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Kinetic Analysis of Ion-Exclusion Chromatography by the Moment Method

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Abstract

The separation of sodium chloride and alcohols by ion exclusion was studied by an pulse response technique. Kinetic parameters were evaluated by the moment method. The HETP was calculated and the contributions of each mass transfer process to the HETP were elucidated. Both axial dispersion and intraparticle diffusion were dominant for alcohols. Agreement between experimental and calculated elution curves is excellent.

INTRODUCTION

Ion exclusion is a process for separating strong electrolytes from weak electrolytes and nonelectrolytes by the Donnan effect. This is a contrary process to ion retardation of the previous paper (*1*). This process was first utilized by Wheaton and Bauman (*2*) and has been studied by many investigators (*3, 4*). However, it seems that little study has been done on the rate process, which is important to predict the elution curve and separation efficiency.

In this paper, ion exclusion for the alcohol-sodium chloride-water system was measured using the cation-exchange resin Dowex 50W-X8. The pulse response technique was applied and the moment method was employed for the analysis of elution curves. The effects of axial dispersion, intraparticle diffusion, and liquid film mass transfer on the transport phenomena in chromatography were revealed.

THEORY

The basic theoretical equations of moment analysis for the ion exclusion process is the same as that for the ion retardation process in the previous paper (*1*). The model accounted for axial dispersion, liquid film mass transport, and intraparticle diffusion. For linear isotherm, solutions of the mass balance equations give for the first absolute and second central moments

$$\mu_1' = \frac{z\varepsilon_B}{u}\left(1 + \frac{1-\varepsilon_B}{\varepsilon_B}K\right) + \frac{t_0}{2} \tag{1}$$

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

The first absolute and second central moments are obtained from the experimental response curves with the following relations:

$$\mu_1' = \int_0^\infty tC(t)dt \Big/ \int_0^\infty C(t)dt \tag{3}$$

$$\mu_2 = \int_0^\infty (t - \mu_1')^2 C(t)dt \Big/ \int_0^\infty C(t)dt \tag{4}$$

The column efficiency may be evaluated by the height equivalent to a theoretical plate (HETP) in plate theory. HETP in chromatography is expressed in terms of moments:

$$\begin{aligned} H &= \mu_2 z/(\mu_1')^2 \\ &= \frac{2u}{\varepsilon_B}\left\{\frac{1-\varepsilon_B}{\varepsilon_B}\frac{KR^2}{\bar{D}}\left(\frac{1}{15} + \frac{\bar{D}K}{3Rk_f}\right)\left(1 + \frac{1-\varepsilon_B}{\varepsilon_B}K\right)^{-2} + \frac{D_L\varepsilon_B^2}{u^2}\right\} \end{aligned} \tag{5}$$

EXPERIMENTAL

Chromatographic peaks for pulse injection of an aqueous solution of sodium chloride and alcohols were measured in a packed bed at 303 K. The experimental apparatus is almost the same as that used in the previous work (*1*). The column was a glass tube of 18 mm i.d. and 0.90 m height. Distilled water was used as the eluant. The resin used was the cation-exchange resin Dowex 50W-X8. It was sieved in distilled water, and the portion of 0.385 mm in average diameter was adopted. The resin was conditioned in the usual manner and changed to the sodium form. The density of swollen resin was 1210 kg/m^3. Samples of 5×10^{-7} m^3 were introduced and concentrations were measured by a conductivity meter for sodium chloride and by a differential refractometer for alcohols. For pulse response analysis, the sample solution consisted of either sodium chloride of 100 mol/m^3 or alcohol of 2000 mol/m^3. For a separation study between sodium chloride and alcohols, the sample solution consisted of sodium chloride and an alcohol such as methyl, ethyl, or *n*-propyl alcohol.

RESULT

First Moment Analysis

In ion-exclusion chromatography, sodium chloride is excluded in the sodium form from the resin by the Donnan effect. Then it is anticipated that adsorption equilibrium constant for sodium chloride will be much less than unity. On the elution curves for sodium chloride and alcohols, the former is eluted earlier than the latter because alcohols are not excluded by the resin.

