

$$\begin{aligned}
\frac{\partial F}{\partial X_j} &= -2 \sum_i [g(\tau_i) - \hat{g}(\tau_i)] \frac{\partial \hat{g}(\tau_i)}{\partial X_j} \\
&= -2 \sum_i [g(\tau_i) - \hat{g}(\tau_i)] A \exp(-\beta^2 \tau_i^2 / 4) \frac{\partial (FT[P(\omega)])}{\partial X_j} \\
&= -2 \sum_i [g(\tau_i) - \hat{g}(\tau_i)] A \exp(-\beta^2 \tau_i^2 / 4) \left(FT \left[\frac{\partial P(\omega)}{\partial X_j} \right] \right) \quad (\text{A3})
\end{aligned}$$

where the last step uses Leibnitz's rule.²⁸

Now the spectrum, eq 8, can be written in the form

$$P(\omega|X) = C \operatorname{Im} \left[\frac{N}{D(\omega)} \right] \quad (\text{A4})$$

where C is a constant, independent of the surface properties

$$N = i\omega\eta(m + q) + \epsilon q^2 \quad (\text{A5})$$

and $D(\omega)$ is defined by eq 3. Differentiating eq A4 with respect to one of the surface parameters yields

$$\frac{\partial P(\omega|X)}{\partial X_j} = C \operatorname{Im} \left(\frac{N}{D} \left[\frac{\partial N / \partial X_j}{N} - \frac{\partial D / \partial X_j}{D} \right] \right) \quad (\text{A6})$$

provided the X_j are real. The derivatives of F (eq A3) with respect to the surface properties can then be coded for computation by using eq A6 and the derivatives of the simpler functions N and D :

$$\begin{aligned}
\frac{\partial N}{\partial \gamma_0} &= \frac{\partial N}{\partial \gamma'} \\
&= 0 \quad (\text{A7})
\end{aligned}$$

$$\begin{aligned}
\frac{\partial N}{\partial \epsilon_0} &= \frac{1}{i\omega} \frac{\partial N}{\partial \epsilon'} \\
&= q^2 \quad (\text{A8})
\end{aligned}$$

$$\begin{aligned}
\frac{\partial D}{\partial \gamma_0} &= \frac{1}{i\omega} \frac{\partial D}{\partial \gamma'} \\
&= q^2 [\epsilon q^2 + i\omega(m + q)] \quad (\text{A9})
\end{aligned}$$

$$\begin{aligned}
\frac{\partial D}{\partial \epsilon_0} &= \frac{1}{i\omega} \frac{\partial D}{\partial \epsilon'} \\
&= q^2 [\gamma q^2 + i\omega(m + q) - \omega^2 \rho / q] \quad (\text{A10})
\end{aligned}$$

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An Extended Langmuir Model for Adsorption of Gas Mixtures on Heterogeneous Surfaces

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A model is presented for calculating the adsorption from gas mixtures on energetically heterogeneous adsorbents. It assumes a uniform distribution of adsorption energies and the applicability of the extended Langmuir model for adsorption from gas mixtures on each patch of surface of uniform energy. The model can be used directly to calculate mixed gas adsorption with only pure gas data at, at least, two temperatures. However, a special case of the model is derived which allows for an analytical solution and which requires pure gas data only at one temperature. The analytical form of the model is tested against considerable mixed gas adsorption data with satisfactory results. The model also compares well with other models. Moreover, it is explicit with respect to the component amount adsorbed from a gas mixture, is noniterative, and provides savings in computation.

Introduction

Predictive models for mixture adsorption are necessary in the design and modeling of adsorbers and adsorption processes (Yang, 1987). The amount of computation involved in adsorber design is directly related to the degree of complexity of these models. Although there are many theories and models in the literature which provide an understanding of the adsorption equilibria on a heterogeneous surface, they are seldom used in adsorber design calculations because they are computationally complex, requiring an iterative solution. The purpose of this paper is to derive a simple, noniterative model for predicting mixed gas adsorption on heterogeneous surfaces.

