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Correlation and Calculation of Multicomponent Adsorption Equilibria Data Using a Generalized Adsorption Isotherm

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Abstract. Enhanced by the need for reliable and accurate data of multicomponent gas adsorption equilibria on porous solids like activated carbons or zeolites, a new method to measure and correlate coadsorption equilibria has been developed. This method is a combination of gravimetric or volumetric measurements of the total load of pure or multicomponent adsorbates (Staudt, 1994; Gregg and Sing, 1982) and a correlation and calculation procedure using a new adsorption isotherm (AI) (Keller, 1990). This AI is thermodynamically consistent and describes adsorbates with fractal dimension for single- or multicomponent systems and load dependent adsorption energies. This method allows calculation of partial loads of multicomponent coadsorption equilibria from pure component data and the total loads of the mixture adsorption equilibria. This will be demonstrated for binary and ternary adsorption equilibria of CH_4, C_2H_4 and C_2H_6 on activated carbon (Reich et al., 1980).

Keywords: multicomponent adsorption, coadsorption, fractal dimension, adsorption isotherm, heat of adsorption

Introduction.

For the optimal design of processes using adsorption phenomena, accurate adsorption equilibria data for mono- and multicomponent systems are needed. This data can be gained by elaborate adsorption experiments or by models on adsorption equilibria. In today's literature many different types of adsorption isotherms are used to describe adsorption equilibria. But most of them are limited to special cases of adsorption systems, for example the low pressure regime, or they do not take into account real gas effects or the fact that adsorption energies normally will depend on the amount adsorbed etc. As a consequence of these limitations we have developed a generalized Adsorption Isotherm (AI) for gas adsorption equilibria on porous solids (Keller, 1990). This AI is thermodynamically consistent and can describe adsorbates with fractal dimension for mono- or multicomponent systems ($N \geq 1$) and load dependent adsorption energies being in equilibrium with real or ideal gas adsorptives. Using this new AI, it is possible to calculate the partial loads of components included in a multicomponent adsorbate from the pure component AI data and the total amount adsorbed of the binary or ternary adsorbate. In contrast to the RAST (Real Adsorbed Solution Theory) the knowledge of the partial loads of multicomponent adsorption equilibria is not necessary for the determination of the cross interaction parameters. Only the total amount adsorbed must be known and can be determinated in principle by simple volumetric or gravimetric experiments (Staudt et al., 1993; Staudt, 1994).

Theory

Adsorption Isotherm

We consider a multicomponent adsorbate on a surface of an inert porous solid, being in equilibrium with the gas phase at constant temperature T (Keller, 1990). The adsorbate may exchange molecules with

the adsorptive which can be described by its temperature T and the partial pressures p_i $(i = 1 \ldots N)$ of its components. Assuming that

(1) the adsorbate is a thermodynamic system in the sense of Schottky with the fractal dimension $0 \le D \le 3$,
(2) the spreading pressure is an internal variable in the sense of Bridgman, Meixner and Kestin,
(3) thermodynamic equilibrium exists between the adsorbate and the adsorptive, i.e., there is chemical equilibrium between each component of the fluid and the adsorbed phase,

one can derive the Gibbs equation of the adsorbate

$$dG = -S\,dT + A\,d\pi + \sum_{i=1}^{N} \mu_i\,dn_i, \qquad (1)$$

and the Gibbs-Duhem relations

$$G = \sum_{i=1}^{N} \mu_i n_i, \qquad (2)$$

as thermodynamic consistency conditions for adsorption isotherms. Additional conditions can be calculated from the Maxwell-relations corresponding to the Gibbs equation (1). From these conditional equations a fairly general class of thermodynamically consistent AIs can be derived which can be written as:

$$\begin{aligned} n_i(T, p_1, \ldots, p_N, m^S) &= n_\infty(T, m^S) \cdot \Phi\left(\sum_k (c_k \cdot f_k)^{\alpha_k} \right) \\ &\quad \times \left[\alpha_i \cdot (c_i \cdot f_i)^{\alpha_i} + \frac{f_i}{RT} \sum_m \alpha_m \cdot (c_m \cdot f_m)^{\alpha_m} \right. \\ &\quad \left. \cdot \left(\frac{\partial q_m}{\partial f_i} \right)_T \right], \quad i, k = 1, \ldots, N, \\ c_k &= f_{k_\infty} \cdot e^{-q_k/(RT)}, \qquad f_{k_\infty} = \text{const.} \end{aligned} \qquad (3)$$

