

# A HYBRID ISOTHERM EQUATION FOR MOBILE MOLECULES ADSORBED ON HETEROGENEOUS SURFACE OF RANDOM TOPOGRAPHY

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A new type of isotherm equation is presented for mobile molecules adsorbed on a heterogeneous surface of random topography. The basic idea of the adsorption model is that molecules moving around on the surface spend more time on sites interacting with lower energy; the probability on each site is determined from the energy term that pulls the system toward more stable states and the entropy term that maximizes the number of combinatorial configurations on sites. The hybrid isotherm equation was applied to single- and mixed-gas adsorptions on MS-13X and on H-mordenite by assuming two sites. The site fractions were found to be important quantities for correlating the single-gas isotherms, while the assignments of sites were crucially important for the interpretation of mixed-gas adsorptions. This theory suggests that the large negative deviations from Raoult's law observed for systems of  $C_3H_8 + CO_2$  and  $C_3H_8 + H_2S$  on H-mordenite are due to the negative site correlations, which means that the lower-energy sites do not compete with each other.

## Introduction

Surface heterogeneity is an important factor affecting the adsorption equilibria on microporous adsorbents widely used in chemical industries. Since molecules have a tendency to be adsorbed on an energetically more stable site or region, the heat evolved from adsorption on a heterogeneous surface increases with decreasing amount adsorbed and such an isotherm hardly follows Henry's law even at low surface coverage.

Isotherm equations based on statistical thermodynamics have been described by either the localized or the mobile model<sup>3,12</sup>. In the localized model, molecules are assumed to be confined in small regions of molecular size, called sites, and the heterogeneous surface has been modeled by postulating a distribution function for site energies<sup>12,13</sup>. In a case where one molecule occupies one site, which is known as the Langmuir model, the relative locations of the sites have little meaning; however, in the multi-site occupancy model studied by one of the authors<sup>7</sup>, information on site locations is required. In the mobile model, molecules are assumed to move around on a surface like a fluid, and the patchwise surface model<sup>11</sup> is the only model that has been used for adsorption on heterogeneous surfaces. We recently applied the patch model to correlate the adsorption isotherms on active carbons<sup>8,9</sup> and reported that the results were fairly good.

Zeolites consist of several units composed of silicon, aluminium, oxygen, and cations such as sodium or calcium. Therefore, the active sites are considered to be dispersed in random topography on a surface. However, no theory has been proposed for mobile molecules adsorbed on such a surface, although light molecules are considered to be mobile in zeolites.

This paper deals with the isotherm equation based on the mobile model on a heterogeneous surface of random topography, which may be characterized as a hybrid of the mobile and random-site models. The theory has been applied to pure- and mixed-gas adsorptions on commercial zeolites, and a suggestion is made that the experimental negative deviations from Raoult's law are attributable to the negative correlation of energy sites for each molecule.

## 1. Theory

### 1.1 Molecular model and partition function

To make the description simple, we first deal with  $N$  molecules of pure component confined in a two-dimensional region having the surface area  $A$  and at temperature  $T$ . When molecules move around on a homogeneous surface, the partition function of a system  $Q(N, A, T)$  is written as<sup>3</sup>

$$Q = \frac{1}{N!} \left( \frac{j^s A_f}{A^2} \right)^N \exp\left( -\frac{E_v}{kT} - \frac{E_h}{kT} \right) \quad (1)$$

where  $\Lambda (= h/(2\pi mkT)^{1/2})$  is the de Broglie wave length,  $j^s$  the molecular partition function on the surface,  $A_f$  the free area available to each molecule,

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$E_v$  the potential energy vertical to the surface and  $E_h$  the horizontal potential energy related to the attractive part of intermolecular interactions.

The free area  $A_f$  represents the repulsive part of intermolecular forces; the scaled particle theory is used as in the previous work<sup>8)</sup>

$$\ln\left(\frac{A_f}{A}\right) = \ln(1-\eta) - \frac{\eta}{(1-\eta)} \quad (2)$$

where  $\eta$  is the dimensionless surface density for hard discs of diameter  $d$ .

$$\eta = \pi d^2 N / 4A = \beta N / A \quad (3)$$

$\beta$  ( $= \pi d^2 / 4$ ) is the cross-sectional area of a molecule.

For an energetically heterogeneous surface, we adopt the concept of sites which are regions characterizing the depth of real potential field changing with location. The surface is divided into  $M$  sites being classified into  $s$  different kinds of sites,  $M_a, M_b, \dots, M_s$ . Then  $E_v$  is expressed by the sum of site-molecule interaction energies as

$$E_v = - \sum_{m=a}^s N_m \varepsilon_m \quad (4)$$

where  $N_m$  is the number of  $m$ th sites attached to or occupied by a segment of a molecule and  $\varepsilon_m$  is the potential energy between site  $m$  and the segment.

