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An Equilibrium Relation for Gas Adsorption Applications

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Abstract. A new multicomponent equilibrium relation is proposed for engineering applications. This relation is based on a lattice model for mixtures of unequally sized molecules. An approximation is introduced for loading-dependent enthalpies of adsorption that simplifies the energy balance in fixed-bed models and allows efficient solution of the equation set in process simulations. Comparisons are made with nonideal binary data in the literature.

Keywords: adsorption equilibrium, lattice theory, pressure swing adsorption

Introduction

Important gas separation and purification processes are based on the selective adsorption of components from the gas phase by a solid adsorbent. Accurate predictions of multicomponent equilibria from pure-component data or limited mixture data are required for accurate process modeling. An additional concern is the simplicity of the equilibrium calculation, since simulations of adsorption processes are computationally intense. Thus, both accuracy and computational simplicity determine the efficiency of the equilibrium model in process simulations (Malek and Farooq, 1996).

In addition to efficiency, it is desirable for the equilibrium relation to have a theoretical basis, to have the proper low-pressure limit, and to have well-behaved enthalpies of adsorption. If the latter requirements are not satisfied, extrapolations beyond experimental conditions are more uncertain. A further requirement of an equilibrium relation is an explicit temperature dependence, since gas separation processes are usually nonisothermal.

The purpose of this paper is to present a new multicomponent equilibrium relation for process engineering applications. An objective is to represent molecular size differences of mixture components and adsorbent heterogeneity in a simple, computationally tractable fashion. The relation is based on the lattice theory of adsorption, and it meets the requirements outlined above. Following a discussion of the lattice model, example applications are given to experimental data from the literature.

Lattice Theory

Adsorption of a single layer of molecules on a lattice of adsorption sites is a simple idealization of physical adsorption on solid surfaces. In this model, an adsorbate molecule is localized on a set of adsorption sites and does not translate parallel to the surface. In general, an adsorbate molecule can occupy multiple sites, and different types of molecules in a mixture can have different sizes. When each adsorbate molecule occupies a single site, we recover the well-known Langmuir model.

Lattice models have also been used for liquids and are the basis for methods of estimating thermodynamic properties of liquid solutions (see Prausnitz et al., 1986). A lattice theory for adsorption is formally obtained from a lattice theory for liquid solutions by treating one of the components in the liquid mixture (a monomer) as a vacant site. Recently, Russell and LeVan (1996) transformed Guggenheim's (1952) lattice theory of solutions into a gas adsorption theory by the foregoing procedure. The equilibrium relation for adsorption of an ideal gas mixture on a uniform

surface with no adsorbate–adsorbate interactions may be written as

$$P_j(T,\underline{\theta}) = \frac{\theta_j\left[1-\sum_i \frac{2\theta_i(r_i-1)}{z}\right]^{r_j-1}}{A_j \exp\left(\frac{-\Delta h_j}{RT}\right)\left(1-\sum_i r_i\theta_i\right)^{r_j}} \quad (1)$$

where P_j is the partial pressure of component j in the gas phase, $\theta_j = n_j/m$ is a dimensionless loading of component j on the adsorbent, and $\underline{\theta}$ is the set of loadings for all mixture components. Equation (1) can be derived from the result of Russell and LeVan by applying the relation

$$\Delta h_j = -RT^2\left(\frac{\partial \ln P_j}{\partial T}\right)_{\underline{\theta}} \quad (2)$$

for the isosteric enthalpy of adsorption of component j and assuming that $\Delta h_j \neq \Delta h_j(T)$.

The physical model underlying Eq. (1) is a random distribution of chain-like molecules with sizes r_i ($i = 1, 2, \ldots$) on a uniform lattice with m adsorption sites of coordination number z. The parameters in Eq. (1) are $\{m, z, r_i, A_i, \Delta h_i\}$; these parameters are independent of temperature, either due to the nature of the physical model (m, z, r_i) or by assumption (Δh_i).

Enthalpy of Adsorption

For most adsorbate–adsorbent systems, the isosteric enthalpy of adsorption is a function of the amount adsorbed. This is due to adsorbent heterogeneity and adsorbate–adsorbate interactions (see Rudzinski and Everett, 1992). Often, adsorbent heterogeneity is more important than adsorbate–adsorbate interactions, and the isosteric enthalpy of adsorption decreases in magnitude with loading.

