

MASS TRANSFER CHARACTERISTICS of m-CRESOL, QUINOLINE AND 1-NAPHTHOL IN A SILICA GEL COLUMN

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Abstract—The mass transport characteristics of m-cresol, quinoline and 1-naphthol in a silica gel column were investigated. Model equations were obtained with linear isotherm, and the equilibrium constant and the overall mass transfer coefficient were also obtained with first two moments. The theoretical chromatographic curves predicted by using above two parameters were in a good agreement with the experiment. Contribution of individual resistances on overall mass transfer resistances was estimated. The results showed that the contribution of the external mass transfer resistances was almost uniform but that of the axial dispersion was diminished as increasing the flow rates. In the most of the experimental regions the internal mass transfer resistances played a major role in the overall resistances.

INTRODUCTION

The investigation of mass transport phenomena in the chromatographic column is essential to obtain the optimal operating condition for the equipments using principles of the chromatography such as the simulated moving bed and moving feed port chromatography.

The analysis of the response to input disturbances has been used to study the dynamic behavior of process equipment particularly for chromatographic systems. Smith and colleagues[1-3] drew some useful informations on the transport phenomena in gas-solid chromatography using a series of equations relating the mass transport parameters in the column with the statistical moments of the entry and exit pulse derived by Kucera[4]. Gangwal et al.[5] suggested a Fourier analysis, and Haynes[6] considered time domain solution. Hsu and Haynes[7] employed a combined frequency domain and fitting in the time domain. Fourier analysis method normally involves larger computer times than the moment method and it requires to restrict the use of high frequencies in some cases. Borsma-Klein and Moulijin[8] performed a comparative study of moment analysis, Fourier analysis and fitting in the time domain. A review of this topic was recently presented by Ruthven[9]. However, works related to those techniques have mostly been applied for gaseous systems in spite of that the general features of the liquid systems are analogized with those of the gase-

ous systems. This may be due to the difficulties often associated with liquid experiments or to the lack of informations on the system in comparison with those of gases.

In the present work, three solutes, m-cresol, quinoline and 1-naphthol were considered for liquid chromatographic separation. Silica gel(Lichroprep SI 100, Merck Co.) was used as a chromatographic medium and mixing solvent of 0.3% isopropanol in n-hexane as an eluent. The model equations were established based on the linearity of the equilibrium isotherm. The first two moments were derived from the solution in the Laplace domain. The object of present work is to investigate the mass transport characteristics of m-cresol, quinoline and 1-naphthol in the chromatographic column.

MATHEMATICAL MODEL

Adsorption of the solutes from a flowing liquid onto the porous particles in a chromatographic column was considered. With assumptions of constant space velocity along the column axis and the axial dispersed plug flow, the differential mass balance for the fluid phase was described by

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

In the model equations for chromatographic column, it should be considered both mass transfer taking place outside film as well as within the particles. In order to express mass transfer rate into the particle, the linear

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driving force approximation model was assumed. Then the mass transport into the particle is expressed by following relationships;

$$\rho_p \frac{dq}{dt} = \frac{3}{R} k_r (C - C_s) = \frac{3}{R} k_{os} \rho_p (q_s - q) \quad (2)$$

where the second part represents the mass transfer rate throughout the external mass boundary around the particles. Initial conditions were

$$C = q = 0 \quad (3)$$

and boundary conditions were assumed as follows;

$$C = C_{in}, \quad 0 < t < t_{in} \quad z = 0 \quad (4)$$

$$C = \text{finite}, \quad t > 0 \quad z \rightarrow \text{infinite} \quad (5)$$

Since the adsorption is markedly faster than the mass transfer rate, the local equilibrium at the particle surface is established. Hence

$$q_s = q_s(C_s). \quad (6)$$

When the equilibrium relationship is linear, the mass transfer resistances and axial dispersion are linear additive [9]. The model equation can be reduced as follows;

$$\epsilon \frac{\partial C}{\partial t} + \epsilon v \frac{\partial C}{\partial z} + (1 - \epsilon) \rho_p \frac{\partial q}{\partial t} = 0 \quad (7)$$

$$\frac{dq}{dt} = \frac{3}{R} k_{os} (KC - q) \quad (8)$$

where

$$\frac{1}{k_{os}} = \frac{\rho_p K}{k_r} + \frac{1}{k_s} + \frac{3D_a [1 + (1 - \epsilon) \rho_p K / \epsilon]}{Rv^2 (1 - \epsilon) \rho_p K / \epsilon} \quad (9)$$

