Theory of Adsorbed Solutions: Analysis of One-Dimensional Systems

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A general formulation for 1-D multicomponent localized adsorption is presented, as well as a new mixing function that varies with only temperature and spreading pressure. An understanding of this mixing function completely determines the solution thermodynamics of the system. A closed-form expression for the adsorbed-phase excess Gibbs energy exhibiting an explicit dependence on the spreading pressure is thus obtained. The empirical expression proposed in the literature for the adsorbed-phase excess Gibbs energy is found to be consistent with the exact solution obtained in one dimension. The new mixing function further suggests the possibility of considering a binary adsorbed solution as the adsorption of a pseudo adsorbate.

Introduction

Separation processes based on the adsorption of microporous materials, such as zeolites and active carbons, are widely used in the chemical industry. In the designing of such processes, it is essential to know the adsorption equilibria of the mixture at hand. However, experimental data on multicomponent adsorption isotherms are scarce and difficult to obtain, and only very limited data are available even for binary systems. The needed information must therefore be deduced mostly from single-component isotherms.

A multicomponent adsorbed phase can be considered as an adsorbed solution. By introducing proper reference states, properties of mixing can be defined as those of a liquid mixture. For example, in an ideal adsorbed solution where the excess Gibbs energy vanishes, the adsorption from a mixed gas can be predicted from single-component isotherms (Myers and Prausnitz, 1965). More frequently, however, the adsorbed phase is nonideal. If binary data of a nonideal adsorbed solution are available, they can be fitted to empirical equations with correlation parameters. These parameters are then used to predict the needed multicomponent equilibrium properties. Without binary adsorption data, the prediction of multicomponent adsorption equilibria will be very difficult.

While many of these correlation equations for binary adsorption are taken from those of liquid mixtures, there exist important differences between the liquid and the adsorbed phases. To begin with, there is an extra degree of freedom in the adsorbed phase due to the presence of the solid. Therefore, the excess Gibbs energy in an adsorbed phase depends on the spreading pressure, in addition to the temperature and the composition. The correlation equations developed for liquid mixture provide no clue to the spreading pressure dependence of the adsorbed-phase excess Gibbs energy.

An empirical equation relating the adsorbed-phase excess Gibbs energy and the spreading pressure has been suggested by Valenzuela and Myers (1989) after examining an extensive survey of literature data. This empirical equation has been tested with experimental as well as computer simulation results of many binary adsorbed solutions (Karavias and Myers, 1992; Dunne and Myers, 1994; Talu et al., 1995). However, only at the asymptotic limit of low coverage can this empirical equation be theoretically derived. There is yet not theoretical support for its correctness at higher coverages.

Although adsorption is a two-dimensional phenomenon, the analysis of adsorption in an artificial one-dimensional system is often very rewarding. For example, Monson (1990) has successfully modeled the volume exclusion effect due to unequal

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adsorbate sizes in a confined one-dimensional system. The volume exclusion effects suggested by one-dimensional analysis have been explicitly included in a lattice model (Van Tassel et al., 1994) for the adsorption of small molecules in cage-type zeolites. On the practical side, there do exist zeolites (such as Mordenite and ZSM-11) with one-dimensional channel structures. Thus, using a one-dimensional model, the isotherm for xenon adsorbed in Mordenite (Mitchell et al., 1994), as well as the mixed adsorption of water and ethanol in silicalite (Farhadpour and Fong, 1992), have been accurately reproduced and studied.

In this article, a general theory for the multicomponent localized adsorption in one dimension is formulated. This formulation leads to the introduction of a relatively simple mixing function, from which the complete solution thermodynamics of the adsorbed phase can be deduced. We then compare the excess Gibbs energy derived from our one-dimensional model to the empirical equation used in the literature, and discuss some consequences suggested by the one-dimensional analysis.

Theory

Single-component adsorption in one dimension

For orientation purposes as well as for the purpose of fixing notation and reference states, we first consider the adsorption of a single-component (one species) on a ring of N lattice sites. The limit $N \to \infty$ will be taken when considering the thermodynamics.