When  $\varepsilon_m$  is greater than others,  $N_m$  will increase for a system to attain energetically more stable states; however, the compensation effect will work against increasing the ordering in the whole system. We take the effect into consideration by a function  $\Omega$ , which we call an ordering function. It counts the number of combinatorial configurations with a set of variables  $\{N_m\}$  and compares this number to that of random configurations with  $\{N_m^*\}$ . By taking the quasi-chemical approximation<sup>2,7)</sup>, we may write  $\Omega$  as

$$\ln \Omega = \sum_{m=a}^s \frac{N_m! (M_m - N_m)!}{N_m! (M_m - N_m^*)!} \quad (5)$$

This expression is known to include some impossible configurations because segments of each molecule are allowed to occupy all the sites independently<sup>3)</sup>. However, at present it serves as a useful approximation for obtaining an analytical expression for  $\Omega$ . If one site accommodates just one molecule, the above expression is exact.

When the sites are distributed randomly, the horizontal interaction energy  $E_h$  may be expressed under the assumption that the radial molecular distribution function is unity; that is

$$E_h = -N^2 \alpha / A \quad (6)$$

where  $\alpha$  is a constant related to the intermolecular attractive potential.

The partition function for the present molecular model is finally written as

$$\ln Q = N \ln \left[ \frac{j^s e A (1-\eta)}{N A^2} \right] + \frac{N \eta}{(1-\eta)} + \frac{N^2 \alpha}{A k T} + \sum_{m=a}^s \ln \left[ \frac{N_m^*! (M_m - N_m)!}{N_m! (M_m - N_m^*)!} \right] + \frac{N_m \varepsilon_m}{k T} \quad (7)$$

A set of variables ( $N_m$ ) is determined from the principle of free energy minimization, which corresponds to maximizing  $\ln Q$ , under the constraint condition that

$$\sum_{m=a}^s N_m - n N = 0 \quad (8)$$

where  $n$  is the number of sites occupied by a molecule.

## 1.2 Surface coverage and site coverages

The undetermined multiplier method is useful to determine the stationary point of Eq. (7) subject to Eq. (8). Since the mathematical procedures are almost the same as those previously developed by the authors<sup>7)</sup>, the resultant expressions will be given.

The surface coverage  $\theta$ , the site coverages  $\{\theta_m\}$ , and the site fractions  $\{f_m\}$  are defined as follows.

$$\theta = n N / M \quad (9)$$

$$\theta_m = N_m / M_m \quad (m = a, b, \dots, s) \quad (10)$$

$$f_m = M_m / M \quad (m = a, b, \dots, s) \quad (11)$$

If we take site  $a$  as a reference site, the stationary condition with respect to  $\{N_m\}$  yields the relation between the site coverages  $\theta_m$  and  $\theta_a$  as

$$\frac{\theta_m}{1-\theta_m} \exp\left(-\frac{\varepsilon_m}{kT}\right) = \frac{\theta_a}{1-\theta_a} \exp\left(-\frac{\varepsilon_a}{kT}\right) \quad (m = b, \dots, s) \quad (12)$$

The site coverages  $\{\theta_m\}$  are then given as

$$\theta_m = \frac{r_m \Gamma \theta}{1 + (r_m \Gamma - 1) \theta} \quad (m = a, b, \dots, s) \quad (13)$$

where  $r_m$  and  $\Gamma$  are parameters defined as

$$r_m = \exp[(\varepsilon_m - \varepsilon_a) / kT] \quad (m = a, b, \dots, s) \quad (14)$$

$$\frac{\theta_a}{1-\theta_a} = \Gamma \frac{\theta}{1-\theta} \quad (15)$$

The parameter  $r_m$  is the ratio of the Boltzmann factors related to site  $m$  and site  $a$ .  $\Gamma$  is proportional to the activity  $\theta_a / (1-\theta_a)$  of a molecule on site  $a$ . Therefore, we may call it the local activity coefficient on a reference site\*.  $\Gamma$  is unity if the surface is

\* The parameter  $\Gamma$  defined in Eq. (15) is equivalent to  $Y/Y^*$  defined in the previous work<sup>7)</sup>. We adopt  $\Gamma$  because it is easy to grasp its physical meaning.

homogeneous; it is less than unity if the reference site has the highest energy (the smallest value of  $\varepsilon$ ). The constraint Eq. (8), which is rewritten as  $\sum_m f_m \theta_m = \theta$ , yields a nonlinear equation in an unknown  $\Gamma$ .

$$\sum_{m=a}^s \left[ \frac{f_m r_m \Gamma}{1 + (r_m \Gamma - 1)\theta} \right] - 1 = 0 \quad (16)$$

When  $\Gamma$  is evaluated by solving the above equation, a set of site coverages  $\{\theta_m\}$  are calculated from Eq. (13).

