On the Gonzalez-Holland Model for Adsorption of Gas Mixtures

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Recently, Gonzalez and Holland (1970, 1971) derived interesting equations for multilayer adsorption isotherm of m-component gas mixtures on homogeneous surfaces:

$$\Theta_{(m)}^{M} = \frac{\Phi_{(m)1}}{1+\Phi_{(m)1}}\left[1 + \nu\Phi_{(m)1} + \nu^3\Phi_{(m)1}^{2} + \dots + \nu^{\frac{n(n-1)}{2}}\Phi_{(m)1}^{n-1}\right] \quad (1a)$$

and

$$\Theta_{(m)}^{M} = \Phi_{(m)1}\,\Omega_{n-1} \Big/ \left[\prod_{j=0}^{n-1}\left(1+\nu^j\Phi_{(m)1}\right)\right] \quad (1b)$$

In the above equations

$$\Phi_{(m)j} = \sum_{i=1}^{m} K_{j,i}\,p_i \qquad (1 \leq j \leq n-1) \quad (2)$$

$$\nu = \frac{K_{j+1,i}}{K_{j,i}} = \frac{\phi_{(m)j+1}}{\phi_{(m)j}} \qquad (1 \leq j \leq n-1) \quad (3)$$

$$\Omega_{n-1} = \Omega_{n-2}(1+\nu^{n-1}\Phi_{(m)1}) + \nu^{\frac{(n-1)n}{2}}\Phi_{(m)1} \quad \text{for} \quad n \geq 2$$
$$\Omega_0 = 1 \quad (4)$$

Equation (1*a*) has been derived on the assumption that the adsorption of all components in the second and higher layers is small relative to the adsorption of the components in the first layer. When the above assumption is not made, the more general result given by Equation (1*b*) is obtained. Both Equations (1*a*) and (1*b*) have been obtained on the basis of a Langmuir model with three additional assumptions characterizing the formation of mixed multilayer.

1. The adsorption of a given molecule in a given layer is independent of the identity of the molecule adsorbed beneath it in the previous layer.
2. The ratio of parameters characterizing the formation of the $(j+1)^{\text{th}}$ and j^{th} layer is constant, and it is independent of the kind of the component.
3. The adsorption layers are treated as independent; that is, the adsorption potential of the i^{th} component in the j^{th} layer $\mu_{j,i}$ is equal to the chemical potential of the i^{th} component in the gas phase ($\mu_{j,i} = \mu_i$).

However, the BET equation is based on the assumption that formation of the j^{th} layer depends upon formation of the $(j-1)^{\text{th}}$ layer; $\mu_{j,i} \neq \mu_i$ (see Hill, 1952).

Assumption 3 makes possible the separation of monolayer and multilayer effects in total adsorption; that is, the multilayer adsorption isotherm may be presented in the form of the product of the monolayer isotherm and a certain function describing the formation of the multilayer.

In this note it will be shown that assumption 3 seems to be too rough. If assumptions 1 and 2 are good enough for adsorption of similar components, then assumption 3 can be satisfied for the systems characterized by a small multilayer effect. This problem will be discussed on the example of adsorption of binary gas mixtures on homogeneous surfaces on the basis of the model proposed by Berezin and Kiselev (1972*a*) for adsorption of pure gases.

For this purpose, the model of Berezin and Kiselev will be generalized to adsorption of the mixture of gases A and B on a homogeneous surface. According to this model, the multilayer adsorption process may be represented by series of the following reactions:

$$\text{first layer}\begin{cases} A + S \rightleftharpoons A_1 & \text{with reaction constant } K_{1,A_1} \\ B + S \rightleftharpoons B_1 & \text{with constant } K_{1,B_1} \end{cases} \quad (5a)$$

$$\text{second layer}\begin{cases} A + A_1 \rightleftharpoons A_1A & \text{with constant } K_{2,A_1A} \\ A + B_1 \rightleftharpoons B_1A & \text{with constant } K_{2,B_1A} \\ B + A_1 \rightleftharpoons A_1B & \text{with constant } K_{2,A_1B} \\ B + B_1 \rightleftharpoons B_1B & \text{with constant } K_{2,B_1B} \end{cases} \quad (5b)$$

