

AN ADSORPTION ISOTHERM OF MULTI-SITE OCCUPANCY MODEL FOR HOMOGENEOUS SURFACE

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An adsorption isotherm equation is derived from a localized monolayer model in which each molecule occupies multi-site on a homogeneous surface. The resultant expression is the same as that of Honig and Mueller (1962) for single-component adsorption derived from a fractional-sized vacancy model. An expression for multi-component adsorption is presented here.

The applicability of the adsorption equation is tested for systems of hydrocarbons and carbon dioxide on activated carbon, molecular sieving carbon 5A and Molecular Sieve 5A. Parameters determined from a best fit to single-component adsorption data are consistent with the physical properties of molecular sizes and the BET surface area of adsorbent. Adsorptions of binary mixtures are predicted fairly satisfactorily by use of the parameters obtained from single-component data.

Introduction

The adsorption equilibrium relation is one of the fundamental properties in the design of adsorption equipment. Single-component adsorption isotherms have been correlated widely in practice by means of empirical expressions such as the Freundlich equation, Dubinin's volume-filling theory, etc. The Langmuir equation has a theoretical basis, being derived from a localized adsorption model in which a molecule occupies one active site.^{2,5)} For real systems, however, decreases of adsorption capacity due to decreases of sorbate concentration are more gradual than those predicted from the Langmuir equation. The gradual decrease of adsorption has been interpreted as a heterogeneous characteristic of a surface.¹⁵⁾

Multi-component adsorptions have been correlated by means of either a descriptive method of evaluating the separation factor¹²⁾ or thermodynamic methods which use the activity coefficients and the spreading pressures for an adsorbed phase.^{8,19)}

In the present work the applicability of a simple adsorption isotherm based on statistical thermodynamics is tested for both single- and multi-adsorptions; it is derived from a localized model in which a molecule occupies multi-site on a homogeneous surface. The resultant expression is essen-

tially the same as that of Honig and Mueller⁶⁾ for single-component adsorption derived from the vacant solution theory. A similar expression was suggested by Henry⁴⁾ for single- and multi-adsorptions from the kinetic theory. The applicability of the equations, however, has not been investigated yet.

1. Adsorption Isotherm

Let M be the number of independent active sites of a homogeneous surface and N be the number of adsorbed molecules. When a molecule occupies n neighboring sites, the partition function of the adsorbed phase $Q(N, M, T)$ may be written as

$$Q = j_s^N g(N, M) \exp \left\{ \frac{N\varepsilon}{kT} + \frac{(nN)^2 u}{2MkT} \right\} \quad (1)$$

where j_s is the internal and vibrational partition function of an adsorbed molecule; $-\varepsilon$ is the adsorption energy per molecule for adsorbate-surface interactions and u is a molecular interaction parameter for adsorbate-adsorbate interactions. The combinatorial factor $g(N, M)$, which is the number of distinguishable ways of distributing N adsorbed molecules over M sites, may be expressed by following a similar procedure of Flory¹⁾ as

$$g(N, M) = \frac{M!}{N!(M-nN)!} \cdot \frac{\zeta^N}{M^{(n-1)N}} \quad (2)$$

where ζ is a parameter relating to flexibility and the symmetric number of a molecule.

The chemical potential of the adsorbate on the

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surface μ^s is derived from partial differentiation of $-kT \ln Q$ with respect to N .

$$\frac{\mu^s}{kT} = -\ln(j_s \zeta) + \ln\left(\frac{N}{M}\right) - n \ln\left(\frac{M-nN}{M}\right) - \frac{\varepsilon}{kT} - \frac{n^2 Nu}{MkT} \quad (3)$$

The chemical potential for an ideal gas is

$$\frac{\mu^g}{kT} = \ln\left(\frac{P\Lambda^3}{j_g kT}\right) \quad (4)$$

An adsorption isotherm is obtained by equating μ^s and μ^g ; it is written in the surface coverage expression, $\theta = nN/M$, as

$$\ln(nKP) = \ln \theta - n \ln(1-\theta) - nu\theta/kT \quad (5)$$

where K is an adsorption equilibrium constant.

$$K = \frac{j_s \zeta}{j_g} \cdot \frac{\Lambda^3}{kT} \cdot \exp\left(\frac{\varepsilon}{kT}\right) \quad (6)$$

In the special case where $u=0$, Eq. (5) becomes

$$nKP = \frac{\theta}{(1-\theta)^n} \quad (5')$$

Equation (5') is identical to the Langmuir equation when $n=1$. Equation (5) reduces to Henry's law when the surface coverage is small enough.