The chemical potential of a component in the surface phase  $\mu^s$  is derived from the conventional thermodynamic formula as

$$\begin{aligned} \frac{\mu^s}{kT} &= - \left[ \frac{\partial \ln Q}{\partial N} \right]_{T,A} \\ &= \ln \left( \frac{\Lambda^2}{j^s \beta} \right) + \ln \left( \frac{\eta}{1-\eta} \right) + \frac{(3-2\eta)\eta}{(1-\eta)^2} \\ &\quad - \frac{2\alpha\eta}{\beta kT} + n \left( \ln \Gamma - \frac{\varepsilon_a}{kT} \right) \end{aligned} \quad (17)$$

### 1.3 Isotherm equation

Since the chemical potential of a component in a gas phase is given by  $\mu^g/kT = \ln(\phi p \Lambda^3 / j^s kT)$ , the isotherm equation is obtained by equating the two chemical potentials,  $\mu^s = \mu^g$ . The resultant isotherm expression is

$$\ln(K\phi p) = \ln \left( \frac{\eta}{1-\eta} \right) + \frac{(3-2\eta)\eta}{(1-\eta)^2} - \frac{v\eta}{kT} + n \ln \Gamma \quad (18)$$

where  $k$  is the adsorption equilibrium constant defined by the adsorption energy for site  $a$  as

$$\ln K = \ln \left( \frac{j^s \beta \Lambda}{j^s kT} \right) + \frac{n\varepsilon_a}{kT} \quad (19)$$

and  $v (= 2\alpha/\beta)$  is the molecular interaction parameter.

The isotherm equation for multicomponent adsorption is extended in a straight way; the final expressions for a  $k$ -component system are given as

$$\begin{aligned} \ln(K_i \phi_i y_i p) &= \ln \left( \frac{\eta_i}{1-\eta} \right) + \frac{\eta}{(1-\eta)} + \left( \sum_{j=1}^k \frac{\beta_i \eta_j}{\beta_j} \right) \\ &\quad \times \frac{(2-\eta)}{(1-\eta)^2} - \sum_{j=1}^k \frac{v_{ij} \eta_j}{kT} + n_i \ln \Gamma_i \\ &\quad (i=1, 2, \dots, k) \end{aligned} \quad (20)$$

where  $y_i$  is the mole fraction in gas phase,  $v_{ij}$  the cross interaction parameter and  $\eta = \sum_j \eta_j$ . The subscripts  $i$  and  $j$  refer to components  $i$  and  $j$  respectively. The local activity coefficient  $\Gamma_i$  is calculated from the  $k$  simultaneous equations given as

$$\sum_{m=a}^s \frac{f_m r_m \Gamma_i}{1 + \sum_{j=1}^k (r_m \Gamma_j - 1)\theta_j} - 1 = 0 \quad (i=1, 2, \dots, k) \quad (21)$$

## 2. Applications

### 2.1 Data reduction method

The hybrid isotherm equation for pure-gas adsorption is given by Eq. (18), which requires three kinds of parameters representing surface characteristics ( $A$ ,  $\{f_m\}$ ), surface-molecule interactions ( $n$ ,  $\beta$ ,  $K$  and  $\{r_m\}$ ) and molecule-molecule interactions ( $v$ ). In correlating the experimental amount adsorbed per mass of adsorbent  $q$ , we use  $q^\circ$ , the maximum amount of the adsorbate, instead of the specific surface area  $A$  and the molecular area  $\beta$ . We define the surface coverage of the adsorbate  $\theta$  as  $q/q^\circ$ , which is related to the packing density  $\eta$  as

$$\theta = q/q^\circ = \eta/\eta_{\max} \quad (22)$$

where  $\eta_{\max}$  is 0.907 for close-packed hard discs. The number of sites occupied by a molecule,  $n$ , is rather arbitrary since the site is a fictitious concept to simplify the real complex potential field on a surface. When a large value of  $n$  is assigned, the interaction energy between a site  $m$  and a segment of molecule  $\varepsilon_m$  becomes small, resulting in a small value of  $r_m$ .