.... and so on. The constants of reactions (5*a*) and (5*b*) may be expressed by the following equations:

$$K_{1,A_1} = \frac{\Theta_{A_1}}{p_A[1-\Theta_{(2)}]} \qquad K_{1,B_1} = \frac{\Theta_{B_1}}{p_B[1-\Theta_{(2)}]} \quad (6)$$

and

$$K_{2,A_1A} = \frac{\Theta_{A_1A}}{p_A \cdot \Theta_{A_1}} \qquad K_{2,B_1A} = \frac{\Theta_{B_1A}}{p_A \cdot \Theta_{B_1}}$$
$$K_{2,A_1B} = \frac{\Theta_{A_1B}}{p_B \cdot \Theta_{A_1}} \qquad K_{2,B_1B} = \frac{\Theta_{B_1B}}{p_B \cdot \Theta_{B_1}} \quad (7)$$

According to this model, $\Theta_{(2)}$ and $\Theta_{(2)}^{M}$ are expressed by

$$\Theta_2 = \Theta_{A_1} + \Theta_{B_1} + \Theta_{A_1A} + \Theta_{B_1B} + \Theta_{A_1B} + \Theta_{B_1A} \quad (8)$$

and

$$\Theta_{(2)}^{M} = \Theta_{A_1} + \Theta_{B_1} + 2(\Theta_{A_1A} + \Theta_{B_1B} + \Theta_{A_1B} + \Theta_{B_1A}) \quad (9)$$

From Equations (8), (9), (6), and (7) we obtain

$$\Theta_{(2)}^{M} = \frac{K_{1,A_1}p_A + K_{1,B_1}p_B + 2f(p_A, p_B)}{1 + K_{1,A_1}p_A + K_{1,B_1}p_B + f(p_A, p_B)} \quad (10)$$

where

$$f(p_A, p_B) = K_{2,A_1A}K_{1,A_1}{p_A}^2 + K_{2,B_1B}K_{1,B_1}{p_B}^2 + (K_{2,A_1B}K_{1,A_1} + K_{2,B_1A}K_{1,B_1})p_Ap_B$$

Equation (10) is a general expression for bilayer adsorption isotherm of binary gas mixtures.

Now, we shall apply assumptions (1) and (2) of Gonzalez and Holland to adsorption isotherm (10). These assumptions can be written in the form

$$1.\quad K_{2,A_1A} = K_{2,B_1A} \qquad K_{2,B_1B} = K_{2,A_1B}$$

$$2.\quad \frac{K_{2,A_1A}}{K_{1,A_1}} = \frac{K_{2,B_1B}}{K_{1,B_1}} = \frac{\Phi_{(2)2}}{\Phi_{(2)1}} = \nu \tag{11}$$

where

$$\Phi_{(2)2} = K_{2,A_1A}p_A + K_{2,B_1B}p_B$$

$$\Phi_{(2)1} = K_{1,A_1}p_A + K_{1,B_1}p_B \tag{12}$$

Using Equations (11) and (12) in Equation (10), we get

$$\overset{M}{\Phi}_{(2)} = \frac{\Phi_{(2)1}(1 + 2\Phi_{(2)2})}{1 + \Phi_{(2)1}(1 + \Phi_{(2)2})} = \frac{\Phi_{(2)1}(1 + 2\nu\Phi_{(2)1})}{1 + \Phi_{(2)1}(1 + \nu\Phi_{(2)1})} \tag{13}$$

However, Equations (1*a*) and (1*b*) of Gonzalez and Holland give the following isotherms for bilayer adsorption of binary gas mixtures:

$$\overset{M}{\Theta}_{(2)} = \frac{\Phi_{(2)1}(1 + 2\Phi_{(2)2})}{1 + \Phi_{(2)1}} = \frac{\Phi_{(2)1}(1 + 2\nu\Phi_{(2)1})}{1 + \Phi_{(2)1}} \tag{14a}$$

and

$$\overset{M}{\Theta}_{(2)} = \frac{\Phi_{(2)1}(1 + 2\Phi_{(2)2})}{(1 + \Phi_{(2)1})(1 + \Phi_{(2)2})} = \frac{\Phi_{(2)1}(1 + 2\nu\Phi_{(2)1})}{(1 + \Phi_{(2)1})(1 + \nu\Phi_{(2)1})} \tag{14b}$$

A comparison of these equations shows that Equation (13) lies between those of Gonzalez and Holland (14*a*) and (14*b*); that is

$$\overset{M}{\Theta}_{(2)}\ [\text{Equation } (14b)] < \overset{M}{\Theta}_{(2)}\ [\text{Equation } (13)] < \overset{M}{\Theta}_{(2)}\ [\text{Equation } (14a)]$$