The general methodology for studying surface energetic heterogeneity is to consider a pure gas isotherm applied locally to describe adsorption on a uniform patch of surface and then integrate it over a distribution of adsorption energies (Ross and Olivier, 1964). Depending on the choice of the local isotherm and the type of energy distribution, different global isotherms can be derived (Sircar and Myers, 1984). To apply this methodology to mixed gas adsorption, two approaches are possible: The first approach involves calculating the adsorption isotherm for a pure gas on a heterogeneous surface and then using this pure gas isotherm to determine the mixed gas adsorption isotherm (Myers, 1984). The alternate approach is to assume a mixture adsorption iso-

therm on a uniform patch of surface and integrate it over a distribution of energies (Nakahara, 1986; Valenzuela et al., 1988; Moon and Tien, 1988).

In this work, the extended Langmuir (EL) model is used to describe mixed gas adsorption on each patch of surface of uniform energy, and the distribution of energies is described by a uniform distribution. Although the EL model is not thermodynamically consistent, unless the values of q_m are the same for all components in a gas mixture, it remains the most useful model in the design and modeling of adsorber behavior (Yang, 1987). LeVan and Vermeulen, 1981, compared the predictions of the EL model with those of ideal adsorbed solution (IAS) theory and showed that the error caused by the difference in values of q_m of various components in a mixture is rather small. Moreover, there are many models in the literature which suffer from a lack of thermodynamic consistency; nevertheless, they are still useful for the prediction of mixed gas adsorption equilibria. The critique of different models given by Sircar and Myers (1973) and that given by Talu and Myers (1988) exemplify this point.

Derivation of Proposed Model

Adsorption on an energetically heterogeneous surface can be described by the following equation (Ross and Olivier, 1964):

$$n(T, P) = \int_{\epsilon_{\min}}^{\epsilon_{\max}} n(T, P, \epsilon) f(\epsilon) d\epsilon \quad (1)$$

where $n(T, P)$ is the amount adsorbed on the heterogeneous surface at temperature T and pressure P , $n(T, P, \epsilon)$ is the amount adsorbed on a homogeneous patch with energy ϵ , $f(\epsilon)$ is the normalized distribution function, and ϵ_{\min} and ϵ_{\max} are the minimum and maximum energies, respectively. Assuming that adsorption on a homogeneous surface can be described by the Langmuir isotherm ($n(T, P, \epsilon) = q_m b P / (1 + b P)$, where $b = b_0 \exp(\epsilon / RT)$) and that the adsorption energy distribution can be approximated by a uniform distribution, eq 1 gives (Myers, 1984)

$$n(T, P) = \frac{q_m}{2s} \ln \frac{1 + \bar{b} P e^s}{1 + \bar{b} P e^s} \quad (2)$$

where

$$\bar{b} = b_0 \exp(\bar{\epsilon} / RT) \quad (2a)$$

$$s = 3^{1/2} \sigma / RT \quad (2b)$$

The parameters $\bar{\epsilon}$ and σ are the mean and square root of variance of energy, q_m and b are the Langmuir constants, and s is the heterogeneity parameter related to the spread of the energy distribution.

For adsorption of an N -component gas mixture on a heterogeneous surface, a joint probability function is needed for the energy distribution, which reflects the fact that, in addition to the distribution of adsorption sites, there are N adsorption energies for each adsorption site (Jaroniec and Rudzinski, 1975). By assuming "perfect positive correlation", i.e., the ordering of the sites from low to high energy is the same for each adsorbate, the integral containing the conditional probability function can be simplified to give the amount adsorbed from a gas mixture, n_i , of the i th component as

$$n_i = \int_0^\infty n_i(T, P, y, \epsilon_1, \epsilon_2, \dots, \epsilon_N) f(\epsilon_i) d\epsilon_i \quad (3)$$

where the function n_i in the integral is the amount of the i th component adsorbed from a mixture on a homo-

geneous surface. In the proposed model, the EL model is used to describe adsorption of component i from a mixture on a homogeneous patch of surface ($n_i(T, P, y, \epsilon_1, \epsilon_2, \dots, \epsilon_N)$). It is given by

$$n_i(T, P, y) = \frac{q_{m,i} b_i P y_i}{1 + \sum (b_j P y_j)} \quad (4)$$

where $b_j = b_{0,j} \exp(\epsilon_j / RT)$.

