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ADSORPTION EQUILIBRIA FOR m-CRESOL, QUINOLINE, AND 1-NAPHTHOL ONTO SILICA GEL

Jeong Ki MOON, Dong Kwon KEUM, 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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Abstract—Adsorption isotherms for m-cresol, quinoline, and 1-naphthol onto silica gel in n-hexane at 30°C were measured in the concentration range of 1-30 mole/m^3. The experimental results for m-cresol and quinoline were well represented by the generalized Toth isotherm, and for 1-naphthol by the superimposed two sites Langmuir model. At low concentrations the adsorbed amounts onto silica gel were decreased in sequence of quinoline, 1-naphthol, and m-cresol. However as the concentration increased, the sequence was reversed.

For binary systems, the competitive adsorption was quantitatively studied by introducing the competitive adsorption coefficient. The relative affinity of quinoline with respect to silica surface was larger than those of the other two components.

INTRODUCTION

The equipments packed with adsorbents for adsorption separation have been used widely in recent years to separate mixture of hydrocarbons into different chemical types. To design these apparatuses, the information of adsorption equilibria is necessary [1,2].

Most isotherms for the single component contain a number of parameters as shown in Table 1. The Langmuir model [3-5] has a good representation only in a limited span (over 20 to 30% of the saturation amount) at the midrange of adsorption values. Also this isotherm is inadequate for a system where the surface has inhomogeneity and for a system with multilayer adsorption. Nevertheless it serves as a logical basis for modifications and improvements of adsorption models since it describes the simplest case of adsorption which behaves as an ideal solute within finite adsorption space. While the Freundlich isotherm[6-8] is relevant for highly heterogeneous surfaces. But it does not reduce to Henry's relation at concentrations approaching zero, so its applicability is restricted to a limited concentration range. To fulfill these disadvantages involved in the previous two isotherms, Redlich and Peterson[9] proposed an empirical equation combined the Langmuir isotherm with Freundlich isotherm. Toth[10] proposed a new isotherm to investigate the adsorption of gases onto the heterogeneous surface, and his idea was extended to predict adsorption of solutes from liquid solutions[11]. But the original Toth's equation was valid only for monolayer adsorption on heterogeneous surface. Therefore this model was extended to a generalized form which takes into account either the surface heterogeneity(lateral interaction) or the interaction energy in the vertical direction(multilayer). Recently, Dabrowski et al.[12] applied Toth's isotherm for investigating adsorption of single solute from the dilute solution. Koresh and Soffer[3] modified the Langmuir equation which had the two limitations: the surface homogeneity and monolayer adsorption. They proposed the independent two sites and the superimposed two sites Langmuir model. In the latter model, it was assumed that adsorption at the second site was not independent but associated with molecules already adsorbed at first site. Quantitatively, the adsorption capacity available for the second site is proportional to the amount adsorbed at the first site.

The isotherms to express the multicomponent system are divided into two groups as shown in Table 2. The first group uses only the parameters obtained from the single component system whereas the second group requires the bisolute experimental data to obtain the parameters for competitive adsorption. The Langmuir competitive isotherm was originally derived

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*To whom all correspondence should be addressed.

Table 1. Isotherms for single component adsorption

Type	Relationship	Parameters	Characteristics
Langmuir	$q=\frac{q_m bC}{1+bC}$	q_m, b	homogeneous monolayer
Freundlich	$q=aC^m$	a, m	heterogeneous not reduce to Henry's law
Redlich and Peterson	$q=\frac{aC}{1+bC^m}$	a, b, m	combined Langmuir and Freundlich
Radke and Prausnitz	$\frac{1}{q}=\frac{a}{C}+\frac{b}{C^m}$	a, b, m	combined Langmuir and Freundlich
Toth	$q=aC/(b+C^m)^{1/m}$	a, b, m	heterogeneous monolayer
Generalized Toth	$q=\frac{a(C/b)^m}{1+(C/b)^m-(C/b)^n}$	a, b, m, n	heterogeneous multilayer
Two-site Langmuir Model	$q=\frac{a_1C}{1+b_1C}+\frac{a_2C}{1+b_2C}$	a_1, b_1 a_2, b_2	independent two-site
	$q=\frac{a_1C}{1+b_1C}(1+\frac{a_2C}{1+b_2C})$		superimposed two site