The void fraction of the bed and the adsorption equilibrium constant for alcohols were determined from the first moment. Figure 1 shows plots of $(\mu_1' - t_0)/2$ versus $1/u$ for sodium chloride and alcohols. Since the value of t_0 is about 10 s, it is negligible. The data fall on straight lines through the origin. Equation (1) may be simplified if the second term in the parentheses is negligible:

$$(\mu_1')_{\mathrm{NaCl}} - t_0/2 = z\varepsilon_B/u \tag{6}$$

Thus from sodium chloride data the void fraction of the bed ε_B was calculated to be 0.377. The slope of the line in Fig. 1 gave the adsorption equilibrium constant K for alcohols as summarized in Table 1. The value of K for sodium chloride could not be determined from the first moment.

Second Moment Analysis

The second moment, expressed in Eq. (2), consists of separate and additive terms of kinetic constants based on axial dispersion, intraparticle diffusion, and liquid film mass transport.

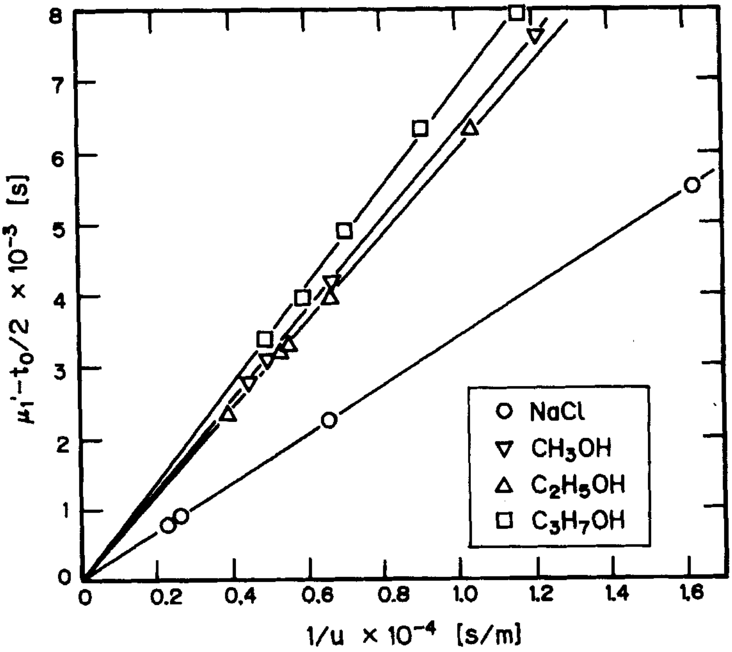

FIG. 1. First absolute moment plots.

TABLE 1
Estimated Parameters at 303 K

	NaCl	CH_3OH	C_2H_5OH	C_3H_7OH
K (m^3/m^3)	0.0269	0.515	0.474	0.608
$D_m \times 10^9$ (m^2/s)	1.81	2.05	1.58	1.32
Sc	444	394	509	609
$k_f \times 10^5$ (m/s)	2.32	2.56	2.08	1.80
		Linear Regression		
η	8.29	15.9	12.7	9.64
$D \times 10^{10}$ (m^2/s)	2.10	4.72	1.62	0.534
		Nonlinear Optimization		
K (m^3/m^3)	0.0203	—	—	—
η	7.38	15.3	12.1	9.48
$D \times 10^{10}$ (m^2/s)	1.61	4.31	1.55	0.529

The axial dispersion in a liquid system is proportional to the flow rate (*1, 6*):

$$D_L = \eta R u \tag{7}$$

Thus the value D_L/u may be constant.

The liquid film mass transfer coefficient can be represented by the following correlation reported by Wakao et al. (*7*):

$$2k_f R/D_m = 2 + 1.45\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3} \tag{8}$$

Two methods to determine the kinetic parameters from the second moment are represented: linear regression and nonlinear optimization.

(1) Linear Regression

The term of the liquid film mass transfer might be less important on the second moment as reported in the previous paper (*1*). If the effect of flow rate on the second term of Eq. (8) is less dominant, the liquid film mass transfer coefficient can be assumed to be constant in the flow rate range of this work. From Eq. (2) the plots $(\mu_2 - t_0^2/12)u/2z\varepsilon_B$ versus $1/u$ might give a straight line with the following slope and intercept:

$$\text{slope} = \frac{D_L\varepsilon_B^2}{u}\left(1 + \frac{1-\varepsilon_B}{\varepsilon_B}K\right)^2 \tag{9}$$

$$\text{intercept} = \frac{1-\varepsilon_B}{\varepsilon_B}\frac{KR^2}{\bar{D}}\left(\frac{1}{15} + \frac{\bar{D}K}{3Rk_f}\right) \tag{10}$$

Figure 2 shows plots of $(\mu_2 - t_0^2/12)u/2z\varepsilon_B$ versus $1/u$. It is evident that there exist linear relations.