The parameters $q_{m,i}$ and b_i correspond to the pure gas Langmuir constants for component i , and y_i is the mole fraction of component i in the gas phase. The proposed model also assumes a uniform distribution of energies for all components in the gas mixture:

$$f(\epsilon_i) = 1/(\epsilon_{i,\max} - \epsilon_{i,\min}) \quad \text{for } \epsilon_{i,\min} \leq \epsilon_i \leq \epsilon_{i,\max} \\ f(\epsilon_i) = 0 \quad \text{for } \epsilon_i < \epsilon_{i,\min} \text{ and } \epsilon_i > \epsilon_{i,\max} \quad (5)$$

where the mean energy $\bar{\epsilon}_i = (\epsilon_{i,\max} + \epsilon_{i,\min})/2$ and the square root of variance $\sigma_i = (\epsilon_{i,\max} - \epsilon_{i,\min})/(2(3)^{1/2})$.

To simplify the integration in eq 3, Valenzuela et al. (1988) assumed that the cumulative energy distribution function was the same for all components in the gas mixture, i.e.

$$F(\epsilon_i) = F(\epsilon_j) \quad (6)$$

where $F(\epsilon) = \int_0^\epsilon f(\epsilon) d\epsilon$. For a uniform distribution, eq 6 becomes

$$\frac{\epsilon_i - \epsilon_{i,\min}}{\sigma_i} = \frac{\epsilon_j - \epsilon_{j,\min}}{\sigma_j} \quad (7)$$

Combining eq 4-7 and substituting into eq 3 yield

$$n_i = \int_{\epsilon_{i,\min}}^{\epsilon_{i,\max}} \frac{q_{m,i} b_{0,i} P y_i \exp(\epsilon_i / RT)}{1 + P \sum_{j=1}^N b_{0,j} y_j \exp(\epsilon_j / RT)} \frac{1}{(\epsilon_{i,\max} - \epsilon_{i,\min})} d\epsilon_i \quad (8)$$

where $\epsilon_j = (\epsilon_i - \epsilon_{i,\min}) \sigma_j / \sigma_i + \epsilon_{j,\min}$. Equation 8 can be written

$$n_i = \Omega_i \int_{\epsilon_{i,\min}}^{\epsilon_{i,\max}} \frac{\exp(\epsilon_i / RT)}{1 + \sum_{j=1}^N \nu_{ij} \exp[\sigma_j / \sigma_i (\epsilon_i / RT)]} d\epsilon_i \quad (9)$$

where

$$\Omega_i = q_{m,i} b_{0,i} P y_i / (\epsilon_{i,\max} - \epsilon_{i,\min})$$

$$\nu_{ij} = P b_{0,j} y_j \exp(\epsilon_{j,\min} - \sigma_j \epsilon_{i,\min} / \sigma_i)$$

Equation 9 describes the adsorption of component i from a gas mixture on a heterogeneous surface. It is referred to here as the numerical heterogeneous extended Langmuir (NHEL) model. Although eq 9 requires numerical integration, it is explicit with respect to the component amount adsorbed. According to eq 2 and 5, pure gas adsorption isotherms are required for each component in the gas mixture at, at least, two temperatures to evaluate the limits of integration ($\epsilon_{i,\min}$ and $\epsilon_{i,\max}$) in eq 9. Nevertheless, a special case of eq 9 allows for an analytical solution to be obtained which requires pure gas isotherms only at one temperature.

