 \tag{8}$$

$$\mu_2 = \frac{2z}{v}\left\{\frac{1-\varepsilon_B}{\varepsilon_B}\,\frac{KR^2}{\bar{D}}\left(\frac{1}{15} + \frac{\bar{D}K}{3Rk_f}\right) + \frac{D_L}{v^2}\left(1 + \frac{1-\varepsilon_B}{\varepsilon_B}K\right)^2\right\} + \frac{t_0^2}{12} \tag{9}$$

The first absolute moment, μ_1', characterizes the position of the center of gravity of the chromatographic curve, whereas the second central moment, μ_2, depends on the width of the curve.

The theoretical equations, Eqs. (1) to (7), were solved analytically by Rasmuson et al. (*11*) and the analytical solution was given in terms of an infinite integral.

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EXPERIMENTAL

The experimental apparatus is shown in Fig. 1. The glass column of 95.5 mm i.d. and 0.9 m height was maintained at 30°C. Distilled water in the head tank 1 flowed to the top of the column 5 through thermostat 2 at 30°C. The

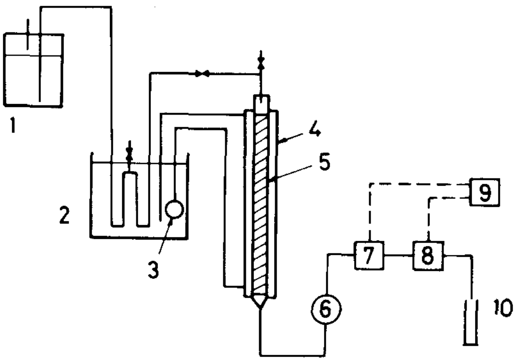

FIG. 1. Experimental apparatus: (1) head tank, (2) thermostat, (3) pump, (4) thermostat tube, (5) resin bed, (6) pump, (7) conductivity meter, (8) differential refractometer, (9) recorder, (10) measuring cylinder.

flow rate was regulated by changing the rotation of pump 6 and measured by measuring cylinder 10. Samples of 2×10^{-7} m^3 were introduced at the inlet of the column, and concentrations were measured by conductivity meter 7 for the electrolyte and by differential refractometer 8 for the nonelectrolyte simultaneously. The sample solution consisted of sodium chloride of 1000 mol/m^3 as electrolyte and sucrose of 100 mol/m^3 as nonelectrolyte.

The resin used was Dowex Retardion AG 11A8 (50–100 mesh) and was sieved in distilled water. Its average diameter was 0.324 mm. The apparent density of the resin was 714 kg/m^3 (measured by a picnometer). The moisture content was obtained from the difference of wet resin (centrifugal dehydrated at 50 rps for 10 min) and dry resin (vaccum dried at 90°C) and was 0.382. The resin true density and void fraction of resin were calculated from these values as 1280 kg/m^3 and 0.443, respectively. The void fraction in the bed, ε_B, was obtained as 0.419 by weighting the resin in the column.

Adsorption equilibrium isotherms for the resin were measured in the following manner. An amount of well-washed resin was weighed into a tube with a screw cap, sodium chloride solution was added, and the tube was sealed. After equilibrium was reached in about 50 h at 30°C, the equilibrated solution was titrated with silver nitrate solution using potassium chromate as indicator (the Mohr method).

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RESULTS

Adsorption equilibrium isotherms of the ion retardation resin in sodium chloride solution are shown in Fig. 2. Since the data were on a straight line through the origin, the adsorption isotherms might be linear. However, the results of Rice et al. (7) were nonlinear. The adsorption equilibrium for sucrose could not be measurable because the amount of adsorption was low.

