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Adsorption Characteristics of Cresols with Eluent Composition in Adsorption Chromatography

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Abstract

Adsorption characteristics of cresol isomers in adsorption chromatography were investigated in a system where the binary eluent containing ethyl acetate as a modifier in *n*-hexane was used. The method of moments was used to estimate the equilibrium constant and the rate parameters. The agreement between the experimental and theoretical results calculated by the orthogonal collocation method was excellent. The equilibrium constant and rate parameters for each cresol were empirically correlated with eluent composition. As the eluent composition increased, the retention time and the front of the response curve became faster and sharper, respectively. By using the modifier in a weak solvent, mixtures of *o-/m*-cresols and *o-/p*-cresols were easily separated whereas that of *m-/p*-cresols was not. The values on the scale of axial eddy dispersion were much larger than those of the gas system. For *o*-cresol, these values diminished with increasing eluent composition, while for *m*- and *p*-cresols the trend was reversed. For all systems, both intraparticle mass transfer and axial dispersion were dominant.

I. INTRODUCTION

The use of a polar adsorbent to separate polar compounds is generally acceptable. The mass transfer resistances are very large if the solvent is nonpolar. Since mobile phase molecules compete with solute molecules for adsorption sites in adsorption chromatography, a mixed mobile phase manipulates the adsorption characteristics. Thus, it is common to use an eluent containing a strong solvent to adjust the selectivity and to separate the mixture efficiently. Also, a systematic investigation of the effects of a strongly sorbed additive on column performance is important for an understanding of such processes as gradient elution chromatography. Recently, Sadroddin and Guiochon (*1*, *2*) discussed the phenomena

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theoretically and experimentally associated with the elution of a single component eluted with a binary mobile phase.

To design such adsorption equipment, information for the equilibrium isotherm and the rate parameters is essential. The main methods for estimating such parameters are: curve fitting in the time domain (*3*), fitting in the Fourier domain (*4*), fitting in the Laplace domain (*5*), and the method of moments. The method of moments was first presented by Kubin (*6*) and Kucera (*7*), and this method has been used extensively by several investigators (*8–12*). Among them, the first is applicable only to nonlinear systems and the others are confined to linear systems.

Aside from complications, solvent mixtures are chromatographically equivalent to pure solvents (*13*). Therefore, the various relationships derived for pure solvents are equally applicable to solvent mixtures. Also, since a binary polar eluent decreases the adsorption capacity of a polar adsorbent, the linear part of the isotherm for eluates is widened. From these points, the experimental results on eluent composition can be analyzed by the theory of linear chromatography.

Neuzil et al. (*14*) developed simulated moving-bed chromatography for the separation of cresols by using zeolite and phenol as the adsorbent and desorbent, respectively. The present work studies the column performance of cresols in a chromatographic medium packed with silica gel (Lichroprep SI 100, Merck Co.) when ethyl acetate in *n*-hexane is used as a strongly sorbed additive. The equilibrium constant, the intraparticle mass transfer coefficient, and the axial dispersion coefficient with eluent compositions were estimated by the method of moments. Also investigated were the effects of eluent composition on the equilibrium constant, the rate parameters, and the elution profile.

II. BASIC EQUATION

The equations governing the process are those for an isothermal system, disregarding radial gradients in velocity and concentration.

The solute balance in the fluid phase is

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial z} + \beta\rho_p\frac{q}{t} = D_a\frac{\partial^2 C}{\partial z^2} \qquad (1)$$

When the equilibrium relationship between the mobile and the stationary phases is linear, it is given as

$$q_s = K(S)C_s, \qquad q^* = K(S)C, \qquad q = K(S)C^* \qquad (2)$$

where S denotes the eluent composition.

In order to express the mass transfer rate into the particle, the linear driving force approximation (LDFA) model is assumed.