An analytical solution to eq 9 can be obtained by assuming $\sigma_j / \sigma_i = 1.0$, i.e., the variance of the energy distribution is the same for all components in the gas mixture, or

$$\sigma_1 = \sigma_2 = \dots = \sigma_N = \dots = \bar{\sigma} \quad (10)$$

where $\bar{\sigma}$ is the average value of σ . This assumption is

Table I. Model Parameters for Pure Gas Adsorption Isotherms

system	<i>T</i> , K	Langmuir ^e		LRC ^f			LUD ^g		
		<i>q_m</i> , mol/kg	<i>b</i> , 1/atm	<i>q_m</i> , mol/kg	<i>b</i> , 1/atm	η	<i>q_m</i> , mol/kg	\bar{b} , 1/atm	<i>s</i>
CH ₄ ^a	212.7	7.169	8.231×10^{-1}	8.594	1.690×10^0	0.635	8.323	5.439×10^{-1}	2.824
C ₂ H ₆ ^a	212.7	6.684	$3.974 \times 10^{+1}$	8.172	$1.540 \times 10^{+1}$	0.489	7.800	1.948×10^{-1}	4.016
C ₂ H ₄ ^a	212.7	7.237	$1.605 \times 10^{+1}$	9.717	8.879×10^0	0.428	9.434	5.365×10^0	4.843
CH ₄ ^a	260.2	6.109	2.351×10^{-1}	7.126	4.557×10^{-1}	0.765	7.104	1.617×10^{-1}	2.096
C ₂ H ₆ ^a	260.2	5.998	4.101×10^0	7.274	5.188×10^0	0.539	6.874	2.675×10^0	3.418
C ₂ H ₄ ^a	260.2	6.228	2.381×10^0	7.703	3.557×10^0	0.565	7.333	1.441×10^0	3.245
CH ₄ ^a	301.4	5.216	1.029×10^{-1}	5.762	1.617×10^{-1}	0.878	5.812	8.821×10^{-2}	1.429
C ₂ H ₆ ^a	301.4	5.263	1.161×10^0	6.099	1.970×10^0	0.684	5.950	8.527×10^{-1}	2.514
C ₂ H ₄ ^a	301.4	5.411	7.79×10^{-1}	6.568	1.396×10^0	0.674	6.541	4.557×10^{-1}	2.683
CH ₄ ^b	296.0	6.149	1.764×10^{-1}	6.111	1.617×10^{-1}	1.021	6.387	1.617×10^{-1}	1.414
CO ₂ ^b	296.0	9.643	3.235×10^{-1}	10.140	4.557×10^{-1}	0.876	10.020	2.792×10^{-1}	1.301
H ₂ ^b	296.0	5.738	5.877×10^{-3}	20.520	4.631×10^{-3}	0.807	9.818	1.470×10^{-3}	1.951
CO ^b	296.0	6.686	8.821×10^{-2}	6.639	1.617×10^{-1}	0.811	6.723	5.879×10^{-2}	1.880
C ₂ H ₆ ^c	303.0	2.170	$1.935 \times 10^{+1}$	2.689	$1.120 \times 10^{+1}$	0.651	2.621	$1.060 \times 10^{+1}$	2.698
C ₃ H ₈ ^c	303.0	1.861	$1.367 \times 10^{+2}$	2.080	$4.695 \times 10^{+1}$	0.602	2.002	$1.184 \times 10^{+2}$	3.065
C ₂ H ₆ ^c	323.0	2.032	9.069×10^0	2.498	6.807×10^0	0.724	2.882	3.204×10^0	3.015
C ₃ H ₈ ^c	323.0	1.772	$6.895 \times 10^{+1}$	2.067	$2.839 \times 10^{+1}$	0.585	1.984	$5.407 \times 10^{+1}$	3.222
O ₂ ^d	273.0	17.110	7.349×10^{-2}	23.800	5.879×10^{-2}	0.987	18.130	7.349×10^{-2}	0.459
CO ^d	273.0	14.560	4.410×10^{-2}	14.980	1.764×10^{-1}	0.997	15.080	1.617×10^{-1}	0.354
O ₂ ^d	373.0	5.663	4.410×10^{-2}	1.084	1.911×10^{-1}	1.122	5.906	4.410×10^{-2}	0.478
CO ^d	373.0	3.110	2.941×10^{-2}	4.350	8.821×10^{-2}	0.980	3.162	1.176×10^{-1}	0.111

