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Vacancy Solution Theory of Adsorption From Gas Mixtures

A new correlation that improves predictions of gas mixture adsorption equilibria from single-component adsorption isotherm data is developed, based on the vacancy solution theory. In this theory, the adsorbed phase and the gas phase are treated as two vacancy solutions. The vacancy is an imaginary solvent occupying spaces that will be filled by adsorbates. The composition relationship between the two phases is derived from thermodynamic equilibrium criteria. The non-ideality of the adsorbed solution is accounted for by an activity coefficient, whose composition dependence is described by the Wilson equation. For an adsorption system, the binary parameters, adsorbate and vacancy, can be obtained from regression of the pure gas adsorption data with the vacancy solution isotherm equation. These parameters are then used to predict multicomponent adsorption equilibrium, assuming that the adsorbate-adsorbate interactions are negligible. The new correlation has been tested on two different kinds of binary adsorption systems. The new method is more general, simpler to apply, and more accurate than other available models. The predictions can be further improved by taking into account the adsorbate-adsorbate interactions.

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SCOPE

Numerous industrial purification and bulk separation processes involve gas mixture adsorption. To design such processes, multicomponent equilibrium data are needed. Since it is very tedious to collect the mixture data, a reliable way to estimate the mixture equilibrium from single-component adsorption isotherm data is preferred. While a number of correlations have been developed for this purpose, all have some limitations. Consider the ideal adsorbed solution model of Myers and Prausnitz (1965) or the simplified statistical thermodynamic model of Ruthven (1976). The former is subjected to the assumption that the adsorbed mixture behaves ideally, and it can not predict non-ideal behavior such as adsorption azeotropes. The latter method can predict the non-ideality caused by size differences of the adsorbed molecules, but has been specifically developed for adsorption on zeolites and cannot be applied to other substrates.

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The objective of our work is to develop and evaluate a generalized correlation that accurately predicts gas mixture adsorption equilibrium from pure gas adsorption isotherms over wide ranges of conditions. Binary adsorption data of two different kinds of systems have been used to evaluate the new correlation. The two sets of data are binary mixtures of O_2, N_2, and CO on zeolite 10X at 144.3 K, 172.0 K, 227.6 K and 273.2 K and 1 bar total pressure (Danner and Wenzel 1969, Nolan, 1978), and that of light hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_8, nC_4H_{10} and also CO_2) on Nuxit-AL activated carbon at 293.2 K or 333.2 K or both, with approximately 1 bar total pressure (Szepesy and Illés 1963).

CONCLUSIONS AND SIGNIFICANCE

A new mixture correlation for gas adsorption is developed, utilizing the modified vacancy solution model introduced by Suwanayuen and Danner (1980). The correlation gives satisfactory predictions of adsorption phase diagrams for binary mixtures of O_2, N_2, and CO on zeolite 10X and light hydrocarbons on Nuxit-AL activated carbon, over wide ranges of temperature. These predictions are slightly better than those given by the simplified statistical thermodynamic model (Ruthven 1976) and very similar to those obtained from the ideal adsorbed solution model (Myers and Prausnitz 1965). The accurate results are obtained from the new method, however, with a decreased complexity of calculations. Evaluations of the new correlation suggest that it should predict equally well mixture adsorption data for less ideal systems than those presently under study. The activity coefficients (evaluated from pure component data only) allow the new method to account for system nonideality.

The dividing surface which has been used in developing our correlation makes the method quite general. The dividing surface can represent adsorbed mixtures on any kind of adsorbent. In addition, mixture adsorption equilibria in which the adsorbates have different capacities can be treated. Accordingly, the developed model is applicable to all gas adsorption systems.

In this work, adsorbate-adsorbate interactions have generally been assumed to be insignificant compared to other interactions, such as the adsorbate-adsorbent heterogeneous effect and the adsorbing molecule-adsorbed molecule interaction. For systems like the binary adsorption of light hydrocarbons, this assumption seems to be appropriate, as supported by the excellent predictions obtained. For the adsorption of O_2, N_2, and CO binary mixtures, the predictions could still be improved by taking into account the adsorbate-adsorbate interactions. An approximate method of accounting for these interactions is shown to be useful.

The ideal adsorbed solution model of Sircar and Myers (1973) has been derived from the vacancy solution theory by defining the dividing surface such that the surface excess of the vacancy is always zero.

At present, multicomponent gas adsorption correlations are usually developed from one of three different kinds of models: two-dimensional gas, adsorbed solution, or statistical thermodynamic. An extension of the two-dimensional gas theory, in which an adsorbed phase is assumed to obey the van der Waals equation of state, has been developed by Hoory and Prausnitz (1967) for predicting mixture adsorption equilibria. The accuracy of this model depends on the values of the van der Waals parameters, which may not be able to contain all the available information from the pure-component data. Therefore, the correlation was reported by Danner and Choi (1978) to be inferior to the ideal adsorbed solution method introduced by Myers and Prausnitz (1965).

The generalized correlation based on solution theory was introduced later, by Sircar and Myers (1973). Depending on the standard state chosen for the adsorbed phase, this theory can be shown to be equivalent to other methods available in the literature. The adsorbed phase, however, must always be assumed to an ideal mixture. The rigorous application of this theory is thus limited.

The simplified statistical thermodynamic theory of Ruthven (1976) was derived specifically for an adsorption equilibrium on zeolites and cannot be applied to other adsorption systems. While this correlation gives good predictions of binary gas mixture adsorption equilibria on zeolites, it is practical only for binary systems because of the complexity of its mathematical form.