The results for impulse response by the column method are shown below. A column packed with glass beads of the same size as the resin was prepared to obtain the axial dispersion coefficient. Since there was no adsorption for glass beads, adsorption equilibrium coefficient K could be zero in Eqs. (8) and (9).

$$(\mu_1')_{\text{inert}} = z/v + t_0/2 \tag{10}$$

$$(\mu_2)_{\text{inert}} = 2(D_L/v^2)(z/v) + t_0^2/12 \tag{11}$$

Plots of $(\mu_1')_{\text{inert}} - t_0/2$ versus $1/v$ gave a straight line through the origin, and

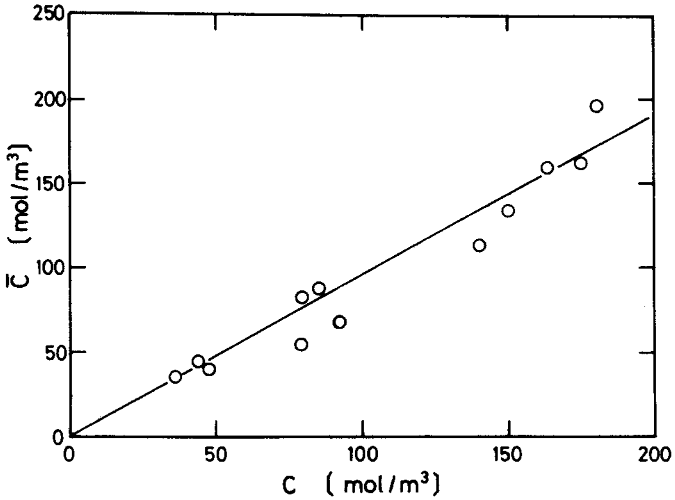

FIG. 2. Equilibrium isotherms for sodium chloride at 30°C.

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the slope should be the height z from Eq. (10). The value of z obtained was almost equal to that of direct measurement. Equation (11) indicates that the plots of $\{(\mu_2)_{\text{inert}} - t_0^2/12\}/(2z/v)$ versus $1/v$ should lie on a straight line with a slope of D_L/v through the origin. Figure 3 shows the evaluated axial dispersion coefficient for sodium chloride and sucrose. There is no distinction between sodium chloride and sucrose, and the data fall on a straight line through the origin. The axial dispersion coefficient might be expressed as

$$D_L = 0.00175\,v \tag{12}$$

The other kinetic parameters can be obtained from the impulse response of the resin packed column. It is evident from Eq. (8) that the plots of $(\mu_1') - t_0/2$ versus $1/v$ should fall on a straight line with a slope of $(z/\varepsilon_B)\{\varepsilon_B + (1 - \varepsilon_B)K\}$ through the origin. Therefore, the adsorption equilibrium coefficient could be obtained from the slope. Figure 4 shows the results, and the data fall on a straight line through the origin. The evaluated value for sodium chloride was 0.474. It was difficult to evaluate the value for sucrose because the slope of the line was close to z.

In the second central moment expressed in Eq. (9), there are three unknown parameters: the axial dispersion coefficient D_L, the intraparticle

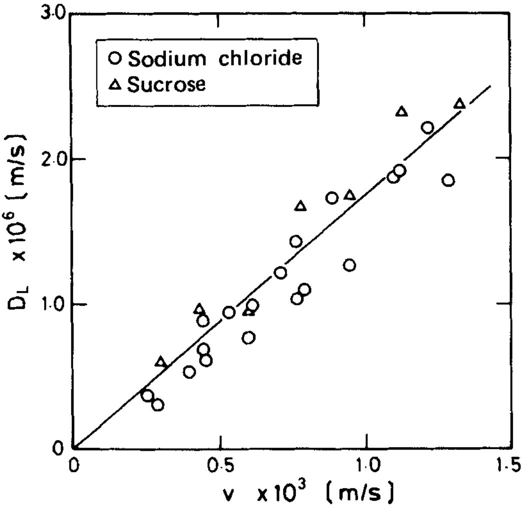

FIG. 3. Axial dispersion coefficients in glass beads column.

