

DIFFUSIONAL INTERFERENCE IN LIQUID PHASE COUNTER-ADSORPTIONS

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Abstract—A surface diffusion model with diffusional interference has been presented for the analysis of multicomponent adsorption of phenols by activated carbon. Surface diffusion coefficients for multicomponent adsorptions were estimated from the relationship between the surface diffusion coefficient of each species and the surface coverage. The diffusional interference coefficients, W_{ij} , was determined from experimental counter-adsorption data. The numerical values of W_{ij} were in the range of 0.4-0.9, which show that the introduction of diffusional interference is necessary to analyze multicomponent counter-adsorptions properly. The proposed model successfully simulates the behaviour of phenols-activated carbon system in a batch adsorber.

INTRODUCTION

For accurate predictions of adsorption data, intraparticle diffusion becomes the major concern because it is usually the rate-controlling step in these processes [1]. Intraparticle diffusion within porous adsorbents depends on the mechanism of adsorbate transport: pore diffusion, surface diffusion or combined diffusion [1,2]. When the adsorbent has relatively large surface area and high adsorption capacity, it has been known that the surface diffusion in the adsorbed state along the pore wall is dominant [3,4].

The surface diffusion coefficient, D_s , depends strongly on the amount of adsorbates adsorbed [5-8]. Since the adsorbent has energetically heterogeneous surfaces, the interaction energy between adsorbable molecules and the surface varies with the surface loading [9,10]. This concentration dependence has been studied by several investigator [5,7,8]. Moon and Lee [7] proposed an empirical concentration dependence of D_s on the amount adsorbed for liquid phase adsorption of phenols by activated carbon.

The surface migration of adsorbed molecules has been regarded as a random walk process of hopping molecules on the surface [9,10]. This is related to the interaction energy between adsorbable molecules and the surface. The concentration dependence of D_s ,

therefore, may be represented by a function of the surface coverage, θ , because the interaction energy decreases due to the shielding effect of adsorbed molecules.

$$D_s = f(\theta) \quad (1)$$

Although this dependence of D_s has been studied in terms of the amount adsorbed [5,7,8], the extension of this dependence of multicomponent adsorptions has not been carried out so far. The direct use of D_s determined from single species systems will cause considerable discrepancy between measured and predicted values in the analysis of multicomponent adsorption processes. On the other hand, when two or more species in the adsorbed state diffuse on the surface, mutual interactions between diffusing molecules are usually not negligible. Particularly, for the case of counter-adsorptions, it is hard to find a suitable method for representing the diffusional interference. Some workers [2,11] have used the assumption that the surface flux of a species is proportional to the concentration gradient of each species. Then, the flux may be described by the following equation:

$$N_{si} = \rho_s \sum_{j=1}^n D_{sj} \frac{\partial Q_j}{\partial r} \quad (2)$$

This is an extension of Fick's law to the multicomponent system by using the phenomenological con-

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cept [11]. Eq. (2) can be rewritten by introducing the diffusional interference coefficient, W_{ij} , as follows:

$$N_{si} = \rho_p D_{si} \sum_{j=1}^n W_{ij} \frac{\partial Q_j}{\partial r} . \quad (3)$$

Where W_{ij} ($= D_{sj}/D_{si}$) represents the effect of the concentration gradient of the j -th species on the flux of the i -th species.

In this study, we address a multicomponent surface diffusion model with diffusional interference. The surface diffusion coefficients, D_s , for multicomponent systems are estimated from the surface coverage of each species, θ_s , or the total surface coverages, θ_T , and W_{ij} is calculated from the counter-adsorption data of binary systems.

THEORETICAL

In developing the surface diffusion model, some assumptions have been made [1,2,5,7]: The concentration of adsorbates in the batch is uniform. The adsorption of adsorbates in the batch is uniform. The adsorbents are spherical particles with identical radius and diffusion is very slow, local equilibrium is established at the external surface of particles. The film mass transfer coefficient can be assumed to be constant regardless of the bulk concentration in the batch. Furthermore, the amount of adsorbates in the liquid in pores can be neglected because it is much less than that adsorbed on the surface [1,2,7].