$$\rho_p \frac{dq}{dt} = \frac{3}{R_p} k_f (C - C_s)$$

$$= \frac{3}{R_p} k_s \rho_p (q_s - q) \tag{3}$$

$$= \frac{3}{R_p} k_o \rho_p (q^* - q) \tag{4}$$

where

$$\frac{1}{k_o} = \frac{\rho_p K}{k_f} + \frac{1}{k_s} \tag{5}$$

The above set of differential equations is subject to the following initial and boundary conditions:

$$C = q = 0 \quad \text{at } t = 0 \tag{6}$$

$$C = C_{in}, \quad 0 \leq t \leq t_{in}, \quad \text{otherwise } C = 0 \text{ at } z = 0 \tag{7}$$

$$\partial C / \partial z = 0, \quad t > 0 \text{ at } z = L \tag{8}$$

Then the system of equations can be solved in the Laplace domain. Solution of the system is

$$C(s,z) = \frac{C_{in}}{s} [1 - \exp(-st_{in})] \exp(-\delta z) \tag{9}$$

where

$$\delta = \frac{1}{2} \left[-\frac{v}{D_a} + \left\{ \left(\frac{v}{D_a} \right)^2 + 4H(s) \right\}^{1/2} \right] \tag{10}$$

$$H(s) = \frac{s}{D_a} \left[1 + \frac{\frac{3}{R_p} \beta \rho_p K k_o}{s + \frac{3}{R_p} k_o} \right] \tag{11}$$

Experimental moments of chromatographic peaks are known to be simply related to limits of derivatives of the Laplace transformed concentration (*8–12*). The final relations for the first absolute and the second central moments are as follows:

$$\mu_1' = \frac{t_{in}}{2} + (1 + \beta\rho_p K)\frac{L}{v} \tag{12}$$

$$\mu_2 = \frac{t_{in}^2}{12} + \frac{2R_p}{3}\beta\rho_p K\left[\frac{1}{k_o} + \frac{3}{R_p}\frac{(1 + \beta\rho_p K)^2}{\beta\rho_p K}\frac{D_a}{v^2}\right]\frac{L}{v} \tag{13}$$

While the first absolute moment locates the peak, the second central moment is a measure of band spreading.

III. EXPERIMENTAL

The adsorbent was Lichroprep SI 100 (Merck Co.), and the properties of the adsorbent are listed elsewhere (*15*). The stainless-steel column (Alltech) was 10 mm i.d. with a length of 250 mm. The solutes investigated were research-grade cresol isomers (Merck Co.). The mobile phases were mixtures of *n*-hexane and ethyl acetate. The eluent compositions were 1, 3, 5, and 7 × 10^{-2} v/v fractions of ethyl acetate.

Before being packed, the adsorbent was activated in a furnace at 200°C for 24 h. The column was equilibrated with the same mobile phases prior to the start of the experiments until steady-state was reached. A high-pressure metering pump (Eldex, AA-100-S) was used, and the flow rates were controlled by a micrometer. The concentration was measured with a differential refractometer (Waters Associates M410).

The column void fraction, ϵ, was 0.332, and all the experiments were performed at 30°C. The volumetric flow rates were varied between 1 and 4 mL/min for the determination of moments. The feed concentration, C_{in}, and the injection time, t_{in}, were fixed at 10 mol/m^3 and 4 min, respectively. The volume actually injected was calculated from the time spent in the injection port.

IV. RESULTS AND DISCUSSION

Since the first absolute moment is influenced by the parameters which describe the geometry of the column and the equilibrium parameter, the equilibrium constant, K, in Eq. (12) is determined from a plot of $(\mu_1' - t_{in}/2)$ versus (L/v). The plot for each cresol at S = 0.03 is shown in Fig. 1, and the curves prove that the assumption of a linear isotherm is valid because the linearity requirement is fulfilled. At all eluent compositions

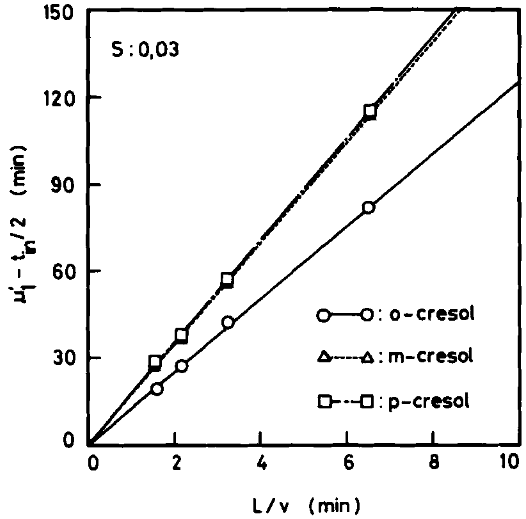

FIG. 1. Plot of ($\mu_1' - t_{in}/2$) vs L/v for each cresol at $S = 0.03$.

the data points were located on straight lines within an average deviation of 2%.