Number the sites by $i = 1, 2, \ldots, N$ and, under periodic boundary conditions, it is understood that $i = 1$ and $i = N+1$ refer to the same site. We introduce site variables $n_i = 1, 0$ for, respectively, when the ith site is occupied and vacant. Let two molecules occupying neighboring sites interact with an energy $-J$, and ascribe to each molecule a site energy $-\epsilon$ and a chemical potential μ. Then the grand partition function of the adsorbed system is

$$\Xi(X,\lambda) = \sum_{n_i = 0,1} \prod_{i=1}^{N} T(n_i, n_{i+1}), \tag{1}$$

where

$$T(n,n') = X^{nn'} \lambda^{n}, \qquad n,n' = 0,1, \tag{2}$$

$X = e^{\beta J}$, $\lambda = e^{\beta(\mu+\epsilon)}$, and $\beta = 1/kT$. This defines a one-component lattice gas (Lee and Yang, 1952), for which the equation of state is given by

$$\frac{\beta \Pi L}{N} = \frac{1}{N} \ln \Xi(X,\lambda),$$

where Π is the spreading tension, and L is the length of the system. In the thermodynamic limit, the equation of state becomes

$$\beta \Pi l = \frac{\Omega(X,\lambda)}{kT} \equiv \lim_{N \to \infty} N^{-1} \ln \Xi(X,\lambda), \tag{3}$$

or, simply $\Omega(X,\lambda) = \Pi l$, where $l \equiv \lim_{N\to\infty} L/N$ is the nearest-neighbor distance between sites. The average density of the occupied sites, or the coverage, is given by

$$\theta = \lambda \frac{\partial}{\partial \lambda} \left[\frac{\Omega(X,\lambda)}{kT} \right]. \tag{4}$$

It is understood that Eq. 4 serves to eliminate μ in the canonical formulation under a fixed θ.

To evaluate $\Omega(X,\lambda)$, it is convenient (see, for example, Pathria, 1972; Reichl, 1980) to regard $T(n, n')$ as elements of a 2×2 matrix

$$\boldsymbol{T} = \begin{pmatrix} 1 & 1 \\ \lambda & X\lambda \end{pmatrix}. \tag{5}$$

The summations in Eq. 1 can now be considered as taking a trace, and Eq. 1 can be rewritten as

$$\Xi(X,\lambda) = \mathrm{Tr}\,\boldsymbol{T}^{N} = Z_+^N + Z_-^N, \tag{6}$$

where $Z_\pm$ are the two eigenvalues of $\boldsymbol{T}$. Explicitly, $Z_\pm$ are the roots of the characteristic equation

$$Z^2 - (1 + \lambda X)Z + \lambda(X-1) = 0, \tag{7}$$

or, equivalently,

$$Z_\pm = (1 + \lambda X)/2 \pm \zeta/2, \tag{8}$$

where $\zeta = \sqrt{4\lambda + (1 - \lambda X)^2}$. Only Z_+, the larger of the two eigenvalues, survives in the thermodynamic limit, Eq. 3, and one obtains the following closed-form expression

$$\frac{\Omega(X,\lambda)}{kT} \equiv \ln Z_+(X,\lambda), \tag{9}$$

and hence the equation of state

$$\beta \Pi l = \ln Z_+(X,\lambda). \tag{10}$$

It is clear that we have $Z_+ \geq 0$ and $Z_+ = 1$, corresponding to $\Pi = 0$ or, equivalently, when the molecules are far apart.

Substituting Eqs. 8 and 9 into Eq. 4, one obtains the adsorption isotherm

$$\theta = \frac{X\lambda + (X^2\lambda^2 - X\lambda + 2\lambda)/\zeta}{1 + X\lambda + \zeta}. \tag{11}$$

This is equivalent to the implicit isotherm obtained by Hill (1960) using a canonical quasi-chemical approach.

Alternately, the characteristic equation, Eq. 7, can be written as

$$\Delta(\beta, \lambda, Z_+) = 0, \tag{12}$$

where

$$\Delta(\beta,\lambda,Z_+) \equiv 1-\lambda/W \tag{13}$$

$$W \equiv \frac{Z_+(Z_+-1)}{1+X(Z_+-1)}. \tag{14}$$

The forms of these equations are suggestive in later considerations.

Multicomponent adsorption in one dimension

The theory presented in the preceding section will now be generalized to the adsorption of K kinds of molecules. Let the interaction energy be $-J_{ij}$ between molecules of types i and j, where $i,j=1, 2, \ldots, K$. To each molecule of type i, associate an energy $-\epsilon_i$ and a chemical potential μ_i. Then, the grand partition function of the system is, as in Eq. 1,

$$\Xi(X,\lambda) = \sum_{n_i=0,\ldots,K} \prod_{i=1}^{N} T(n_i,n_{i+1}), \tag{15}$$

where

$$T(n,n') = X_{nn'}\lambda_n, \qquad n,n'=0,1,2,\ldots,K, \tag{16}$$

with $X_{ij} = X_{ji} = \exp(\beta J_{ij})$, $\lambda_i = \exp[\beta(\epsilon_i+\mu_i)]$ for $i, j=1,2,\ldots,K$ and $X_{0n} = X_{n0} = \lambda_0 = 1$. For a large system the coverage of the ith molecular type is

$$\theta_i = \lambda_i \frac{\partial}{\partial\lambda_i}\left[\frac{\Omega(X,\lambda)}{kT}\right]_{\lambda_j,\beta}, \quad i=1,2,\ldots,K. \tag{17}$$

Again, Eq. 17 serves to eliminate μ_i in a canonical formulation under fixed θ_i.

