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High Pressure Adsorption Data of Methane, Nitrogen, Carbon Dioxide and their Binary and Ternary Mixtures on Activated Carbon

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Abstract. Adsorption equilibria of the gases CH_4, N_2, and CO_2 and their binary and ternary mixtures on activated carbon Norit R1 Extra have been measured in the pressure range $0 \leq P \leq 6\,\text{MPa}$ at $T = 298\,\text{K}$. Pure gas adsorption equilibria were measured gravimetrically. Coadsorption data of the three binary mixtures CH_4/N_2, CH_4/CO_2, and CO_2/N_2 were obtained by the volume-gravimetric method. Isotherms of five ternary mixtures $CH_4/CO_2/N_2$ were measured using the volumetric-chromatographic method. First, we present in a short overview the method and procedure of measurement. In a second part, the measured data of pressures, surface excess amounts adsorbed and absolute amounts adsorbed are presented and analyzed. In the last part of the paper the resulting pure gas adsorption data are correlated using a generalized dual-site Langmuir isotherm. Mixture adsorption can be predicted by this model using only pure component parameters with fair accuracy. Results are presented and discussed in several tables and figures.

Keywords: activated carbon, gas adsorption, coadsorption equilibria data, adsorption isotherm, Langmuir isotherm, dual-site

Introduction

Measurements of pure component gas adsorption isotherms are the most simple ones in adsorption science and technology. These measurements are so common, that automated commercial systems are available today, at least for a certain set of gases and range of pressure and temperature. On the other hand, almost all applications of adsorption processes for separation of gases and liquids involve mixtures. Thus, the development, design and operation of these processes require knowledge of mixture equilibria, i.e., coadsorption isotherms rather than pure component isotherms. There are models available in literature to predict the mixture behavior from pure component isotherms, i.e., the Ideal Adsorbed Solution Theory or the Mixed-Langmuir model (Myers and Prausnitz, 1965; Markham and Benton, 1931). The accuracy of these predictions usually is not sufficient to allow an engineer to economically design an adsorption separation process. Therefore, to check the accuracy of the predictions as well as to improve existing models or to develop new theories accurate mixture data are required. These data should cover a range of pressure, concentration, and temperature relevant for technical processes, causing normally strongly nonideal behavior of both adsorbate and adsorptive. For this purpose in this study gas adsorption equilibria of methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), and their binary and ternary mixtures have been measured up to pressures $P = 6\,\text{MPa}$ at constant temperature $T = 298\,\text{K}$ on microporous activated carbon (AC) Norit R1 Extra. Pure gas equilibria were measured gravimetrically. Coadsorption equilibria of the binary mixtures CH_4/CO_2, N_2/CO_2, and CO_2/N_2 have been

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measured for three (nearly constant) sorptive concentrations of each mixture using the volume-gravimetric method (Keller et al., 1992). Adsorption equilibria of five ternary mixtures $CH_4/CO_2/N_2$ were measured using the volumetric-chromatographic method. By using the Helium volume of the adsorbent, the surface excess amounts adsorbed can be obtained using the measurement techniques mentioned above. Introducing a physically appropriate model for the volume of the adsorbate (Staudt et al., 1993; Keller et al., 1999), it is also possible to calculate from these data the total amounts adsorbed for all single- and multi-component adsorption equilibria considered.

We start in giving an overview on the measurement procedures and data analyzing methods in the first section of this paper. The resulting data have been checked for thermodynamic consistency. These data are listed in tables and compared with the predictions of a modified dual-site Langmuir model, the results being presented in several figures in the last section of the paper.

Experimental

The experimental setup for volume-gravimetric-chromatographic measurements of pure and mixed gas adsorption equilibria is sketched in Fig. 1. The gas mixture can be prepared in a storage vessel (*SV*, volume $V_{SV} \cong 10\,\mathrm{dm}^3$). The adsorption vessel (*AV*, volume $V_{AV} \cong 1.4\,\mathrm{dm}^3$) contains a microbalance (*MB*, two beam balance, Sartorius, Germany, sensitivity $1\,\mu$g). One bucket of the balance is filled with a sample of the adsorbent ($m^S \cong 2\,$g); the counterweights of the balance are lead balls ($m^B \cong m^S$). A pump (*CP*, Brey, Germany) can circulate the gas mixture in the storage vessel and the overall system to avoid concentration differences during equilibration. Concentration of an adsorptive sample can be measured with a gas chromatograph (*GC*, Perkin Elmer 8600, UK). Pressures are measured at four different locations using high precision pressure transducers (burster, Germany, $\Delta P = \pm 0.0001 \cdot P_{\max}$). Temperatures are measured at five different locations using resistance thermometers (Pt100, burster, Germany, $\Delta T = \pm 0.03\,$K). The equipment is thermostated with three water thermostats (Haake, Germany); it can be evacuated by a vacuum pump (*VP*, Balzers, Germany, $p \le 1\,$Pa) and is connected to a gas supply system (*GS*, DruVa, Germany). For detailed information about the equipment refer to literature (Keller et al., 1992; Tomalla et al., 1994).

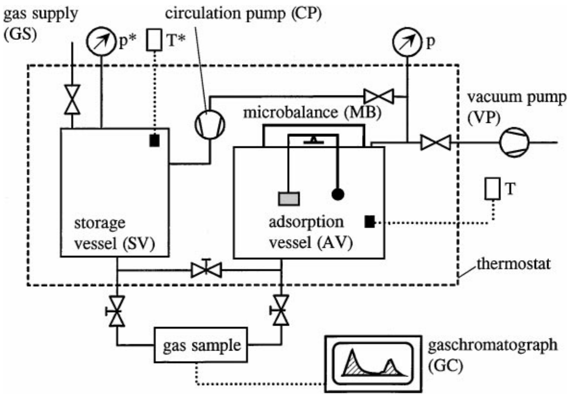

Figure 1. Schematic diagram of the volume-gravimetric-chromatographic equipment.