^a BPL activated carbon (Reich et al., 1980). ^b PCB activated carbon (Ritter and Yang, 1987). ^c Molecular sieve carbon (Nakahara et al., 1974, 1981). ^d Silica (Markham and Benton, 1931). ^e $n = q_m bP / (1 + bP)$. ^f $n = q_m bP^\eta / (1 + bP^\eta)$. ^g $n = (q_m / 2s) \ln(1 + bPe^s) / (1 + bPe^{-s})$ (eq 2).

reasonable for the case where the values of s_i of each component in a gas mixture are not markedly different. From eq 10 and 7

$$\epsilon_j = \epsilon_i + (\epsilon_{i,\min} - \epsilon_{j,\min}) \text{ or } \epsilon_j = \epsilon_i + \delta_{ij} \quad (11)$$

The minimum and maximum energies for component j can be written with respect to a reference component i as

$$\epsilon_{j,\min} = \epsilon_{i,\min} + \delta_{ij} \quad (12a)$$

$$\epsilon_{j,\max} = \epsilon_{i,\max} + \delta_{ij} \quad (12b)$$

Substituting eq 10–12 in eq 9 gives

$$n_i = \Omega_i \int_{\epsilon_{i,\min}}^{\epsilon_{i,\max}} \frac{\exp(\epsilon_i/RT)}{1 + \left(\sum_{j=1}^N \nu_{ij} \right) \exp(\epsilon_i/RT)} d\epsilon_i \quad (13)$$

Equation 13 as opposed to eq 9 can be easily integrated because the exponential term in the denominator of the integral is taken out of the summation. Integration and rearrangement of eq 13 give

$$n_i(T, P, y) = \frac{q_{m,i} \bar{b}_i P y_i}{2\bar{s}\alpha} \ln \frac{1 + \alpha \exp(\bar{s})}{1 + \alpha \exp(-\bar{s})} \quad (14)$$

where

$$\alpha = \sum_{j=1}^N \bar{b}_j P y_j \quad (14a)$$

$$\bar{s} = \frac{1}{N} \sum_{j=1}^N s_j \quad (14b)$$

$$\bar{b}_j = b_{j,0} \exp(\bar{\epsilon}_j/RT) \quad (14c)$$

$$s_j = \frac{3^{1/2}}{RT} \sigma_j \quad (14d)$$

Equation 14 describes the adsorption of component i from an N -component gas mixture on a heterogeneous surface. It is referred to here as the analytical heterogeneous extended Langmuir (AHEL) model. The param-

eters needed to use eq 14 can be obtained from the pure gas adsorption isotherms of each component in the gas mixture. Moreover, pure gas adsorption data are required only at one temperature, which makes eq 14 more readily applicable than eq 9. It is worth noting that for $j = 1$ (single component) eq 14 reduces to eq 2, and for $s \rightarrow 0$ (a homogeneous surface) it reduces to the EL model (eq 4).

Results and Discussion

The analytical heterogeneous extended Langmuir (AHEL) model (eq 14) is more convenient to use than the numerical HEL (NHEL) model (eq 9); therefore, the AHEL model is tested against experimental data of 16 binary gas mixtures comprised of 120 data points. The AHEL model predictions are also compared to the predictions from three other models: the extended Langmuir (EL) model (Markham and Benton, 1931), the loading ratio correlation (LRC) (Wojciechowski et al., 1985), and the heterogeneous ideal adsorbed solution (HIAS) theory (Myers, 1984). These models, like the AHEL and NHEL models, require information only from pure gas data for the prediction of mixed gas adsorption. In addition, the AHEL model is compared to the NHEL by using the predictions from 6 of the 16 binary systems to test the assumption of the use of an average value of s in eq 9.

Correlation of Pure Gas Adsorption Data. The pure gas adsorption data of 21 gas-adsorbent systems were fitted by using nonlinear regression to three isotherms: the LRC isotherm given by

$$n = \frac{q_m b P^\eta}{1 + b P^\eta} \quad (15)$$

the Langmuir isotherm (eq 15 with $\eta = 1.0$), and the LUD isotherm (eq 2). The parameter η is related to the spread of the energy distribution. All the experimental data were fitted first to the two-parameter Langmuir isotherm; then, these parameters were used as initial guesses for fitting the data to the three-parameter LRC and LUD isotherms. The resulting parameters are given in Table I.