The solution in Laplace domain (see Appendix) obtained by taking Laplace transform of above equations is given by

$$C(s, z) = \frac{C_{in} [1 - \exp(-st_{in})] \exp[-\frac{z}{v} (s + \frac{ghKs}{s+h})]}{s} \quad (10)$$

where

$$g = (1 - \epsilon) \rho_p / \epsilon, \quad h = 3k_{os} / R. \quad (11)$$

Moment technique for parameter estimation

The solution, Eqn(10), does not appear simple to invert the transform. But it is possible to obtain easily explicit expressions for the moments of chromatographic curve in real time domain. The *n*th moments(*m_n*) of the response curve at the bed exit can be obtained from the limit equation expressed as

$$m_n = \int_0^\infty t^n C(t, L_t) dt = (-1)^n \lim_{s \rightarrow 0} \frac{d^n C(s, L_t)}{ds^n} \quad (12)$$

In practice, only the first and second moments from a column can be measured accurately enough to be useful. The first absolute moment is defined by

$$\mu'_1 = \frac{\int_0^\infty tC dt}{\int_0^\infty C dt} = \frac{m_1}{m_0} \quad (13)$$

and the physical meaning of this is the center of gravity of the peak or mean retention time. The second central moment is

$$\mu_2 = \frac{\int_0^\infty (t - \mu'_1)^2 C dt}{\int_0^\infty C dt} = \frac{m_2}{m_0} - \mu_1'^2 \quad (14)$$

The solution, Eqn(10), in the Laplace domain can be substituted into Eqn(12) to evaluate *m₀*, *m₁*, *m₂*. Hence the first absolute moment was obtained by Eqn (13)

$$\mu'_1 = \frac{t_{in}}{2} + \frac{L_t}{v} (1 + \frac{1 - \epsilon}{\epsilon} \rho_p K) \quad (15)$$

and above relation shows that the retention time is independent from mass transfer parameters and is a function of equilibrium parameter, K. Similarly the second central moment with Eqn(14) was given as

$$\mu_2 = \frac{t_{in}^2}{12} + \frac{2L_t}{v} \frac{R}{3} \frac{\rho_p K}{k_{os}} \quad (16)$$

Since the μ'_1 and μ_2 are obtained from experimental response curve, the equilibrium constant(K) and overall mass transfer coefficient(*k_{os}*) can also be determined.

EXPERIMENTAL

The experimental equipments were shown schematically in Figure 1. The column was made from 1/2 inches stainless steel tube. Water of constant temperature was pumped through water jackets on the outside of the column to maintain the required temperature, and all experiments were carried out at 30°C. Feed and solvent were introduced by downflow mode with the high pressure metering pump(Eldex, AA-100-S), and flow rates were controlled by setting the micro-meter.

Lichroprep SI 100(Merck Co.), which is a kind of silica gel, was used as adsorbent. The apparent density by mercury porosity meter and radius of particles were 614 kg/m³ and 3.25 × 10⁻⁵ m, respectively and further details were in elsewhere[10]. Quinoline, m-cresol and 1-naphthol of research grade were used as adsorbates. The eluent used was the mixture of 0.3 volume % isopropanol in n-hexane.

Solvent was sufficiently supplied into the column prior to the start of experiment in order to wet the adsorbent completely. The experiments were carried out under the operating conditions shown in Table 1. The response peaks at the column outlet were measured

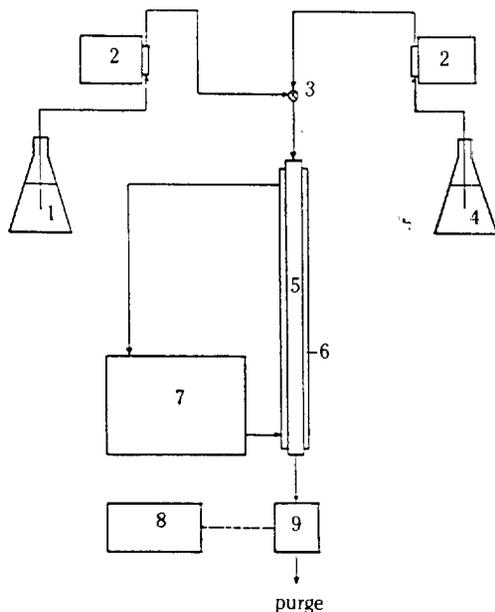


Fig. 1. Schematic experimental apparatus.