Similar to Eq. 5, $T(n, n')$ can be regarded as elements of a $(K+1)\times(K+1)$ matrix

$$T = \begin{pmatrix} 1 & 1 & 1 & \cdots & 1 \\ \lambda_1 & X_{11}\lambda_1 & X_{12}\lambda_1 & \cdots & X_{1K}\lambda_1 \\ \lambda_2 & X_{21}\lambda_2 & X_{22}\lambda_2 & \cdots & X_{2K}\lambda_2 \\ \cdots & \cdots & \cdots & \ddots & \cdots \\ \lambda_K & X_{K1}\lambda_K & X_{k2}\lambda_K & \cdots & X_{KK}\lambda_K \end{pmatrix}. \tag{18}$$

Then, Eq. 15 becomes

$$\Xi(X,\lambda) = \mathrm{Tr}\, T^N = Z_1^N + Z_2^N + Z_3^N + \ldots + Z_{K+1}^N, \tag{19}$$

where $Z_1, Z_2, \ldots, Z_{K+1}$ are the eigenvalues of T. Since all elements of T are positive, the largest eigenvalue is positive. Explicitly, the characteristic equation of Eq. 18 can be written as

$$\begin{vmatrix} 1-Z & 1 & 1 & \cdots & 1 \\ \lambda_1 & X_{11}\lambda_1 - Z & X_{12}\lambda_1 & \cdots & X_{1K}\lambda_1 \\ \lambda_2 & X_{21}\lambda_2 & X_{22}\lambda_2 - Z & \cdots & X_{2K}\lambda_K \\ \cdots & \cdots & \cdots & \ddots & \cdots \\ \lambda_K & X_{K1}\lambda_K & X_{K2}\lambda_K & \cdots & X_{KK}\lambda_K - Z \end{vmatrix} = 0. \tag{20}$$

After some elementary manipulations of adding rows and/or columns, Eq. 20 can be transformed to

$$\begin{vmatrix} 1 & -1/W_{11} & -1/W_{22} & \cdots & -1/W_{KK} \\ 0 & \lambda_1/W_{11}-1 & \lambda_1/W_{12} & \cdots & \lambda_1/W_{1K} \\ 0 & \lambda_2/W_{21} & \lambda/W_{22}-1 & \cdots & \lambda_2/W_{2K} \\ \cdots & \cdots & \cdots & \ddots & \cdots \\ 0 & \lambda_K/W_{K1} & \lambda_K/W_{K2} & \cdots & \lambda_K/W_{KK}-1 \end{vmatrix} = 0, \tag{21}$$

where

$$W_{ij} \equiv \frac{Z(Z-1)}{1+X_{ij}(Z-1)}. \tag{22}$$

We can now cross out the first row and column in Eq. 21, and obtain the following elegant expression for the characteristic equation:

$$\Delta(\beta,\lambda,Z) \equiv \det\left|\frac{\lambda_i}{W_{ij}} - \delta_{ij}\right| = 0, \tag{23}$$

where δ_{ij} is the Kronecker delta that equals 1 if $i=j$, and 0 otherwise. Note that the $K\times K$ determinant in Eq. 23 can be systematically evaluated for any given K.

In the thermodynamic limit, one obtains

$$\frac{1}{kT}\Omega(X,\lambda) \equiv \ln Z_{\max}, \tag{24}$$

and hence the equation of state

$$\beta\Pi l = \ln Z_{\max}, \tag{25}$$

where $Z_{\max}$ is the largest eigenvalue. The standard procedure at this point is to solve $Z=Z_{\max}$ from Eq. 23 and to compute $\theta_i = \partial \ln Z/\partial \ln \lambda_i$. But one can also consider Eq. 23 as an equation implicitly relating $Z_{\max}$, and thus Π, with λ_i without actually solving it. This is the approach we adopt in the following discussion.