According to this model, adsorption occurs at the outer surface of particles, which can be described by adsorption isotherms, followed by the surface diffusion within the particle. The governing equations for this model are written by introducing dimensionless variables and groups as follows.

Mass balance of the i -th species in the batch:

$$\frac{\partial \xi_i}{\partial \tau} = -\alpha \lambda_i (\xi_i - \xi_{si}) \quad (4)$$

$$\xi_i = 1 \text{ at } \tau = 0 . \quad (5)$$

Mass balance in the particle:

$$\frac{\partial \Psi_i}{\partial \tau} = \gamma_i \sum_{j=1}^n W_{ij} \left(\frac{\partial^2 \Psi_j}{\partial x^2} + \frac{2}{x} \frac{\partial \Psi_j}{\partial x} \right) \quad (6)$$

$$\Psi_i = \Psi_{oi} \text{ at } \tau = 0, 0 < x < 1 \quad (7)$$

$$\sum_{j=1}^n W_{ij} \frac{\partial \Psi_j}{\partial x} = 0 \text{ at } x = 0, \tau > 0 \quad (8)$$

$$\sum_{j=1}^n W_{ij} \frac{\partial \Psi_j}{\partial x} = Bi_i (\xi_i - \xi_{si}) \text{ at } x = 1, \tau > 0 . \quad (9)$$

Here, the dimensionless variables are defined as follows:

$$\xi_i = C_i / C_{oi}, \Psi_i = Q_i / Q_{oi}, x = r / R \text{ and } \tau = vt / L .$$

The dimensionless group, Bi_i represents the Biot number for the i -th species and α , γ , and λ are the dimensionless groups which are dependent on process variables of the adsorption system.

$$Bi_i = \frac{K_{si} R C_{oi}}{\rho_p D_{si} Q_{oi}}, \alpha = \frac{m \epsilon_p}{V \rho_p}, \gamma_i = \frac{L D_{si}}{v R^2}$$

$$\text{and } \lambda_i = \frac{3 L K_{si}}{v R \epsilon_p}$$

Eqs. (4) and (6) are related with the boundary condition of Eq. (9) at the external surface of the particle.

The surface concentration, ξ_{si} , in Eq. (9) is calculated from the amount of adsorbates adsorbed at a previous time by using a multicomponent adsorption isotherm. For multicomponent adsorptions, the ideal adsorbed solution (IAS) theory which is thermodynamically consistent has been applied [12,13]. A great advantage of this theory is to require only single component adsorption data in predicting multicomponent adsorption equilibria. However, the incorporation of the IAS theory into the model equations with diffusional interference causes considerable computational expenses. In this study, adsorption equilibria at the external surface of particles are represented by a Freundlich-type multicomponent isotherm which gave good predictions for binary adsorption data [14]. This adsorption isotherm is:

$$Q_i = \frac{k_i (C_{si})^{(P_i + B_i)}}{\sum_{j=1}^n A_{ij} (C_{sj}) B_{ij}} \quad (10)$$

where k_i and P_i are the Freundlich coefficient and the reciprocal of the Freundlich exponent, respectively. A_{ij} and B_{ij} are interrelated parameters which can be determined from binary adsorption data. Numerical values of parameters in Eq. (10) are given in Table 1. The Newton's iterative method can be used to evaluate C_{si} or ξ_{si} from Eq. (10). Eqs. (4)-(9) were solved numerically by employing the Crank-Nicholson finite difference method. The set of generalized tridiagonal matrices was transformed into a band form to use an algorithm for the solution of the band matrix [15]. The details of the band matrix and the computer programs are listed elsewhere [16].