It is noteworthy that the slope of the surface coverage θ against the logarithm of pressure, $\log P$, decreases with increasing value of n ; however, it increases with increasing u . The critical point of two-dimensional phase separation is obtained from the stability condition as

$$(u/kT)_c = (1 + \sqrt{n})^2/n \quad (7)$$

and

$$\theta_c = 1/(1 + \sqrt{n}) \quad (8)$$

though the phase-splitting seldom happens to be realized in practical conditions.

An adsorption energy per mole of adsorbate $-E$ ($= -L\varepsilon$) is calculated from the temperature dependence of $\ln K$.

$$E = R \frac{\partial \ln K}{\partial (1/T)} + \frac{RT}{2} \quad (9)$$

where R is the gas constant.

Multi-component adsorption isotherm is obtained as

$$\ln(n_i K_i p_i) = \ln \theta_i - n_i \ln\left(1 - \sum_j \theta_j\right) - n_i \sum_j \theta_j u_{ij}/kT \quad (i=1, 2, \dots, k) \quad (10)$$

where p_i is the partial pressure of component i . When

all the values of u_{ij} are zero, Eq. (10) becomes

$$n_i K_i p_i = \frac{\theta_i}{\left(1 - \sum_{j=1}^n \theta_j\right)^{n_i}} \quad (10')$$

Honig and Mueller⁶⁾ suggested essentially the same expression as Eq. (5) from the vacant solution theory in which a molecule is assumed to occupy one site and an imaginary site occupies a fractional site. From the kinetic theory, Henry⁴⁾ suggested Eqs. (5') and (10'). Equation (10) is a general expression for multi-component adsorption when each adsorbate molecule occupies several sites, interacting with each other.

2. Application

Let W be the experimental adsorption per gram of adsorbent, W^* be hypothetical W of full coverage and W^\bullet be the amount of active sites per gram of adsorbent. The surface coverage θ is calculated as

$$\theta = W/W^* \quad (11)$$

The maximum adsorption capacity W^* is related to W^\bullet and n as

$$W^* = W^\bullet/n \quad (12)$$

Then the isotherm equation has parameters of W^\bullet , n , $K(T)$ and u to be specified; W^\bullet is a characteristic property of a solid adsorbent and n is characteristic of the relative size of an adsorbate molecule to the distance of neighboring active sites. Both W^\bullet and n are temperature-independent. As noted in the preceding section, the parameters of n and u play a compensating role; therefore, the value of u was assumed to be zero at first. When non-zero value for u was judged to be required from the data analysis, it was assumed to be temperature-independent. Parameters were evaluated by means of a non-linear least square method by Marquardt⁷⁾; the following objective function (O.F.) was used in the present work.

$$\text{O.F.} = \sum_{(\text{adsorbate})} \sum_{(\text{data points})} (W_{\text{cal.}} - W_{\text{obs.}})^2 \quad (13)$$

The approximate value of W^\bullet may be estimated from the experimental BET surface area being divided by the area allocated to a unit site of the surface, though the BET equation itself should be examined in the light of the multi-site occupancy model. If a graphite structure is assumed for the surface of activated carbon, the unit area per site is evaluated as $5.24 \times 10^{-2} \text{ nm}^2$ or converted to $31.5 \text{ m}^2 \cdot \text{mmol}^{-1}$.

An approximate value for u , possibly a maximum one, may be estimated from Eq. (14), details of which are given in Appendix.

$$u = 3.44(\varepsilon_{LJ}/n) \quad (14)$$

where ε_{LJ} is the force constant for the Lennard-Jones

Table 1. Parameters determined from single-component adsorption isotherms on Nuxit-AL