Table 2. Isotherms for multicomponent adsorption

	Investigators	Type
I	Butler and Ockrent (1930)	$q_i=\frac{a_iC_i}{1+\Sigma b_jC_j}$, $j=1, N$
	Redlich and Peterson (1959)	$q_i=\frac{a_iC_i}{1+\Sigma b_jC_{ji}^m}$, $j=1, N$
	Jain and Snoeyink (1973)	$q_1=\frac{(q_{m1}-q_{m2})b_1C_1}{1+b_1C_1}+\frac{q_{m2}b_1C_1}{1+b_1C_1+b_2C_2}$ $q_2=\frac{q_{m2}b_2C_2}{1+b_1C_1+b_2C_2}$
II	Sheindorf et al. (1981)	$q_i=a_iC_i(\Sigma\alpha_{ij}C_j)^{m_i-1}$, $j=1, N$
	Fritz and Schlünder (1981)	$q_i=\frac{a_iC_{ii}^m}{b_i+\Sigma a_{ij}C_{jj}^m}$, $j=1, N$

I: First group
II: Second group

by Butler and Ockrent[13]. This isotherm can be only applicable when each component obeys a Langmuir behavior in a single component system. Jain and Snoeyink[15] proposed a modified version of Langmuir isotherm under the hypothesis that a certain amounts of adsorption occurred without competition. Another method for predicting multicomponent equilibria is the IAS(Ideal Adsorbed Solution) theory. This theory was first derived by Myers and Prausnitz[16] to predict the adsorption of gases on solids and extended by Radke and Prausnitz[4] to the liquid phase adsorption in dilute solutions. Sheindorf et al.[6,14,17] extended the Freundlich isotherm into multicomponent systems by introducing the competitive coefficient. This coefficient was determined from the correlation of the binary experimental data. Fritz and Schlünder[7,18] proposed the generalized multicomponent isotherm as an empirical equation. Although it required many experimental data, this model has been used by several investigators since it can predict experimental data with reasonable accuracy.

The objects of present study are to select a relevant isotherm and to investigate the adsorption characteristics of m-cresol, quinoline, and 1-naphthol on silica gel.

EXPERIMENTALS

Since the presence of hydroxyl groups on silica gel imparts a degree of polarity to the surface, molecules which can form hydrogen bonds and unsaturated hydrocarbons which can form complexes are adsorbed in preference to nonpolar molecules. Because of these characteristics of adsorption, silica gel has been widely used to separate aromatic compounds[19,20]. Hence Lichroprep SI 100 (Merck Co.) which is a kind of silica gel was selected as an adsorbent. The solvent was n-hexane, and the solutes used were m-cresol, quinoline, and 1-naphthol, and these are in coal tar.

The solvent was pretreated by Kieselgel 60 (Merck Co.) to remove the impurities, the adsorbent was activated in a furnace for about two days at 200°C before experiments.

The usual procedure was started with pipetting 100 ml volume of organic solution of m-cresol, quinoline, and 1-naphthol of given concentration into a 500 ml Erlenmeyer flask containing carefully weighted quantity of adsorbents. The bottles were then shaken continuously in an incubator shaker controlled at 30°C for a week. After equilibrium was attained the adsorbent was allowed to settle for at least 1 hr before a sample was removed for analysis of the concentration. Filtration of the sample to remove any suspended particle was accomplished with a syringe filter holder and 0.45-μ filters. Liquid chromatography was used for sample analysis. The adsorbed amounts were calculated from the following relation

$$q=\frac{V}{W}(C_o-C) \qquad (1)$$

where C_0 is the initial concentration, V the fluid phase volume, and W the adsorbent weight in solution.

RESULTS AND DISCUSSIONS

1. Single component system

The standard deviations of experimental data fr the models were summarized in Table 3. As shown in this table, the experimental results for m-cresol and quinoline were supremely described by the generalized Toth isotherm, for 1-naphthol the superimposed two sites Langmuir model. Fig. 1 represented the behavior of adsorption equilibria for each component at 30°C. The solid lines for each component represented the theoretical values of the models in Table 4. The adsorbed amounts for each component decreased in sequence of quinoline, 1-naphthol, and m-cresol when the concentrations were low.