The equilibrium constants for each component against the composition of the eluent are given in Fig. 2. Those constants diminished with increasing solvent composition. This means that ethyl acetate competes with cresols for adsorption sites. The equilibrium constants for each component were empirically correlated with solvent compositions, S:

$$K = A_1 S^{B_1} \tag{14}$$

The parameters evaluated are listed in Table 1. Figure 3 shows the separation factors defined by the ratio of the equilibrium constants between cresols with eluent composition. That is,

$$\alpha_{i,j} = K_j / K_i \tag{15}$$

In this figure, each line was obtained by using the parameters in Table 1, and the subscripts 1, 2, and 3 represent *o*-, *m*-, and *p*-cresols, respectively. In general, the mixture is easily separated when the separation factor is larger than 1.2 (*16*). This figure reveals that α_{12} and α_{13} diminish with increasing eluent composition larger than 1.2, whereas α_{23} has values of about 1.0 except at $S = 0.01$.

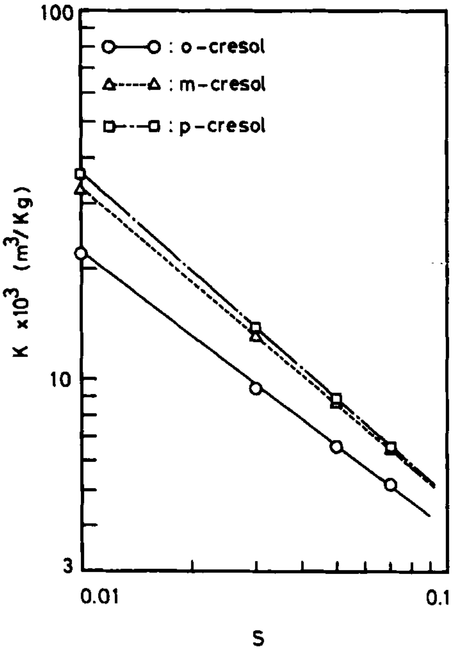

FIG. 2. Equilibrium constant with eluent composition for cresols.

In general, the external mass transfer and axial dispersion coefficients are not independent of the eluent flow rate in liquid systems. The external mass transfer coefficient was obtained from the correlation equation proposed by Merk et al. (*17*), and the molecular diffusivity was from the Hayduk and Minhas correlation (*18*). The values of the external mass transfer coefficient were nearly constant with velocity and with solvent

TABLE 1
Parameter Values of Equilibrium Constants and Rate Parameters for Cresols

		o-Cresol	*m*-Cresol	*p*-Cresol
K	A_1	7.0764×10^{-4}	7.2234×10^{-4}	6.5315×10^{-4}
	B_1	−0.74751	−0.82932	−0.87197
k_s	A_2	1.1966×10^{-2}	7.9310×10^{-3}	6.0309×10^{-2}
	B_2	1.0914	1.2649	1.7053
τ	A_3	8.8578	26.9980	55.9360
	B_3	−0.15335	0.20063	0.43576

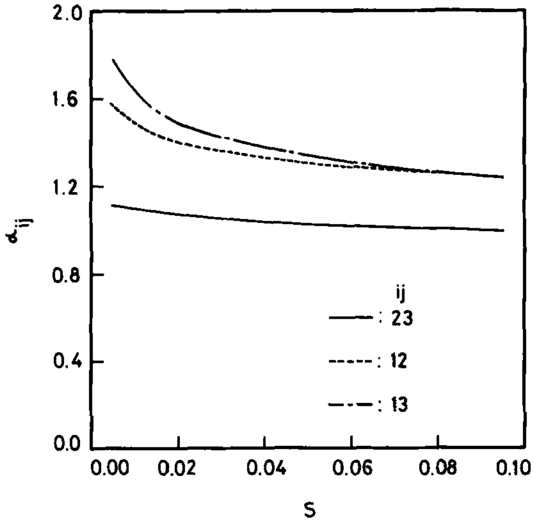

FIG. 3. Separation factor with the eluent compositions for each mixture (1, *o*-cresol; 2, *m*-cresol; 3, *p*-cresol).

composition because of low Reynolds number. The final average values are listed in Table 2 for each component. Axial dispersion in a packed bed is usually divided into molecular diffusion and eddy diffusion:

$$D_a = D_{AB} + R_p \tau v \qquad (16)$$

Since the molecular diffusivities are small in liquid systems, the axial dispersion in liquid chromatography is directly proportional to bulk mixing in the interstitial phase (*11*, *19*, *20*).