Component	n	$W^* = 3.12 \text{ mmol} \cdot \text{g}^{-1} \quad u = 0 \text{ (Assumed value)}$				Av. dev.* [mmol · g ⁻¹]	No. of data pts.
		20°C	40°C	60°C	90°C		
CH ₄	3.69	0.373	0.239	0.143	0.0824	0.014	86
C ₂ H ₂	3.38	3.94	1.91	1.04	0.526	0.036	53
C ₂ H ₄	3.55	4.08	2.08	1.16	0.522	0.049	109
C ₂ H ₆	3.63	6.01	3.07	1.62	0.766	0.047	121
C ₃ H ₆	4.30	83.4	26.4	13.8	4.91	0.049	87
C ₃ H ₈	4.45	84.6	32.2	16.0	5.50	0.034	120
<i>n</i> -C ₄ H ₁₀	5.22	394	214	98.5	30.3	0.085	50
CO ₂	2.69	1.28	0.593	0.374	0.188	0.060	94

* Average deviation, $\sum_{(\text{data points})} |W_{\text{cal.}} - W_{\text{obs.}}| / (\text{No. of data points})$

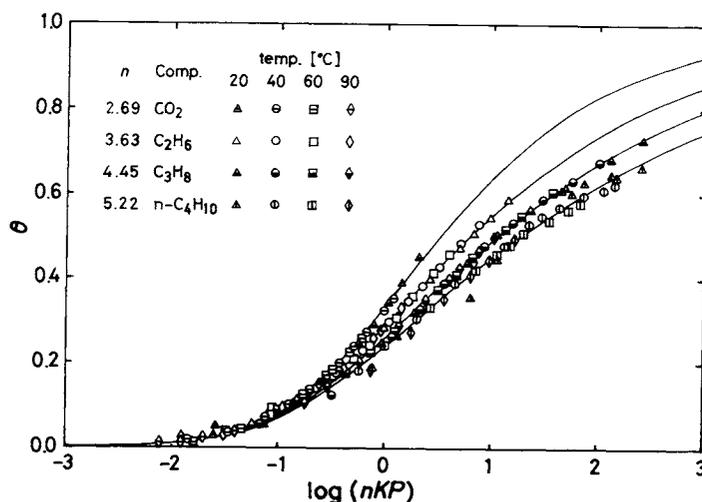


Fig. 1. Single-component adsorption isotherms of hydrocarbons and carbon dioxide on activated carbon Nuxit-AL. Experimental data are from Szepesy and Illés.^{16,17}

6–12 potential.

2.1 Activated carbon

Adsorption isotherms of seven hydrocarbons and carbon dioxide on activated carbon Nuxit-AL, both gases and gas mixtures adsorptions reported by Szepesy and Illés,^{16–18} were analyzed by use of Eqs. (5') and (10'). The value of 31.18 mmol/g for W^* is obtained from a fit to single-component adsorption isotherms. Parameters obtained from a best fit are summarized in **Table 1** along with the average deviation for each component. **Figure 1** shows the experimental and the calculated surface coverages against $\log(nKP)$ for several hydrocarbons and carbon dioxide. Approximately 40% of data points selected at random are shown in the figure to avoid confusion. Data points for *n*-butane are scattered. The average deviation is 0.045 mmol/g over 720 data points. The calculated values for n increase with increasing molecular sizes of the adsorbates; an exception is methane, the value n of which is close to that of ethane.

Figure 2 shows adsorption isotherms of binary

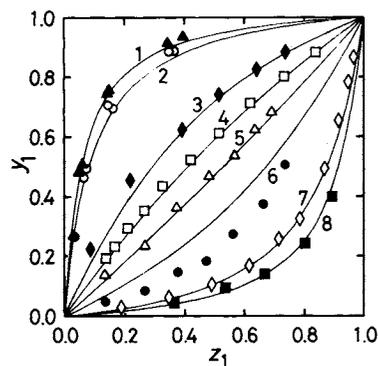


Fig. 2. Equilibrium diagrams of binary mixtures on activated carbon Nuxit-AL at 20°C and 760 mmHg: (1) CH₄ + C₂H₄; (2) CH₄ + C₂H₆; (3) CO₂ + C₂H₄; (4) C₂H₄ + C₂H₆; (5) C₃H₆ + C₃H₈; (6) *n*-C₄H₁₀ + C₃H₈; (7) C₃H₈ + C₂H₆; (8) C₃H₆ + C₂H₄. The first substance is denoted as component 1 and the second as 2. Experimental data are from Szepesy and Illés.¹⁸

mixtures at 20°C. Legends in the figure represent experimental data points; curves are predictions calculated from Eq. (10'). Agreement between experi-

Table 2. Parameters determined from single-component adsorption isotherms on molecular sieving carbon 5A