Adsorbent heterogeneity can be modeled in a rigorous fashion (e.g., with a patch model), but results are often not practical from an engineering perspective; for example, calculations can become too slow for simulations of pressure swing adsorption (PSA) cycles. Thus, a simple approximation is proposed to account for loading-dependent enthalpies. It is assumed that Δh_j varies with θ_j independently of adsorption of other mixture components. That is,

$$\Delta h_j = \Delta h_j(\theta_j). \quad (3)$$

In other words, enthalpies of mixture components are the same as they would be if the components were alone on the surface. Equation (3) satisfies differential and integral consistency tests for heats of adsorption (Dunne et al., 1997). This approximation is introduced in order to capture the salient effects of loading-dependent enthalpies while maintaining computational efficiency. The equilibrium equations can be written as implicit functions ($\theta_i = f_i(\underline{\theta}); i = 1, 2, \ldots$), and together with conservation and rate equations can be solved as a differential–algebraic set. This method is much more efficient than solving the equilibrium equations separately. Also, the calculation of the heat of adsorption in the energy balance is greatly simplified since Δh_j is independent of temperature and loading ($i \neq j$). The function $\Delta h_j(\theta_j)$ should be smooth, nonpositive, and finite on the entire domain $0 \leq \theta_j < 1/r_j$.

As an example, the simple exponential function

$$\Delta h_j = \Delta h_j^o \exp(-k_j\theta_j), \quad (4)$$

where k_j is a constant, is chosen for Δh_j in Eq. (1). The constant k_j will usually be greater than zero, giving a decreasing (in magnitude) enthalpy of adsorption with loading; however, k_j can also be less than or equal to zero.

Selectivity

A measure of the partitioning of two components between fluid and adsorbed phases is the selectivity, defined by

$$s_{1,2} = \frac{x_1/y_1}{x_2/y_2}. \quad (5)$$

It follows from Eq. (1) that $s_{1,2}$ for the lattice model is given by

$$s_{1,2} = \frac{A_1}{A_2}\exp\left(\frac{\Delta h_2 - \Delta h_1}{RT}\right) \times \left[\frac{z(1-\sum_i r_i\theta_i)}{z-\sum_i 2\theta_i(r_i-1)}\right]^{r_1-r_2}. \quad (6)$$

From Eq. (6), we see that $s_{1,2}$ has the proper limiting behavior as $P \to 0$ (Henry's law). Also, we see that $s_{1,2}$ is proportional to the product of an enthalpic term and an entropic term. Adsorbent heterogeneity often causes a decrease in $s_{1,2}$ with loading ($\Delta h_2 - \Delta h_1$ decreases). Molecular size differences can also cause a decrease in $s_{1,2}$ with loading, as discussed below.

Configurational Entropy and Flory's Approximation

To focus on the entropic contribution to $s_{1,2}$, we set $\Delta h_1 = \Delta h_1^o$ and $\Delta h_2 = \Delta h_2^o$ in Eq. (6) to obtain

$$s_{1,2} = s_{1,2}^o \left[\frac{z(1 - \sum_i r_i \theta_i)}{z - \sum_i 2\theta_i (r_i - 1)} \right]^{r_1 - r_2}. \qquad (7)$$

The parameter r is related to the size of an adsorbate molecule and is proportional to the area occupied by the molecule on the surface (Nitta et al., 1984); strictly, r is the number of lattice sites occupied by the molecule. When $r_1 = r_2$ in Eq. (7), the entropic contribution to $s_{1,2}$ vanishes, and $s_{1,2}$ is constant. The importance of the entropic contribution increases as the difference $r_1 - r_2$ increases.

An important simplification of Eq. (7) (or Eq. (1)) is formally obtained by setting $z = \infty$. Following Guggenheim (1952), this simplification will be called Flory's approximation. When this approximation is applied to Eq. (7), we obtain the selectivity for the so-called multisite Langmuir model. The meaning of Flory's approximation is that the segments comprising a molecule are assumed to be mutually independent, as if they were not connected. This can be readily seen from the kinetic derivation of the multisite Langmuir equation (Henry, 1922). Thus, Flory's approximation overestimates the configurational degeneracy (entropy) of the system

The significance of molecular size differences and Flory's approximation on the selectivity is demonstrated in Fig. 1. The abscissa in Fig. 1 is the fraction of the surface that is covered by adsorbate molecules, and the curves are plots of Eq. (7) with $z = 6$ and $z = \infty$ (the solid lines are nearly independent of x_1). We see that the selectivity for the larger molecule diminishes with surface coverage and that the diminution is more rapid for larger values of $r_1 - r_2$. This is because the likelihood of finding r contiguous adsorption sites decreases more rapidly with surface coverage for larger values of r. Also from Fig. 1, we see that the accuracy of Flory's approximation decreases as the difference of molecular sizes increases.