- 1: Feed reservoir
- 2: High pressure pump
- 3: Three way valve
- 4: Solvent reservoir
- 5: Column
- 6: Water jacket
- 7: Water bath
- 8: Recorder
- 9: Detector

Table 1. Experimental conditions

Flow rate	10^{-6} - 4×10^{-6} (m ³ /min)
Injection time(t _{in})	4 (min)
Input concentration(C _{in})	9 (mole/m ³)
Bed length(L _i)	0.3, 0.4, 0.5, 0.6 (m)
Bed porosity(ε)	0.336 (-)
Temperature	30°C
Particle density(ρ _p)	614 (kg/m ³)

using differential refractometer (R401, Waters), and the transmission curves of the concentration versus time were generated by Digitizer (Summagraphics, mm1812) and calibration curve.

RESULTS AND DISCUSSION

The adsorption equilibrium constant(K) and the overall mass transfer coefficient(k_{os}) can be obtained by the Eqn(15) and (16). By Eqn(15), the plot of (μ₁t_{in}/2) vs L_i/v should be a straight line through the origin since K is independent from the flow rates. Such plot of the moment generated from the experimental curves was given in Figure 2. It was shown that the linearity requirement is fulfilled, and it means that the

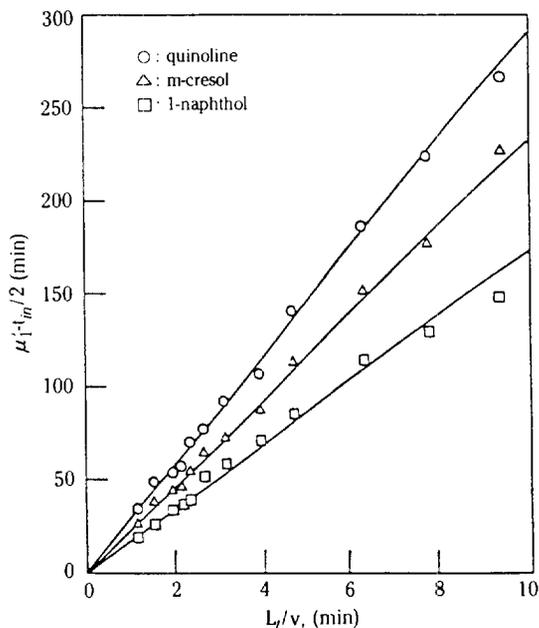


Fig. 2. Plot of (μ₁t_{in}/2) vs L_i/v.

assumption of the linear isotherm is valid. Thus the value of K was obtained from the slope of the line, and this result for each component was listed at the first column in Table 3.

The second central moments, μ₂, of the chromatographic curves are under the influence of the fluid velocity(v), the properties which characterize the column and the adsorbent (L_i, ε, R, ρ_p), the injection time (t_{in}), the equilibrium constant(K) and the overall mass transfer coefficient which includes both the effects of axial dispersion and mass transfer resistances. In order to analyze the experimental data, Eqn(16) with Eqn(9) was transformed into the following form

$$\frac{3(\mu_2 - t_{in}^2/12)\epsilon v}{2(1-\epsilon)RL_i\rho_p K} = E_t = E_r + E_s + E_D/Rv^2 \tag{17}$$

where

$$E_t = 1/k_{os}, E_r = \rho_p K/k_r, E_s = 1/k_s, E_D = E'_D \cdot D_a, E'_D = 3[1 + (1-\epsilon)\rho_p K/\epsilon]^2 / [(1-\epsilon)\rho_p K/\epsilon]$$

E_r, E_s and E_D represent the effect of the external mass transfer, the internal diffusion and the axial dispersion, respectively. To predict the external mass transfer coefficient in column Merck et al.[11] have proposed the empirical equation in form that

$$k_r = \frac{[1 + 1.5(1-\epsilon)]D_L}{2R} (2 + FSc^{1/3}Re_p^{0.5}) \tag{18}$$

where

$$F = 0.664 [1 + (\frac{0.0557 Re_p^{0.3} Sc^{2/3}}{1 + 2.44 (Sc^{2/3} - 1) Re_p^{-0.1}})^2]$$

Table 2. External mass transfer coefficient with flow rates

$F_R \times 10^6$	$k_f \times 10^2$ (m/min)		
	m-cresol	quinoline	1-naphthol
1.0	1.3159	1.1897	1.1610
1.5	1.3163	1.2000	1.1613
2.0	1.3166	1.2003	1.1615
2.5	1.3168	1.2005	1.1618
3.0	1.3170	1.2007	1.1620
3.5	1.3173	1.2009	1.1622
4.0	1.3175	1.2011	1.1623