The total amount of sites  $q^*$  is related to  $n$  and  $q^\circ$  as

$$q^* = nq^\circ \quad (23)$$

It may also be related to the conventional BET surface area  $S_{\text{BET}}$  through the area of unit site  $A_{\text{site}}$ .

$$q^* = \eta_{\max} S_{\text{BET}} / A_{\text{site}} L \quad (24)$$

where  $L$  is the Avogadro constant. In the present study we presume  $q^*$  to be an adsorbent characteristic firstly and either  $n$  or  $q^\circ$  is treated as an adjustable parameter for each molecule.

The adsorption equilibrium constant  $K$  at a temperature  $T$  is calculated from two parameters  $K_0$  and  $\varepsilon_0$  defined at a reference temperature  $T_0 (= 298.15 \text{ K})$  as

$$\ln K = \ln K_0 - \frac{1}{2} \ln \left( \frac{T}{T_0} \right) + \frac{\varepsilon_0}{k} \left[ \frac{1}{T} - \frac{1}{T_0} \right] \quad (25)$$

The molecular interaction parameter  $v$  is estimated as  $v = 4.8\varepsilon_{\text{LJ}}^8$ , where  $\varepsilon_{\text{LJ}}$  is the energy depth of the Lennard-Jones potential.

Molecular sieve 13X (MS-13X) and H-mordenite were selected for applications of the hybrid isotherm equation mainly because experimental data for pure- and mixed-gas adsorptions are available and that some binary mixtures are known to form highly nonideal solutions in the adsorbed phase.

**Table 1.** Parameters determined from single-component adsorption isotherms

Component	$f_b$ [—]	$n$ [—]	$q^o$ [mol/kg]	$v/k$ [K]	$K_o$ [kPa <sup>-1</sup> ]	$\epsilon_o/k$ [K]	$\Delta\epsilon/k$ [—]	$\Delta q^{**}$ [mol/kg]
Molecular sieve 13X ( $q^* = 11.4 \text{ mol} \cdot \text{kg}^{-1}$ )								
CO <sub>2</sub>	0.22	1.34	8.50	937*	$1.21 \times 10^{-2}$	3452	972	0.055 (30)
C <sub>2</sub> H <sub>4</sub>	0.22	2.14	5.34	1079*	$2.43 \times 10^{-2}$	3466	675	0.032 (66)
C <sub>2</sub> H <sub>6</sub>	0.22	2.15	5.30	1035*	$1.49 \times 10^{-2}$	3135	1	0.030 (60)
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.22	4.41	2.58	1584*	0.359	4081	464	0.047 (45)
H-mordenite ( $q^* = 8.2 \text{ mol} \cdot \text{kg}^{-1}$ )								
CO <sub>2</sub>	0.08	1.45	5.66	937*	$1.08 \times 10^{-2}$	3281	1412	0.031 (93)
H <sub>2</sub> S	0.20	1.73	4.74	1445*	$3.39 \times 10^{-2}$	3365	1240	0.023 (69)
C <sub>3</sub> H <sub>8</sub>	0.30	2.82	2.91	1138*	$4.32 \times 10^{-4}$	2021	1121	0.013 (92)
C <sub>3</sub> H <sub>8</sub>	0.08	4.27	1.92	1138*	$8.28 \times 10^{-2}$	3596	875	0.030 (92)

The value of  $q^o$  is calculated from  $q^*$  and  $n$  as  $q^o = q^*/n$ .

\*) Estimated from the Lennard-Jones potential depth ( $v = 4.8\epsilon_{LJ}$ ).

The values for  $\epsilon_{LJ}$  were taken from Reid, Prausnitz and Poling<sup>10</sup>.

\*\*) Average deviation,  $\sum_j |\Delta q|/n$ . The numbers in parentheses refer to the number of data points,  $n$ .

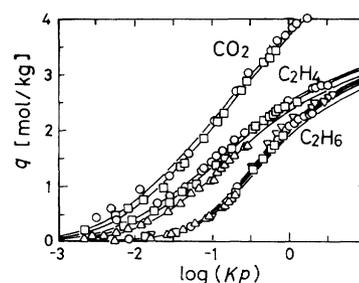
Only two types of sites, a and b, are presumed in correlating the pure component data because our knowledge of surface energy distribution is limited at present. Site b is assumed to be more active than site a ( $\Delta\epsilon = \epsilon_b - \epsilon_a > 0$ ). Since the inner surface of zeolites is exposed by oxygen atoms or cations<sup>15</sup>, the total amount of sites  $q^*$  may be estimated from the amount of oxygen per mass of adsorbent. For MS-13X we fixed a value of 11.4 mol/kg for  $q^*$ , which is half the amount of oxygen atoms in the adsorbent ( $\text{Na}_4\text{Al}_4\text{Si}_5\text{O}_{18} + 20 \text{ wt}\% \text{ binder}$ ), and 0.22 for  $f_b$ , which is estimated from the ratio of the amount of sodium to that of oxygen. Changing the value for  $q^*$  by 20–25% affected the average deviations very little in correlating the pure-gas isotherms because there remained four parameters,  $n$ ,  $K_o$ ,  $\epsilon_o$  and  $\Delta\epsilon$ , to be relaxed. The value of  $f_b$  seems a little sensitive to the correlational results, but 0.22 was used for all gases.