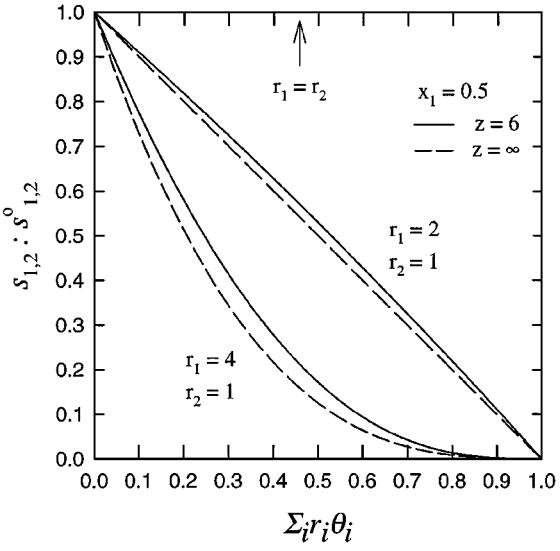

Figure 1. Selectivity for the larger molecule in a binary mixture.

Gibbs Adsorption Isotherm

The analogue of the Gibbs-Duhem equation for adsorption of an ideal gas is

$$\mathcal{A} d\pi = RT \sum_i n_i d \ln P_i \quad \text{constant } T. \qquad (8)$$

Theories for a homogeneous adsorbed phase must satisfy Eq. (8) for thermodynamic consistency. A necessary (but not sufficient) condition for satisfaction of Eq. (8) for a binary mixture is

$$\left(\frac{\partial \ln P_1}{\partial n_2} \right)_{T,n_1} = \left(\frac{\partial \ln P_2}{\partial n_1} \right)_{T,n_2}. \qquad (9)$$

Equation (9) follows from Eq. (8) by using the fact that the order of differentiation of crossed partial derivatives is immaterial for continuous derivatives. It can readily be shown that Eqs. (1) and (3) satisfy condition (9).

The integration of Eq. (8) for a pure component is required for ideal adsorbed solution (IAS) calculations (Myers and Prausnitz, 1965). This integration can be performed analytically with Eqs. (1) and (4). The result is

$$\frac{\pi \mathcal{A}}{RT} = \frac{zm}{2} \ln \left[1 - \frac{2\theta(r-1)}{z} \right] - m \ln(1 - r\theta) - \frac{m \Delta h^o}{RT} \left[\frac{1}{k} - \frac{1}{k \exp(k\theta)} - \frac{\theta}{\exp(k\theta)} \right]. \qquad (10)$$

Examples

The lattice model discussed in the previous section, with Eq. (4) for $\Delta h_j(\theta_j)$, was applied to experimental data of Reich et al. (1980) for adsorption of methane and ethane on BPL activated carbon and of Talu and

Table 1. Parameter values in Eq. (1) for data of Reich et al. and Talu and Zwiebel.

	BPL carbon		H-mordenite	
Parameter	CH_4	C_2H_6	H_2S	C_3H_8
m(mol kg^{-1})	34.85	34.85	11.80	11.80
r	3.285	3.559	2.257	5.800
A(kPa^{-1})	1.555×10^{-7}	7.729×10^{-8}	8.209×10^{-8}	7.265×10^{-8}
Δh^o(kJ mol^{-1})	−18.01	−27.11	−41.48	−37.56
k	0.3264	0.7055	1.387	1.217

Zwiebel (1986) for adsorption of hydrogen sulfide and propane on H-mordenite. These data sets are well known for deviations from ideal behavior.

The parameters in Eq. (1) are $\{m, r_i, A_i, \Delta h_i^o, k_i\}$. As indicated previously, these parameters are independent of temperature. The parameter m is a property of the adsorbent and is the same for all adsorbates. The value of z was chosen a priori as $z = 6$. Thus, the number of adjustable parameters in the model is $4 \times$ (number of gases) $+ 1$. These parameters were determined from fits to multiple pure-component isotherms and are given in Table 1. Excellent fits were obtained for both data sets.

Predictions of Eq. (1) are compared with experimental mixture data of Reich et al. in Fig. 2 and Table 2. Also shown are predictions for an ideal adsorbed solution with the same pure-component isotherms. We see from Fig. 2 that predicted selectivities by the lattice model are in relatively good agreement with data, whereas the IAS mixing rule does not accurately predict the sharp decline in selectivity with total pressure. Mean deviations in Table 2 show that predictions of the lattice model are better than IAS, except at $T = 213$ K where the lattice model over-predicts the methane loading. Molecular size differences are not significant for this system (similar values of r), and differences between Eq. (1) and IAS are enthalpic in origin (adsorbent heterogeneity).