Component	n	$W^* = 10.9 \text{ mmol} \cdot \text{g}^{-1} \quad u = 0 \text{ (Assumed value)}$			Av. dev. [mmol · g ⁻¹]	No. of data pts.
		5.4°C	K [kPa ⁻¹] 30°C	50°C		
CH ₄	2.81	3.80×10^{-3}	1.78×10^{-3}		0.010	18
C ₂ H ₄	3.06	0.108*	3.96×10^{-2}	1.70×10^{-2}	0.022	32
C ₂ H ₆	3.22	0.199*	6.05×10^{-2}	2.54×10^{-2}	0.014	33
C ₃ H ₆	3.71	3.79*	1.13	0.395	0.018	35
C ₃ H ₈	4.17	1.67	0.827	0.363	0.026	32
<i>n</i> -C ₄ H ₁₀	4.89	55.3	13.8	2.18	0.024	34
<i>n</i> -C ₅ H ₁₂	5.72		62.7		0.013	10

* values at 5.5°C.

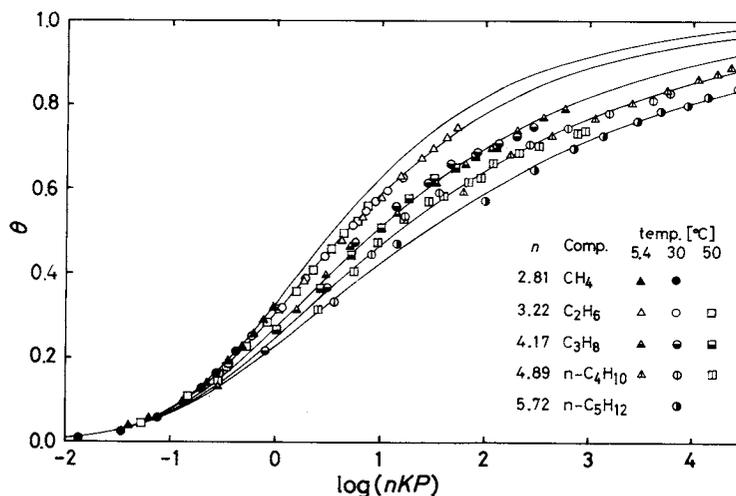


Fig. 3. Single-component adsorption isotherms of saturated hydrocarbons on molecular sieving carbon 5A. Experimental data are from Nakahara *et al.*¹⁰⁾

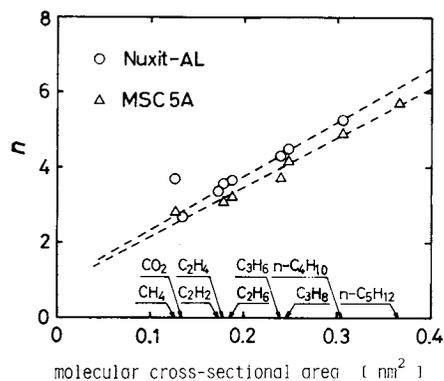


Fig. 4. Relationship between parameter n and molecular area projected on a plane.

ments and predictions is satisfactory except for the *n*-butane + propane system (numbered 6).

2.2 Molecular sieving carbon (MSC) 5A

Single-component adsorption isotherms of seven hydrocarbons on MSC-5A were presented at 5.4, 30, and 50°C by Nakahara, Hirata and Omori.¹⁰⁾ The value of $10.91 \text{ mmol} \cdot \text{g}^{-1}$ for W^* , determined by use of Eq. (5'), is about half the value of $20.6 \text{ mmol} \cdot \text{g}^{-1}$

calculated from the BET surface area of $650 \text{ m}^2 \cdot \text{g}^{-1}$ divided by the unit area of $31.5 \text{ m}^2 \cdot \text{mmol}^{-1}$. **Figure 3** shows the experimental and the calculated adsorption isotherms for saturated hydrocarbons of methane to *n*-pentane. Determined parameters and average deviations are listed in **Table 2**. The values of n for each adsorbate are similar to those determined from the data on the activated carbon Nuxit-AL except for methane. **Figure 4** shows plots of n against molecular area projected on a plane. The molecular areas were calculated by means of compiled values for the van der Waals radii and bond lengths.¹¹⁾

Another method of parameter evaluation is applied by use of Eq. (5) to the experimental data, by fixing the value of $20.6 \text{ mmol} \cdot \text{g}^{-1}$ for W^* ; the parameter u is now relaxed to be optimized by assuming the same value for all the saturated hydrocarbons. The determined value for u/k is 141 K, which is comparable to 136 K calculated from Eq. (13) with the force constant ($\epsilon/k = 215.7 \text{ K}^{13}$) for ethane. The standard deviation of the amounts of adsorption calculated from Eq. (5) is almost the same as that from Eq. (5').