EXPERIMENTAL

The adsorbent used in this study was a granular

Table 1. Parameters of adsorption isotherms

Single component systems			Binary systems						
Component	k_i	P_i	Component (1)/(2)	A_{12}	A_{21}	B_{11}	B_{22}	B_{12}	B_{21}
Phenol	1.705	0.235	Phenol/PCP	2.639	0.222	0.287	0.488	0.738	0.564
PCP	2.575	0.141	Phenol/PNP	6.489	0.036	0.608	0.818	0.838	0.986
PNP	2.327	0.131	PCP/PNP	1.383	0.476	0.690	0.857	0.797	0.926

$$A_{11} = A_{22} = 1.0$$

Table 2. Properties of activated carbon used

Property	Unit
Real density	kg/m ³
Apparent particle density	kg/m ³
Surface area (BET)	m ² /kg
Porosity	
Mean pore radius	nm
Particle diameter	m

activated carbon, F-400, manufactured by Calgon Co. The properties of this carbon are given in Table 2. The average particle diameter of the adsorbent used was estimated to be 0.92×10^{-3} m from the sieve openings. All carbon particles were boiled in distilled water for 48 hr and then washed to remove impurities.

The adsorbates studied were phenol, p-chlorophenol(PCP), and p-nitrophenol(PNP) which are common industrial contaminants. Stock solutions of each species were made up by dissolving the reagent grade chemicals in distilled, deionized, and activated carbon-filtered water. Binary solutions were prepared by adding stock solutions at various concentrations. The concentrations of individual species in solution were determined by using UV spectrometry. Absorbences were measured at different wavelengths for multicomponent systems.

Adsorption experiments were conducted in a Carberry-type batch adsorber used in previous studies [7,16]. All the experiments were carried out at approximately 500 rpm so that the film mass transfer coefficient, K_f , would be nearly constant [7,16]. The detailed estimation method for K_f has been discussed in the literature [17].

RESULTS AND DISCUSSIONS

In analyzing the adsorption rate of multicomponent systems, the surface diffusion coefficients deter-

Table 3. Coefficient of Eq. (11) for adsorbates

Adsorbate	$D_s^* \times 10^{12}$ (m ² /s)	n
Phenol	11.27	1.251
PCP	5.11	0.994
PNP	3.13	0.799

mined from single component systems have been used by many investigators [2,5,6]. It should, however, be noted that the distribution of adsorption energy of a species depends on the amount of all of the species adsorbed. The interaction energy between adsorbable molecules and the surface usually decreases with the surface coverage, θ , because of the progressive filling of adsorption sites according to the relative adsorption energy. The relation between the surface diffusion coefficient and the surface coverage, therefore, is likely to be a good representation in dealing with multicomponent systems. The dependence of D_s on θ can be derived from the relation between D_s and Q obtained in a previous work [7].

$$D_s = D_s^* (\theta)^n \quad (11)$$

Table 3 shows the parameters of Eq. (11). The surface coverage of the i -th species may be calculated by:

$$\theta_i = Q_i / Q_{mi} \quad (12)$$

where Q_{mi} is the amount of adsorption for monolayer coverage. Q_{mi} can be calculated from the molar volume at the normal boiling point (Le Bas volume) [18] and the available surface area of activated carbon. In this study, the surface area was estimated from the amount of PCP adsorbed, which approaches a constant value, shown in Fig. 1 as a matter of convenience. The specific surface area obtained by the nitrogen adsorption can not be used properly because the critical diameters of phenols are about two times that of nitrogen. This calculation can be regarded as a

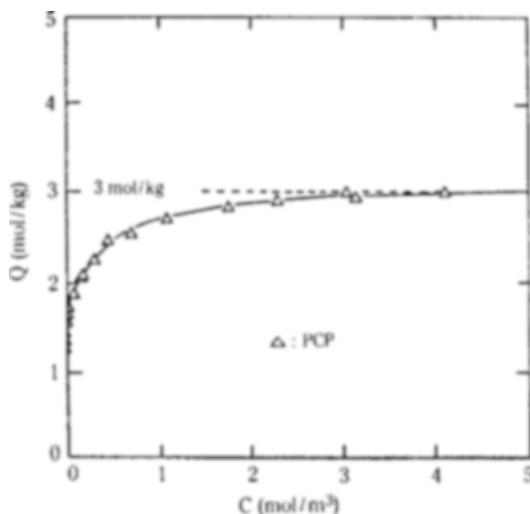


Fig. 1. Amount of PCP adsorbed on activated carbon at 20°C.