Predictions are compared with data of Talu and Zwiebel in Fig. 3 and Table 2. Predictions of the lattice model are in relatively good agreement with data for this highly nonideal system, including a correct prediction of an azeotrope at low propane mole fractions in Fig. 3. Molecular size differences are

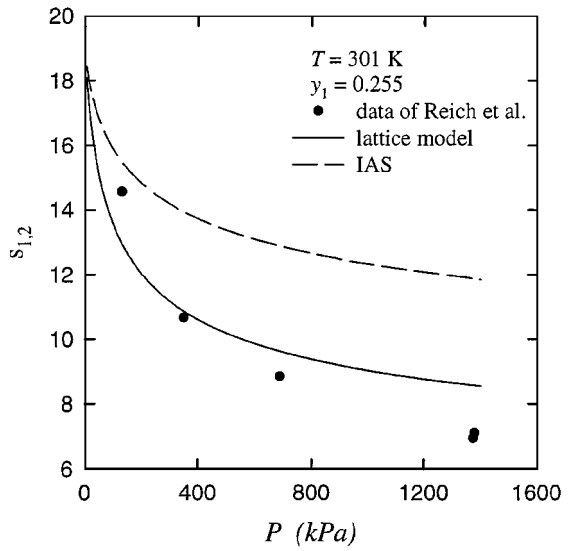

Figure 2. Comparison of predicted selectivities by the lattice model and IAS with experimental data for ethane (1) and methane (2) adsorbed in BPL carbon.

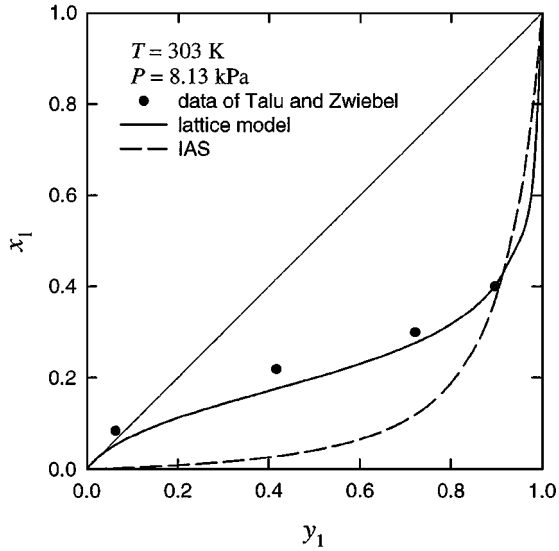

Figure 3. Equilibrium composition diagram for propane (1) hydrogen sulfide (2) mixtures adsorbed on H-mordenite at constant temperature and pressure.

Table 2. Mean deviations between predicted and experimental loadings for components in binary mixtures.

				Lattice model		IAS	
Adsorbates	Adsorbent	T(K)	N_{data}	D_1	D_2	D_1	D_2
C_2H_6(1)–CH_4(2)	BPL carbon	213	9	2.89	75.2	1.95	33.1
C_2H_6(1)–CH_4(2)	BPL carbon	260	3	1.19	20.8	2.49	21.4
C_2H_6(1)–CH_4(2)	BPL carbon	301	14	2.38	22.6	3.14	40.6
C_3H_8(1)–H_2S(2)	H-mordenite	303	8	13.4	16.3	41.8	35.2

$$D_i = \frac{100}{N_{\text{data}}} \sum_{k=1}^{N_{\text{data}}} \left| \frac{n_i^{\text{calc}} - n_i^{\text{exp}}}{n_i^{\text{exp}}} \right|_k ; \; N_{\text{data}} = \text{No. of data points}$$

significant for this system, as well as adsorbent heterogeneity.

Conclusions

A new equilibrium relation is proposed for engineering applications. This relation has a basis in the lattice theory of adsorption and represents molecular size differences of mixture components and variable heats of adsorption in a simple, computationally manageable fashion. The model has the proper low-pressure limit (Henry's law), it is consistent with the Gibbs adsorption isotherm, and the isosteric enthalpy of adsorption is well-behaved over the entire range of loadings. The parameters in the model are independent of temperature and can be determined from pure-gas isotherms, allowing predictions of mixture properties.

Comparisons with literature data show that mixture predictions can be relatively accurate for nonideal systems. In addition to accuracy, computational efficiency in process simulations can be obtained by writing the equilibrium equations as implicit functions in the overall differential–algebraic set.

Nomenclature

A	pre-exponential factor in Henry constant	Pa^{-1}
$\mathcal{A}$	specific area	$\text{m}^2\ \text{kg}^{-1}$
Δh	isosteric enthalpy of adsorption	J mol^{-1}
m	number of adsorption sites per unit mass of adsorbent	mol kg^{-1}
n	amount adsorbed per unit mass of adsorbent	mol kg^{-1}
r	parameter related to size of adsorbate molecule	—
R	gas constant	$\text{J mol}^{-1}\ \text{K}^{-1}$
T	absolute temperature	K
x	mole fraction in adsorbed phase	—
y	mole fraction in gas phase	—
z	coordination number of lattice	—

Greek Letters

π	spreading pressure	N m^{-1}

Superscripts

o limiting value as $P \to 0$

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