In general the first layer of strongly adsorbed water on the silica gel was remained without changing below 200°C, and the hydrogen bonded water was not displaced by n-hexane. Over the first layer, the solutes were adsorbed by the interaction between the hydrogen bonded water and the solute[20]. Hence these interaction forces determine the adsorbed amounts of each component.

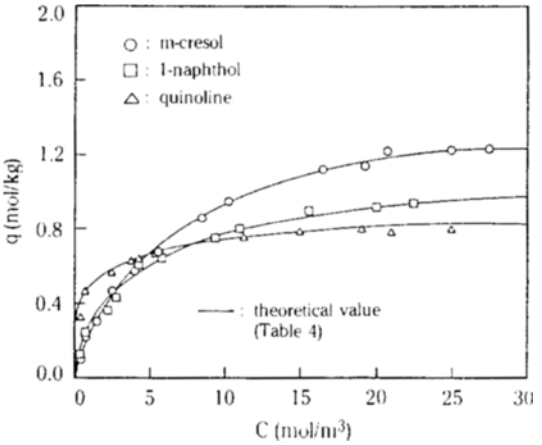

Fig. 1. Equilibrium isotherms for each component at 30°C.

Since the atomic nitrogen in quinoline is located in the aromatic ring whereas atomic oxygen in 1-naphthol or m-cresol is not, quinoline has the larger resonance stabilization than the other two components[21]. It means that the interacting force of quinoline to water molecules is larger than that of 1-naphthol or m-cresol. Therefore the more amounts of quinoline will be adsorbed than the others at the same conditions as shown in present results. On the other hand, electron-releasing substituent ($-CH_3$) on m-cresol decreased the electronic density and concentrated the negative charge on atomic oxygen so that the resonance stabilization of m-cresol was larger than that of 1-naphthol. However the hydrogen bonding force was very large as each molecule interacted linearly as 1-naphthol, therefore m-cresol which had the steric hindrance originated from $-CH_3$ substituent[21] might have lesser bonding force to water molecules than 1-naphthol. Several investigators[14,22,23] reported that when the value of exponent parameter of the Freundlich isotherm became small, the affinity of a component increased. As shown in Table 5, the values of exponent for present systems decreased in sequence of m-cresol, 1-naphthol, and quinoline. These results confirmed quantita-

Table 3. Standard deviation(%) between experimental data and model equation for single component

model	m-cresol	quinoline	1-naphtol
Langmuir	2.2681	9.3602	3.6589
Freundlich	6.0903	6.8571	4.3846
Toth	1.8307	6.9872	2.3438
Redlich and Peterson	1.9660	7.1964	2.6963
Radke and Prausnitz	1.9660	7.1964	2.6963
Generalized Toth	1.5604	6.8560	2.0260
Independent two site	1.8310	6.9863	3.6829
Superimposed two site	2.3582	7.7377	1.8997

* Percent standard deviation was defined as

$$SD\,(\%) = \frac{1}{N_d}\,\Sigma\left|(q_{cal}-q_{exp})/q_{exp}\right| \times 100$$

Table 4. Best single component isotherm obtained for each component

m-cresol (generalized Toth's isotherm)

$$q = \frac{0.118\,C^{0.660}}{1+0.09\,C^{0.660}-0.60\,C^{0.140}}$$

quinoline (generalized Toth's isotherm)

$$q = \frac{0.524\,C^{0.146}}{1+0.55\,C^{0.146}-0.52\,C^{0.157}}$$

1-naphtol (superimposed two site Langmuir model)

$$q = \frac{1.128\,C}{1+4.692\,C}\left(1+\frac{0.555C}{1+0.148\,C}\right)$$

Table 5. The values of parameter of the Freundlich isotherm for each component

component	a	m
m-cresol	0.31825	0.43439
1-naphthol	0.33716	0.34265
quinoline	0.51276	0.14959

Table 6. Standard deviation(%) between experimental data and model equation for multicomponent

model	m-cresol (1)/ quinoline (2)		1-naphtol(1)/ quinoline (2)	
	SD_1	SD_2	SD_1	SD_2
Langmuir	483.00	4.17	159.90	8.89
IAS	86.76	12.87	89.82	6.49
Sheindorf	42.50	53.30	15.09	63.66
Redlich Peterson	109.30	13.05	244.00	6.87
Jain Snoeyink	7.45	4.82	10.07	8.89
Fritz Schlünder	5.52	3.64	6.70	2.87