The rate parameters are easily estimated from the second central moment. When the equilibrium relationship is linear, the contributions of the mass transfer resistances and axial dispersion are linearly additive (*21*). Equation (13) is rearranged together with Eq. (16) to give

$$\frac{3(\mu_2 - t_{in}^2/12)v}{2LR_p\beta\rho_pK} = \frac{1}{k_T}$$

$$= \frac{\rho_pK}{k_f} + \frac{1}{k_s} + 3\frac{(1+\beta\rho_pK)^2}{\beta\rho_pK}\frac{\tau}{v} \qquad (17)$$

$$= R_T = R_{ext} + R_{int} + R_{axi} \qquad (18)$$

From a plot of the left-hand side with respect to $1/v$ in Eq. (17), the intraparticle mass transfer coefficient and the axial dispersion coefficient

TABLE 2
The External Mass Transfer Coefficient with Solvent Strength

	S	k_f ($\times$ 10^2 m/min)
o-Cresol	0.01	2.149
	0.03	2.132
	0.05	2.121
	0.07	2.105
	Average	2.130
m-Cresol	0.01	2.093
	0.03	2.077
	0.05	2.066
	0.07	2.050
	Average	2.070
p-Cresol	0.01	2.203
	0.03	2.186
	0.05	2.175
	0.07	2.159
	Average	2.180

can be evaluated from the intercept and slope, respectively. This plot for each component at S = 0.03 is shown in Fig. 4. All the data were on straight lines within an average deviation of 4%.

The estimated rate parameters at each eluent composition are given in Figs. 5 and 6. These parameters for each cresol were empirically correlated with solvent composition:

$$k_s = A_2 S^{B_2}, \qquad \tau = A_3 S^{B_3} \tag{19}$$

The correlated parameters are listed in Table 1. Figure 5 demonstrates that the intraparticle mass transfer coefficients for each cresol depend strongly upon the eluent composition because the adsorption affinities of cresols to the adsorbent diminish with increasing ethyl acetate composition. As shown in Fig. 6, when S increased, the values of scale of axial eddy dispersion, τ, decreased for *o*-cresol whereas it showed a reverse trend for *m*- and *p*-cresols. τ normally has a value of about 1 for gas systems (*21*), and Keum and Lee (*11*) reported that this parameter also had a value of around 1 even in liquid systems when the intraparticle mass transfer resistance played a major role. However, some investigators (*12, 19*) reported that in liquid systems this value is much larger than 1 when the contributions of the other resistances are significant. In the present work, the order of magnitude

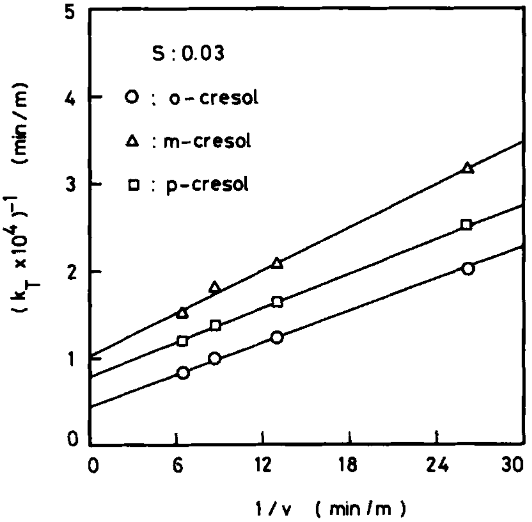

FIG. 4. Plot of $1/k_T$ vs $1/v$ for each cresol at $S = 0.03$.

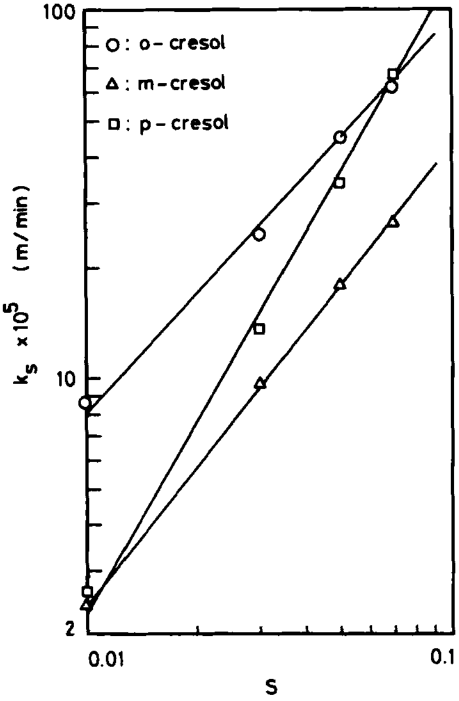

FIG. 5. Intraparticle mass transfer coefficients with eluent composition for cresols.