Against this background, there is a need for a general and simple correlation that predicts accurately multicomponent equilibrium data from the single-component data for any adsorption system. Such a correlation can be obtained from the solution thermodynamic treatment if the non-ideality in the adsorbed solution is appropriately accounted for. In another paper (Suwanayuen and Danner 1980), we present a new gas adsorption isotherm equation. It is based on a vacancy solution theory in which the adsorbed phase interactions are accounted for in terms of an activity coefficient. In this article, the vacancy solution theory is extended to gas mixture adsorption equilibria.

DERIVATION

The present vacancy solution theory is analogous to the one introduced by Dubinin (1977), but has been modified by applying a procedure suggested by the work of Lucassen-Reynders (1972, 1973, 1976). In the modified method, the gas mixture adsorption equilibrium is considered to be an equilibrium between two vacancy solutions corresponding to the gas and adsorbed phases. The properties of the adsorbed solution are represented in terms of excess properties with an unusual dividing surface, the definition of which is suggested by Lucassen-Reynders. The details of this model as well as the development of a pure gas adsorption isotherm equation is given elsewhere (Suwanayuen and Danner 1980). The isotherm equation is

$$p = \left[\frac{n_1^{s,\infty}}{b_1} \frac{\theta}{1-\theta} \right] \left[\Lambda_{13} \cdot \frac{1-(1-\Lambda_{31})\theta}{\Lambda_{13} + (1-\Lambda_{13})\theta} \right]$$
$$\exp\left[-\frac{\Lambda_{31}(1-\Lambda_{31})\theta}{1-(1-\Lambda_{31})\theta} - \frac{(1-\Lambda_{13})\theta}{\Lambda_{13}+(1-\Lambda_{13})\theta} \right] \quad (1)$$

Here, the equilibrium correlation is developed for binary gas mixture adsorption only, although the method can also apply to multicomponent systems. According to our model, the binary mixture adsorption equilibrium becomes an equilibrium between ternary vacancy solutions, the third component of which is the vacancy defined to be the solvent of the system. The chemical potential of component i in the vacancy solution subjected to the solid force field (the adsorbed phase) can be expressed by the equation given by Lucassen-Reynders (1972, 1973, 1976)

$$\mu_i^s = \mu_i^{os} + RT \ln \gamma_i^s x_i^s + \pi \bar{a}_i \quad (2)$$

The chemical potential for an adsorbate in the gas phase is expressed by the usual equation for a gas mixture.

$$\mu_i^g = \mu_i^{*g} + RT \ln \phi_i y_i P \quad (3)$$

An equilibrium equation governing the distribution of an adsorbate between the adsorbed and the gas phase is then obtained by equating Equation (2) to Equation (3) and rearranging.

$$\phi_i y_i P = \gamma_i^s x_i^s \exp\left(\frac{\Delta G_i^o}{RT} \right) \exp\left(\frac{\pi \bar{a}_i}{RT} \right) \quad (4)$$

The standard state free energy of adsorption is defined as

$$\Delta G_i^o = \mu_i^{os} - \mu_i^{*g} \quad (5)$$

Equation (4) relates the mole fraction of component i in the binary gas mixture, y_i, to that of component i in the adsorbed phase, x_i^s, which is based on the total moles of the adsorbed ternary vacancy solution. The experimental mole fraction, x_i, is, however, based on the total moles of the corresponding binary mixture of adsorbates. The relationship between the two fractions is needed in order to interpret experimental data. Since

$$n_m^{s,\infty} = n_1^s + n_2^s + n_3^s \quad (6)$$

and

$$n_m^s = n_1^s + n_2^s \quad (7)$$

one can write the following

$$x_i^s = \frac{n_i^s}{n_1^s + n_2^s + n_3^s} \cdot \frac{n_1^s + n_2^s}{n_1^s + n_2^s} = \frac{x_i n_m^s}{n_m^{s,\infty}} = x_i \theta, \quad i = 1 \text{ or } 2 \quad (8)$$

and

$$x_3^s = 1 - x_1^s - x_2^s = 1 - \frac{n_m^s}{n_m^{s,\infty}} = 1 - \theta \quad (9)$$

Substituting x_i^s from Equation (8) into Equation (4), the equilibrium equation becomes:

$$\phi_i y_i P = \gamma_i^s x_i \frac{n_m^s}{n_m^{s,\infty}} \exp\left(\frac{\Delta G_i^o}{RT} \right) \exp\left(\frac{\pi \bar{a}_i}{RT} \right) \quad (10)$$

All terms on the right hand side, except x_i and n_m^s, can be obtained in terms of the binary vacancy solution parameters (i.e., from pure component adsorption data). The adsorption equation of state expressing the spreading pressure as a function of the vacancy partial molar area, activity coefficient, and adsorbed composition has been derived in another article (Suwanayuen and Danner 1980).

$$\pi = -\frac{RT}{\bar{a}_3} \ln \gamma_3^s x_3^s \quad (11)$$

The composition dependence of the activity coefficient is assumed to obey the Wilson equation whose general form (Prausnitz 1969) is as follows

$$\ln \gamma_k = 1 - \ln \left[\sum_{j=1}^{n} x_j \Lambda_{kj} \right] - \sum_{i=1}^{n} \left[\frac{x_i \Lambda_{ik}}{\sum_{j=1}^{n} x_j \Lambda_{ij}} \right] \quad (12)$$

The main advantage is that this equation can predict an activity coefficient for a multicomponent system from binary parameters only. A multicomponent adsorption activity coefficient can be calculated if all relevant binary parameters are known.