* Percent standard deviation was defined as

$$SD_i(\%) = \frac{1}{N_d} \Sigma \left|(q_{i,cal} - q_{i,exp})/q_{i,exp}\right| \times 100$$

Table 7. The values of parameter of the Langmuir isotherm in Table 1

component	b	q_m
m-cresol	0.16784	1.50179
1-naphthol	0.28695	1.06540
quinoline	2.13530	0.75811

Table 8. The values of each parameter of the model proposed by Fritz and Schlünder for two binary systems

m-cresol(1)-quinoline(2) system

$$q_1 = \frac{1.3411\ C_1^{0.52755}}{1+0.14989\ C_1^{0.77044}+5.2899\ C_2^{0.15226}}$$

$$q_2 = \frac{1.3532\ C_2^{0.60595}}{1+0.14759\ C_1^{0.88594}+1.3925\ C_2^{0.63853}}$$

1-naphthol(1)- quinoline(2) system

$$q_1 = \frac{1.4053\ C_1^{0.45846}}{1+2.7901\ C_1^{0.043771}+2.9106\ C_2^{0.43122}}$$

$$q_2 = \frac{1.4768\ C_2^{0.44462}}{1+0.087271\ C_1^{0.86471}+2.2025\ C_2^{0.29374}}$$

tively the above analysis.

As the concentration increased, the solutes were adsorbed with bilayer or multilayer. This states that the adsorbed amounts were influenced by the magnitudes of the lateral and longitudinal interaction force [3,12]. Therefore the relative interaction forces between them determine the adsorbed amounts. That is, 1-naphthol or m-cresol interacts with them by the hydrogen bonding force originated from -OH group, while quinoline interacts with them by van der Waals force. Furthermore m-cresol is less bulky than 1-naphthol and the CH_3 group is substituted into the meta position, thus the more amounts of m-cresol were adsorbed than 1-naphtol at the same initial concentrations. While the least amounts of quinoline were adsorbed[19,21]. Summing up, when the concentration was high, the adsorbed amounts increased in the order of quinoline, 1-naphthol, and m-cresol as shown in Fig. 1.

2. Binary system

Table 6 indicates the standard deviations between the experimental results and the models. As shown in the table, the IAS(Ideal Adsorbed Solution) theory shows large standard deviations because this theory is well fitted with the experimental results in dilute solutions. However the models presented by Jain and Snoeyink[15], Fritz and Schlünder[7,18] described the experimental results well. From the former model it can be seen that a certain amount of adsorption occurred without competition because the available capacity for each component was different[15,23]. The ultimate adsorbed amounts for each component were calculated from the Langmuir isotherm for the single component systems, and the values of each parameter were listed in Table 7. Here the values of q_m in this table confirmed the above results. Among the models listed in Table 2, the model proposed by Fritz and Schlünder[7,18] had the lowest standard deviation but it is a empirical equation which has the more numbers of parameter than the others. The values of each parameter to this model were presented in Table 8.

Fig. 2 and 3 represented the equilibrium data for the mixtures of m-cresol and quinoline in the presence of various initial concentrations of the other component. These figures revealed that the amounts of quinoline adsorbed were less influenced by m-cresol whereas the adsorption of m-cresol was more

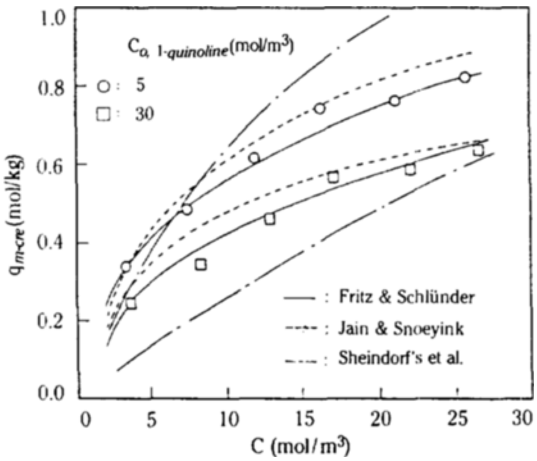

Fig. 2. Equilibrium isotherms for m-cresol in the presence of quinoline at 30°C.

