

CONCENTRATION DEPENDENCE OF INTRAPARTICLE MASS TRANSFER COEFFICIENTS IN SILICA GEL FOR *m*-CRESOL, QUINOLINE AND 1-NAPHTHOL IN *n*-HEXANE

DONG KWON KEUM, JEONG KI MOON AND WON KOOK LEE

*Department of Chemical Engineering Korea Advanced Institute of Science and Technology
P.O. BOX 131 Dongdaemun, Seoul 130-650, Korea*

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Introduction

Investigation of the rates of mass transfer into porous particles is essential to the understanding of separation processes such as chromatography and ion exchange, and thus it is important to predict intraparticle mass transfer coefficients by either theoretical or experimental methods. But the present theoretical methods are not yet well developed in systems where adsorption and diffusion in solid phase are important. Thus experimental methods would be useful.

Komiyama and Smith¹⁾ have correlated the surface diffusion coefficients to a function of the pseudo-adsorption equilibrium constants in a system with nonlinear isotherms in order to investigate the concentration dependence of surface diffusion in the aqueous liquid phase. Also, Sudo *et al.*⁸⁾ found that the surface diffusion coefficients can be correlated in terms of the final amount adsorbed, and Neretnieks⁶⁾ assumed that the surface diffusion coefficient was exponentially dependent on the adsorbed phase concentration when the Temkin isotherm is applicable.

More recently, Suzuki and Fujii⁹⁾ obtained the dependence of the surface diffusion coefficient on the amount adsorbed by Wicke-Kallenbach type in steady-state diffusion experiment, and Moon and Lee⁴⁾ have suggested an empirical equation in terms of the time-average amount adsorbed.

In this work the adsorption of *m*-cresol, quinoline and 1-naphthol onto silica gel in hexane was carried out in a batch reactor, whereas most previous works were done in aqueous solution. By superimposition of the theoretical concentration onto the experimental data, the intraparticle mass transfer coefficients were calculated. The main purpose of this work is to investigate the concentration dependence of the intraparticle mass transfer coefficients.

1. Basic Equation

The following assumptions for model equations were introduced. i) The bulk liquid in the vessel is perfectly mixed. ii) The rate of adsorption is much faster than that of diffusion, and hence local equilibrium at the particle surface is maintained during the overall run time. iii) The particle is spherical. iv) For diffusion into the solid, the linear driving force approximation (LDFA) model is applicable.

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Overall mass balance:

$$V(C - C_0) + Wq = 0 \quad (1)$$

Mass balance for solid phase:

$$\rho_p \frac{dp}{dt} = \frac{3}{R} k_s \rho_p (q_s - q) \quad (2)$$

$$= \frac{3}{R} k_f (C - C_s) \quad (3)$$

Equilibrium at particle surface:

$$q_s = q_s(C_s) \quad (4)$$

Initial conditions:

$$C = C_0, \quad q = 0 \quad (5)$$

Equation (3) represents the mass transfer rate through the external surface film at the particles. From Eq. (2) and Eq. (3) the following relation is derived.

$$q_s = q + \phi(C - C_s) \quad (6)$$

in which ϕ represents the relative importance of resistances in the external film and in the interior of the solid, and is equal to $k_f/k_s\rho_p$. If ϕ approaches infinity, the overall mass transfer rate is controlled by the intraparticle diffusion, and if ϕ approaches zero the film diffusion is the rate-controlling step.

2. Experimental

Materials: Silica gel as adsorbent, having average diameter of 32.5 microns and apparent density of 614 kg/m³, and quinoline, *m*-cresol and 1-naphthol of research grade as solute, and *n*-hexane as solvent were used in the experiments.