A value of 8.2 mol/kg was estimated for  $q^*$  of H-mordenite through Eq. (24) by considering the small adsorption capacity. After several trials for site fraction  $f_b$ , disparately different values were assigned for three gases, CO<sub>2</sub>, H<sub>2</sub>S and C<sub>3</sub>H<sub>8</sub>, on H-mordenite since the experimental data for pure-gas isotherms were not correlated satisfactorily when  $f_b$  had been fixed at some value.

The four parameters,  $n$ ,  $K_o$ ,  $\epsilon_o$  and  $\Delta\epsilon$ , were determined by the nonlinear-least-square method to fit the experimental isotherms at several temperatures. The Marquardt method<sup>5</sup>) was used for the optimization; the objective function was chosen as the sum of the square residuals  $\sum (q_{\text{cal}} - q_{\text{exp}})^2$ .

## 2.2 Adsorptions on molecular sieve 13X

Hyun and Danner<sup>4</sup>) reported single-component adsorption data for carbon dioxide (CO<sub>2</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and isobutane (*i*-C<sub>4</sub>H<sub>10</sub>) on MS-13X at several temperatures between 273 K and



**Fig. 1.** Amounts of pure CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> adsorbed on MS-13X: (○) 298.15 K, (□) 323.15 K, (△) 373.15 K, (▽) 273.15 K

373 K and pressures up to 138 kPa. The parameters determined for the four gases are listed in **Table 1** along with average deviations and number of data points.

**Figure 1** shows the experimental and the calculated amounts of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> against  $Kp$  on a semilogarithmic scale. The agreement between theory and experiments is good for the three gases; however, we observe systematic deviations for CO<sub>2</sub> in the region of low surface coverage where the experimental values for  $q$  are larger than the calculated ones. This may suggest that more active sites for CO<sub>2</sub> are present by several percent in MS-13X.

**Figure 2** shows similar plots for *i*-C<sub>4</sub>H<sub>10</sub> at three temperatures. Though the correlations by the hybrid model are fairly good, the experimental values for  $q$  in the region of high surface coverage tend to become saturated more rapidly than the calculated curves. In addition, the maximum amount  $q^o$  seems to decrease with increasing temperature. On careful inspection of Fig. 1 this observation has been found in isotherms of C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. We consider that the discrepancy at high surface coverages may be attributed to the curved surface in a zeolite crystal and that the mobile term ( $A_f$ ) in the partition

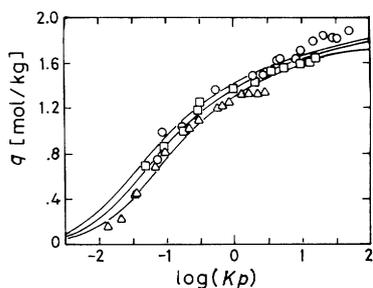


Fig. 2. Amounts of *i*-C<sub>4</sub>H<sub>10</sub> adsorbed on MS-13X: (○) 298.15 K, (□) 323.15 K, (△) 373.15 K

function should be altered.

Predictions of binary-gas adsorptions were made with four mixtures at 298.15 K and 137.8 kPa. The mixtures and data sources compared with the predictions are as follows.

- (1) C<sub>2</sub>H<sub>6</sub> + C<sub>2</sub>H<sub>4</sub><sup>1)</sup>      (2) C<sub>2</sub>H<sub>4</sub> + CO<sub>2</sub><sup>4)</sup>  
 (3) *i*-C<sub>4</sub>H<sub>10</sub> + C<sub>2</sub>H<sub>4</sub><sup>4)</sup>      (4) *i*-C<sub>4</sub>H<sub>10</sub> + C<sub>2</sub>H<sub>6</sub><sup>4)</sup>