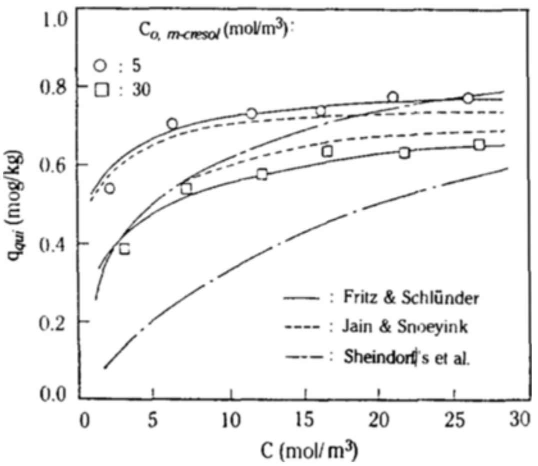

Fig. 3. Equilibrium isotherms for quinoline in the presence of m-cresol at 30°C.

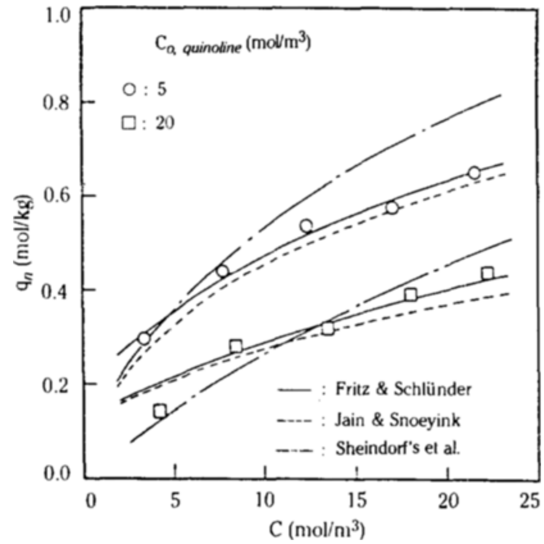

Fig. 4. Equilibrium isotherms for 1-naphthol in the presence of quinoline at 30°C.

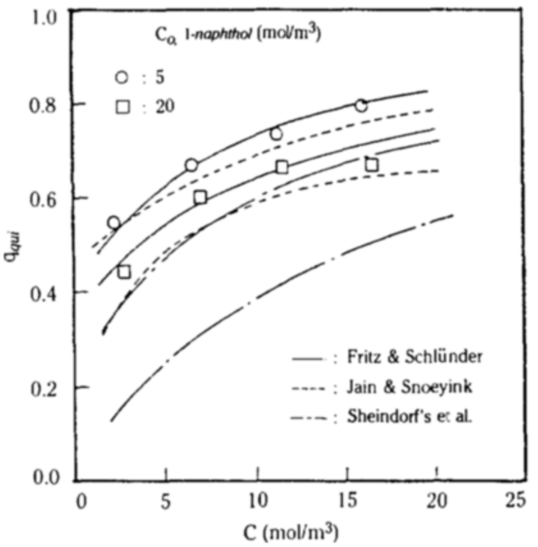

Fig. 5. Equilibrium isotherms for quinoline in the presence of 1-naphthol at 30°C.

affected by quinoline. Fig. 4 and 5 showed the effects of competitive adsorption for 1-naphthol-quinoline system. From these figures it can be seen that the adsorbed amounts of 1-naphthol decreased largely as the concentration of quinoline increased, but the amounts of quinoline and adsorbed were less influenced by 1-naphthol.

The results for two binary systems exhibited a same trend. These phenomena were resulted from the higher affinity of quinoline with respect to silica surface than the other two components[19,21].