Apparatus: Equilibrium adsorption data were obtained by an incubator shaken continuously for a week at 30°C. The configuration of the batch reactor is nearly analogous to the slurry type utilized by Mistic *et al.*²⁾ Experimental apparatus and procedure are described elsewhere.³⁾

3. Results and Discussion

The isotherms were well described by Toth's isotherm¹¹⁾ within a few percent error. The isotherm equations for each solute are expressed in a concentration range of 1–30 mol/m³ as follows.

m-Cresol

$$q_s = \frac{0.12C_s^{0.66}}{1 + 0.09C_s^{0.66} - 0.60C_s^{0.14}} \quad (7)$$

Quinoline

$$q_s = \frac{0.52C_s^{0.15}}{1 + 0.55C_s^{0.15} - 0.52C_s^{0.16}} \quad (8)$$

1-Naphthol

$$q_s = \frac{0.15C_s^{0.52}}{1 + 0.14C_s^{0.52} - 0.62C_s^{0.12}} \quad (9)$$

Table 1. Intraparticle mass transfer coefficient obtained from each run

Run	(mol/m ³) C ₀	k _s × 10 ⁷ , (m/s)			
		(kg) W × 10 ³	<i>m</i> -Cresol	Quinoline	1-Naphthol
1	5	3.750	—	—	0.94
2	5	5.625	—	—	0.96
3	9	3.750	0.51	0.87	0.95
4	9	5.625	0.64	0.88	1.00
5	15	3.750	0.63	0.91	1.22
6	15	5.625	0.64	0.89	1.26
7	20	3.750	0.66	1.02	1.30
8	20	5.625	0.70	1.10	1.37
9	25	3.750	1.05	1.53	—
10	25	5.625	0.99	1.48	—
11	30	3.750	1.39	1.63	—
12	30	5.625	1.34	1.69	—
k _f × 10 ⁴ , (m/s)			1.57	1.43	1.39

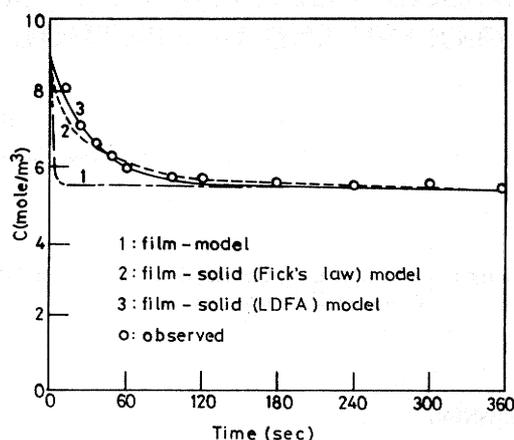


Fig. 1. Comparison of experimental data with theoretical curve for run 3 of *m*-Cresol in Table 1.

[For film-solid (Fick's law) diffusion model, the value of D_s was obtained from the relation $k_s = 5D_s/R$.]

Mistic *et al.*²⁾ proposed an empirical equation to predict the external mass transfer coefficient in a stirred batch vessel with nonlinear isotherm, and the external mass transfer coefficient for each solute obtained from this equation is shown in the bottom row in Table 1.

Typical experimental data and theoretical concentration curve for *m*-cresol are shown in Fig. 1. Two concentration profiles for Fick's diffusion equation and the LDFA model appear to be quite comparable except those in the earlier time region. The differences between the two models in the earlier time region are likely caused by the intrinsic characteristics of the models. But the LDFA model has reasonable accuracy for the systems encountered here over the whole range of time. Thus the intraparticle mass transfer coefficient was obtained by the superimposition of the concentration-time curve based on the LDFA model onto the experimental data, and the

resulting values are listed in Table 1. This figure also shows that the concentration curve for the film model instantaneously reaches equilibrium state. A similar tendency was found for 1-naphthol and quinoline. These results confirm that the diffusion in solid phase is the rate-controlling step.

Concentration dependence of k_s : In Table 1 it is clear that k_s increases with C_0 . This means that k_s is dependent on the solute concentration in solid phase which may be caused by decrease of average bonding forces between the adsorbates and the surface with increasing surface coverage.

To investigate the concentration dependence of the rates of mass transfer into particles, Muraki *et al.*,⁵⁾ Suzuki and Fujii⁹⁾ and Suzuki and Kawazoe¹⁰⁾ suggested an empirical equation for systems where the Freundlich isotherm was applicable. Here, the following empirical equation of exponential type, presented by Neretnieks,⁶⁾ is proposed.

$$k_s = k_0 \exp(\beta \bar{q}) \quad (10)$$

in which β is an empirical parameter and \bar{q} is the time average of the solute concentration in solid phase, expressed as

$$\bar{q} = \frac{1}{t_m} \int_0^{t_m} q(t) dt \quad (11)$$

where t_m is the time required to reach equilibrium. In the present work, t_m was defined as the time to reach to 98% of the value of the equilibrium concentration, which can be determined from the equality of operating line, Eq. (1), and the equilibrium relation, Eq. (4).