It should be noted that the overall average errors were 6.3%, 2.0%, and 2.3%, respectively, for the Langmuir, LRC, and LUD isotherms. Thus, as anticipated, the three-parameter models (LRC and LUD) fitted the data better than the two-parameter Langmuir isotherm.

The parameter s in the LUD isotherm and the parameter η in the LRC model are a measure of the spread of the distribution of adsorption energies. As s approaches zero and η approaches unity, the surface approaches homogeneity. By use of these parameters, some interesting observations can be made from the results given in Table I regarding the extent of heterogeneity of different adsorbents. Silica gel appeared to have the most homogeneous surface among all four adsorbents. This is consistent with the nature and structure of silica gel, which is formed from colloidal, polymerized silica with silanol groups (Si-OH) on its surface. PCB-activated carbon appeared to be more homogeneous than BPL carbon. This difference may be caused by the difference in "ash content" (i.e., metal oxide residue upon combustion). The approximate ash contents of PCB and BPL activated carbons are 2% and 10%, respectively. The molecular sieve carbon appeared to be highly heterogeneous. Such a heterogeneity, however, may be derived from structural heterogeneity (Jaroniec, 1987), as the molecular sieve carbon has a micropore distribution between 3 and 7 Å, which is unique among all four adsorbents.

Prediction of Mixed Gas Adsorption Data. This section compares the predictions of binary adsorption equilibria from the AHLE, EL, LRC, and HIAS models. The AHLE and EL models are given by eq 14 and 4, respectively. The LRC model for adsorption of component i from a gas mixture (Wojciechowski, 1985) is given by

$$n_i = \frac{q_{m,i} b_i (P y_i)^{\eta_i}}{1 + \sum_{j=1}^N b_j (P y_j)^{\eta_j}} \quad (16)$$

which may be derived by assuming a quasi-Gaussian energy distribution. The parameters $q_{m,i}$, b_i , and η_i correspond to the pure gas isotherm parameters of component i . The HIAS calculations were similar to those used by Myers (1984). It should be noted that this was the only model (of the four) which required not only a numerical integration routine but also an iterative scheme to solve for n_i . To make a fair comparison between the AHLE and HIAS models, the LUD isotherm (eq 2) was used in the HIAS model with the same parameters listed in Table I.

A comparison of the predictions from the four models (AHLE, EL, LRC, and HIAS) is given in Table II. The comparison is based on the average relative errors of the moles adsorbed for each component:

$$\text{avg rel err} = \frac{100}{N_t} \sum_{i=1}^{N_t} \text{abs} \left(\frac{n_{\text{exp}} - n_{\text{cal}}}{n_{\text{exp}}} \right) \quad (17)$$

where N_t is the number of data points and n is the moles adsorbed of a component in the gas mixture. An overall comparison of the predictions from the same four models for the four different adsorbents is given in Table III. The average errors were calculated by summing over both components in the mixture.

The comparison between the AHLE and HIAS models (see Tables II and III) shows that the predictions from the two models were very similar. However, since the HIAS model is computationally complex, its use requires considerable CPU time in modeling adsorber dynamics. A comparison of the AHLE model to the two nonitera-

Table II. Comparison of Model Predictions to Experimental Mixture Adsorption Equilibria