For the estimation of the liquid-film mass transfer coefficient, molecular diffusivities were calculated from the Wilke-Chang equation (*8*) for alcohols and from Robinson et al. (*9*) for sodium chloride. The estimated values are shown in Table 1. The calculated values of k_f at the average flow rate $u = 1.5 \times 10^{-4}$ m/s are shown in Table 1. The effect of flow rate on the value of k_f was less than 10% under these experimental conditions.

The slope and intercept of the lines in Fig. 2 were calculated by the least-square method. The values of η in Eq. (7) were calculated from the

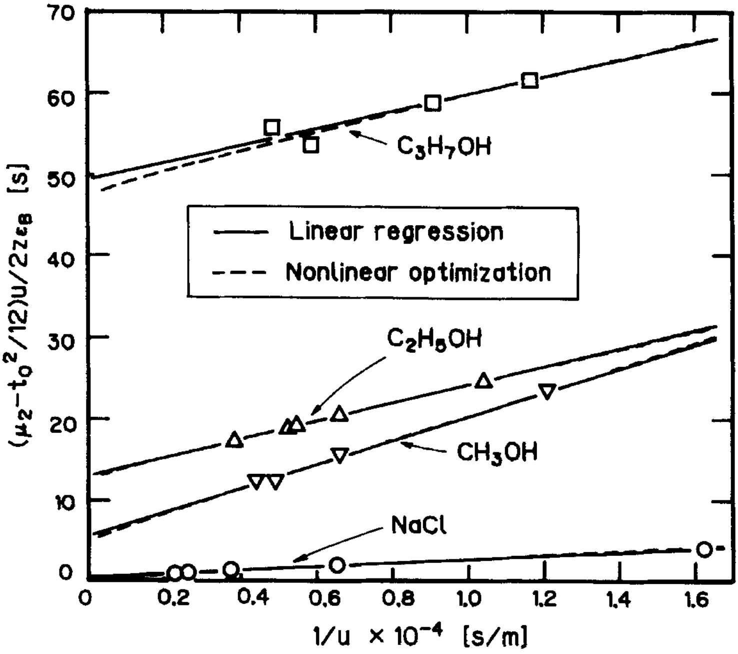

FIG. 2. Second central moment plots.

slopes. The intraparticle diffusivities were calculated from the intercept using k_f at the average flow rate.

As for sodium chloride, the slope may be approximated by $(D_L/u)\varepsilon_B^2$ because the term $(1 - \varepsilon_B)K/\varepsilon_B$ is much less than unity. However, the intraparticle diffusivity could not be calculated from the intercept because the values of K and $\bar{D}$ are not separate. Therefore, the intraparticle diffusivity was not obtained from the moment method but it was estimated from the correlation of Kataoka (*10*). The ratio of intraparticle diffusivity $\bar{D}$ to molecular diffusivity D_m was estimated to be 0.116. The intraparticle diffusivity was calculated to be 2.10×10^{-10} m^2/s. The adsorption equilibrium coefficient K was calculated to be 2.69×10^{-2} from the intercept using $\bar{D}$ obtained above. As a result of the small value of K, the assumption made in the calculation of ε_B from the first moment of sodium chloride was adequate.

(2) Nonlinear Optimization Method

If the dependence of the flow rate on the liquid film mass transfer coefficient cannot be neglected in the second moment, kinetic parameters cannot be determined by a simple linear regression because of the nonlinearity of the second moment expression with respect to the flow rate. Consequently, the nonlinear optimization method was adopted as used by Ghim et al. (*11*).

At first, three parameters such as K, η, and $\bar{D}$ were determined from the second moment of sodium chloride by the Simplex method. As for alcohols, two parameters such as η and $\bar{D}$ were determined using the value of K obtained from the first moment. The estimated kinetic parameters are presented in Table 1.

DISCUSSION

The kinetic parameters determined by the linear regression, which assumed a negligible effect of the flow rate on k_f, were in fair agreement with those determined by nonlinear optimization as shown in Table 1.

The broken lines in Fig. 2 indicate the values calculated by using kinetic parameters. Compared to the straight solid lines obtained by linear regression, only a little difference exists in the high flow rate region.