Adsorption isotherms of binary mixtures of ethane

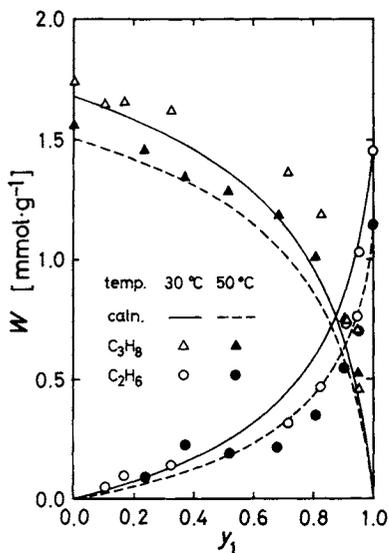


Fig. 5. Amount adsorbed for system $C_2H_6(1) + C_3H_8(2)$ on molecular sieving carbon 5A at 100 mmHg. Experimental data are from Nakahara *et al.*⁹⁾

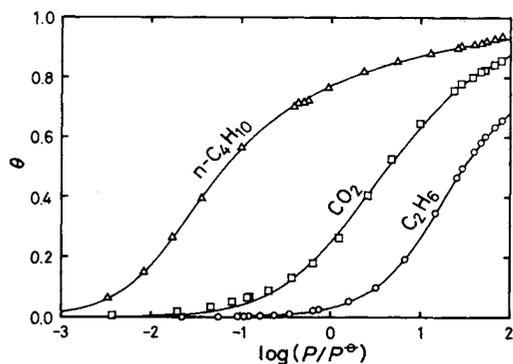


Fig. 6. Single-component adsorption isotherms in Molecular Sieve 5A at 35°C. Experimental data are from Glessner and Myers³⁾; $P^{\ominus} = 1$ kPa.

and propane, reported by Nakahara, Hirata and Komatsu,⁹⁾ are compared with the prediction through Eq. (10'). The calculated isotherms in Fig. 5 are close to those predicted by the ideal adsorbed solution⁸⁾; the two predictions do not represent the experiments satisfactorily.

2.3 Molecular Sieve 5A

Single-component adsorption isotherms of ethane, *n*-butane, and carbon dioxide presented by Glessner and Myers³⁾ are shown in Fig. 6. The solid curves are calculated by means of Eq. (5); the parameters determined from a best fit are given in Table 3. The value for W^* is fixed at 9.06 mmol/g, which was determined by Shigetomi *et al.*¹⁴⁾ from fitting to water adsorption in Molecular Sieve 4A by use of the localized and nonlocalized adsorption model. In a parameter-optimization procedure, the values of (u/k) for ethane and *n*-butane are assumed to be same; the value of (u/k) for carbon dioxide happens to be zero, which was the lowest limit presumed for the param-

Table 3. Parameters determined from single-component adsorption isotherms on Molecular Sieve 5A at 35°C ($W^* = 9.06$ mmol/g*)

	n	u/k [K]	K [kPa ⁻¹]
C_2H_6	2.92	286	0.0110
$n-C_4H_{10}$	4.32	286	4.65
CO_2	1.86	0*	0.230

* Assumed value.

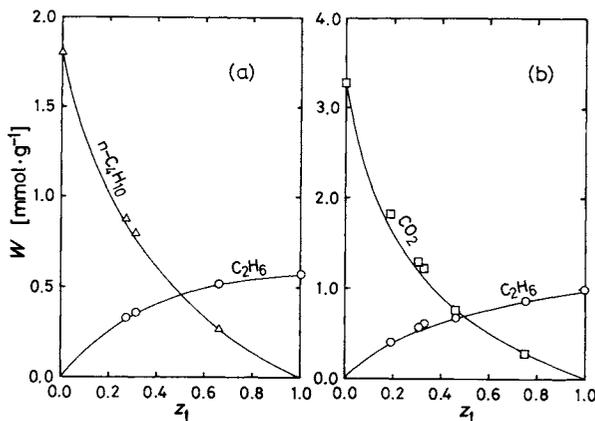


Fig. 7. Amount adsorbed at 35°C in Molecular Sieve 5A: (a) $C_2H_6(1) + n-C_4H_{10}(2)$ (at 48 mmHg) and (b) $C_2H_6(1) + CO_2(2)$ (at 95 mmHg). Experimental data are from Glessner and Myers.³⁾