reasonable method if the liquid phase adsorption does not involve multilayer formation [19] and the molecular diameter and Q_m of phenols calculated are listed in Table 4. The total surface coverage, θ_T , can be obtained by:

$$\theta_T = \sum_{j=1}^n \theta_j. \quad (13)$$

When D_s was evaluated from Eq. (11), the average values of surface coverage were used since the surface loading of each species varies with respect to time and position during the adsorption. To ascertain the applicability of Eq. (11), two different surface diffusion coefficients were calculated from θ_i and θ_T , respectively, and they were used in predicting the adsorption data for simultaneous binary adsorption of phenols with activated carbon. Table 5 shows that D_s estimated from θ_T gives good predictions comparable to experimental data in all cases. The mean deviation, σ , is expressed as follows:

$$\sigma = \frac{1}{N} \sum_{j=1}^n |(\xi_{meas} - \xi_{calc})_j|. \quad (14)$$

Figs. 2 and 3 show the typical variation of bulk concentrations in the batch with respect to the square root of time. The points represent experimental data. While the centered lines are the predicted results by using D_s obtained from θ_T , the broken lines are those from θ_i . In these calculations, the diffusional interference coefficients, W_{ij} ($i \neq j$), were taken as zero. These results show that the use of Eq. (11) in estimating D_s for multicomponent systems is more accurate than the direct use of D_s obtained in single species

Table 4. Molecular diameter and Q_m calculated

Adsorbate	Molecular weight	Molecular diameter (nm)*	Q_m (mol/kg)
Phenol	94.11	0.690	3.39
PCP	128.56	0.733	3.00
PNP	139.11	0.738	2.96

*from the molar volume (Le Bas Volume) [18]

systems. If the species in a mixture have similar adsorptive and diffusive properties, it is reasonable to assume that the effect of the surface coverage formed by all the species will be similar.

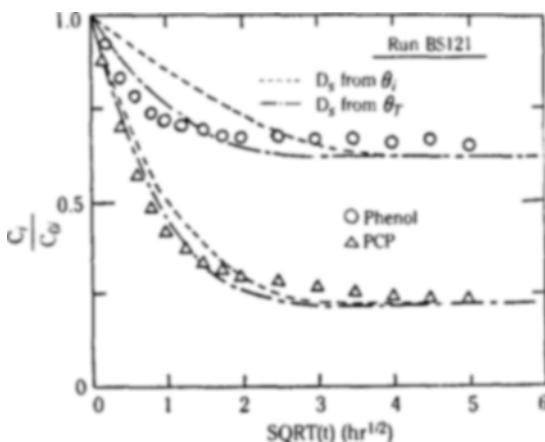
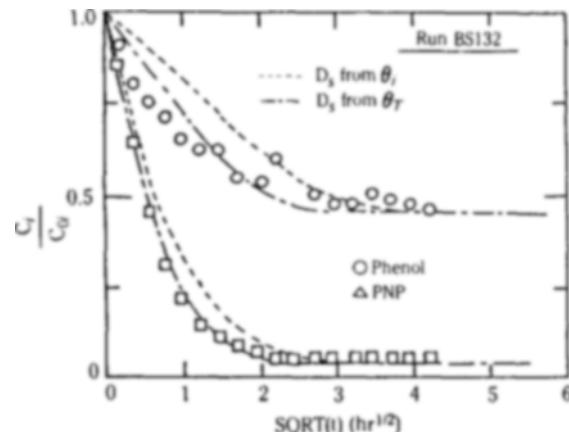
The surface diffusion coefficients have been obtained by superimposing predicted concentration-time curves onto experimental curves such as a kind of graphical comparison [2,6]. From Figs. 2 and 3, it can be concluded that D_s estimated in this work gives relatively good predictions. Small deviations between measured and predicted values, when equilibrium is established, are caused by inaccurate adsorption isotherms. This indicates that the determination of accurate adsorption isotherms is an important basis for the analysis of multicomponent adsorptions.