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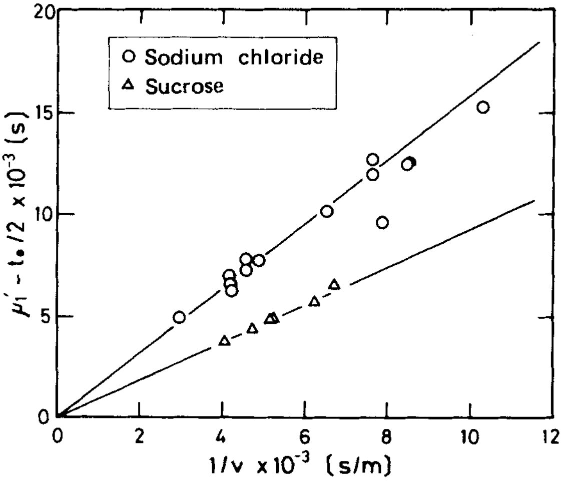

FIG. 4. First absolute moment for resin column.

diffusivity $\bar{D}$, and the liquid film mass transfer coefficient k_f. For the axial dispersion coefficient, the result of the glass beads column was applied to the resin column.

The following correlation, reported by Wakao et al. (*12*), was used for the liquid film mass transfer coefficient:

$$2k_fR/D_m = 2 + 1.45\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3} \tag{13}$$

The molecular diffusivities D_m in Eq. (13) were 1.81×10^{-9} m^2/s for sodium chloride and 0.532×10^{-9} m^2/s for sucrose.

Therefore, only intraparticle diffusivity $\bar{D}$ remains as an unknown parameter in the second central moment. Applying the values of K, D_L, and k_f to the experimentally obtained second central moment, intraparticle diffusivity $\bar{D}$ was obtained as 1.74×10^{-11} m^2/s for sodium chloride and 3.69×10^{11} m^2/s for sucrose.

The intraparticle diffusivities for sodium chloride reported by Foo et al. (*8*) are 2.60×10^{-12} m^2/s at 10°C and 3.03×10^{-11} m^2/s at 50°C by the column method, and 3.2×10^{-12} m^2/s at 10°C and 3.50×10^{-11} m^2/s at 50°C by the batch study. These values were interpolated to be 1.78×10^{-11} m^2/s at 30°C. This value agrees well with the value obtained at 30°C in our study.

Figure 5 shows the result of the impulse response for sodium chloride and sucrose. Sucrose is scarcely adsorbed in the resin and is eluted quickly. On the other hand, sodium chloride is adsorbed and eluted slowly by the ion retardation effect. Both components could then be separated. The solid line in Fig. 5 indicates the experimental results and the dotted line indicates the results calculated by an analytical solution (*11*) of the theoretical equations. The calculation was performed by numerical integration of the oscillatory function by using the kinetic parameters obtained.

DISCUSSION

To evaluate the relative importance of three mass transfer resistances, each contribution to the second central moment was estimated. Figure 6 shows the effect of flow rate on the relative importance of the respective resistance for sodium chloride. The solid line is the result calculated by the parameters obtained. The symbols indicate the values calculated from experimental data. The film resistance was less than 1% for any flow rate. The axial dispersion resistance was dominant at low flow rates while the intraparticle resistance became important as the flow rate increased. For