With the equation of state, Eq. 25, the function $W_{ij}(X, Z_{\max})$ can be considered as a function $W_{ij}(\beta,\Pi)$. The implicit characteristic equation, Eq. 23, then becomes

$$\Delta(\beta,\lambda,\Pi) \equiv \det\left|\frac{\lambda_i}{W_{ij}(\beta,\Pi)} - \delta_{ij}\right| = 0. \tag{26}$$

For single-component systems, we have

$$\Delta(\beta,\lambda,\Pi) \equiv 1-\lambda/W(\beta,\Pi), \tag{27}$$

and for binary adsorption systems

$$\Delta(\lambda,\beta,\Pi) \equiv 1-\lambda_1/W_{11}-\lambda_2/W_{22}+\left[1-\frac{1}{\eta_{12}}\right]\frac{\lambda_1\lambda_2}{W_{11}W_{22}} = 0, \tag{28}$$

where we have defined a *mixing function*

$$\eta_{12}(\beta,\Pi) \equiv \frac{W_{12}^2}{W_{11}W_{22}}. \tag{29}$$

The coverage θ_i is now given explicitly as a function of Π by

$$\theta_i = \left(\frac{\beta\partial\Omega}{\partial\ln\lambda_i}\right)_{\beta,\lambda_j} = -\left(\frac{\partial\Delta}{\partial\ln\lambda_i}\right)_{\Pi,\beta,\lambda_j} \Bigg/ \left(\frac{\partial\Delta}{\beta l\partial\Pi}\right)_{\beta,\lambda_j,\lambda_i}. \tag{30}$$

This completes the thermodynamic formulation of multicomponent adsorption on a one-dimensional lattice. The thermodynamics of the system is now completely determined if all $W_{ij}(\beta,\Pi)$ are known.

Physical meanings of the W function

For a single-component adsorption system, Eq. 27 suggests that the W function is nothing but the chemical activity λ expressed in terms of the spreading pressure and the temperature. This is not a function that one can measure experimentally. However, from the function $W(\Pi)$ the coverage is found to be

$$\theta(\Pi) = \frac{l}{kT}\frac{W}{(\partial W/\partial\Pi)_\beta}.$$

Thus, one will be able to obtain the $W(\Pi)$ function from the experimental isotherm. At infinite dilution, we have $\lim_{\Pi\to 0} W(\Pi) = 0$ and $\lim_{\Pi\to 0}[dW/d\Pi] = l/kT$ from Eq. 14. In other words, the localized adsorption in one dimension obeys Henry's law

$$\lim_{\lambda\to 0}\left(\frac{d\theta}{d\lambda}\right) = -\frac{\theta}{\lambda}.$$

In the limit of large spreading pressure, we have

$$\lim_{\Pi\to\infty}[\partial W/\partial\Pi]_\beta = \frac{l}{XkT}e^{\beta\Pi l},$$

which is different from the limiting values obtained from classic equations such as Langmuir or Volmer isotherms.

Notice that for binary adsorption cases, the function $W_{12}(\Pi)$ is of the same form as the pure component function $W_{11}(\Pi)$, but with a different interaction. Thus W_{12} can be considered as the W function of a pseudocomponent adsorbed in one dimension. The similarity of functional forms for W_{12} and W_{11} will be important in our later discussions.

Longuet-Higgins (1958) has derived an equation of state similar to Eq. 23 for one-dimensional fluid mixtures using a constant-pressure ensemble. In his formulation, the corresponding W_{ij} function appears as an integral

$$W_{ij}(\beta,P) = (\Lambda_i\Lambda_j)^{1/2}\left[\int_0^\infty e^{-\beta u_{ij}(r)}e^{-\beta Pr}dr\right]^{-1}, \tag{31}$$

where u_{ij} is a distance-dependent interaction potential between species i and j, and Λ_i is the de Broglie wavelength of the ith species. However, simple replacement of the one-dimensional pressure P with the spreading pressure Π does not change Eq. 31 to a correct description of mobile adsorption systems. Particularly, W_{ij} becomes infinite unless the interaction potential u_{ij} has a finite range.

Activity coefficient and the excess Gibbs energy

The complete thermodynamics of adsorption in one dimension has been solved in the previous sections. We will now recast these results in more familiar terms, such as the activity coefficient and the excess Gibbs energy.

The excess Gibbs energy of an adsorbed solution is defined (Myers and Prausnitz, 1965) relative to pure-component systems at the same temperature and spreading pressure. Thus, under a fixed temperature

$$\frac{g^{ex}}{RT} \equiv \sum_i x_i\ln\gamma_i = \sum_i x_i\ln\frac{f_i}{x_if_i^*} = \frac{A}{RT}\int_0^\Pi\left[\frac{1}{\Sigma_i n_i} - \sum_i\frac{x_i}{n_i^*}\right]d\Pi, \tag{32}$$

where f_i is the fugacity, x_i the composition, n_i the amount adsorbed per unit area (or unit length in one dimension), A the total surface area (length) of the system, and * indicates quantities of the single-component reference state at the system spreading pressure.