The values of β and k_0 were determined from the slope and intercept of the plot of $\ln(k_s)$ versus \bar{q} . Such plots are shown in Fig. 2, and the values of β and k_0 obtained for each solute are given in Table 2. From the values of β for each solute it can be seen that the degree of concentration dependence on k_s increases in the order 1-naphthol, *m*-cresol and quinoline.

Conclusion

Adsorption equilibrium data of *m*-cresol, quinoline and 1-naphthol onto silica gel in *n*-hexane were measured and all solutes were well expressed by Toth's isotherm. In addition, adsorption rates were observed in a finite batch reactor. To obtain the intraparticle mass transfer coefficients as a model parameter the linear driving force approximation model was applied. The effect of external film diffusion was considered, but was so small as to be negligible.

The concentration dependence of the intraparticle mass transfer coefficient could be empirically represented by an exponential function of the time average value of the solute concentration in solid phase. The results can be used as a first approximation

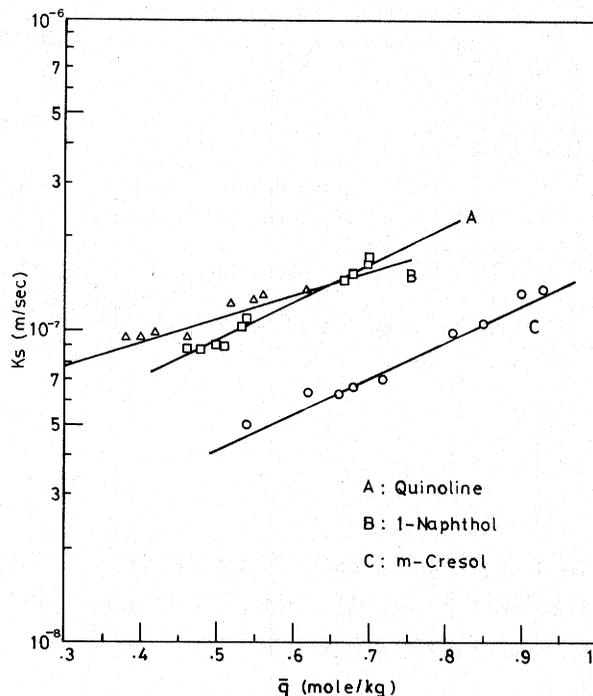


Fig. 2. k_s vs. \bar{q} for each solute [(A): Quinoline; (B): 1-Naphthol; (C): *m*-Cresol]

Table 2. Range of time average values of solute concentration in solid phase and parameters of Eq. 10

Solute	Range of \bar{q}	$k_0 \times 10^7$	β	r
<i>m</i> -Cresol	0.54–0.93	0.11	2.66	0.98
Quinoline	0.46–0.70	0.23	2.82	0.99
1-Naphthol	0.38–0.62	0.47	1.75	0.95

to estimate the concentration dependence of the intraparticle mass transfer coefficients.

Nomenclature

C	= solute concentration in fluid phase	[mol/m ³]
C_0	= initial solute concentration in fluid phase	[mol/m ³]
C_s	= solute concentration in fluid phase at particle surfaces	[mol/m ³]
k_f	= external mass transfer coefficient	[m/s]
k_s	= intraparticle mass transfer coefficient	[m/s]
k_0	= intraparticle mass transfer coefficient at zero surface loading	[m/s]
q	= volume average solute concentration in solid phase	[mol/kg]
\bar{q}	= time average concentration of q as defined by Eq. 11	[mol/kg]
q_s	= solute concentration in solid phase at particle surface	[mol/kg]
R	= particle radius	[m]
r	= correlation coefficient	[—]
t	= time	[s]
t_m	= time required to reach equilibrium	[s]
V	= solution volume	[m ³]
W	= adsorbent weights	[kg]

β	= empirical parameter in Eq. 10	[kg/mol]
ρ_p	= density of particle	[kg/m ³]
ϕ	= $k_f/k_s\rho_p$	[m ³ /kg]

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