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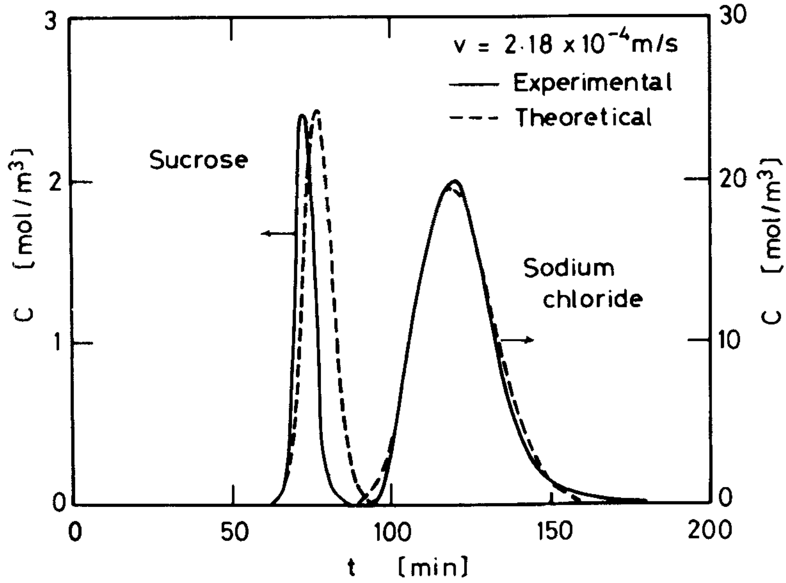

FIG. 5. Separation of sodium chloride and sucrose.

sucrose the axial dispersion was dominant for any flow rate and the intraparticle resistance was only a small contribution, even at high flow rates, because of slight adsorption of sucrose. Consequently, the intraparticle diffusivity for sucrose calculated by the second moment might be inaccurate.

CONCLUSION

The separation of sodium chloride and sucrose was investigated by an ion retardation resin using the column method. The kinetic parameters were obtained by applying the moment method. Experimental chromatograms agreed well with theoretical curves.

Ion retardation may be advantageous for high ionic concentrations compared with ion exchange because regeneration agents are unnecessary.

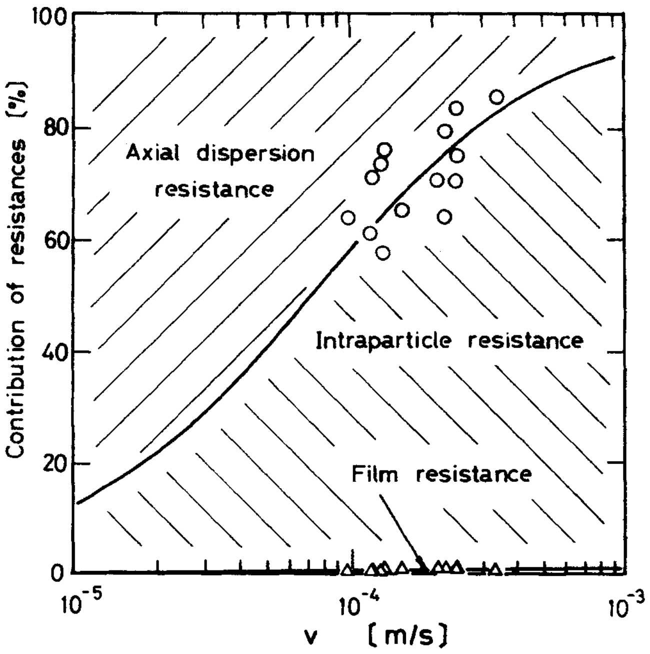

FIG. 6. Contribution of resistances for sodium chloride.

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SYMBOLS

C	fluid phase concentration (mol/m^3)
$\bar{C}$	solid phase concentration (mol/m^3)
C^*	fluid phase concentration at liquid-solid interface (mol/m^3)
D_L	axial dispersion coefficient (m^2/s)
$\bar{D}$	intraparticle diffusivity (m^2/s)
D_m	molecular diffusivity (m^2/s)
K	adsorption equilibrium constant (m^3/m^3)
k_f	liquid film mass transfer coefficient (m/s)
R	radius of the spherical particle (m)
Re	Reynolds number
r	radial coordinate in the spherical particle

Sc	Schmidt number
t	time (s)
t_0	injection time (s)
v	linear velocity of fluid in the interparticle space (m/s)
z	coordinate along the length of the column

Subscripts

inert	glass beads column
o	feed

Greek

ε_B	interparticle void fraction in the bed
μ_n	nth central moment of the chromatographic curve
μ'_n	nth absolute moment of the chromatographic curve

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