Since

$$\gamma_i \equiv \frac{f_i}{x_if_i^*} = \frac{e^{\beta\mu_i}}{x_ie^{\beta\mu_i^*}} = \frac{\lambda_i}{x_i\lambda_i^*}, \tag{33}$$

and from Eq. 27 we know $\lambda_i^* = W_{ii}(\Pi^*) = W_{ii}(\Pi)$, therefore we can write

$$x_i\gamma_i = \lambda_i/\lambda_i^* = \lambda_i/W_{ii}. \tag{34}$$

With this relation, the binary characteristic equation, Eq. 28, reduces to

$$\Delta \equiv 1-(x_1\gamma_1+x_2\gamma_2)+(1-\eta_{12}^{-1})x_1x_2\gamma_1\gamma_2 = 0. \tag{35}$$

We now have an explicit equation relating activity coefficients to compositions and the mixing function η_{12} (Π).

Another relation relating γ_1 and γ_2 is obtained by taking the ratio of species coverages. Using Eq. 30, one finds

$$\frac{x_1}{x_2} = \frac{\theta_1}{\theta_2} = \frac{\lambda_1(\partial\Delta/\partial\lambda_1)_{\Pi,\beta,\lambda_2}}{\lambda_2(\partial\Delta/\partial\lambda_2)_{\Pi,\beta,\lambda_1}} = \frac{1-x_2\gamma_2}{1-x_1\gamma_1}. \tag{36}$$

Eliminating γ_2 from Eqs. 35 and 36, a quadratic equation for γ_1 is obtained as

$$(1-\eta_{12}^{-1})x_1^2\gamma_1^2 - [\eta^{-1}(x_2-x_1)+2x_1]\gamma_1 + 1 = 0, \tag{37}$$

which yields

$$\gamma_{1\pm} = \frac{x_2 - x_1 + 2x_1\eta_{12} \pm \sqrt{(x_2 - x_1)^2 + 4x_1x_2\eta_{12}}}{2(\eta_{12} - 1)x_1^2}$$

$$= 1\frac{x_2}{x_1}\left[\frac{\sqrt{1 - 4x_1x_2 + 4x_1x_2\eta_{12}} \pm 1}{\sqrt{1 - 4x_1x_2 + 4x_1x_2\eta_{12}} \mp 1}\right]. \qquad (38)$$

The quantity inside the square root is always positive. However, the root γ_{1+} leads to negative values when $\eta < 1$ and extremely large values when $\eta > 1$. This is unphysical and the positive root is thus discarded. The proper expression for γ_1 is now given by

$$\gamma_1 = 1 + \frac{x_2}{x_1}\left[\frac{\sqrt{1 + 4x_1x_2(\eta_{12} - 1)} - 1}{\sqrt{1 + 4x_1x_2(\eta_{12} - 1)} + 1}\right]. \qquad (39)$$

In a similar fashion one obtains an expression for γ_2 given by Eq. 39 with x_1 and x_2 interchanged. From Eq. 39 it is clear that $\gamma_i > 1$ if $\eta_{12} > 1$ and vice versa. Consequently, g^{ex}/RT as defined in Eq. 32 has the same sign as $\ln \eta_{12}$.

We have now arrived at an explicit expression for the activity coefficient, and thus the excess Gibbs energy, in terms of the composition and the mixing function. This is an exact solution for one-dimensional adsorption systems, and is the first closed-form expression ever obtained for the adsorbed-phase excess Gibbs energy exhibiting an explicit dependence on the spreading pressure.

Other related excess properties of the adsorbed solution can also be derived in terms of the mixing function and the compositions. For example, the excess area of mixing defined (Talu et al., 1995) by

$$a^{ex} = \frac{A}{\Sigma n_i} - \Sigma\frac{Ax_i}{n_i^*} = \left(\frac{\partial g^{ex}}{\partial \Pi}\right)_{\beta,x} \qquad (40)$$

can be derived from Eq. 39 to give

$$a^{ex} = \frac{2x_1x_2RT}{1 + \sqrt{1 + 4x_1x_2(\eta_{12} - 1)}}\left(\frac{\partial \ln \eta_{12}}{\partial \Pi}\right)_{\beta}. \qquad (41)$$

From the excess area and the excess Gibbs energy, the individual coverage can be calculated.

Although we have only demonstrated the derivations in a binary case, the same approach can easily be extended to multicomponent systems. For a K-component system, there will be $K - 1$ independent equations similar to Eq. 36. The activity coefficients can thus be solved in terms of compositions and the pairwise mixing functions $\eta_{ij}(\Pi)$.