For the ternary vacancy solution, these parameters are Λ_{13}, Λ_{31}, Λ_{23}, Λ_{32}, Λ_{12}, and Λ_{21}. The first four parameters account for adsorbate-vacancy interactions caused by nonideality in the adsorbed phase, and they can be obtained from regression of Equation (1) with the corresponding experimental pure component adsorption data. The last two parameters represent adsorbate-adsorbate interactions in the absence of solid when their molecules are arranged and constricted in a similar manner as caused by the solid. Thus, these parameters must be estimated from theoretical considerations or regressed from experimental mixture adsorption data. Equation (12) when applied to a ternary vacancy solution system reduces to:

$$\ln \gamma_i^s = 1 - \ln (x_i^s + x_j^s \Lambda_{ij} + x_3^s \Lambda_{i3}) - \left(\frac{x_i^s}{x_i^s + x_j^s \Lambda_{ij} + x_3^s \Lambda_{i3}} + \frac{x_j^s \Lambda_{ji}}{x_i^s \Lambda_{ji} + x_j^s + x_3^s \Lambda_{j3}} + \frac{x_3^s \Lambda_{3i}}{x_i^s \Lambda_{3i} + x_j^s \Lambda_{3j} + x_3^s} \right) \quad \text{for } i, j = 1, 2 \text{ or } 2, 1 \quad (13)$$

$$\ln \gamma_3^s = 1 - \ln (x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s) - \left(\frac{x_1^s \Lambda_{13}}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} + \frac{x_2^s \Lambda_{23}}{x_1^s \Lambda_{21} + x_2^s + x_3^s \Lambda_{23}} + \frac{x_3^s}{x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s} \right) \quad (14)$$

For systems which have similar adsorbates, the problem can be simplified by neglecting the interactions between different adsorbates (i.e., setting Λ_{12} and Λ_{21} equal to unity). If this is not the case, the adsorbate interactions must be approximated in some manner or determined from the mixture data itself. For now, we will neglect these interactions, but will discuss a method of estimating them later on.

The remaining tasks are 1) to introduce the dividing surface definition since the surface excess mole fraction, as well as the other properties, depend on this definition and 2) to obtain an expression for the exponential term containing the pure component standard state free energy of adsorption. The dividing surface is defined with the convention introduced by Lucassen-Reynders (1972). The definition of the surface is given such that the limiting adsorption concentration is the average of those of the adsorbates

$$\Gamma_m^\infty \equiv \left(\frac{\Gamma_1}{\Gamma_1 + \Gamma_2} \right) \Gamma_1^\infty + \left(\frac{\Gamma_2}{\Gamma_1 + \Gamma_2} \right) \Gamma_2^\infty \quad (15)$$

where

$$\Gamma_m{}^\infty = \Gamma_1 + \Gamma_2 + \Gamma_3 \tag{16}$$

This definition has the advantage of allowing the description of adsorbed mixtures containing adsorbates which have unequal values of the saturation amount. Multiplying by the total area of the surface, A,

$$n_m{}^{s,\infty} = x_1 n_1{}^{s,\infty} + x_2 n_2{}^{s,\infty} \tag{17}$$

The expressions for the partial molar areas can then be derived from the following equation (Lucassen-Reynders, 1972)

$$\frac{1}{\bar{a}_i} = \Gamma_i - \Gamma_j \left(\frac{\partial \Gamma_i}{\partial \Gamma_j}\right)_{T,P,\Gamma_k/\Gamma_j}, \quad i \neq j \quad \text{and} \quad k \neq i, j \tag{18}$$

Thus

$$\bar{a}_3 = \frac{A}{n_m{}^{s,\infty}} \tag{19}$$

and

$$\bar{a}_i = \bar{a}_3 + \left(1 - \frac{n_i{}^{s,\infty}}{n_m{}^{s,\infty}}\right)\frac{A}{n_m{}^s}, \quad i = 1 \text{ or } 2 \tag{20}$$

Combining Equations (11), (19), and (20) one obtains

$$-\frac{\pi \bar{a}_i}{RT} = \left[1 + \frac{n_m{}^{s,\infty} - n_i{}^{s,\infty}}{n_m{}^s}\right] \ln \gamma_3{}^s x_3{}^s \tag{21}$$

The standard state free energy of adsorption is actually defined by Equation (4).

$$\exp\left(\frac{\Delta G_i{}^o}{RT}\right) \equiv \left(\frac{\phi_i y_i P}{\gamma_i{}^s x_i{}^s}\right) \exp\left(-\frac{\pi \bar{a}_i}{RT}\right) \tag{22}$$

Since this relationship is true for the whole range of composition, it is possible to apply it to the condition such that the spreading pressure approaches zero (i.e., infinite dilution), and there is only one adsorbate present (i.e. pure component adsorption). In this case

$$x_i{}^s = \theta = n_i{}^s / n_i{}^{s,\infty}$$

$$y_i = 1$$

$$\phi_i \to 1$$

and

$$\pi \to 0$$

or

$$\exp\left(\frac{\pi \bar{a}_i}{RT}\right) \to 1$$

Thus

$$\exp\left(\frac{\Delta G_i{}^o}{RT}\right) = n_i{}^{s,\infty} \cdot \lim_{x_i{}^s \to 0}\left(\frac{1}{\gamma_i{}^s}\right) \cdot \lim_{p \to 0}\left(\frac{p}{n_i{}^s}\right) \tag{23}$$