The height equivalent to a theoretical plate (HETP) was calculated from the experimental data. Figure 3 shows the experimentally obtained HETP together with HETP calculated by Eq. (5) using the determined kinetic parameters. The values of HETP increased with the flow rate for both sodium chloride and alcohols. As the molecular weights of alcohols increased, the values of HETP were increased, and then the intraparticle diffusivities were decreased.

To evaluate the relative importance of the three mass transfer resistances, the contribution of each resistance to HETP was calculated. Figure 4 shows the effect of the flow rate on the relative importance of the respective resistance for sodium chloride. While the liquid film mass transfer resistance was negligible, the axial dispersion was dominant for low flow rate and it occupied about 80% of the total resistance in this experimental flow rate.

Figure 5 shows the relative importance of the flow rate for alcohols. The resistance of liquid film mass transfer is about 5 to 10% for three kinds of alcohol. The resistance of intraparticle diffusion and axial dispersion

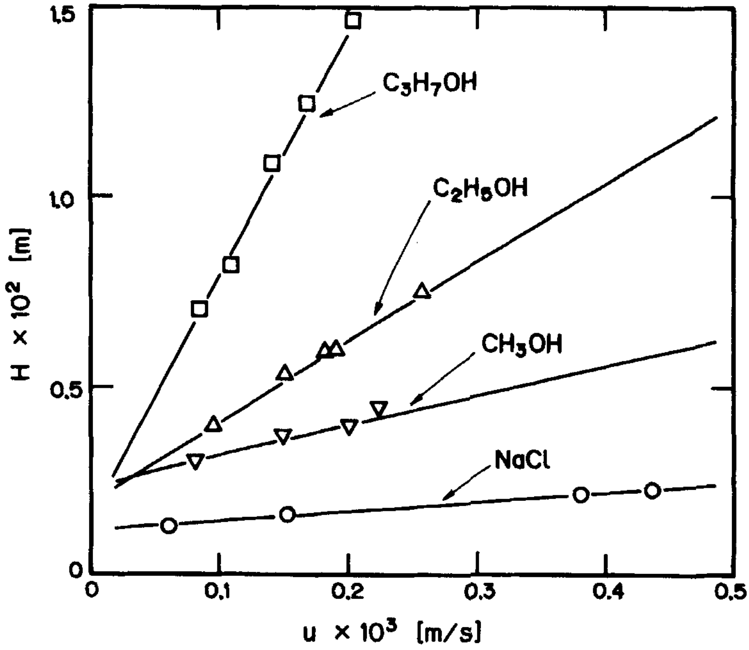

FIG. 3. Dependence of HETP on flow rate.

were equally dominant for ethyl alcohol in this experimental flow rate. For methyl alcohol, intraparticle resistance was less important than axial dispersion. On the other hand, intraparticle resistance was more important for propyl alcohol. Thus intraparticle resistance increased as the molecular weight increased.

Since liquid film resistance was less important for sodium chloride and alcohols, linear regression for the second moment gave satisfactory results. Therefore, the linear regression may be recommended to determine kinetic parameters from the second moment because the nonlinear optimization method could give diverse values, unless appropriate initial values were used.

Typical elution curves for sodium chloride and methyl alcohol are shown in Fig. 6. The solid line indicates the experimental result and the broken line indicates the theoretical curve which was calculated with kinetic parameters obtained by using the analytical equation solved by Rasmuson et al. (*12*). Sodium chloride and methyl alcohol were separated satisfactory by ion exclusion. Agreement between experimental and calculated curves was excellent.