Numerical Investigations

We now take a closer look at the mixing function η_{12} derived for one-dimensional systems. With Eqs. 22 and 25, Eq. 29 can be converted to

$$\eta_{12} - 1 = \frac{\chi}{[\chi + 1]^2}\left[\chi\left(\frac{1}{\nu^2} - 1\right) + 2\left(\frac{h}{\nu} - 1\right)\right], \qquad (42)$$

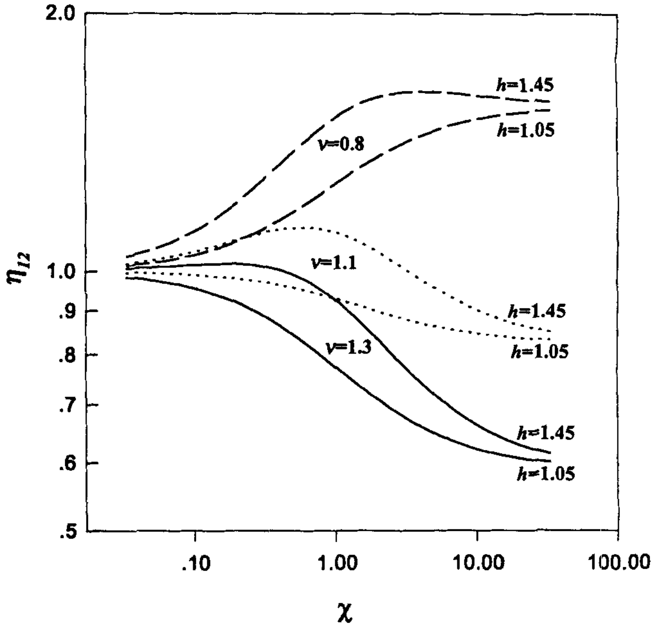

Figure 1. Variation of the one-dimensional mixing function η_{12} with energy parameters h, ν, and χ.

The solid lines are for cases with $\upsilon = 1.3$, the dotted lines are for $\nu = 1.1$, and the dashed lines are for $\nu = 0.8$. The values of h are marked in the figure.

where

$$h \equiv (X_{11} + X_{22})/2\sqrt{X_{11}X_{22}} \geq 1, \quad \nu \equiv X_{12}/\sqrt{X_{11}X_{22}}$$

$$\text{and} \quad \chi \equiv X_{12}(e^{\beta\Pi l} - 1).$$

The dependence of η_{12} on the parameters h, ν, and χ is illustrated in Figure 1. Note that the mixture becomes an ideal solution when $h = 1$ and $\nu = 1$, or equivalently, when $X_{11} = X_{22} = X_{12}$. This will be the case when both adsorbates act identically. As suggested by Eq. 42, the mixing function η_{12} will be smaller than 1 when $\nu > h > 1$, that is, when there is a strong association between the species. Conversely, when there is a repulsive force between the species, and thus $\nu < 1 < h$, we will have $\eta_{12} > 1$. For intermediate cases where $h \geq \nu \geq 1$, η_{12} will still be smaller than 1 for large χ.

The parameter h can be considered as an indication of the relative magnitude of X_{11} and X_{22}. If we assign a new parameter $\omega \equiv X_{11}/X_{22}$ when $X_{11} \leq X_{22}$ and vice versa, then h is related to ω as $h = 1 - (1 - \omega)^2/2\omega$. For ω in the range from 0.4 to 1, the corresponding h varies only between 1.45 and 1.0. The mixing function η_{12} for selected values of ν and h is shown in Figure 1. As indicated in Figure 1, the parameter ν has a larger effect on the value of η_{12} than the parameter h. From purely energetic considerations, Figure 1 suggests that the mixing function η should have a numerical value between 0.5 and 2 if the two species are not too different.

Excess Gibbs energy

Valenzuela and Myers (1989) have found that, for a binary adsorbed solution under constant spreading pressure, the excess Gibbs energy is symmetrical with respect to the inter-