Substituting the limits of Equations (1) and (12) into Equation (23) gives

$$\exp\left(\frac{\Delta G_i{}^o}{RT}\right) = \frac{n_i{}^{s,\infty}}{b_i} \Lambda_{i3} \exp\left(\Lambda_{3i} - 1\right) \tag{24}$$

The final equilibrium equation for the distribution of adsorbate i is now obtained by substituting Equation (24) into Equation (10).

$$\phi_i y_i P = \gamma_i{}^s x_i n_m{}^s \frac{n_i{}^{s,\infty} \Lambda_{i3}}{n_m{}^{s,\infty} b_i} \exp(\Lambda_{3i} - 1) \exp\left(\frac{\pi \bar{a}_i}{RT}\right) \tag{25}$$

There are, for binary adsorption, two similar independent equations corresponding to the two adsorbates. For adsorption at moderate pressure, the gas mixture is approximately ideal, and thus the fugacity coefficient is usually set equal to unity.

According to Equations (8), (9), (11), (13), (14), (19) and (20), the activity coefficients and the spreading pressure depend only on the pure component parameters, the adsorbed phase composition, x_i, and the total volume adsorbed, $n_m{}^s$. The two equilibrium equations as expressed by Equation (25) can thus be used to solve for its two unknown variables, for example, y_i and $n_m{}^s$ at a given x_i. The solution is obtained by trial and error.

CALCULATION PROCEDURE

The procedure for calculating the equilibrium composition relationship (i.e., the adsorption phase diagrams) and the total amount adsorbed, $n_m{}^s$ using only the parameters obtained from the single-component adsorption data is as follows:

1. Use Equation (1) to obtain $n_i{}^{s,\infty}$, b_i, Λ_{i3} and Λ_{3i} for each pure component from regression of the experimental isotherm data.
2. Select an $x_1 . (x_2 = 1 - x_1)$.
3. Use Equation (17) to calculate $n_m{}^{s,\infty}$.
4. Use Equation (21) for $\pi \bar{a}_i / RT$.
5. Use Equations (13) and (14) for the activity coefficients.
6. Solve the two equilibrium equations (corresponding to adsorbate 1 and 2) as expressed by Equation (25) simultaneously for y_1 $(y_2 = 1 - y_1)$ and $n_m{}^s$, by trial and error.

At moderate pressures, the fugacity coefficients can be set equal to one, and the two independent equations can be summed to eliminate y_i, permitting a simpler solution for $n_m{}^s$.

The correlation can also be extended to predict multicomponent adsorption systems without any complication. The equilibrium equation (25) is still applicable; however, the equations for the activity coefficients (Equation 12) become more complex.

ADSORBATE—ADSORBATE INTERACTIONS

A limitation of the new correlation is the assumption that the interactions between different types of adsorbed molecules are negligible. That is, the Wilson parameters, Λ_{12} and Λ_{21}, in Equations (13) and (14) have been set equal to unity. The model would be improved if values of these two parameters could be determined. At present, these can only be estimated from an equation analogous to that introduced by Wilson for a bulk liquid mixture (Prausnitz, 1969)

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp - \left(\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{26}$$

To apply this equation to the binary mixture of adsorbed molecules, the size ratio, v_j/v_i, is first defined to be that at the limiting adsorption. Equation (26) thus becomes

$$\Lambda_{ij} = \frac{n_i{}^{s,\infty}}{n_j{}^{s,\infty}} \exp - \left(\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{27}$$

The remaining task is to obtain the energies of interaction, λ_{ii} and λ_{ij}. The i-i energies of interaction between pure bulk liquid molecules can be approximated according to Reid et al. (1977) by

$$\lambda_{ii} = \frac{-2}{z}\left(\Delta H_{v_i} - RT\right) \tag{28}$$

For an adsorption system, the analogy to the enthalpy of vaporization ΔH_{v_i} is the enthalpy of desorption which is the difference between the enthalpy state of molecules restricted in the adsorbed phase and that of random molecules in the vapor phase. The value of the enthalpy of desorption for each adsorbate should be calculated at the mixture equilibrium condition. As a first approximation, the isosteric enthalpy of desorption at infinite dilution may be used instead.

$$\lambda_{ii} = \frac{-2}{z}\left(-q^{\theta}_{st} - RT\right) \tag{29}$$

The coordination number z of a molecule in the adsorbed phase, at present, can not be determined because it is dependent on both the coverage and the adsorption system. It has therefore been obtained empirically, as described in the evaluation section.

Finally, the cross coefficient λ_{ij} is assumed to be a geometric mean of the pure component coefficients, λ_{ii} and λ_{jj}

$$\lambda_{ij} = (\lambda_{ii}\lambda_{jj})^{1/2} \tag{30}$$

In this manner, the Wilson parameters, Λ_{12} and Λ_{21}, can be approximated by using information from the pure component adsorption data only.