eter u/k . Almost the same values as those in Table 3 were obtained for a set of parameters when W^* is relaxed to be optimized. Since Molecular Sieve 5A has three different types of atoms, oxygen, Na^+ , and Ca^{2+} , on the surface, the active sites may be heterogeneous. In the case of carbon dioxide, as shown in Fig. 6, the experimental adsorption capacities at lower pressures are higher than the calculated line, which shows that there is an appreciable fraction of strongly active sites on the surface.

In Fig. 7 adsorption isotherms of binary mixtures in Molecular Sieve 5A are shown. The curves are predictions by using the parameters in Table 3 under the assumption of the arithmetic means for u_{ij} ; $u_{ij} = (u_{ii} + u_{jj})/2$. Agreement between the theory and the experiments is satisfactory.

Concluding Remarks

An adsorption isotherm of a multi-site occupancy model for a homogeneous surface, given by Eq. (10) as a general expression for multi-component adsorption, has been applied successfully to systems of hydrocarbons and carbon dioxide on activated carbon, MSC-5A, and Molecular Sieve 5A. Simple expressions without molecular interactions, Eqs. (5') and (10'), work well for adsorbents of activated carbon and molecular sieving carbon. Adsorptions of

binary mixtures are predicted fairly satisfactorily by use of the parameters determined from single-component adsorption data. An important feature of the isotherm equation is that the slope of adsorption capacity against pressure decreases with increasing value of parameter n , the number of sites occupied by a molecule. Though ambiguous extrapolations of spreading pressures of each component are often required by the thermodynamic methods,^{8,19)} an analytical expression of Eq. (10) or Eq. (10') does not require any knowledge of spreading pressures in calculating multi-component adsorption isotherms.

For polar adsorbents, such as Molecular Sieves, activated aluminum, etc., surface heterogeneity should be taken into account for correlating adsorption isotherms.

Appendix

Relation between the molecular interaction parameter u and the force constant ϵ_{LJ}

It is assumed that molecular interactions among adsorbed molecules are pairwise additive and that each pair-energy is represented by the Lennard-Jones 6-12 potential.

$$\phi(r) = 4\epsilon_{LJ} \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} \quad (\text{A-1})$$

If the adsorbed molecules are distributed at random, the total energy of the system due to molecular interactions U may be given as

$$U = \frac{N}{2} \int_{\sigma}^{\infty} \phi(r) \frac{N}{A} \cdot 2\pi r dr$$

$$= \frac{3}{5} \cdot \frac{\pi \epsilon_{LJ} (\sigma N)^2}{A} \quad (\text{A-2})$$

An alternative expression of U is obtained by assuming that the molecular interaction energy is counted from neighboring sites occupied by other molecules.

$$U = -\frac{1}{2} unN\theta \quad (\text{A-3})$$

where u is the molecular potential energy allocated to a site; it is related to ϵ_{LJ} as

$$u = \frac{6\pi}{5} \cdot \frac{\epsilon_{LJ}}{n} \cdot \frac{M\sigma^2}{nA} \quad (\text{A-4})$$

When spherical particles of diameter a are packed most closely, the packing fraction over the surface is 0.907.

$$\frac{\pi}{4} \cdot \frac{Ma^2}{nA} = 0.907 \quad (\text{A-5})$$

Since a may be equal to $(2)^{1/6}\sigma$ for a (6-12) potential, we obtain the relation

$$u = 3.44(\epsilon_{LJ}/n) \quad (\text{A-6})$$

It should be noted that Eq. (A-2) assumes that the radial distribution function for adsorbed molecules is unity, which might be a poor assumption due to adsorbate-surface interactions.

