Multicomponent Adsorption Equilibrium: Henry's Law Limit for Pore-Filling Models

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Introduction

Pore-filling models have long been used to correlate the effects of pressure and temperature on the adsorption of gases. Most of these models are based on the Polanyi potential theory (Lewis et al., 1950a; Grant and Manes, 1966; Dubinin, 1975; Mehta and Danner, 1985; Doong and Yang, 1988). A recent model is instead based on an Antoine-type equation (Hacskaylo and LeVan, 1985). We will restrict our discussion to models with common assumptions of a "liquid-like" adsorbed phase and a dependence of fractional filling of the pore volume on adsorbate pressure. When these models are extended to a mixed adsorbed phase, it is generally assumed that the adsorption potential or reference pressure of each component can be calculated from the mixture adsorbate volume (Lewis et al., 1950b; Grant and Manes, 1966). The fugacities of the vapor and adsorbed phases of each component are frequently related for pore-filling models by the expression

$$Py_i = \gamma_i x_i P_i^o(\theta) \qquad \text{(constant } T\text{)} \tag{1}$$

where θ is the total fractional filling of the pore volume with all components and $P_i^o(\theta)$ is the reference pressure of pure component i at the θ of the mixture. θ is defined assuming all molecules have equal access to the entire pore volume. The applicability of Eq. 1 to pore-filling models at low loading and the development of an improved expression are the subjects of this note.

Henry's Law Limit

A fundamental test for any adsorption equilibrium relation is its behavior in the limit of low loading. In this limit, for the adsorption of a vapor of a single component, the amount adsorbed becomes directly proportional to the pressure of the vapor (Hill, 1960), and we write the pure component isotherm as

$$P = kn \tag{2}$$

For pore-filling models, with $\theta = n/n_{max}$, Eq. 2 becomes

$$P = K\theta \tag{3}$$

In Eqs. 2 and 3, k and K represent Henry's law constants and are functions of temperature. Pure component models based on the Polanyi potential theory do not reduce to a linear isotherm at low loading and thus cannot satisfy this Henry's law limit (Ruthven, 1984). The model based on the Antoine equation does reduce to a linear isotherm.

For a mixture at low loading, the amount of each component adsorbed is proportional to its partial pressure (Hill, 1960); thus,

$$Py_i = k_i n_i \tag{4}$$

or, for a pore filling model,

$$Py_i = K_i \theta_i \tag{5}$$

where n_i is the number of moles of component i adsorbed and θ_i is the fractional filling of the pore volume with component i. This means the adsorbed components behave independently, not being influenced by the presence of each other. The fractional filling of the pore volume with each component θ_i can be related to the total fractional filling of the pore volume by the volume fraction w_i; thus, we have

$$\theta_i = w_i \theta \tag{6}$$

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where

$$w_i = \frac{x_i v_i}{\Sigma_j x_j v_j} \tag{7}$$

in which v_i is the molar volume of component i. Substituting Eq. 6 into Eq. 5 we obtain

$$P y_i = K_i w_i \theta \tag{8}$$

For the Henry's law limit, we have $P_i^o(\theta) = K_i \theta$, which gives

$$P y_i = w_i P_i^o(\theta) \tag{9}$$

This expression represents the pore-filling relation for a mixture at low loading. It indicates that volume fraction is the relevant measure of concentration for pore-filling models at low-loading. The appearance of the volume fraction is a direct result of assuming that the components act independently in the limit of low loading.

Thermodynamic Consistency

We will now redevelop Eq. 9 from an established thermodynamic approach. For an ideal adsorbed solution, Myers and Prausnitz (1965) wrote

$$P y_i = x_i P_i^o(\pi) \tag{10}$$

where π is the mixture spreading pressure. π is calculated for a pure component from

$$\frac{\pi A}{RT} = \int_o^{P_i^o(\pi)} \frac{n}{P}\, dP \tag{11}$$

We can replace n for pure component i by $n_i = \theta n_{max_i}$ and apply Eq. 3 for the Henry's law limit to get

$$P_i^o(\pi) = \frac{K_i}{n_{max_i}} \frac{\pi A}{RT} \tag{12}$$

The Gibbs adsorption isotherm can be written for an ideal mixture as (Gibbs, 1928)

$$\frac{A}{RT}\, d\pi = \sum_i \frac{n_i}{P_i}\, dP_i \tag{13}$$

For linear isotherms, Eq. 13 can be integrated to give

$$\frac{\pi A}{RT} = \sum_i n_i = n_{tot} \tag{14}$$

Now, since $P_i^o(\pi)$ is evaluated at π of the mixture we can substitute Eq. 14 into Eq. 12 to get

$$P_i^o(\pi) = K_i \frac{n_{tot}}{n_{max_i}} \tag{15}$$

Substituting Eq. 15 into the equilibrium expression Eq. 10, gives Eq. 5 which leads as before to Eq. 9. Thus, changing the reference pressure from $P_i^o(\pi)$ to $P_i^o(\theta)$ results in a fundamental change in the equilibrium expression at low-loading.

Discussion

We will now consider the application of Eq. 1 to the low loading limit. Equation 9 is the correct expression for this limit. To make Eq. 1 agree with Eq. 9, the activity coefficient in Eq. 1 must be $\gamma_i = w_i/x_i$ to correctly represent the Henry's law limit. This is not desirable since real solutions are expected to approach ideal behavior at infinite dilution. For the special case when the components of the mixture have equal molar volumes, the mole fraction and the volume fraction become equivalent and Eq. 1 with $\gamma_i = 1$ is correct.

The low-loading limit should be treated as the ideal case. For liquid mixtures it is generally assumed that for an ideal solution the fugacity of each component is directly proportional to its mole fraction (Prausnitz et al., 1985)

$$f_i = H_i x_i \tag{16}$$

where

$$H_i = H_i(T, P) \tag{17}$$

The mole fraction is chosen as the appropriate measure of concentration based on a rough kinetic argument (Denbigh, 1955; Lewis et al., 1961). The choice of the mole fraction gives rise to two ideal cases, Raoult's law and Henry's law, depending on the choice of H_i. We have shown that Henry's law defined in this way does not yield the correct expression for pore-filling models.

To define an ideal solution for adsorption in the Henry's law limit with the reference pressure $P_i^o(\theta)$, the measure of concentration must be the volume fraction; thus, we have

$$f_i = H_i w_i \tag{18}$$

where

$$H_i = P_i^o(\theta, T) = K_i(T)\theta \tag{19}$$

Again, if the molar volumes of all components are the same, Eqs. 16 and 18 are equivalent, with H_i for adsorption given by Eq. 19.

Acknowledgment

The authors are grateful to the National Science Foundation (Grant CBT-8417673) and the Petroleum Research Fund (Grant 18418-AC7) for financial support.

Notation

A = adsorbent area, m^2/kg
f = fugacity, MPa
H = proportionality constant
k, K = Henry's law constants
n = adsorbed-phase concentration, mol/kg
n_{max} = adsorbed-phase concentration at filling of pore volume, mol/kg
n_{tot} = total adsorbed-phase concentration, mol/kg
P = pressure, MPa
P^o = reference pressure, MPa
R = gas constant
T = temperature, K
v = molar volume, m^3/mol

w = volume fraction in adsorbed phase
x = mole fraction in adsorbed phase
y = mole fraction in gas phase

Greek letters

γ = activity coefficient
π = spreading pressure, N/m
θ = fraction of pore volume filled

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Manuscript received June 10, 1988, and revision received Aug. 8, 1988.