Equation (13) is approximately a simple average of the two Equations (14*a*) and (14*b*). Both Equations (14*a*) and (14*b*) are of the same type; they are the product of the monolayer coverage and a certain function describing the formation of the multilayer. Restriction of assumption 3 for second and higher layers only (that is, $j = 2, 3, \ldots, n - 1$) gives more general equations of adsorption isotherms [see first versions of Equations (13), (14*a*), and (14*b*)]. In these equations the monolayer and multilayer effects are separated; therefore, these forms are very useful for studying the adsorption of gas mixtures on highly heterogeneous surfaces (Jaroniec, 1976). However, study of adsorption on heterogeneous surfaces by using the local isotherm (13) are more difficult. This problem will be discussed in more detail.

The generalization of Equation (13) for *n*-layer adsorption leads to the following expression:

$$\overset{M}{\Theta}_{(2)} = \frac{\sum_{j=1}^{n} j\nu^{\frac{j(j-1)}{2}} g(p_A, p_B)}{1 + \sum_{j=1}^{n} \nu^{\frac{j(j-1)}{2}} g(p_A, p_B)} \tag{15}$$

where

$$g(p_A, p_B) = \sum_{i=0}^{j} \binom{j}{i} K_{1,A_1}^{i} K_{1,B_1}^{j-i} p_A^{i} p_B^{j-i}$$

Equation (15) may be rewritten in a slightly different form:

$$\overset{M}{\Theta}_{(2)} = \frac{\Phi_{(2)1}\,\varphi_{(2)}{}^{*}}{1 + \Phi_{(2)1}\,\varphi_{(2)}} \tag{16}$$

where

$$\varphi_{(2)}{}^{*} = 1 + 2\nu\Phi_{(2)1} + 3\nu^3\Phi_{(2)1}{}^2 + \ldots + n\nu^{\frac{n(n-1)}{2}}\Phi_{(2)1}^{n-1}$$

and

$$\varphi_{(2)} = 1 + \nu\Phi_{(2)1} + \nu^3\Phi_{(2)1}{}^2 + \ldots + \nu^{\frac{n(n-1)}{2}}\Phi_{(2)1}^{n-1}$$

Assuming that function $\varphi_{(2)}$ is close to unity, from Equation (16) we obtain the following adsorption isotherm:

$$\overset{M}{\Theta}_{(2)} = \frac{\Phi_{(2)1}\,\varphi_{(2)}{}^{*}}{1 + \Phi_{(2)1}} \tag{17}$$

Replacing in Equation (17) $\Phi_{(2)1}$ by $\Phi_{(m)1}$ and $\varphi_{(2)}{}^{*}$ by $\varphi_{(m)}{}^{*}$, we get the isotherm very similar to Equation (1*a*).

The combination of the models of Berezin-Kiselev (1972*a*) and Gonzalez-Holland (1970) leads to a general exact form of adsorption isotherm, which for BET assumptions gives the exact form of the BET equation. However, if we use assumption 3 in Equation (16) and assume that the function $\varphi_{(m)}{}^{*}$ is independent upon adsorption energies $\epsilon_1, \epsilon_2, \ldots, \epsilon_m$, the Gonzalez-Holland adsorption isotherms are obtained. These isotherms are very convenient for describing the adsorption of *m*-component gas mixtures on heterogeneous surfaces. It follows from the papers by Jaroniec (1975, 1976) that the multilayer surface coverage $\overset{M}{v}_{(m)}$ for *m*-component mixtures on heterogeneous surfaces is given by the following generalized integral equation:

$$\overset{M}{v}_{(m)}(\mathbf{p}) = \int_{\Delta_{(m)}} \overset{M}{\Theta}_{(m)}(\mathbf{p}, \boldsymbol{\varepsilon})\ \chi_{(m)}(\boldsymbol{\varepsilon})d\boldsymbol{\varepsilon} \tag{18}$$

Using in Equation (18) for $\overset{M}{\Theta}_{(m)}$ in Equation (17), we obtain

$$\overset{M}{v}_{(m)}(\mathbf{p}) = \varphi_{(m)}{}^{*}(\mathbf{p}) \int_{\Delta_{(m)}} \frac{\Phi_{(m)1}(\mathbf{p}, \boldsymbol{\varepsilon})}{1 + \Phi_{(m)1}(\mathbf{p}, \boldsymbol{\varepsilon})} \chi_{(m)}(\boldsymbol{\varepsilon})d\boldsymbol{\varepsilon} \tag{19}$$

The last equation may be useful to describe the adsorption of *m*-component gas mixtures on heterogeneous surfaces.