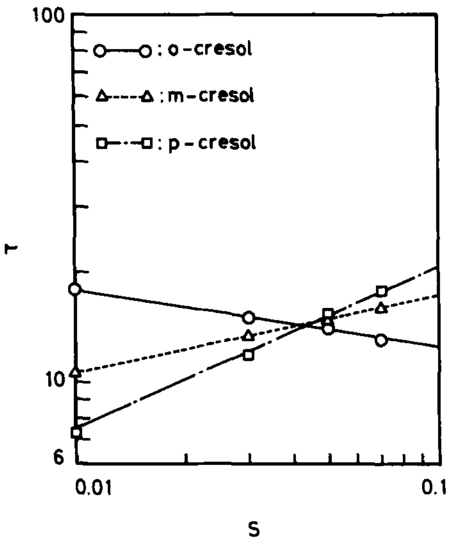

FIG. 6. The values of scale of axial eddy dispersion with eluent composition for cresols.

was the same as that of the latter investigators. Mansour et al. (*22*) also reported that for $L >> d_p$, $Pe_p > 1$, and $Re_p \gtrsim 10$, axial dispersion is negligible. However, the ranges of these numbers in the present work were $0.05 < Re_p < 0.24$ and $0.10 < Pe_p < 0.28$. Thus, axial dispersion is likely to be significant.

To confirm the above results, the relative importance of mass transfer resistances was computed from Eq. (18). Figure 7 shows the effect of eluent composition on the relative dominance of the respective resistances for cresols at $V = 4$ mL/min. The external mass transfer resistance was negligible at all eluent compositions. On the other hand, the contributions of intraparticle mass transfer and axial dispersion were significant. Thus, axial dispersion is significant when the value of axial eddy dispersion is much larger than 1.

Figure 8 shows the effect of eluent composition on the elution profile of *p*-cresol at a fixed flow rate ($V = 3$ mL/min). The theoretical concentration profiles for the individual pulse inputs were calculated by the orthogonal collocation method (*23*) for ease and speed of computation. This figure demonstrates that as the composition of ethyl acetate at a fixed flow rate increases, the retention time and the front of the elution profile become shorter and sharper, respectively, and the maximum concentration of the peak markedly increases. That is, the retention of the sample band and the shape of its profile depend not only on the relative strengths of the

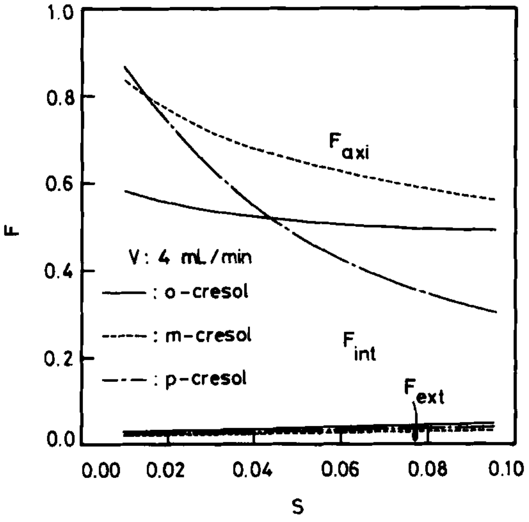

FIG. 7. Effect of solvent composition on relative contribution of each resistance for cresols at V = 4 mL/min.

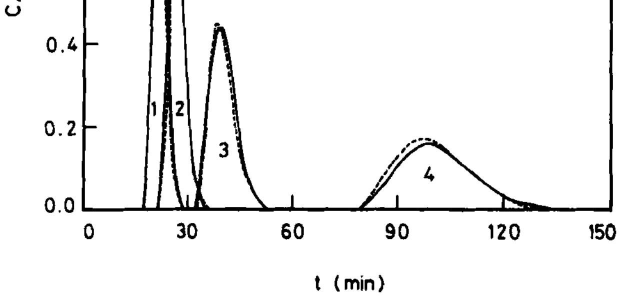

FIG. 8. Influence of the concentration of the strongly sorbed additive in the mobile phase on the elution profile of p-cresol at fixed flow rate (S: 1, 0.07; 2, 0.05; 3, 0.03; 4, 0.01).