RELATIONSHIP BETWEEN THE VACANCY SOLUTION MODEL AND OTHER ADSORBED SOLUTION THEORIES

When the surface definition is adopted so that $\Gamma_3 = 0$, the ternary vacancy solution system is reduced to a binary system of adsorbates. The chemical potential of the adsorbates in the gas phase, assumed to be ideal, can now be presented by

$$\mu_i^g = \mu_i^{*g} + RT \ln y_i P \tag{31}$$

Equating this with the chemical potential of the component in the surface phase as given by Equation (2), the equilibrium equation derived by Sircar and Myers (1973) can be obtained

$$y_i P = \gamma_i^s x_i \exp\left(\frac{\mu_i^{os} - \mu_i^{*g}}{RT}\right) \exp\left(\frac{\pi \bar{a}_i}{RT}\right) \tag{32}$$

By applying the above equation to pure-component adsorption equilibrium at the standard state condition

$$\exp\left(\frac{\mu_i^{os} - \mu_i^{*g}}{RT}\right) = P_i^o \exp\left(\frac{-\pi_i^o a_i^o}{RT}\right) \tag{33}$$

Substituting Equation (33) into Equation (32) gives the equation of Sircar and Myers

$$y_i P = \gamma_i^s x_i P_i^o \exp\left(\frac{\pi \bar{a}_i - \pi_i^o a_i^o}{RT}\right) \tag{34}$$

Before applying this equation, the standard state must be defined. Myers and Prausnitz (1965) selected the standard state to be that condition where the spreading pressures of both pure components are equal to that of the mixture. (Although this definition is reasonable, an extrapolation far beyond the mixture pressure is usually necessary, to raise the value of the spreading pressure of the less strongly adsorbed component to that of the mixture.) With this standard state, Equation (34) reduces to the simple expression of Myers and Prausnitz

$$y_i p(\pi) = \gamma_i^s x_i P_i^o(\pi) \tag{35}$$

In order to use Equation (35), all interactions within the adsorbed mixture have to be neglected, for there is no proper method of estimating the activity coefficients. The equation is analogous to Raoult's law, unable to describe such non-ideal behavior as the formation of azeotropes. Unlike Raoult's law, however, this equation can predict adsorption phase diagrams that are asymmetric, because the standard state pressures of the adsorbates vary as a function of the composition.

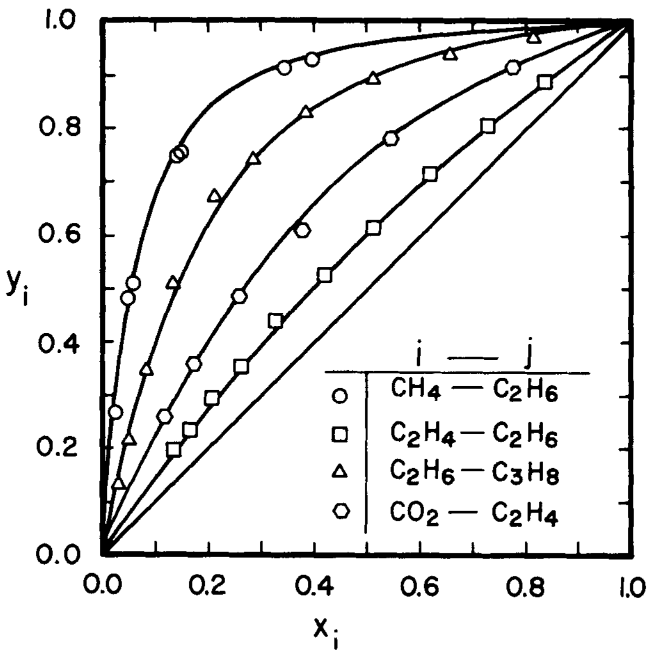

Figure 1. Adsorption phase diagrams for mixtures adsorbed on Nuxit-AL activated carbon at 293.2 K and approximately 1 bar. Points are experimental data of Szepesy and Illés (1963). Solid line—vacancy solution model.

In our approach, the adsorbate-adsorbent as well as the adsorbing molecule-adsorbed molecule interactions are taken into account, by obtaining the Wilson parameters from the pure component behavior. The adsorbate-adsorbate interactions can be approximated as discussed earlier. Accordingly, the new correlation can predict asymmetric adsorption phase diagrams as well as azeotrope formation.

EVALUATION

The new correlation has been tested on two different binary gas mixture adsorption systems: binary mixtures of O_2, N_2, and CO on zeolite 10X at 144.3K, 172.0K, 227.6K and 273.2K and 1 bar total pressure (Danner and Wenzel 1969, Nolan 1978) and those of CH_4, C_2H_4, C_2H_6, C_3H_6, n-C_4H_{10}, and CO_2 on Nuxit-AL activated carbon at either 293.2K or 333.2K or both and approximately 1 bar total pressure (Szepesy and Illés 1963). The gas adsorption isotherm equation based on the vacancy solution theory has been successfully evaluated with the pure-component data of these two systems in other work (Suwanayuen and Danner 1980). The single-component parameters required for the mixture adsorption equilibria predictions are tabulated there.