system	T, K	avg rel err in moles adsorbed for each component, %			
		AHEL	EL	LRC	HIAS
CH ₄	212.7	35.06	51.40	<i>e</i>	23.84
C ₂ H ₆ ^a		3.79	4.75		1.68
CH ₄	212.7	35.52	34.64	<i>e</i>	9.94
C ₂ H ₄ ^a		4.40	5.05		1.17
C ₂ H ₆	212.7	23.56	21.24	30.73	15.86
C ₂ H ₄ ^a		30.17	22.02	30.33	2.72
CH ₄	260.2	16.49	19.03	65.45	13.05
C ₂ H ₆ ^a		2.96	5.79	8.39	3.72
CH ₄	260.2	10.38	12.10	35.73	14.67
C ₂ H ₄ ^a		3.42	6.97	6.62	9.27
CH ₄	301.4	33.84	34.76	24.81	32.63
C ₂ H ₆ ^a		2.95	4.88	4.77	3.63
CH ₄	301.4	22.86	25.89	17.69	26.67
C ₂ H ₄ ^a		6.04	5.57	4.99	5.37
C ₂ H ₆	301.4	8.67	14.71	18.37	19.56
C ₂ H ₄ ^a		17.21	8.36	13.78	22.84
CO	296.0	49.15	71.22	73.09	38.02
CO ₂ ^b		11.22	15.30	11.84	6.56
CH ₄	296.0	9.30	8.79	39.84	40.08
CO ^b		8.71	11.17	85.34	26.71
CH ₄	296.0	35.82	31.25	41.82	10.45
CO ₂ ^b		17.41	16.38	16.62	5.80
CO	296.0	8.62	6.98	7.94	22.87
H ₂ ^b		27.87	23.97	10.80	23.63
C ₂ H ₆	303.0	22.07	31.05	67.02	73.84
C ₃ H ₈ ^c		8.38	12.41	11.95	13.92
C ₂ H ₆	323.0	23.69	35.43	66.58	43.59
C ₃ H ₈ ^c		6.46	13.98	12.46	3.19
O ₂	273.0	3.11	2.95	2.83	24.46
CO ^d		1.40	1.32	2.37	28.81
O ₂	373.0	8.67	8.34	6.68	23.95
CO ^d		3.42	3.89	4.35	35.80

^a BPL activated carbon (Reich et al., 1980). ^b PCB activated carbon (Ritter and Yang, 1987). ^c Molecular sieve carbon (Nakahara et al., 1981). ^d Silica (Markham and Benton, 1931). ^e Errors worse than 100% for at least one component.

Table III. Overall Comparison of Model Predictions to Experimental Mixture Adsorption Equilibria

adsorbent	avg rel err of moles adsorbed, %			
	AHEL	EL	LRC	HIAS
BPL activated carbon	16	18	20	14
PCB activated carbon	21	23	38	22
molecular sieve carbon	15	23	39	35
silica gel	4	4	4	28
avg for all binary mixtures	16.6	18.8	25.0	19.2

tive models (EL and LRC) shows that the AHLE model resulted in better predictions. For example, the average relative errors listed in Table III for the AHLE, EL, and LRC models are 16.6%, 18.8%, and 25%, respectively. Also, the comparison between the predictions from the AHLE and EL models, to some extent, reveals the effect of heterogeneity. Similar to the observations made from the results given in Table I, silica gel seems to be the least heterogeneous.

Comparison of Predictions from AHLE and NHEL Models. The AHLE model was derived from the NHEL model by assuming an average value of s (eq 10) for all the components in the gas mixture. It is, therefore, important to examine the sensitivity of the LUD isotherm to the parameter s . A typical comparison of the LUD isotherms obtained by using the individual values of s and an average value of s is shown in Figure 1 for CH₄ and C₂H₄ on BPL activated carbon at 212.7 K (data source, Reich et al., 1980). The parameters used to evaluate the isotherms in Figure 1 are given in Table I. It is seen from Figure 1 that the LUD isotherms are not very sen-

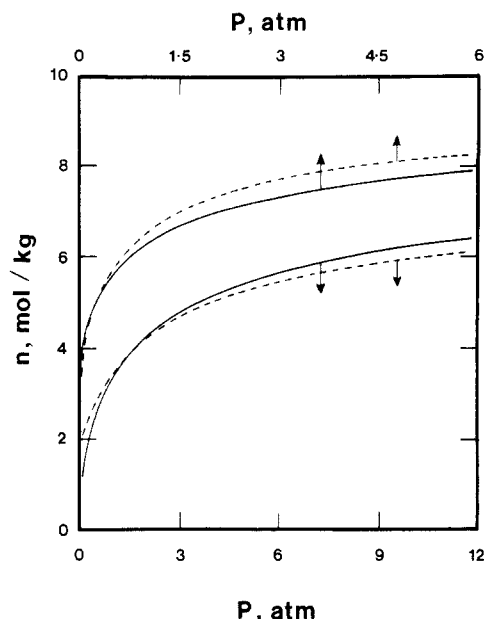


Figure 1. Sensitivity of the LUD isotherm to the parameter s . Solid line, s_i ; dashed line, \bar{s} . The values of s are given in Table I.