Here n_i indicates the number of moles of component $i = 1, 2, \ldots, N$, adsorbed on the mass m^S of adsorbent. The parameter α_i is an exponent related to the (fractal) dimension D of an adsorbate formed by molecules of pure component i and reference component 0

$$\frac{\alpha_i}{\alpha_0} = \left(\frac{r_i}{r_0} \right)^{-D}. \qquad (4)$$

Often the exponents α_i are not equal to 1, this can lead to an inappropriate behaviour in the Henry region (Talu and Myers, 1988). To overcome this difficulty a pressure dependent exponent $\alpha_i(f_i)$ with the limiting condition $\alpha_i(f_i \to 0) = 1$ can be introduced (Staudt et al., 1996).

The limiting load of component i can be calculated by $n_{i_\infty} = \alpha_i \cdot n_\infty$, the parameter f_{i_∞} under special conditions can be interpreted as the "half load pressure" of pure component i and $q_i = q_i(f_1, \ldots, f_N, T)$ as a load dependent adsorption energy, $f_i(p_1, \ldots, p_N, T)$, $i = 1 \ldots N$ indicating the fugacity of component i in the adsorptive. $\Phi = \Phi(f^*)$ is the characteristic function of a single variable f^*

$$f^* = \sum_k (c_k \cdot f_k)^{\alpha_k}$$

describing the type of adsorption. It is due to several general algebraic conditions (Keller, 1990; Staudt, 1994) and, for example, can be chosen as:

$$\text{LF:} \quad \Phi(f^*) = \frac{1}{1 + f^*}, \qquad (5a)$$

$$\text{BET:} \quad \Phi(f^*) = \frac{B}{(1 - f^*)[1 + (B - 1) f^*]}, \qquad (5b)$$

$$\text{AR:} \quad \Phi(f^*) = \frac{D}{(1 - f^*)^{1/2}[1 + D f^*]}. \qquad (5c)$$

According, the AI indicated by Eq. (3) and Eqs. (5a–c) represent thermodynamically consistent generalizations of the LANGMUIR-FREUNDLICH (LF), the BRUNAUER-EMMETT-TELLER (BET) or the ARANOVICH (AR) (Aranovich, 1988) isotherm.

The enthalpy H of the adsorbed phases described by Eqs. (3, 5a–c) is given by (Keller, 1990)

$$\begin{aligned} H^f(T, p, n_1, \ldots, n_N,) - H(T, n_1, \ldots, n_N, m_s) &= \sum_i^N \left\{ \left[q_i - \frac{RT^2}{f_i} \left(\frac{\partial f_i}{\partial T} \right)_p \right] n_i - n_\infty \Phi \frac{f_i q_i}{RT} \right. \\ &\quad \left. \times \sum_m \alpha_m \cdot (c_m \cdot f_m)^{\alpha_m} \cdot \left(\frac{\partial q_m}{\partial f_i} \right)_T \right\} \end{aligned} \qquad (6)$$

where H^f indicates the enthalpy of $n = \sum_i^N n_i$ moles in the adsorptive state.

Heat of Adsorption

We assume the adsorbed phase to be a liquid like phase. Also the heat of adsorption is assumed to be the sum of the interaction energies between the adsorbate and the adsorbens and between the adsorbed molecules. The adsorbens-adsorbate interaction is described by a load- or equivalently pressure dependent (12, 6)—Lennard-Jones potential energy V_{LJ}. The adsorbate-adsorbate interaction may lead to a phase transition among the adsorbed molecules with a phase transition energy approximated by the heat of evaporation of the bulk phase q^{LV} (Staudt, 1994). The heat of adsorption can be written as:

$$q = -V_{\mathrm{LJ}} + q^{\mathrm{LV}}, \tag{7}$$

$$V_{\mathrm{LJ},i} = -E_{\min,i}\left[(L_i)^{d_i} - (L_i)^{d_i-6}\right], \quad L_i = \frac{r_{0i}}{r_i} \tag{7a}$$