It follows from the studies of Gonzalez and Holland (1970, 1971) that their model predicts well the adsorption of binary hydrocarbon mixtures on carbon adsorbents. The studies of Karpinski and Garbacz (1974) and Berezin et al. (1972*b*) showed that the model of Berezin and Kiselev (1972*a*) gives good agreement with the experimental data for pure gas adsorption. For that reason the equations proposed here, derived on the basis of Berezin-Kiselev and Gonzalez-Holland models, should also coincide with the experimental data.

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NOTATION

A, B = molecules of the components A and B, respectively
A_1, B_1 = single associates of the components A and B with the free site of the surface, respectively
A_1A, B_1B, A_1B, B_1A = double associates normal to the surface
$f(p_A, p_B)$ = function, defined by Equation (10)
$g(p_A, p_B)$ = function, defined by Equation (15)

$K_{j,i}$ = constant characterizing the formation of the j^{th} adsorption layer by molecules of the i^{th} component

$K_{1,\beta}$, $K_{2,\beta}$ = equilibrium constants for single ($\beta = A_1, B_1$) and double ($\beta = A_1A, B_1B, A_1B, B_1A$) associates, respectively

p_i = partial pressure of the i^{th} component in a gas mixture

S = free site on the adsorbent surface

Greek Letters

ν = constant, defined for a multilayer adsorption by Equations (3) and (11)

ϵ_i = adsorption energy of the i^{th} component

$\Delta_{(m)}$ = m-dimensional region of possible variations of the adsorption energies of m components

$\Theta_{(m)}$, $\overset{M}{\Theta}_{(m)}$ = total monolayer and multilayer surface coverage for m-component gas mixture on a homogeneous surface, respectively

$\overset{M}{v}_{(m)}$ = multilayer surface coverage for m-component gas mixture on a heterogeneous surface

μ_i = chemical potential of the i^{th} component in the gas phase

$\mu_{j,i}$ = chemical potential of the i^{th} component in the j^{th} adsorption layer

$\Phi_{(m)j}$ = function characteristic for adsorption of m-component gas mixture and for j^{th} adsorption layer, defined by Equation (2)

$\varphi_{(m)}$, $\varphi_{(m)}{}^*$ = functions for adsorption of m-component gas mixtures, defined by Equation (16)

$\chi_{(m)}(\boldsymbol{\varepsilon})$ = m-dimensional distribution of adsorption energies

Ω_{n-1} = function; defined by Equation (4)

Vectors

$\mathbf{p}$ = $(p_1, p_2, \ldots, p_m)$, m-dimensional vector of the partial pressures

$\boldsymbol{\varepsilon}$ = $(\epsilon_1, \epsilon_2, \ldots, \epsilon_m)$, m-dimensional vector of the adsorption energies

$d\boldsymbol{\varepsilon}$ = $d\epsilon_1\, d\epsilon_2 \ldots d\epsilon_m$

Superscript

M = reference for multilayer surface coverage

Subscripts

i = component No. i

j = adsorption layer No. j

m = reference for adsorption of m-component gas mixtures

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Charge Characteristics of Particles in Coal Derived Liquids: Measurement and Origin

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Particles present in the reactor effluent stream of all coal liquefaction processes consist of a mixture of the original mineral matter present in coal, that is, clays, SiO_2, FeS_2, $FeCO_3$, $CaSO_4$, $CaMg(CO_3)_2$, together with unreacted and partially reacted coal residues (Walker et al., 1975). These particles range in size from 0.1 to 100 μm and constitute up to 10 wt. % of the reactor effluent stream depending on the specific process conditions. Subsequent removal of this particulate matter represents one of the major process problems associated with coal liquefaction.

This note summarizes measurements made on the sign of the charges associated with the particulate matter present in an unfiltered Solvent Refined Coal liquid having an initial 3:1 solvent to coal ratio (Wilsonville Run 94, 10-12-76, Monterey feed coal). A mechanism is presented to explain both the origin and sign of the observed charges.

EXPERIMENTS

Direct microscopic observation of particle motion in a DC electric field was used to determine the particle charge characteristics. Owing to the extremely opaque nature of the coal derived liquid, direct observations could only be made in a thin cell. The cell was constructed from a

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