When a species with higher affinity was adsorbed to the activated carbon preloaded with a species with lower affinity, the latter was progressively replaced by the former according to the relative affinity to the adsorbent. Desorbed molecules, then, diffuse from the interior to the external surface of the particle. This phenomenon has been called "displacement effect" or "counter-diffusion effect" [2,3]. Fig. 4 shows the variation of average particle loading of each species for the simultaneous adsorption of phenol-PCP system. The displacement is not observed in simultaneous adsorptions, in general, and for the most cases of simultaneous adsorptions, the concentration-time curves are progressive according to the difference in adsorptive properties. However, the displacement appears explicitly in the counter-adsorptions as shown in Fig. 5. In Runs BS121 and BC121 shown in Figs. 4 and 5, the final equilibrium concentrations are the same even the adsorption methods are different, simultaneous and counter-current. In Fig. 5, the broken line stands for the uptake of PCP in the simultaneous adsorption. This shows that the uptake of PCP in the counter-adsorption is quite retarded because of diffusional interference.

The counter-diffusion effect should be considered in multicomponent fixed-bed adsorptions because

Table 5. D_s estimated and σ between ξ_{meas} and ξ_{calc}

Run	Component	C_0 (mol/m ³)	$D_s \times 10^{12}{}^a$ (m ² /s)	$D_s \times 10^{12}{}^b$ (m ² /s)	$\sigma \times 10^2{}^a$	$\sigma \times 10^2{}^b$
BS121	Phenol	1.03	1.56	7.17	7.31	1.05
	P C P	1.00	2.52	3.57	1.20	0.72
BS122	Phenol	1.01	2.42	5.76	2.42	1.34
	P C P	0.51	1.51	3.00	0.53	0.49
BS123	Phenol	0.50	1.01	6.75	1.47	0.66
	P C P	1.01	2.66	3.40	1.17	0.85
BS124	Phenol	0.51	1.78	4.99	2.45	1.44
	P C P	0.47	1.51	2.67	0.71	0.49
BS132	Phenol	0.96	2.29	5.86	1.98	1.12
	P N P	0.50	1.24	2.06	0.62	0.17
BS134	Phenol	0.47	1.48	4.95	1.21	0.48
	P N P	0.49	1.26	1.85	0.66	0.27
BS231	P C P	1.00	1.64	3.73	1.48	1.32
	P N P	0.97	1.53	2.43	1.52	0.81
BS232	P C P	1.01	2.21	3.46	1.47	1.16
	P N P	0.49	1.02	2.29	1.04	0.63
BS233	P C P	0.52	1.07	3.48	1.46	0.84
	P N P	0.99	1.72	2.30	2.94	1.29
BS234	P C P	0.50	1.42	2.95	0.93	1.03
	P N P	0.49	1.19	2.01	1.09	0.52

^aestimated from θ_i ^bestimated from θ_T **Fig. 2.** Calculated and experimental batch concentrations of binary simultaneous adsorption for phenol-PCP system.**Fig. 3.** Calculated and experimental batch concentrations of binary adsorption for phenol-PNP system.

those are associated with replacement of preadsorbed species by the following species [20,21]. In cases

where the counter-diffusion occurs, the surface diffusion model without diffusional interference between