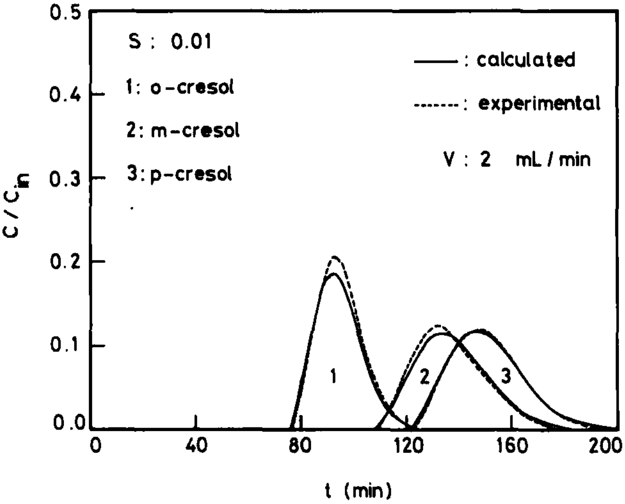

FIG. 9. Elution profiles for each cresol at $S = 0.01$ and $V = 2$ mL/min.

adsorption of the strongly sorbed additive and the sample from their solution in the weak solvent, but also on the column efficiency, the concentration of the strongly sorbed additive in the mobile phase, the column saturation capacity, and the size of the sample pulse. Figure 9 shows the predicted curve together with the experimental data of each cresol at $V =$ 2 mL/min and $S = 0.01$. As discussed previously, the mixture of *m*-/*p*-cresols was not easily separated by single column chromatography. As shown in Figs. 8 and 9, agreement between the model and experiment was fairly good. This confirms that the parameters obtained from the method of moments are very useful for predicting the elution profiles for column systems.

V. CONCLUSIONS

The equilibrium constant and rate parameters were estimated by the method of moments. The theoretical values were calculated by the orthogonal collocation method with these parameter values. Agreement between experimental and calculated results was very good. This confirmed that the method of moments is useful for determining the parameters.

The equilibrium constants and rate parameters for cresols were empirically correlated with eluent composition. When the composition of ethyl acetate in *n*-hexane increased, the equilibrium constants were diminished whereas the intraparticle mass transfer coefficients showed the reverse trend. Thus, as the eluent composition increased, the elution profiles had faster retention and a sharper front, and the maximum concentration of the peak markedly increased. At all eluent compositions, separation factors for mixtures of *o*-/*m*-cresols and *o*-/*p*-cresols were larger than 1.2 whereas those values for *m*-/*p*-cresols were not. The values of axial eddy dispersion were much larger than those of gas systems. These values were diminished with eluent composition for *o*-cresol, while for *m*- and *p*-cresols the values increased.

SYMBOLS

A, B	correlation parameters in Eqs. (14) and (19)
C	average adsorbate bulk concentration (mol/m^3)
C^*	average adsorbate bulk concentration in equilibrium with q (mol/m^3)
D_a	axial dispersion coefficient (m^2/min)
d_p	particle diameter (m)
F	fraction of the relative mass transfer resistance
$H(s)$	function given by Eq. (11)
K	equilibrium constant (m^3/kg)
k_f	external mass transfer coefficient (m/min)
k_o	overall mass transfer coefficient (m/min)
k_s	intraparticle mass transfer coefficient (m/min)
k_T	total mass transfer coefficient defined by Eq. (17) (m/min)
L	total column length (m)
Pe_p	Peclet number, $d_p v / D_a$
q	average adsorbate concentration on the adsorbent (mol/kg)
q^*	average adsorbate concentration on the adsorbent in equilibrium with C (mol/kg)
R_p	particle radius (m)
R_{axi}	axial dispersion resistance
Re_p	particle Reynolds number, $d_p v \rho_l / \mu_l$
R_{ext}	external mass transfer resistance
R_{int}	intraparticle mass transfer resistance
R_T	total mass transfer resistance
S	ethyl acetate volume fraction in solvent
s	Laplace parameter
t	time (min)
V	volumetric flow rate (mL/min)
v	interstitial velocity (m/min)
z	axial distance from column inlet (m)

Subscript

axi	axial
ext	external or film
in	injection

int	intraparticle
s	surface

Greek Letters

ρ_p	apparent particle density (m^3/kg)
β	$(1 - \epsilon)/\epsilon$
μ_1'	first absolute moment
μ_2	second central moment
δ	parameter defined by Eq. (10)
ϵ	interparticle void fraction
τ	scale of axial eddy dispersion
α	separation factor

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