The parameter r_i is the statistical mean distance of the adsorbed molecule of component i from the surface atoms of the adsorbens. Likewise r_{0i} indicates the distance from the surface at which the surface potential energy has its minimum value. In our model we assume the mean relative distance of the adsorbed molecules L_i to depend on the amount adsorbed or likewise on adsorptive's pressure p or, in case of multicomponent systems on the partial pressure p_i of all components as, for example, described by Eq. (7b):

$$L_i = \exp\left(-\sum_j^N l_{ij}\, p_j\right). \tag{7b}$$

The phenomenological parameters l_{ij} have to be determined by numerical optimization. With increasing load of the adsorbate (i.e., increasing pressure in the adsorptive) the attracting interaction between surface and adsorbate normally will decrease. Hence, for exponents d_i we assume the following relation to hold:

$$d_i = d' \exp\left(-\sum_j^N k_{ij}\, p_j\right), \quad d' = 6. \tag{7c}$$

Again the empirical parameters k_{ij} have to be determined by fitting the AI (3) to experimental data. The numerical fitting procedure is based on a Gaussian sum of least squares minimization procedure enhanced by the method of Fletcher and Reeves (Fletcher and Reeves, 1964; Staudt, 1994).

Results

Using the AI (3) with the characteristic function (5a, 5c) adsorption equilibria data (Staudt et al., 1993; Reich et al., 1980; Talu and Zwiebel, 1986; Danner and Choi, 1978; Rübner, 1993) of pure gases (N_2, CH_4, CO, CO_2, Ar, He, C_2H_6, C_2H_4, C_3H_8, H_2S), many of their binary mixtures (CH_4/N_2, CO_2/H_2S, H_2S/C_3H_8, CH_4/CO, CH_4/C_2H_4, CH_4/C_2H_6, C_3H_8/CO_2, C_2H_4/C_2H_6) and ternary mixtures ($C_3H_8/H_2S/CO_2$, $CH_4/C_2H_6/C_2H_4$) on activated carbon and zeolites referring to the pressure range 0–15 MPa and temperature range 212 K–323 K have been correlated.

In this paper results of the optimization procedure of the data of Reich, Danner and Rübner are presented. Reich et al. (1980) measured adsorption equilibria data of CH_4, C_2H_6 and C_2H_4 and their binary and ternary mixtures on activated carbon at $T = 301$ K. Figure 1 shows the pure gas adsorption equilibria data of CH_4 and CO_2 on AC in the pressure range of 0–3.5 MPa. The symbols represent the experimental data and the lines the fit using a generalized LF-AI (3, 5a) with the modified LJ-Potential (7). The dashed lines show the Lennard-Jones-potential V_{LJ} (Eq. (7a)) as a result of this fit. The heat of adsorption q can be calculated by Eq. (7). For the heat of evaporation we choose the values of q^{LV} in Table 1. The mean relative deviation Δm between the experimental and the calculated values of the adsorbed masses ($\Delta m < 1\%$) is smaller than the uncertainty of the experimental data. The fitting parameters are listed in Table 1. All the curves represent AIs of type I (IUPAC classification) reflecting mainly adsorption in the micro- and mesopores of the activated carbon. All adsorption processes seem

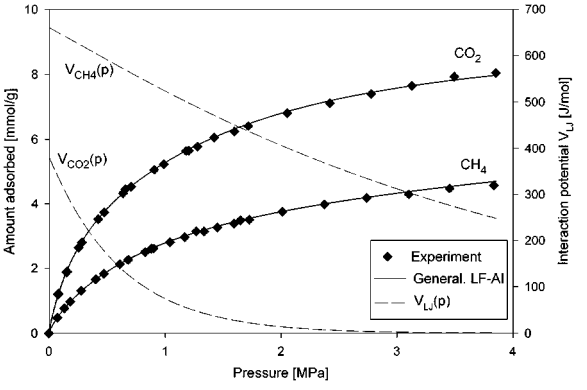

Figure 1. AI of CH_4 and CO_2 on AC at $T = 301$ K, data: (Reich et al., 1980); lines: correlation using gen. LF-AI (3, 5a, 7), dashed lines: calculated interaction potential: Eq. (7a).

Table 1. Parameters for adsorption equilibria of pure gases CH_4, C_2H_6, C_2H_4, CO_2 on AC, $T = 301$ K, data: (Reich et al., 1980); correlation: gen. LF-AI (3, 5a, 7).