Examples of experimental adsorption phase-diagrams are compared with the theoretical curves predicted by Equation (25) for the Nuxit-AL carbon system in Figure 1 and for the zeolite 10X system in Figure 2 and 3. In all calculations, the adsorbate-adsorbate interactions are assumed to be negligible ($\Lambda_{12} = \Lambda_{21} = 1$). The total amounts adsorbed, both experimental and predicted, are plotted in Figures 4 and 5 for the molecular sieves and the activated carbon, respectively. Also shown in Figures

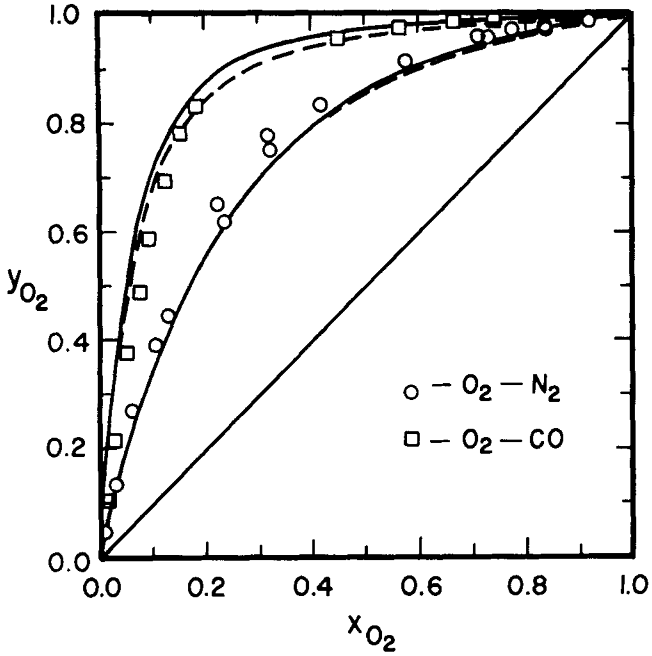

Figure 2. Adsorption phase diagrams for O_2-N_2 and O_2-CO mixtures on zeolite 10X at 227.6 K and 101.3 kPa. Points are experimental data of Nolan (1978): solid line—vacancy solution model; dashed line—simplified statistical thermodynamic model.

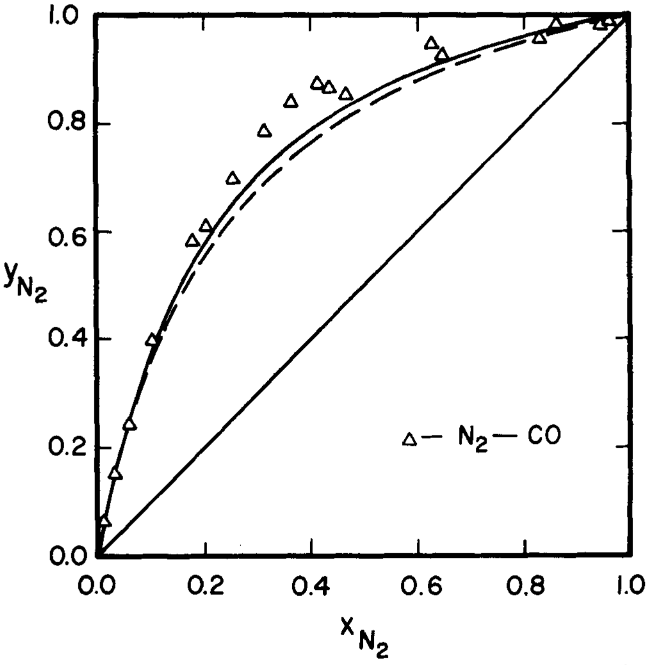

Figure 3. Adsorption phase diagram for N_2-CO mixtures on zeolite 10X at 227.6 K and 101.3 kPa. Points are experimental data of Nolan (1978): solid line—vacancy solution model; dashed line—simplified statistical thermodynamic model.

2, 3 and 5 are the curves predicted by the simplified statistical thermodynamic correlation of Ruthven (1976). The regression parameters used for this correlation are given in Table 1.

For the Nuxit-AL activated carbon system, agreement between the experimental and the calculated data is excellent. The assumption that the adsorbate-adsorbate interactions, especially those caused by size differences, are negligible with respect to other interactions is quite acceptable for hydrocarbons adsorbed on activated carbon.

For the zeolite systems, the predictions of the new correlation are reasonably accurate, but not as accurate as for the carbon systems. Some results are very similar to those predicted by the statistical thermodynamic model. When all the data including those not shown are considered, however, the new method gives better agreement. Predictions of this model can be improved by taking into account the adsorbate-adsorbate interactions through the Wilson parameters, Λ_{12} and Λ_{21}.

An example of this improvement is shown for the O_2-N_2-zeolite 10X system in Figure 6. Λ_{12} and Λ_{21} were estimated by Equations (27), (29) and (30) to be 2.441