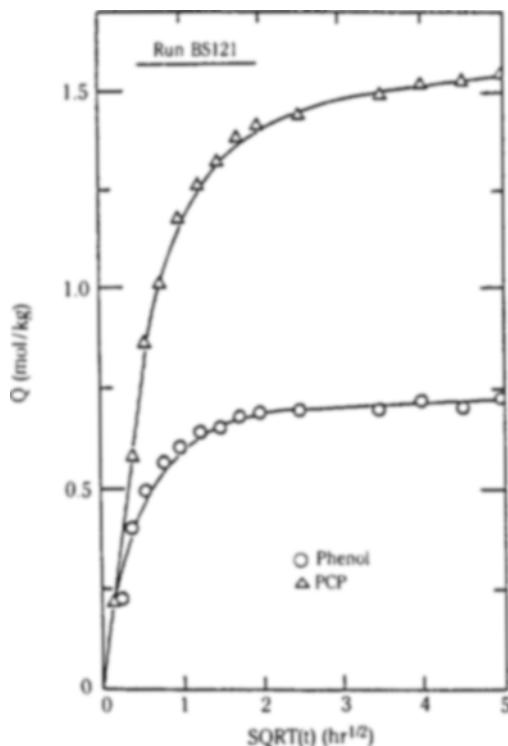


Fig. 4. Variation of Q_i of simultaneous adsorption for phenol-PCP system.

adsorbed species can not generally be used; thus, the model has to be extended to include the counter-diffusion effect. In this study, the species which has lower affinity for the adsorbent is taken as the preadsorbed one to explicitly elucidate the displacement phenomena in the counter-adsorption systems. The affinities of phenols to activated carbon has been known to be in the order: phenol \ll PCP $<$ PNP [14,16].

Fig. 6 shows the predicted concentration-time curves of phenol for the counter-adsorptions of a phenol-PCP system. The most interesting fact shown in Fig. 6 is that the maxima on the curves appear at high values of D_{s1} . This can occur only when D_s of phenol is greater than that of PCP. This phenomenon can be explained logically by the following conjecture; since the affinity of phenol is less than that of PCP, the desorption occurs very fast in earlier times but later phenol is likely to be readSORBED because of the decrease in the bulk concentration of PCP. However, the maxima do not appear in the experimental curves, indicating that the diffusion rate of desorbed species is greatly reduced by the counter-diffusion effect. The diffusion coefficient in the counter-adsorption has been reported to be unreasonably low compared to the

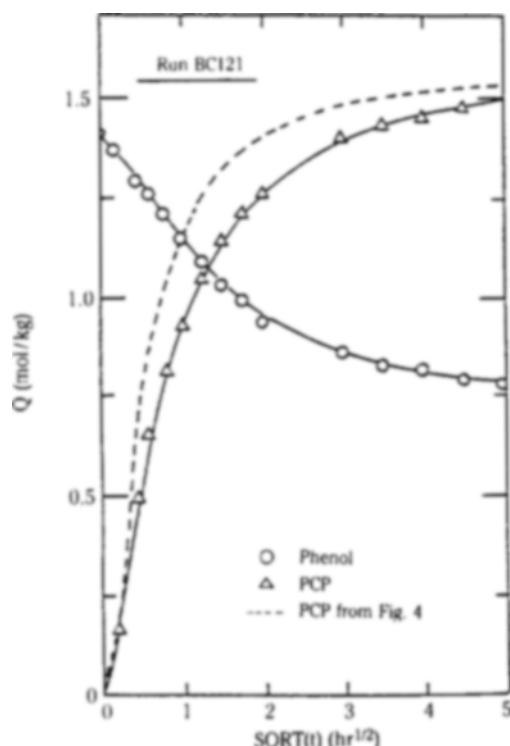


Fig. 5. Variation of Q_i of counter-adsorption for phenol-PCP system.