Parameter		CH_4	C_2H_4	C_2H_6	CO_2
n_∞	mmol/g		10.82		
$p_{i\infty}$	MPa	76.88	67.67	73.01	8.65
$E_{\min,i}$	kJ/kmol	661.0	263.1	265.5	382.2
k_{ij}	1/MPa	0.223	0.675	0.500	1.627
l_{ij}	1/MPa	0.021	0.232	0.238	0.031
α_i	1	0.829	0.683	0.658	0.910
Δm	%		0.70		
q^{LV}	J/mol	8160	13496	14655	6021

to be completely reversible, i.e., do not indicate any type of hysteresis or any other endoreversible or irreversible effect. The heat of adsorption $q = V_{LJ} + q^{LV}$ of CO_2 on AC decreases strongly with increasing pressure (load). At higher pressure the heat of adsorption is equal to the heat of evaporation. In the case of CH_4 the heat of adsorption decreases slowly with increasing pressure (compared to CO_2) i.e., there exists a strong interaction between the adsorbate and the surface with adsorbed molecules.

Only from the total loads of the binary mixture isotherms and the pure gas adsorption isotherms, the loads of single components within the mixture can be calculated. The results of the calculation (optimization procedure) and the experimental data are shown in Figs. 2, 3 and 4 for the mixtures C_2H_6/C_2H_4, CH_4/C_2H_4 and CH_4/C_2H_6. The coincidence of the calculated and experimental values of the partial loads of the components is of the same order as the uncertainty of the experimental data ($\Delta m < 3\%$ for binary mixture).

Figure 5 shows the adsorption equilibria data of the ternary mixture $CH_4/C_2H_6/C_2H_4$ on activated Carbon at $T = 301$ K. The partial loads of the ternary mixture

Table 2. Fitting parameters for adsorption equilibria of binary mixtures CH_4/C_2H_6, CH_4/C_2H_4, C_2H_6/C_2H_4 on AC, $T = 301$ K, data: (Reich et al., 1980); correlation: gen. LF-AI (3, 5a, 7).

Parameter		CH_4/C_2H_6	CH_4/C_2H_4	C_2H_6/C_2H_4
k_{ij}	1/MPa	0.7568	0.3307	1.3788
l_{ij}	1/MPa	2.0080	0.0098	0.0204
k_{ji}	1/MPa	0.0121	0.3785	0.9242
l_{ji}	1/MPa	0.0294	0.0959	0.0029
Δm	%	2.97	2.01	2.93

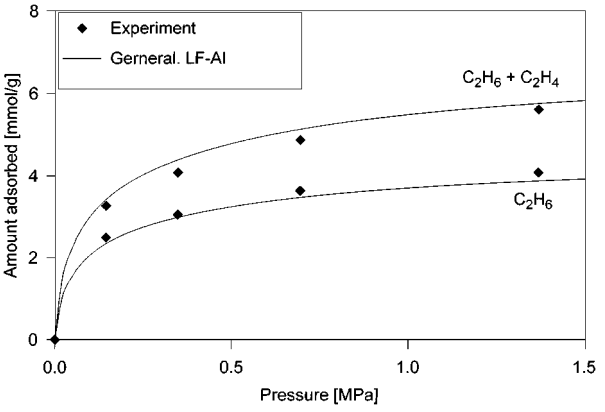

Figure 2. Coadsorption isotherm of C_2H_6/C_2H_4 (68 : 32 mol%) on AC at $T = 301$ K, data: (Reich et al., 1980); correlation/calculation: gen. LF-AI (3, 5a, 7).

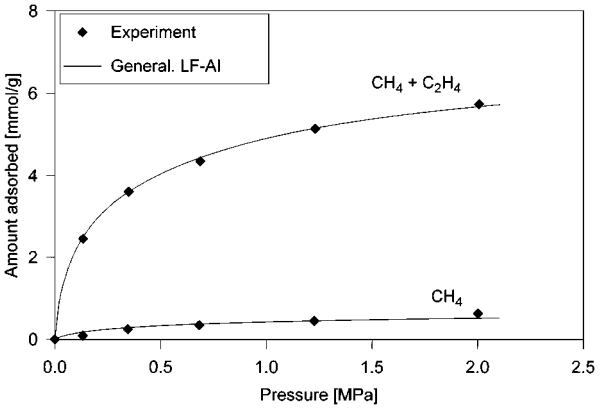

Figure 3. Coadsorption isotherm of CH_4/C_2H_4 (26 : 74 mol%) on AC at $T = 301$ K, data: (Reich et al., 1980); correlation/calculation: gen. LF-AI, Eqs. (3, 5a, 7).

were calculated using only the pure gas isotherms and the total loads of the respective binary mixtures. Agreement between experimental and calculated partial loads is fair ($\Delta m < 6\%$). It can be improved, if we use more information from the experimental data base available (Staudt, 1994).