In addition to the parameters listed in Table 1, the binary interaction parameters  $v_{ij}$  are required in the mixture calculations. They were estimated from the geometric-mean assumption for the parameter  $\alpha$ , not for  $v^8$ ; that is,

$$v_{ij} = (v_{ii}v_{jj}q_j^0/q_i^0)^{1/2} \quad (26)$$

Figure 3 shows a comparison of experimental and predicted mole-fractions in gas phase ( $y_1$ ) against the mole-fraction in adsorbed phase ( $z_1$ ). The agreement between theory and experiments is fairly good for mixtures (1), (2), and (4); however, for mixture (3), *i*-C<sub>4</sub>H<sub>10</sub> + C<sub>2</sub>H<sub>4</sub>, the prediction curve does not represent the experimental results, which show an azeotrope at a mole fraction of approximately 0.7. The azeotropic behavior will be explained by a negative site correlation that will be shown in the next section for mixed-gas adsorptions on H-mordenite. It is noted here that the results predicted by the IAS theory<sup>6)</sup> are almost the same as the theoretical curves shown in Fig. 3.

### 2.3 Adsorptions on H-mordenite

Talu and Zwiebel<sup>14)</sup> reported pure- and mixed-gas adsorptions for CO<sub>2</sub>, H<sub>2</sub>S and C<sub>3</sub>H<sub>8</sub> on H-mordenite (Type Z-900H). Pure-gas isotherms were correlated by the 2-site model with a value of 8.2 mol/kg for  $q^*$ . The parameters optimized are summarized in Table 1, where disparate values for  $f_b$  are found. The site fraction of more active site  $f_b$  was estimated as 0.08 from the ratio of the amounts of sodium and oxygen in H-mordenite (NaAlSi<sub>5</sub>O<sub>12</sub>) in the same manner as that for MS-13X. The value of 0.08 for  $f_b$  yields good correlations for CO<sub>2</sub> at the three temperatures 283, 303, and 323 K as shown in Fig. 4. For C<sub>3</sub>H<sub>8</sub>, however, a larger value of 0.30 for  $f_b$  was chosen to

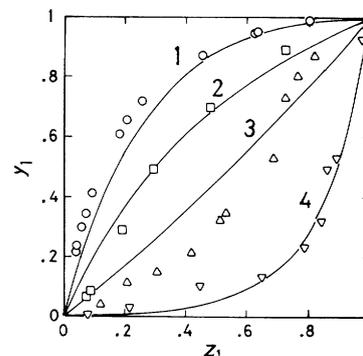


Fig. 3. Mole fractions for binary mixtures on MS-13X at 298.15 K and 137.8 kPa: (1) C<sub>2</sub>H<sub>6</sub> + C<sub>2</sub>H<sub>4</sub>, (2) C<sub>2</sub>H<sub>4</sub> + CO<sub>2</sub>, (3) *i*-C<sub>4</sub>H<sub>10</sub> + C<sub>2</sub>H<sub>4</sub>, (4) *i*-C<sub>4</sub>H<sub>10</sub> + C<sub>2</sub>H<sub>6</sub>; the first is component 1. Solid lines are calculated from the positive site correlation discussed in section 2.3.

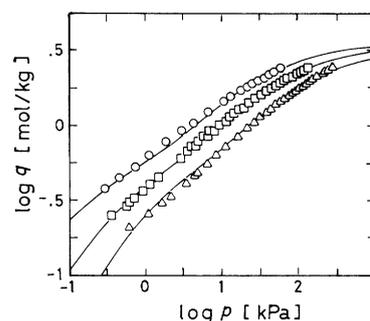


Fig. 4. Isotherms of CO<sub>2</sub> on H-mordenite: (○) 283.2 K, (□) 303.2 K, (△) 323.2 K

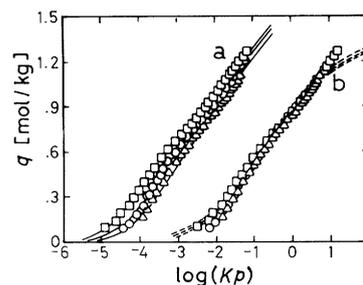


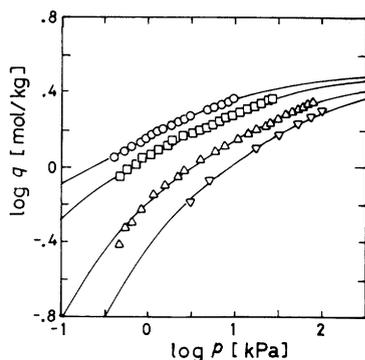
Fig. 5. Comparison of isotherms calculated from different values of  $f_b$  for C<sub>3</sub>H<sub>8</sub> on H-mordenite: (○) 283.1 K, (□) 303.2 K, (△) 324.3 K: (—)  $f_b = 0.30$ ; (----)  $f_b = 0.08$

get satisfactory correlation; in Fig. 5, comparison is made with the two results calculated from the values of 0.30 (solid lines) and 0.08 (dotted lines). The value of 0.20 was assigned for H<sub>2</sub>S and comparison is made with the experimental isotherms at four temperatures in Fig. 6.