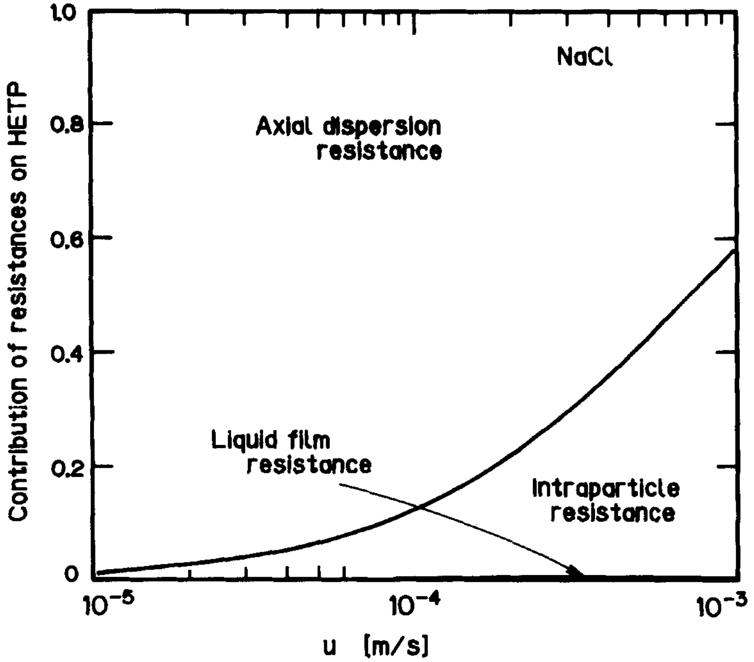

FIG. 5. Effect of flow rate on relative contribution of each resistance to HETP for alcohols.

The comparison of the elution curves for various kind of alcohols is shown in Fig. 7. As the molecular weight increased, the peak concentration became low and the curve width broadened. The experimental curves agreed well with the theoretical curves.

CONCLUSION

Moment analysis of chromatographic elution curves was applied to ion exclusion of sodium chloride and three kind of alcohol in a packed bed of Dowex 50W-X8 resin. The interparticle void fraction in the bed was determined from the first moment of sodium chloride data. The adsorption equilibrium constant was determined from the first moment of alcohol data. The second moment gave information on intraparticle diffusivity, liquid film mass transfer, and axial dispersion. The linear regression and nonlinear optimization method were compared for the analysis of second moment.

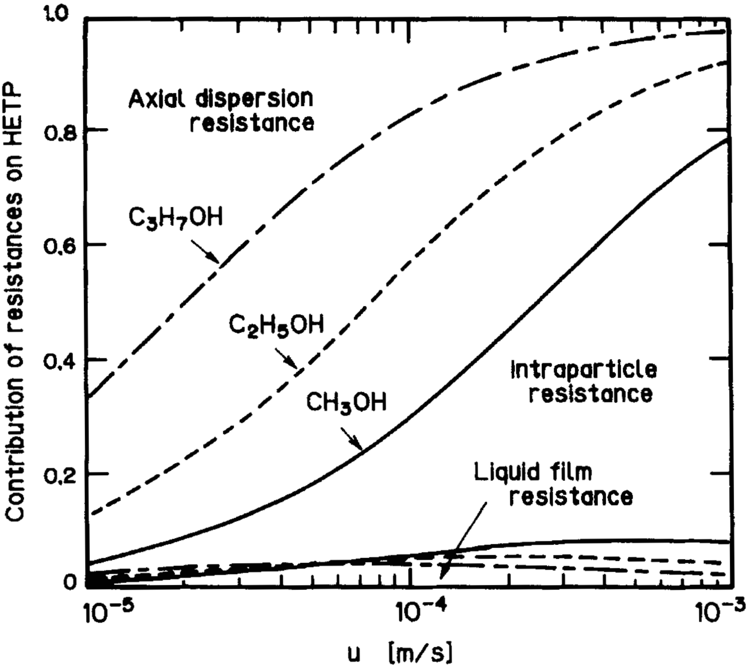

FIG. 5. Effect of flow rate on relative contribution of each resistance to HETP for alcohols.

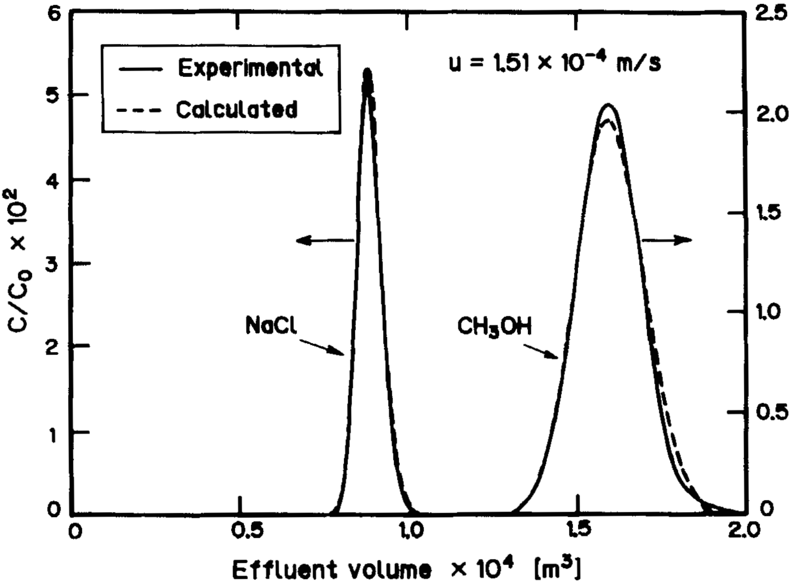

FIG. 6. Comparison of experimental elution curves with the calculated curves.