Danner and Choi (1978) measured adsorption equilibria of the pure components C_2H_6 and C_2H_4 and their binary mixtures on activated carbon at $T = 298$ K and 323 K. Figure 6 shows the phase diagram for $p = 1034$ mmHg and $T = 298$ K. The symbols are the experimental values and the line shows the calculated adsorption equilibria of the mixture using the pure adsorption isotherm and the total load of the binary mixtures. The agreement between the experimental values and the calculated partial loads is $\Delta m < 3\%$.

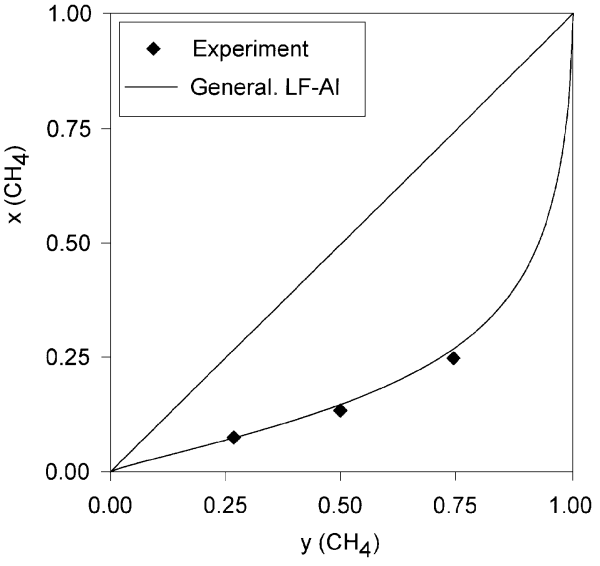

Figure 4. Phase diagram of coadsorption equilibria of CH_4/C_2H_6 on AC at $T = 301$ K, data: (Reich et al., 1980); calculation: gen. LF-AI, Eqs. (3, 5a, 7).

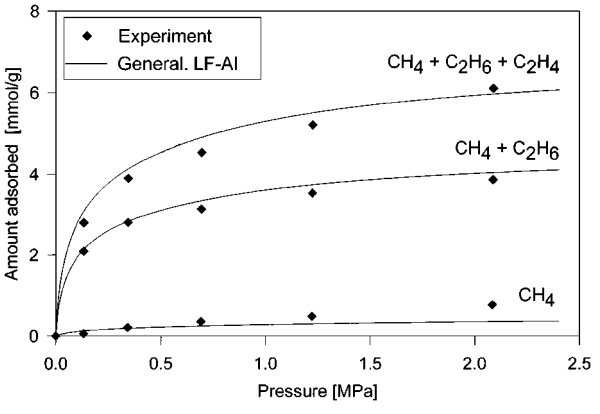

Figure 5. Coadsorption isotherm of $CH_4/C_2H_6/C_2H_4$ (23 : 52 : 25 mol%) on AC at $T = 301$ K, data: (Reich et al., 1980); calculation: gen. LF-AI, Eqs. (3, 5a, 7).

Figure 7 shows the adsorption isotherm of N_2 on activated carbon at 77 K. The data are fitted using the generalized Aranovich adsorption isotherm (Eqs. (3, 5c)) with load (pressure) dependent heat of adsorption (Eqs. (7)). Agreement between experimental data and calculated loads is fair ($\Delta m = 2.68\%$). The heat of adsorption decreases strongly at low pressures down to the heat of evaporation. At higher pressures in the range of capillary condensation the heat of adsorption is equal to the heat of evaporation.

Table 3. Fitting parameters for adsorption equilibria of pure gases C_2H_6 and C_2H_4 and their binary mixtures on AC, $T = 301$ K, data: (Danner and Choi, 1978); correlation/calculation: gen. LF-AI, Eqs. (3, 5a, 7).