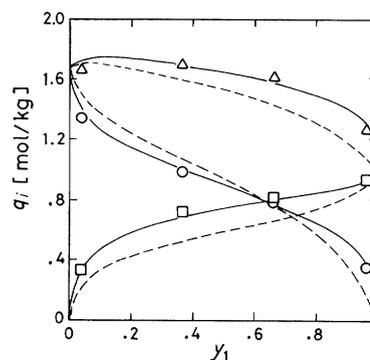
The different values for  $f_b$  assigned for pure gases inevitably divide the surface into at least three regions for binary mixtures of gases. When the lower-energy site for CO<sub>2</sub> ( $f_b = 0.08$ ) is overlapped with the lower-energy site for C<sub>3</sub>H<sub>8</sub> ( $f_b = 0.30$ ), the sites are divided into three fractions, 0.08, 0.22 and 0.70, which we may call the perfect positive correla-

**Table 2.** Site assignments for binary mixtures on H-mordenite

Gas mixture		NEGATIVE correlation			POSITIVE correlation		
C <sub>3</sub> H <sub>8</sub> (1) CO <sub>2</sub> (2)	$f_m$	0.62	0.30	0.08	0.70	0.22	0.08
	$\Delta\varepsilon_{m1}/k$ [K]	0	1121	0	0	1121	1121
	$\Delta\varepsilon_{m2}/k$ [K]	0	0	1412	0	0	1412
C <sub>3</sub> H <sub>8</sub> (1) H <sub>2</sub> S(2)	$f_m$	0.50	0.30	0.20	0.70	0.10	0.20
	$\Delta\varepsilon_{m1}/k$ [K]	0	1121	0	0	1121	1121
	$\Delta\varepsilon_{m2}/k$ [K]	0	0	1240	0	0	1240
CO <sub>2</sub> (1) H <sub>2</sub> S(2)	$f_m$	0.72	0.20	0.08	0.80	0.12	0.08
	$\Delta\varepsilon_{m1}/k$ [K]	0	0	1412	0	0	1412
	$\Delta\varepsilon_{m2}/k$ [K]	0	1240	0	0	1240	1240



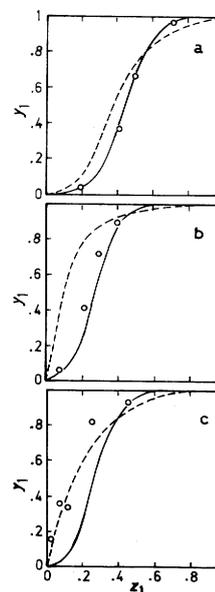
**Fig. 6.** Isotherms of H<sub>2</sub>S on H-mordenite: (○) 283.2 K, (□) 303.2 K, (△) 338.2 K (▽) 378.2 K



**Fig. 7.** Comparison of negative and positive site correlations for predicting the amounts adsorbed on H-mordenite for binary mixtures C<sub>3</sub>H<sub>8</sub>(1) + CO<sub>2</sub>(2) at 303.2 K and 41 kPa: (—) negative; (----) positive

tion for the site energy as used by Valenzuela *et al.*<sup>16)</sup> in their heterogeneous ideal adsorbed solution approach. On the contrary, in the case of negative site correlation the sites on a surface should be divided into the fractions 0.08, 0.30 and 0.62. **Figure 7** shows a comparison of the two predictions with the experimental adsorption data for the system of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> on H-mordenite at 303 K and total pressure of 41 kPa. It is remarkable that the solid lines calculated from the negative correlation fit the binary data better than the broken lines from the perfect positive correlation.

In **Table 2** details of site assignments by the two correlations are summarized for three binary mixtures, and in **Fig. 8** comparisons of the two correlations are made for prediction of the equilibrium compositions by plotting  $y_1$  against  $z_1$ . The negative correlation shown by the solid lines represents the  $y$ - $z$  relations for two binary mixtures, (a) C<sub>3</sub>H<sub>8</sub> + CO<sub>2</sub> and (b) C<sub>3</sub>H<sub>8</sub> + H<sub>2</sub>S, while the perfect positive correlation shown by the broken lines fits to the  $y$ - $z$  relations for the binary mixture (c) CO<sub>2</sub> + H<sub>2</sub>S. These results tell us that the active sites for CO<sub>2</sub> and H<sub>2</sub>S, both having acidic characteristic, are competitive but not competitive with those for C<sub>3</sub>H<sub>8</sub>, a saturated hydrocarbon.