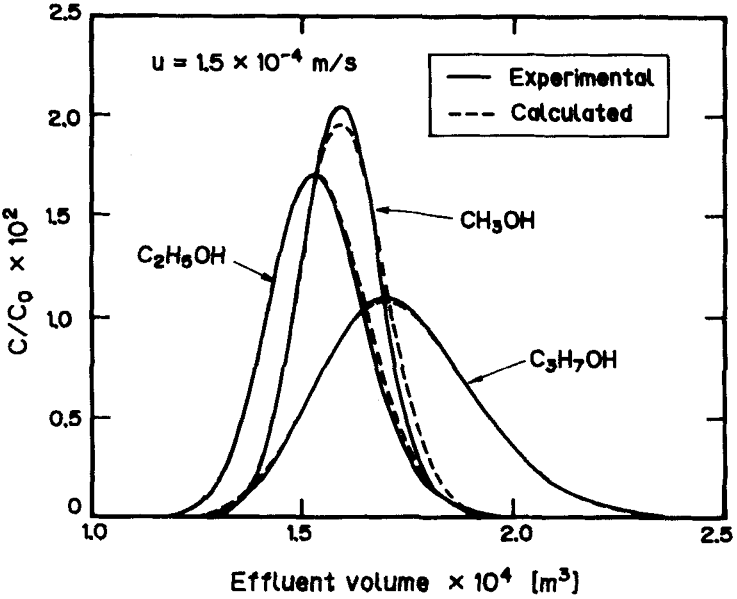

FIG. 7. Comparison of elution curves for various alcohols.

The height equivalent to a theoretical plate (HETP) was calculated and the relative importance of each mass transfer resistance was elucidated. Experimental elution curves were in good agreement with theoretical curves calculated by using the determined kinetic parameters.

SYMBOLS

$C(t)$	fluid phase concentration (mol/m^3)
$\bar{D}$	intraparticle diffusivity (m^2/s)
D_L	axial dispersion coefficient (m^2/s)
D_m	molecular diffusivity (m^2/s)
H	height equivalent to a theoretical plate (m)
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
Sc	Schmidt number
t	time (s)
t_0	injection time (s)

u	superficial velocity (m/s)
z	length of the packed bed (m)

Greek

ε_B	interparticle void fraction in the bed
η	scale of axial eddy dispersion
μ_1'	first absolute moment of the chromatographic curve (s)
μ_2	second central moment of the chromatographic curve (s^2)

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REFERENCES

1. M. Goto, N. Hayashi, and S. Goto, *Sep. Sci. Technol., 18,* 475 (1983).
2. R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem., 45,* 228 (1953).
3. P. C. Nigam, D. Singh, and R. N. Sharma, *Ind. Eng. Chem., Process Des. Dev., 20,* 182 (1981).
4. Y. Tokunaga, H. Waki, and S. Ohashi, *J. Liq. Chromatogr., 6,* 271 (1983).
5. D. M. Ruthven, *Principles of Adsorption and Adsorption Processes,* Wiley, New York, 1984.
6. M. Suzuki, *J. Chem. Eng. Jpn., 7,* 262 (1974).
7. N. Wakao, T. Oshima, and S. Yagi, *Kagaku Kogaku, 22,* 780 (1958).
8. C. R. Wilke and P. Chang, *AIChE J., 1,* 264 (1955).
9. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions,* Butterworths, London, 1959.
10. T. Kataoka, H. Yoshida, and H. Sanada, *J. Chem. Eng. Jpn., 7,* 105 (1974).
11. Y. S. Ghim and H. N. Chang, *Ind. Eng. Chem., Fundam., 21,* 369 (1982).
12. A. Rasmuson and I. Neretrieks, *AIChE J., 26,* 686 (1980).

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