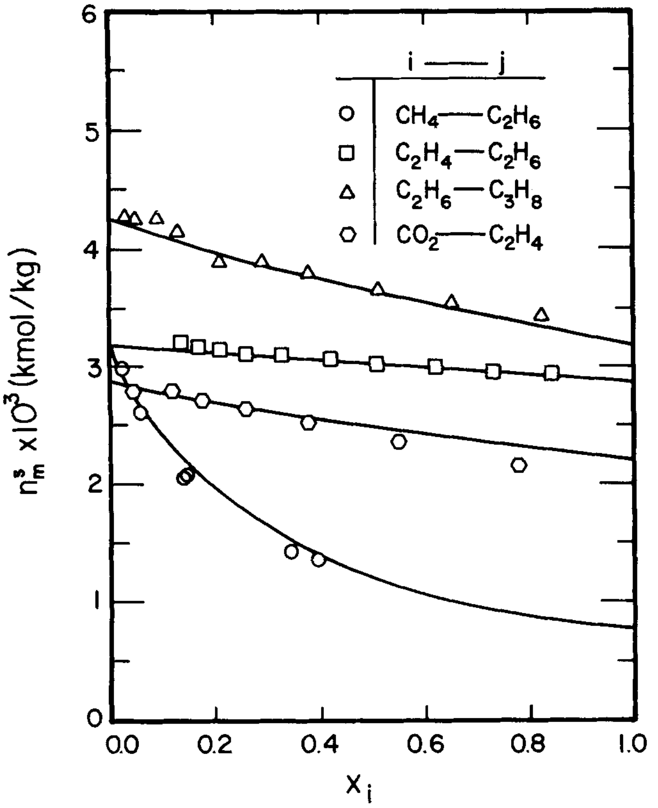

Figure 4. Total volume of mixtures adsorbed on Nuxit-AL activated carbon at 293.2 K and approximately 1 bar. Points are experimental data of Szepesy and Illés (1963). Solid line—vacancy solution model.

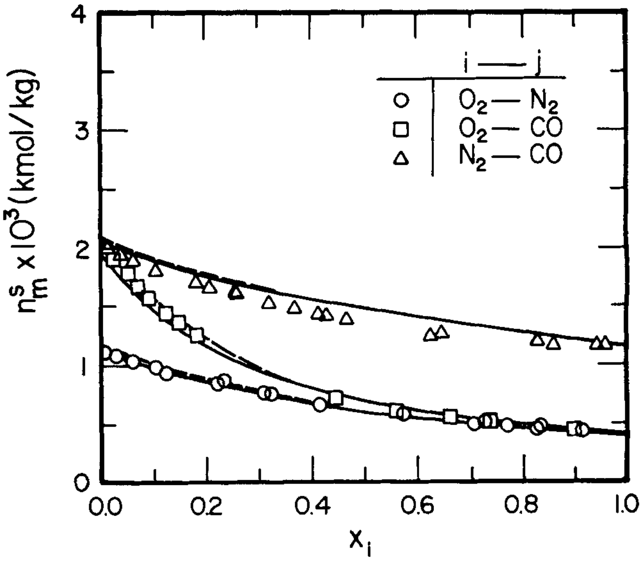

Figure 5. Total volume of O_2-N_2, O_2-CO and N_2-CO mixtures adsorbed on zeolite 10X at 227.6K and 101.3 kPa. Points are experimental data of Nolan (1978): solid line—vacancy solution model; dashed line—simplified statistical thermodynamic model.

TABLE 1. REGRESSION PARAMETERS FOR THE SIMPLIFIED STATISTICAL THERMODYNAMIC CORRELATION OF RUTHVEN (1976) AS APPLIED TO ADSORPTION OF VARIOUS GASES ON ZEOLITE 10X* AT 227.6 K

Gases	Henry's law constant (molecules/ cavity · Pa)	Molecular volume (nm³/ molecules)	Max. number of molecules per cavity
O_2	9.743×10^{-6}	0.04443	20
N_2	6.689×10^{-5}	0.11497	7
CO	3.043×10^{-4}	0.10711	8

* Cavity volume = 0.89435 nm³.
Number of cavities per unit cell = 8.
Number of unit cells per gram anhydrous adsorbent = 0.455×10^{20}.
Amount of anhydrous adsorbent in a pellet = 80%.

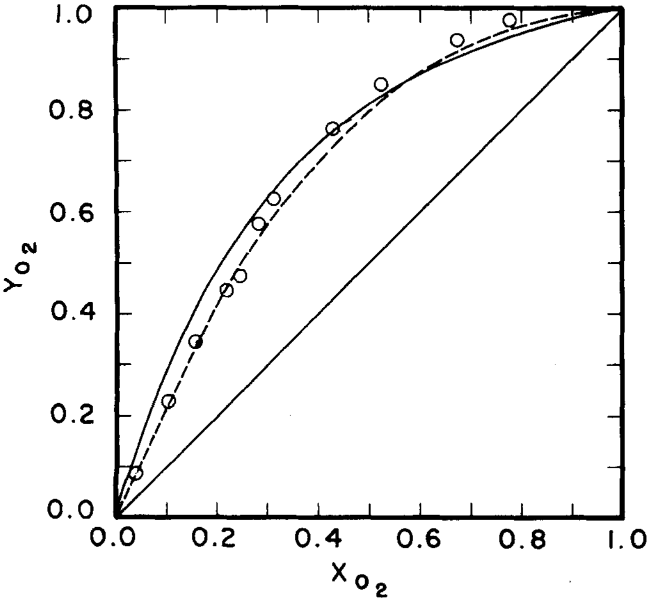

Figure 6. Adsorption phase diagram for O_2-N_2 mixtures on zeolite 10X at 144.3 K and 101.3 kPa. Points are experimental data of Danner and Wenzel (1969): solid line—vacancy solution model with Λ_{12} and Λ_{21} = 1.0; dashed line—vacancy solution model with estimated values of Λ_{12} and Λ_{21}.

and 0.3724, respectively. The improvement observed in this case is typical of that found for the rest of the zeolite systems. For these calculations the coordination number in the zeolite cavity was assumed to be three.