Above equation shows that the external mass transfer coefficient depend on the Reynold number, i.e. flow rates. However the values of k_f calculated under present experimental conditions were nearly constant in spite of the variation of the flow rate as shown in Table 2. It may be caused by small variation of Reynold number with the present experimental conditions. Then E_f and E_s in Eqn(17) can be treated as constant and independent from the flow rates. Suzuki and Smith[12] have suggested that there are two contributors, molecular diffusion and eddy diffusion, so that the axial dispersion coefficient may be expressed by

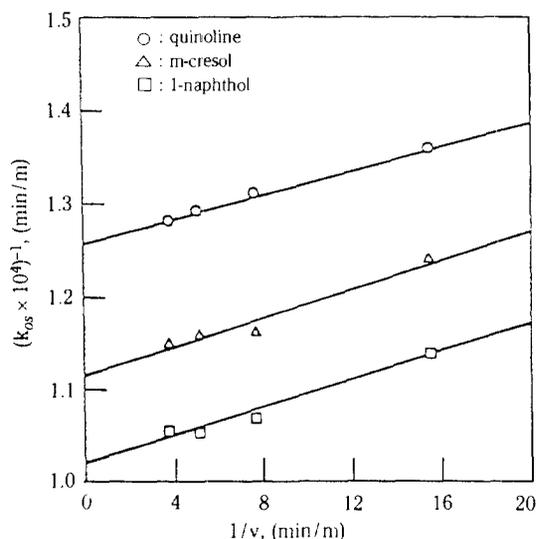
$$D_a = \nu_1 D_L + \nu_2 Rv. \quad (19)$$

Unlike in gaseous system, the axial dispersion in liquid system is directly proportional to v because of small diffusivities[13]. Hence the molecular diffusion term can be dropped, then

$$D_a = \nu_2 Rv. \quad (20)$$

When Eqn(20) is substituted into Eqn(17), the value of $E_f + E_s$ and ν_2 can be obtained from the intercept and slope of the plot of $1/k_{os}$ vs $1/v$. Furthermore the internal mass transfer coefficient(k_s) can be extracted by subtracting E_f from $E_f + E_s$. Such plot of the second moment was given in Figure 3, and the parameters obtained were summarized in Table 3. Ruthven[9] suggested that ν_2 is constants which normally have values of about unity. This value in the present work was almost agreement with the value indicated by Ruthven.

It is interesting to investigate the relative contribution of the individual resistances on the overall mass transfer resistances. The percent contribution of the individual mass transfer resistances for overall mass transfer was given in Table 4. As flow rate increases, resistances of the axial dispersion were diminished, while those of external mass transfer were nearly uniform. In most regions the internal mass transfer resis-

**Fig. 3. Plot of $1/k_{os}$ vs $1/v$.****Table 3. Parameters obtained from moment analysis**

solute	K	$*k_f \times 10^2$	$k_s \times 10^5$	ν_2
m-cresol	0.01836	1.3170	9.7904	1.11
quinoline	0.02298	1.2005	8.8745	0.75
1-naphthol	0.01340	1.1617	10.5610	1.38

* k_f was the average value for flow rate in Table 2.

Table 4. Percent relative contributions of individual resistances on overall mass transfer resistances

$F_R = 1 \times 10^{-6} \text{ m}^3/\text{min}$

solute	E_f/E_t	E_s/E_t	$(E_D/Rv^2)/E_t$
m-cresol	6.91	82.44	10.65
quinoline	8.64	83.71	7.65
1-naphthol	6.22	83.19	10.59

$F_R = 2 \times 10^{-6} \text{ m}^3/\text{min}$

solute	E_f/E_t	E_s/E_t	$(E_D/Rv^2)/E_t$
m-cresol	7.40	88.30	4.30
quinoline	9.04	86.95	4.01
1-naphthol	6.65	88.91	4.44

$F_R = 3 \times 10^{-6} \text{ m}^3/\text{min}$

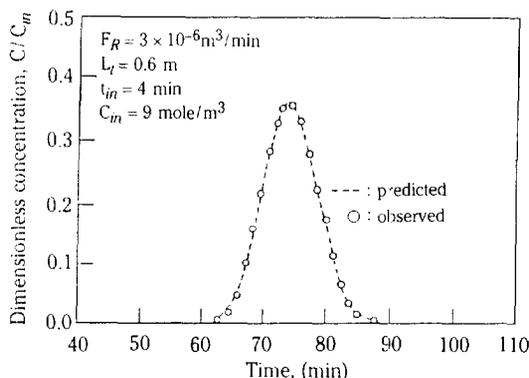
solute	E_f/E_t	E_s/E_t	$(E_D/Rv^2)/E_t$
m-cresol	7.44	88.76	3.80
quinoline	9.11	88.19	2.70
1-naphthol	6.67	89.29	4.04