2-1. Competitive adsorption

The competitive adsorption coefficient shown in Sheindorf's isotherm, α_{ij}, is a good measure of the competitive adsorption between components. This parameter express the degree of the component j influenced to the adsorption equilibrium of the component i. That is to say, the larger the competitive coefficient, the more the effects of component j to the adsorption equilibrium of component i. When α_{ij} is equal to one it is a case that each component i, j, has the equal affinity to the adsorbent surface[6,17]

With a simple manipulation, Sheindorf's isotherm for a binary system can be expressed as follow

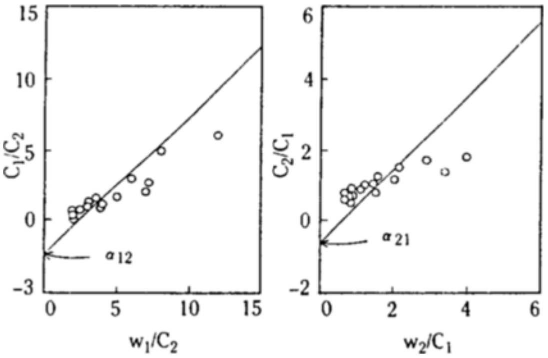

Fig. 6. **Plots of C_i/C_j vs. w_i/C_j.**
(1: 1-naphthol, 2: quinoline)

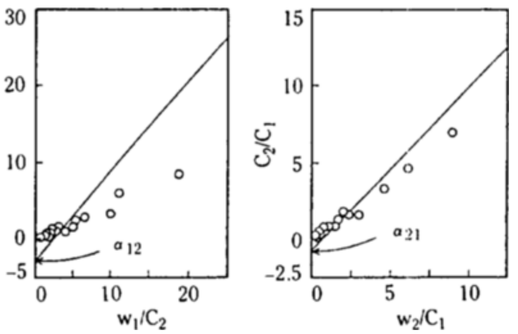

Fig. 7. **Plots of C_i/C_j vs. w_i/C_j.**
(1: m-cresol, 2: quinoline)

$$\frac{C_i}{C_j}=\frac{w_i}{C_i}-\alpha_{ij} \tag{2}$$

where

$$w_i=(a_iC_i/q_i)^{1/(1-m_i)} \tag{3}$$

The plot of C_i/C_j versus w_i/C_j should be a straight line with a slope of unity. Then α_{ij} can be determined from the intercept of this plot. The exponent m_i and the coefficient a_i are constants of the Freundlich isotherm for the single component system. Although the standard deviations were large, as shown in Table 6, this model was used to estimate the relative affinity with respect to the adsorbent quantitatively. Those plots for the two binary systems were shown in Figs. 6 and 7, and α_{ij} obtained are presented in Table 9. As shown in this table, quinoline had the larger affinity to the surface of silica gel than m-cresol or 1-naphthol since α_{12} was larger than α_{21} for each system.

Table 9. Sheindorf's competitive effect coefficients

mixture	α_{12}	α_{21}
m-cresol(1)/quinoline(2)	2.8168	0.5539
1-naphthol(1)/quinoline(2)	2.4510	0.6040

CONCLUSIONS

Liquid phase adsorption of m-cresol, quinoline, and 1-naphthol onto silica gel in n-hexane at 30°C were studied.

The experimental results for the single component system were well respresented by the generalized Toth's isotherm for m-cresol and quinoline, and by the superimposed two sites Langmuir model for 1-naphthol. At low concentration the affinity with respect to silica surface decreased in sequence of quinoline, 1-naphthol, and m-cresol. Whereas the sequence was reversed as the concentration became higher. These results seem to be caused by the lateral and longitudinal interaction force.

For the binary system, the experimental results for each system were well represented by the model proposed by Fritz and Schlünder. From the study of the competitive adsorption with the competitive adsorption coefficient, quinoline had larger affinity with respect to silica surface than 1-naphthol or m-cresol. These results agreed with those for the single component system.

NOMENCLATURE

a : parameter for adsorption isotherm
b, b_1, b_2 : parameters for adsorption isotherm
C : average adsorbate bulk concentration, [mol/m^3]
C_o : initial adsorbate bulk concentration, [mol/m^3]
m : equilibrium parameter
N : numbers of component
N_d : numbers of data point
q : adsorbate concentration on the solid particle, [mol/kg]
q_m : saturation loading, [mol/kg]
V : fluid phase volume, [m^3]
W : mass of adsorbent present in system, [kg]
w_i : parameter defined by $(a_iC_i/q_i)^{1/(1-m_i)}$

Greek Letter

α_{ij} : competition coefficient

Subscript

i,j : of sorbate i, j

Abbreviation

SD : standard deviation

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