We also applied the ideal adsorbed solution theory developed by Myers and Prausnitz to the systems shown. This method gives essentially the same results as obtained from the new model. Therefore, the predicted curve are not shown here. The two adsorption systems evaluated are approximately ideal; the adsorption phase diagrams are quite symmetric and give no indication of azeotrope formation. Where the vacancy solution model can predict azeotropic behavior, the ideal adsorbed solution theory cannot.

In conclusion, the new mixture correlation is believed to be the best of presently available models. Its applicability is more general than that of the ideal adsorbed solution theory or the simplified statistical model. From an applications point of view, the new model is the most convenient to use in computer simulations: Its calculation is simple and direct, and an extrapolation beyond the experimental pressure ranges is not required.

ACKNOWLEDGMENT

Portions of this work were supported under Grant No. GK-18631 from the National Science Foundation and administered through the Center for Air Environment Studies of the Pennsylvania State University. Support of S. Suwanayuen through a grant from Air Products and Chemicals, Inc. is also gratefully acknowledged.

NOTATION

$\bar{a}_i$ = partial molar surface area of i (m²/kmol)

a_i^o = standard state molar area of i (m²/kmol)

A = surface area of adsorbent (m²/kg)

b_i = Henry's Law Constant of i (kmol/kg·kPa)

ΔG_i^o = standard state free energy of adsorption of pure i (J/mol)

ΔH_{vi} = enthalpy of vaporization of liquid i (J/mol)

n_i^o = number of moles of pure i adsorbed at standard state (kmol/kg)

n_i^s = number of moles of i in surface phase (kmol/kg)

$n_i^{s,\infty}$ = maximum number of moles of i in surface phase (kmol/kg)

n_m^s = total number of moles of mixture in surface phase (kmol/kg)

$n_m^{s,\infty}$ = maximum total number of moles of mixture in surface phase (kmol/kg)

p = pressure of pure gas in equilibrium with its adsorbed phase (kPa)

P = total pressure of mixture in equilibrium with its adsorbed phase (kPa)

P_i^o = standard state pressure of pure gas i (kPa)

q^θ_{st} = isosteric enthalpy of adsorption (J/mol)

T = temperature of adsorption system (K)

v_i, v_j = molar liquid volume (m³/kmol)

x_i = mole fraction of i in vacancy-free adsorbed phase

x_i^s = mole fraction of i in adsorbed phase vacancy solution

y_i = mole fraction of i in vacancy-free vapor phase

z = coordination number of an adsorbed molecule

Greek Letters

γ_i^s = activity coefficient of i in adsorbed phase vacancy solution

Γ_i = surface excess concentration of i (kmol/m²)

Γ_i^∞ = maximum surface excess concentration of pure i (kmol/m²)

Γ_m^∞ = maximum surface excess concentration of mixture (kmol/m²)

θ = fractional coverage

λ_{ii} = energy of interaction between two i molecules (J/mol)

λ_{ij} = energy of interaction between molecule i and molecule j (J/mol)

Λ_{ij}, Λ_{ji} = Wilson's parameters for interaction between i and j

μ_i^g = chemical potential of i in bulk gas mixture (J/mol)

μ_i^s = chemical potential of i in adsorbed phase vacancy solution (J/mol)

μ_i^{*g} = standard state chemical potential of pure gas i at 1 bar (J/mol)

μ_i^{os} = standard state chemical potential of pure i in adsorbed phase vacancy solution (J/mol)

π = surface, spreading, or osmotic pressure of adsorbed mixture (N/m)

π_i^o = standard state spreading pressure of pure i (N/m)

ϕ_i = fugacity coefficient of i in bulk gas mixture

Superscripts

g = gas phase value
o = standard state value
s = surface phase value
∞ = value at maximum adsorption limit
$*$ = standard state value at 1 bar total pressure

Subscripts

i, j, k = component i, j, k
m = mixture
n = total number of components in a mixture
1, 2 = adsorbates
3 = vacancy

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The Influence of Mixing on the Antisolvent Induced Agglomeration and Sedimentation of Mineral Matter in Coal Derived Liquids

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There are several ways to remove mineral matter from coal-derived liquids: antisolvent agglomeration and subsequent sedimentation is one. Adding antisolvent to coal liquids causes asphaltenes and/or preasphaltenes in the oil to precipitate. The precipitated asphaltenes then agglomerate the particles, increasing the sedimentation rate. The magnitude of this increase depends on the mixing conditions used to disperse the antisolvent in the oil.

This article discusses the results of sedimentation experiments performed on the antisolvent addition to coal liquids, using an x-ray detection system. The system has the capability of high temperature (up to 315°C) and high pressure (up to 2.75 × 10^6 Pa). The important parameters are the mixing time, the impeller speed, and the antisolvent addition rate. These are studied in detail for the antisolvent Soltrol.

SCOPE

Studied here is the influence of mixing conditions on the antisolvent-induced agglomeration of mineral matter and subsequent settling in coal-derived liquids at 285°C. The commercially available aliphatic hydrocarbon Soltrol-130 is the antisolvent. The variables studied are the antisolvent-to-oil ratio (0.4 to 1.0 by volume), mixing time (2 to 30 min. at a constant mixing speed of 250 rpm), mixing speed (100 to 550 rpm at a constant 30 min.), sequential mixing (mixing at 550 rpm for 2 min. followed by mixing at 250 rpm for various times up to 28 min.) and sequential antisolvent addition (added in two aliquotes, five minutes apart, with the total antisolvent to oil ratio of 0.64 by volume). Previous theories of breakage and agglomerations are extended to model the influence of mixing time and

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