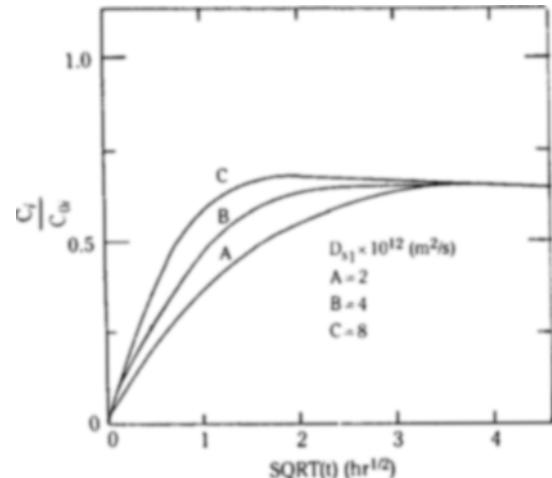


Fig. 6. Calculated batch concentrations of phenol with respect to D_{s1} with $D_{s2} = 4 \times 10^{-12} \text{ m}^2/\text{s}$.

molecular diffusivity in solution [22]. In this work, the counter-diffusion effect for the analysis of multicomponent adsorption systems is considered by introducing diffusional interference coefficients.

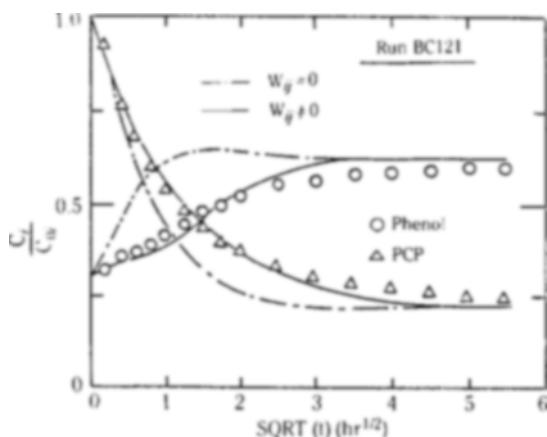


Fig. 7. Counter-adsorption of PCP on activated carbon preloaded with phenol.

Figs. 7 and 8 show the measured and predicted bulk concentrations for counter-adsorptions in the batch in terms of time. The solid lines are the curves predicted by the surface diffusion model for which diffusional interference coefficients are non-zero. In this calculation, D_s was estimated from θ_T and the diffusional interference coefficients were determined by

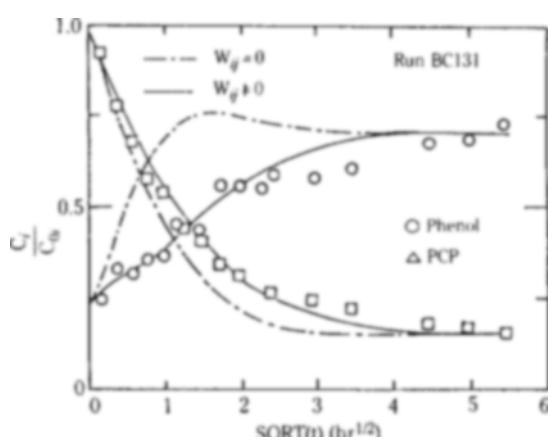


Fig. 8. Counter-adsorption of PNP on activated carbon preloaded with phenol.

superimposing predicted curves onto experimental curves. The values of D_s and W_{ij} used in calculations are listed in Table 6. On the other hand, the centered lines represent the predictions by using the model with $W_{ij} = 0$ ($i \neq j$). The surface diffusion model with W_{ij} ($\neq 0$) gave good predictions as shown in Figs. 7 and 8. At the moment, a correlation between W_{ij} and proper-