**Fig. 8.** Comparison of negative and positive site correlations for predicting the mole fraction of binary mixtures adsorbed on H-mordenite at 303.2 K: (a) C<sub>3</sub>H<sub>8</sub> + CO<sub>2</sub> [41 kPa]; (b) C<sub>3</sub>H<sub>8</sub> + H<sub>2</sub>S [8.1 kPa]; (c) CO<sub>2</sub> + H<sub>2</sub>S [15 kPa]; the first is component 1. (—) negative; (----) positive

## Concluding remarks

A hybrid isotherm equation is derived from a view that the mobile molecules may spend different amounts of time on different energy sites. The key element in describing the picture via the partition function is the ordering function  $\Omega$ , introduced in Eq. (5); it throws a new light on the quasi-chemical approximation originally proposed by Guggenheim for explaining the non-random mixing in liquid mixtures. The hybrid concept does not specify the scaled particle theory for describing the free area; for example, the two-dimensional van der Waals equation would be useful for its simplicity.

The site fractions are sensitive to pure-gas isotherms and the assignment of sites is crucially important for calculating mixed-gas adsorption. It has been shown that the enhancement of adsorption for mixtures  $C_3H_8 + CO_2$  and  $C_3H_8 + H_2S$  on H-mordenite, which are characterized by negative deviations from Raoult's law, is attributable to the negative site correlation.

Note: Computer programs of the hybrid isotherm equation written in FORTRAN are available upon request to T.N.

## Nomenclature

$A$	= surface area	[m <sup>2</sup> ]
$A_f$	= surface free area	[m <sup>2</sup> ]
$A_{site}$	= surface area of a site	[m <sup>2</sup> ]
$d$	= diameter of hard disk	[m]
$E$	= potential energy	[J]
$f_m$	= site fraction	[—]
$h$	= Planck constant	[J·s]
$j$	= internal molecular partition function	[—]
$K$	= adsorption equilibrium constant on a (hypothetical) reference site a	[Pa <sup>-1</sup> ]
$k$	= Boltzmann constant	[J/K]
$L$	= Avogadro constant	[mol <sup>-1</sup> ]
$M$	= total number of sites	[—]
$N$	= number of molecules	[—]
$N_m$	= number of sites attached by a segment of molecule	[—]
$n$	= number of sites occupied by a molecule	[—]
$p$	= pressure	[Pa]
$Q$	= canonical partition function	[—]
$q$	= amount adsorbed per mass of adsorbent	[mol/kg]
$q^o$	= maximum amount adsorbed	[mol/kg]
$q^*$	= total amount of sites	[mol/kg]
$R$	= gas constant	[J/(K·mol)]
$r_m$	= ratio of the Boltzmann factor on site $m$ and that on site a	[—]
$S_{BET}$	= BET surface area	[m <sup>2</sup> /kg]
$T$	= temperature	[K]
$T_o$	= reference temperature (= 298.15 K)	[K]
$v$	= interaction parameter (= $2\alpha/\beta$ )	[J]
$y$	= mole fraction in gas phase	[—]

$z$	= mole fraction in adsorbed phase	[—]
$\alpha$	= molecular interaction parameter	[J·m <sup>2</sup> ]
$\beta$	= molecular cross-sectional area	[m <sup>2</sup> ]
$\Gamma$	= local activity coefficient defined in Eq. (15)	[—]
$\varepsilon_m$	= minus of adsorption energy on site $m$	[J]
$\varepsilon_o$	= minus of molecular adsorption energy on a (hypothetical) reference site a	[J]
$\Delta\varepsilon$	= $\varepsilon_b - \varepsilon_a$	[J]
$\varepsilon_{LJ}$	= energy depth for the Lennard-Jones potential	[J]
$\eta$	= dimensionless surface density	[—]
$\theta$	= surface coverage	[—]
$\theta_m$	= site coverage on site $m$	[—]
$\lambda$	= thermal de Broglie wavelength	[m]
$\mu$	= chemical potential	[J]
$\phi$	= fugacity coefficient	[—]
$\Omega$	= ordering function	[—]

## <Subscripts>

$i$	= component $i$
$ij$	= pair of components $i$ and $j$
$m$	= refers to site $m$
$o$	= refers to a reference temperature

## <Superscripts>

$g$	= refers to gas phase
$s$	= refers to surface or adsorbed phase

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