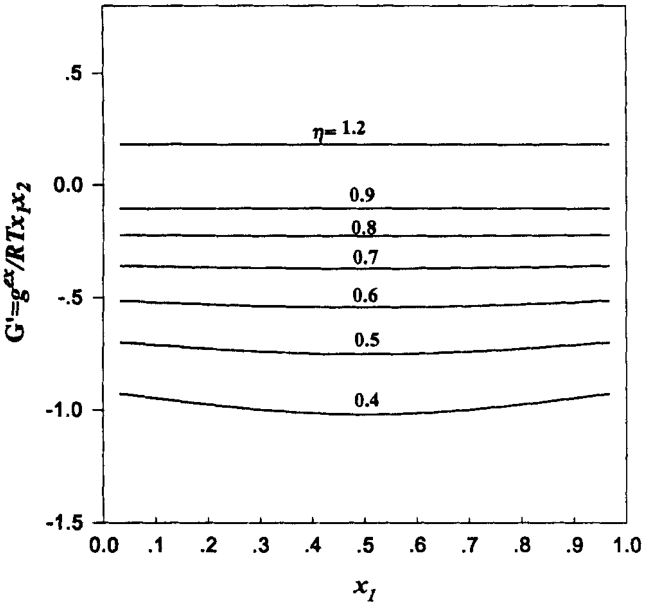

Figure 2. Variation of the function G' calculated from Eqs. 39 and 32 with respect to the composition.

change of compositions. They have thus proposed the empirical equation for the adsorbed-phase excess Gibbs energy

$$\frac{g^{ex}}{x_1 x_2 RT} = G'(\Pi) \approx C(1 - e^{D\Pi}). \tag{43}$$

As shown in Figure 2, the function $G' = g^{ex}/x_1 x_2 RT$ calculated from Eqs. 39 and 32 with fixed value of $\eta_{12}(\Pi)$ is very close to a constant if $0.5 > \eta_{12} > 1.2$. Thus, we have proved that the composition dependence described by Eq. 43 is qualitatively correct, at least for binary adsorption in one dimension.

We next check the spreading pressure dependence proposed by Valenzuela and Myers. Shown in Figure 3 is the plot of the functions G' calculated from the one-dimensional model against $[1 - e^{-\beta\Pi l/\nu}]$. For cases where a negative excess Gibbs energy has been found ($\nu > 1$), G' appears as a nearly straight line in this figure. Therefore, the spreading pressure dependence suggested by Eq. 43 is again correct for one-dimensional systems under reasonable choices of parameters. Figure 3 further reveals that the parameter D in Eq. 43 depends on the temperature, the interspecies interaction ν, and the size of adsorbates l. Such information may be useful for the development of a predictive adsorbed solution theory.

Very large negative excess free energies are often reported in the literature for adsorbed solutions. Comparatively, the value predicted by the one-dimensional model is much smaller. In the one-dimensional model, a very large negative excess Gibbs energy would suggest the existence of a very strong association within the mixture. It is unlikely that strong associations always exist in adsorption systems. Other effects, such as unequal adsorbate sizes and adsorption energy heterogeneity, also must have contributed to the observed excess Gibbs energy. These effects have not been included in the one-dimensional model.

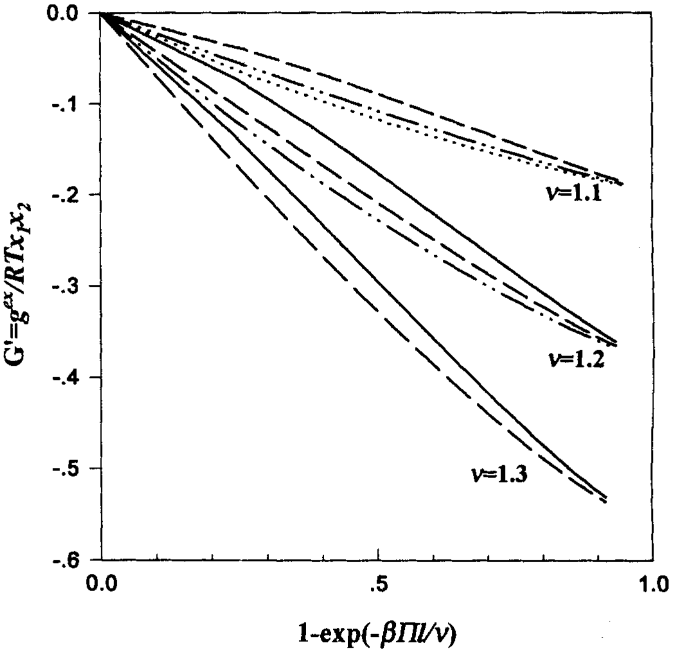

Figure 3. Variation of the function G' calculated from Eqs. 42, 39, and 32 with respect to 1-exp $(-\beta\Pi l/\nu)$.

The solid, dashed, dot-dashed, and dotted lines are for cases with $\omega = 0.6$, 0.7, 0.8, and 0.9, respectively.