Table IV. NHEL Model Parameters^a Characterizing the Adsorption of Methane, Ethylene, and Ethane on Activated Carbon^b

adsorbate	b_0 , 1/atm	ϵ_{\min} , kJ/mol	ϵ_{\max} , kJ/mol
CH ₄	1.204×10^{-3}	6.390	15.130
C ₂ H ₄	1.515×10^{-3}	7.822	22.692
C ₂ H ₆	4.754×10^{-4}	12.081	25.482

^a These parameters were evaluated from the values of b and s (given in Table I) at 212.7 and 301.4 K. ^b Data of Reich et al. (1980).

sitive to the parameter s . This result suggests that there should be only a marginal effect of using an average value of s over the individual s values on the predictions of mixed gas adsorption. This fact is demonstrated next.

A more rigorous test of the use of an average value of s over the individual s values was made by comparing the AHHEL model predictions of the component amount adsorbed from six binary gas mixtures to those from the NHEL model. The CH₄-C₂H₆, CH₄-C₂H₄, and C₂H₆-C₂H₄ systems on BPL activated carbon at 212.7 and 301.4 K (data source, Reich et al., 1980) were selected for this purpose. The pure gas adsorption isotherms for these systems at 212.7 and 301.4 K were used to calculate $b_{0,i}$, $\epsilon_{i,\max}$, and $\epsilon_{i,\min}$ via eq 5, 14c, and 14d. It is apparent, then, that the NHEL model necessarily requires pure gas information at, at least, two temperatures for each component in the gas mixture. The three parameters (b_0 , ϵ_{\max} , ϵ_{\min}) are listed in Table IV, and the comparison of the overall average relative errors in the component moles adsorbed, as predicted by the two models, is given in Table V. It is clearly seen from Table V that the predictions from the AHHEL model were similar to those from the NHEL model. Only two of the six cases (based on the average predictions for the system) demonstrated significant improvement by using the individual values of s along with the tedious numerical integration of eq 9.

In conclusion, the use of an average value of s does have some effect on the predictions from the HEL models. However, since the predictions from the AHHEL model

Table V. Overall Comparison of Predictions from AHHEL Model to NHEL Model

system	T, K	avg rel err in moles adsorbed for each component, %	
		AHHEL	NHEL
CH ₄	212.7	35.06	32.97
C ₂ H ₆ ^a		3.79	3.36
avg		19.43	18.17
CH ₄	212.7	35.53	11.94
C ₂ H ₄ ^a		4.40	6.66
avg		19.96	9.3
C ₂ H ₆	212.7	23.56	17.68
C ₂ H ₄ ^a		30.17	15.53
avg		26.87	16.61
CH ₄	301.4	33.84	31.79
C ₂ H ₆ ^a		2.95	3.37
avg		18.40	17.58
CH ₄	301.4	22.86	17.89
C ₂ H ₄ ^a		6.04	8.53
avg		14.45	13.21
C ₂ H ₆	301.4	8.67	10.34
C ₂ H ₄ ^a		17.21	14.10
avg		12.94	12.22

^a BPL activated carbon (Reich et al. 1980).

were generally better than those from the EL model, and since the AHHEL model is computationally simple, it should be useful for the design and modeling of adsorption processes concerned with the predictions of mixed gas adsorption on heterogeneous surfaces. Moreover, even if the values of s are markedly different, the NHEL model can be used with little additional effort because, like the AHHEL model, it is explicit with respect to n_i and is noniterative.

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