Table 4. Continued.

$$F_R = 4 \times 10^{-6} \text{ m}^3/\text{min}$$

solute	E_f/E_t	E_s/E_t	$(E_D/Rv^2)/E_t$
m-cresol	7.46	89.04	3.50
quinoline	9.17	88.86	1.97
1-naphthol	6.72	90.01	3.27

$$E_t = E_s + E_D/Rv^2$$

**Fig. 4. Comparison of model and experiment for m-cresol.**

tances played the major role. The contribution of the axial dispersion can be vary from almost 100 percents at a very low velocity to zero at a velocity approaching infinity. Hence an erroneous results may be obtained for such parameter as the internal mass transfer coefficient when the axial dispersion is neglected at low flow rates. Only at high velocities would it be possible to neglect this contribution to predict the chromatographic curve.

The rate parameters discussed up to now can be used to obtain the solutions in real time domain. These solutions in the present work were obtained by applying the orthogonal collocation method for ease and simple[14]. Figure 4 shows a comparison between the model and experimental data for m-cresol, and it can be seen in a good agreement between them. It was given a confirmation that the parameters obtained from the moment method are very useful to predict the elution profiles for the column system.

CONCLUSION

The mass transport characteristics of m-cresol, quinoline and 1-naphthol in a silica gel column were investigated. By moment method the equilibrium constant and the overall mass transfer coefficient were obtained and the chromatographic curve calculated with these two parameters was in a good agreement with

the experimental curve. It supported that moment method is very useful to obtain the system parameters. The influence of the individual resistances on the overall mass transfer resistance was also investigated. In the most of experimental regions the internal mass transfer played a major role. When the flow rates were low the contribution of the axial dispersion was existed some extent. It suggests that negligence of the axial dispersion at low flow rate may give an overestimation of the internal mass transfer coefficients, and it would be safe to neglect the axial dispersion at high flow rates.

Appendix: Derivation of Solution in Laplace Domain [Eqn(10)]

Taking Laplace transform of Eqn(7) and (8)

$$sC(s) + v \frac{dC(s)}{dz} + gsQ(s) = 0 \quad (\text{A-1})$$

$$sQ(s) = h [KC(s) - Q(s)] \quad (\text{A-2})$$

where

$$g = (1 - \epsilon) \rho_p / \epsilon, \quad h = 3k_{os}/R.$$

From Eqn(A-1) and (A-2)

$$\frac{dC(s)}{dz} + \frac{s}{v} (1 + \frac{ghK}{s+h}) C(s) = 0. \quad (\text{A-3})$$

The solution of Eqn(A-3) with the boundary condition [Eqn(4)] was given by

$$C(s) = \frac{C_{in}}{s} [1 - \exp(-st_{in})] \exp[-\frac{z}{v} (s + \frac{ghKs}{s+h})]. \quad (\text{A-4})$$

NOMENCLATURE

- C : concentration of the fluid phase [mole/m³]
- C_{in} : input concentration of the fluid phase [mole/m³]
- C_s : concentration of the fluid phase at the particle surface [mole/m³]
- D_a : axial dispersion coefficient [m/min²]
- D_L : molecular diffusivity [mole/m³]
- F_R : flow rate [m³/min]
- K : equilibrium constant [m³/kg]
- k_f : external mass transfer coefficient [m/min]
- k_{os} : overall mass transfer coefficient [m/min]
- k_s : internal mass transfer coefficient [m/min]
- L_t : column length [m]
- m_n : nth moment defined by Eqn(12)
- q : concentration of the solid phase [mole/kg]
- q_s : concentration of solid phase at the particle surface [mole/kg]
- R : particle radius [m]
- Re : Reynold number [-]

- Sc : Schmidt number [-]
 s : variable in Laplace domain
 t : time [min]
 t_m : injection time [min]
 v : interstitial velocity [m/min]
 z : axial coordinate [m]

Greek Letters

- ϵ : void fraction [-]
 ρ_p : apparent density of particle [kg/m³]
 μ'_1 : first absolute moment [min]
 μ_2 : second central moment [min²]
 ν_1, ν_2 : constant in Eqn(20)

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