Furthermore, for localized adsorption systems, a well-defined saturation capacity always exists. A finite saturation capacity does exist for microporous adsorbent where pore condensation (multilayer adsorption) is unimportant. When multilayer adsorption occurs, adsorbed molecules will experience a varying solid potential in different layers. Again, this effect cannot be included in a one-dimensional model.

In spite of these limitations, we have demonstrated that the simple one-dimensional model gives a correct account to the composition and spreading pressure dependences of the excess Gibbs energy observed in real adsorbed solutions. At the very least, we have given the empirical equation, Eq. 43, of Valenzuela and Myers (1989) a new theoretical footing.

An interesting relation has also been found between the function G' calculated from Eq. 39 and the mixing function η_{12} as illustrated in Figure 4. In the limited range of η_{12} given in Figure 1, G' and ln η_{12} are almost numerically equivalent. Minor dependence on the composition sets in only at larger and smaller values of η_{12}. This comparison suggests that the composition-independent part of the adsorbed-phase excess Gibbs energy may be changed to

$$G'(\Pi) \approx \ln \eta_{12} = 2 \ln W_{12}(\Pi) - \ln W_{11}(\Pi) - \ln W_{22}(\Pi).$$

We have mentioned previously that $W_{12}(\Pi)$ can be considered as the chemical activity of a pseudo-adsorbate with an average property of the pure components. Thus, ln η becomes the difference between the free energy of the pseudo-adsorbate and that of the pure species. Judging from the success of Eq. 43 in dealing with many real adsorbed solutions, it may be possible to define a pseudo-adsorbate for those mixtures, and obtain the corresponding W_{12} function. The W_{12}

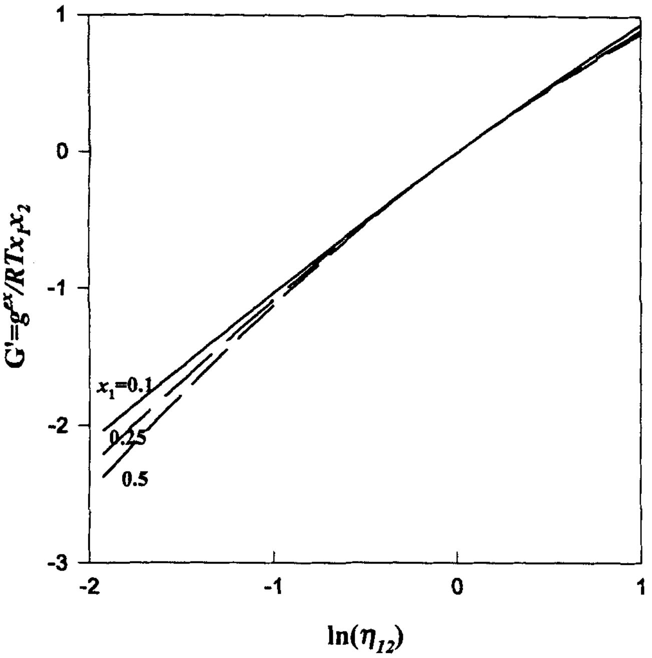

Figure 4. Numerical equivalence of the function G' calculated from Eqs. 39 and 32 and $\ln\eta_{12}$.

function is likely to assume the same form as the single-component W_{ii} functions, with some averaged size and interaction parameters.

We have verified (Chiang and Lee, 1995) that some data on binary adsorption found in the literature can indeed be described by Eqs. 35 to 41 as well as by the empirical equation, Eq. 43. Ternary equilibria predicted using binary parameters are also consistent with the reported data. We are now in the process of correlating the parameters involved in the pseudo-adsorbate W_{12} function with those in the single-component W_{ii} functions.

Conclusions

We have presented the exact solution of a one-dimensional analysis of multicomponent adsorption. A new mixing function $\eta_{ij}(\beta, \Pi)$ is introduced to describe the nonideal mixing of binary adsorbed solutions. The activity coefficients as well as the excess Gibbs energy are then given explicitly in terms of this mixing function and the compositions.

Numerical results indicate that the empirical equation, Eq. 43, suggested by Valenzuela and Myers (1989) for the adsorbed-phase excess Gibbs energy is consistent with the exact solution of a one-dimensional model for reasonable choices of the parameters. The one-dimensional model further provides information concerning the physical meaning of the empirical parameters.

A numerical equivalence between the new mixing function and the composition-independent part of the adsorbed-phase excess Gibbs energy has been discovered. This implies that one may use the adsorption of a pseudocomponent to describe that of a binary mixture. Since only binary mixing functions appeared in the characteristic equation, Eq. 23, our theory can be extended to multicomponent systems in a straightforward fashion.

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Greek letter

$\Omega = \lim_{N \to \infty} \Xi / N$

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