Parameter		C_2H_6	C_2H_4	Parameter		C_2H_6/C_2H_4
n_∞	mmol/g	3.79		k_{ij}	1/MPa	0.0118
$p_{i\infty}$	MPa	11.85	14.49	l_{ij}	1/MPa	0.0020
$E_{\min,i}$	J/mol	285.7	475.3	k_{ji}	1/MPa	0.0086
k_{ij}	1/MPa	0.284	1.242	l_{ji}	1/MPa	0.0010
l_{ij}	1/MPa	0.537	1.433			
α_i	1	1.38	0.96			
Δm	%			2.17		

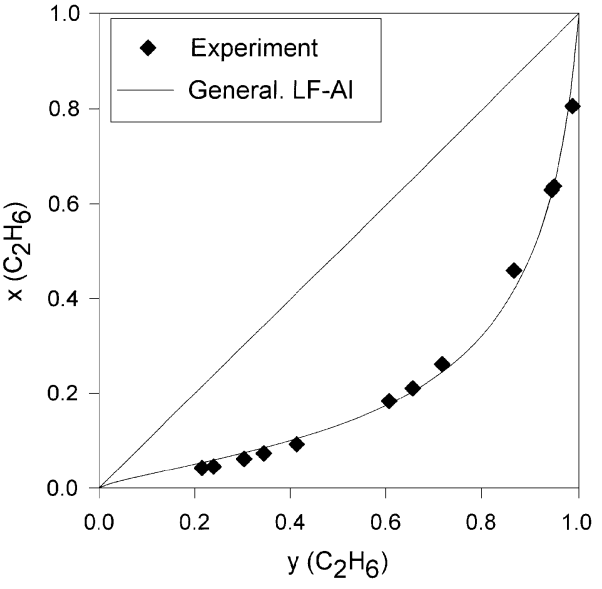

Figure 6. Coadsorption of C_2H_6/C_2H_4 on AC at $T = 298$ K, $p = 1034$ mmHg, data: (Danner and Choi, 1978); calculation gen. LF-AI, Eqs. (3, 5a, 7).

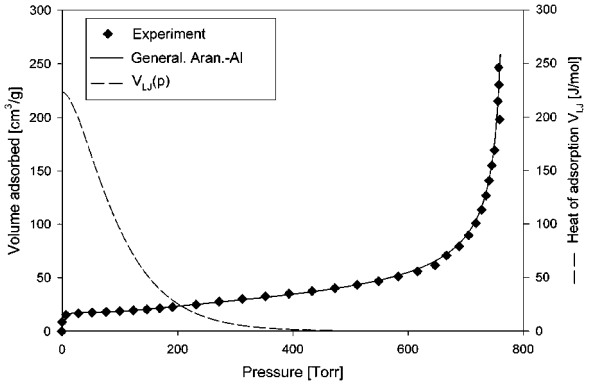

Figure 7. Adsorption of N_2 on AC at $T = 77$ K, data: (Rübner, 1993); correlation: gen. Aran.-AI, Eqs. (3, 5c, 7).

Table 4. Fitting parameters for adsorption equilibria of N_2, on AC $T = 77$ K, data: (Rübner, 1993); correlation: gen. Aran.-AI, Eqs. (3, 5c, 7).

Parameter		N_2
∞	cm^3/g	40.23
D_i	1	28.2
p_{i_∞}	Torr	2.81×10^6
E_{min}	J/mol	188.4
k_{ij}	1/Torr	0.00042
l_{ij}	1/Torr	0.00217
α_i	1	0.468
Δm_i	%	2.68
q^{LV}	J/mol	5544

Conclusions

A new method to calculate coadsorption equilibria with a minimum of experimental informations has been developed. This method is a combination of simple gravimetric or volumetric measurements only of the total load of pure or multicomponent adsorbates and a correlation and calculation procedure using a new adsorption isotherm. With this method it is possible to calculate partial loads of multicomponent coadsorption equilibria. The coincidence of the calculated and experimental values of the partial loads of the components is of the same order as the uncertainty of the experimental data as has been demonstrated.

Nomenclature

A	Surface area, m^2
B, D	Adsorption equilibrium constant
d_i	Exponent in Lennard-Jones potential
f	Fugacity, Pa
f_{i_∞}	Adsorption equilibrium constant of component i, Pa
H	Enthalpy, J/mol
L_i	Coefficient in Lennard-Jones potential energy
k_{ij}, l_{ij}	Coefficients in Lennard-Jones potential energy, 1/Pa
m^s	Mass of adsorbens, g
n_i	Amount adsorbed of component i, mmol/g
n_∞	Limiting amount adsorbed, mmol/g
p	Pressure, Pa
q	Adsorption energy, J/mol
q^{LV}	Heat of evaporation, J/mol
R	Gas constant, J/(mol K)
T	Temperature, K
S	Entropy, J/(mol K)
V_{LJ}	Lennard-Jones potential energy, J/mol
α	Characteristic exponent
Φ	Characteristic function
μ	Chemical potential, J/mol
π	Spreading pressure, N/m

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