Table 6. D_s and W_{ij} used in calculations for counter-adsorptions

Run	Component	C_o (mol/m ³)	Q (mol/kg)	$D_s \times 10^{12a}$ (m ² /s)	w_{12}	w_{21}
BC121	Phenol	0.23	1.40	6.77	0.7	0.9
	PCP	1.01	0.00	3.85		
BC122	Phenol	0.33	1.34	5.61	0.6	0.8
	PCP	0.51	0.00	3.32		
BC123	Phenol	0.07	0.90	6.58	0.5	0.8
	PCP	1.02	0.00	3.76		
BC131	Phenol	0.22	1.56	6.67	0.8	0.6
	PNP	0.96	0.00	2.50		
BC132	Phenol	0.29	1.43	5.74	0.9	0.6
	PNP	0.48	0.00	2.77		
BC133	Phenol	0.03	0.94	5.90	0.7	0.3
	PNP	0.96	0.00	2.31		
BC231	PCP	0.10	1.80	3.99	0.8	0.9
	PNP	0.99	0.00	2.59		
BC232	PCP	0.12	1.77	3.58	0.6	0.9
	PNP	0.50	0.00	2.37		
BC233	PCP	0.03	0.93	3.56	0.5	0.7
	PNP	0.97	0.00	2.37		

^aestimated from θ_T

ties of adsorption systems can not be given because of insufficient experimental data and theoretical grounds. Additional experiments as well as theoretical works should be required to elucidate the characteristics of multicomponent adsorptions more explicitly.

CONCLUDING REMARKS

A surface diffusion model with diffusional interference has been presented to analyze multicomponent adsorption data of phenols to activated carbon in a batch adsorber. The surface diffusion coefficients used were estimated from the surface coverage of each species or the total surface coverage by using the relationship between D_s and θ . When D_s was estimated from θ_T , the model predicted accurately the adsorption data for simultaneous binary adsorptions. This shows that the amount of a species adsorbed affects the surface migration of others in multicomponent adsorptions.

When the counter-adsorption occurs within the particles, the displacement was explicitly observed according to the relative affinity to activated carbon. The presented model was very useful in dealing with counter-adsorptions. The diffusional interference coefficients, W_{ij} , determined were in range of 0.4-0.9, indicating that diffusional interference is severe in counter-adsorptions. This observation indicates that the diffusional interference should be considered in analyzing multicomponent adsorption systems in which the displacement occurs such as fixed-bed adsorptions.

NOMENCLATURE

A_{ij} , B_{ij}	: parameters in Eq. (10)
BI	: Biot number ($= K_f R C_{or} / \rho_p D_s Q_o$)
C	: concentration in the fluid phase [mol/m ³]
C_o	: initial value of C [mol/m ³]
D_s	: surface diffusion coefficient [m ² /s]
D_s^*	: constant factor in Eq. (11) [m ² /s]
$f(\theta)$: function in Eq. (1)
K_f	: film mass transfer coefficient [m/s]
k_i	: Freundlich coefficients in Eq. (10)
L	: characteristic length [m]
m	: mass of adsorbent, kg and number of components
N	: number of data points
N_s	: surface diffusion flux [mol/m ²]
n	: exponent in Eq. (11)
P_i	: reciprocal of Freundlich exponent in Eq. (10)
Q	: amount adsorbed [mol/kg]
Q_o	: initial value of Q [mol/kg]

Q_m	: amount adsorbed for monolayer formation [mol/kg]
R	: radius of particle [m]
r	: radial distance [m]
t	: time [s or hr]
V	: volume of solution [m ³]
v	: characteristic velocity [m/s]
W_{ij}	: diffusional interaction coefficient
x	: dimensionless radial distance

Greek Letters

α	: dimensionless group ($= m \epsilon_p / V \rho_p$)
γ	: dimensionless group ($= LD_{si} / v R^2$)
ϵ_p	: particle porosity
θ	: surface coverage
θ_T	: total surface coverage
λ_i	: dimensionless group ($= 3LK_h / vR\epsilon_p$)
ξ	: normalized concentration of C
ξ_s	: ξ at the outer surface of the particle
ρ_p	: apparent particle density [kg/m ³]
τ	: dimensionless time
σ	: mean deviation defined in Eq. (14)
Ψ	: dimensionless amount adsorbed

Subscripts

0	: initial value
f	: film
i,j	: subscripts for species
m	: monolayer
p	: particle
s	: surface
T	: total

Abbreviations

PCP	: p-chlorophenol
PNP	: p-nitrophenol
meas	: measured value
calc	: calculated value

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