Nomenclature

A	= surface area	[m ²]
E	= desorption energy per mole	[J · mol ⁻¹]
g	= combinatorial factor	[—]

j_g	= internal partition function in gas phase	[—]
j_s	= internal and vibrational partition function of an adsorbed molecule	[—]
K	= adsorption equilibrium constant	[Pa ⁻¹]
k	= Boltzmann constant	[J · K ⁻¹]
L	= Avogadro constant	[mol ⁻¹]
M	= number of active sites on surface	[—]
N	= number of adsorbed molecules on surface	[—]
n	= number of sites occupied by one molecule	[—]
P	= pressure	[Pa]
p_i	= partial pressure	[Pa]
Q	= partition function	[—]
R	= Gas constant	[J · mol ⁻¹ · K ⁻¹]
T	= temperature	[K]
U	= internal energy	[J]
u	= molecular interaction parameter	[J]
W	= amount adsorbed per gram of adsorbent	[mol · g ⁻¹]
W^*	= maximum adsorption capacity per gram of adsorbent	[mol · g ⁻¹]
W^\bullet	= amount of active sites per gram of adsorbent	[mol · g ⁻¹]
y	= mole fraction in gas phase	[—]
z	= mole fraction in adsorbed phase	[—]
ϵ	= desorption energy per molecule	[J]
ϵ_{LJ}	= energy constant for Lennard-Jones potential	[J]
ζ	= a constant relating to flexibility and the symmetric number of a molecule	[—]
θ	= surface coverage	[—]
λ	= thermal de Broglie wavelength	[m]
μ	= chemical potential per molecule	[J]
σ	= collision diameter	[m]
ϕ	= pair-potential function	[J]

<Subscripts>

i	= component i
ij	= pair of components i and j
c	= critical point of phase separation
cal.	= calculated value
obs.	= observed value

<Superscripts>

g	= gas phase
s	= solid or adsorbed phase

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Key Words: Adsorption, Equilibrium, Adsorption Isotherm, Heterogeneous Surface, Group Contribution, Molecular Sieve, Oxygen, Nitrogen, Carbon Monoxide, Multicomponent Adsorption

An adsorption isotherm for a heterogeneous surface is described on the basis of a multi-site occupancy model followed by a group-contribution assumption. Equations of single- and multi-component adsorptions are derived for systems of molecules consisting of several functional groups and a surface composed of active sites of different energies interacting with the groups independently. The isotherm equation reduces to the expression derived by Sparnaay in the special case where a molecule occupies one site of the surface.

The theory is applied to adsorption equilibria for systems of oxygen, nitrogen, and carbon monoxide on Molecular Sieves 5A and 10X. Correlations of single-component isotherms are excellent for nitrogen and oxygen and fairly good for carbon monoxide; predictions of adsorption isotherms of binary gas mixtures are made satisfactorily by means of parameters determined from the best fit to each single-component isotherm.

Introduction

It is known that the influence of surface heterogeneity on a single-component adsorption isotherm is the decrease of the slope of adsorption against pressure. Sparnaay⁷⁾ suggested many types of isotherms having a low slope of adsorption by assuming different kinds of active sites; however, the fundamental equation is based on the Langmuir model, characterized as a localized monolayer in which a molecule occupies one active site.^{2,3)}

In a previous paper concerning a multi-site occupancy model,⁵⁾ the authors pointed out that the slope of an adsorption isotherm decreases with increasing number of sites occupied by a molecule even when a homogeneous surface is assumed. An extension to a heterogeneous surface of the multi-site occupancy model is given here, which may be characterized as a method of group contributions. Numerical examples and an application to adsorp-

tions on Molecular Sieves are included.

1. Theory

1.1 Theoretical framework

To simplify the theoretical treatment, single-component adsorption is considered first. An adsorbent surface is characterized by m different site-groups; the numbers of each site are M_a, M_b, \dots, M_m . The total number of active sites M is the sum of all M_α 's ($\alpha = a, b, \dots, m$). A molecule consists of k groups; the numbers of sites occupied by each group are n_1, n_2, \dots, n_k . Let $-\varepsilon_{\alpha i}$ be the adsorption energy per site when a group i of a molecule is attached on an active site α . The adsorption energies are assumed to be independent of either neighboring groups or neighboring sites.

When N molecules are adsorbed on a heterogeneous surface, the partition function of the system $Q(N, M, T)$ may be written as

$$Q = j_s^N \sum_{\{N_{\alpha i}\}} g(N, M, \{N_{\alpha i}\}) \exp \left\{ \sum_{\alpha} \sum_i N_{\alpha i} \varepsilon_{\alpha i} / kT \right\} \quad (1)$$

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