Measurements

Prior to adsorption the activated carbon has to be prepared, i.e., to be activated or reactivated. Therefore, the adsorbent is heated up to $T = 353\,$K in a Helium (He) atmosphere at $P_{He} = 1\,$MPa. After the temperature has been held constant for at least one hour, the system is evacuated and cooled down again to 298 K. The activation or reactivation of the carbon is considered to be finished if the microbalance signal of the AC sample at minimum pressure and at temperature of measurement is constant and, in case of reactivation, has assumed its value prior to adsorption experiments again. The reproducibility of this procedure (during measurement periods of months with up to 20 reactivations) has been proofed by observing the microbalance signal after reactivation.

For gravimetric measurements of the adsorption of pure gases the pressure in the adsorption vessel (AV) is increased by supplying the pure component sorptive gas. After equilibrium is reached, i.e., the microbalance signal is constant, the data (pressure P, temperature T, and microbalance signal Δm) are measured. Then the pressure of the sorptive is increased again and the next equilibrium data are measured. This procedure is continued until the maximum pressure is reached. Desorption processes have not been considered separately since in former experiments with pure gases even at much lower temperatures no hysteresis effects could be observed. Prior to measurement of the next isotherm, the adsorbent has to be reactivated as described above.

To measure coadsorption equilibria, a gas mixture of given molar concentration y_i^* ($i = 1, 2, 3$), pressure P^*, and temperature T^* is prepared by filling the storage vessel (SV). We apply a truncated virial equation of state (EOS) $\rho = f(P, T, y_i)$ (Jaeschke et al., 1988) to calculate the masses of components of the mixture in the SV, $m_i^* = V_{\mathrm{SV}} \cdot \rho_i(P^*, T^*, y_i^*)$ prior to adsorption. After preparation of the mixture, the valves between SV and AV are opened and adsorption occurs. The mixed gas adsorptive is circulated in the equipment using the pump (CP) until adsorption equilibrium is reached. This is indicated by constant total pressure and a constant microbalance signal. The data measured in the equilibrium state (CP is off) are the pressure P, the temperature T, and the microbalance signal Δm. In case of ternary gas mixture adsorption measurements, the molar concentration of sorptives' components in equilibrium states y_i, have been determined with a gas chromatograph. After this, the adsorption vessel may be evacuated and the adsorbent regenerated to be prepared for the next measurement.

Data Handling

Pure Gas Adsorption Measurements. The microbalance signal Δm, measured at adsorption equilibrium, is proportional to the mass m of pure gas adsorbed in the adsorbent sample attached to the microbalance minus the buoyancy caused by the displacement of the gas phase (density ρ) by the volume of the adsorbent and adsorbate V:

$$\Delta m = m - \rho \cdot V. \tag{1}$$

In this equation the quantities m and V are unknown. Thus, the result of gravimetric measurements of pure gas adsorption equilibria is the so-called reduced mass of adsorbate Ω (Staudt et al. 1993):

$$\Omega \equiv m - \rho \cdot V = \Delta m, \tag{2}$$

being the difference between the mass adsorbed and the buoyancy term. A model for the volume of the adsorbent and the adsorbate V, needed to calculate the mass adsorbed from the measured data, i.e., Eq. (2), is given below.

Binary Gas Mixture Adsorption Measurements. The microbalance signal Δm, measured in adsorption equilibrium, yields the sum of the masses of the components adsorbed $(m_1 + m_2)$ minus the buoyancy term, i.e., the product of gas phase density $\rho(P, T, y_1) = \rho_1(P, T, y_1) + \rho_2(P, T, y_1)$ and the volume of the adsorbent and the adsorbate V:

$$\Delta m = m_1 + m_2 - \rho(P, T, y_1) \cdot V. \tag{3}$$

The material balances for components $i = 1, 2$ deliver relationships between the mass of sorptive's component i prepared in the storage vessel m_i^*, and the sum of the mass of component i being in the gas phase after adsorption equilibrium is reached m_i^{f}, and the mass of component i being adsorbed m_i:

$$m_i^* = m_i + m_i^{\mathrm{f}}, \quad i = 1, 2. \tag{4}$$

The mass of component i prepared in the storage vessel can be calculated using an equation of state:

$$m_i^* = V_{\mathrm{SV}} \cdot \rho_i(P^*, T^*, y_1^*), \quad i = 1, 2. \tag{4a}$$

The mass of component i being in the gas phase in adsorption equilibrium is:

$$m_i^{\mathrm{f}} = \rho_i(P, T, y_1) \cdot (V_{\mathrm{SV}} + V_{\mathrm{AV}} - V), \quad i = 1, 2. \tag{4b}$$

In this equation the sum $(V_{\mathrm{SV}} + V_{\mathrm{AV}} - V)$ is the volume of the gas phase, i.e., the total volume of the storage and the adsorption vessel minus the displacement volume of the adsorbent and the adsorbate V. Combining Eq. (4) with Eqs. (4a) and (4b) yield the equations:

$$\begin{aligned} &V_{\mathrm{SV}} \cdot \rho_i(P^*, T^*, y_1^*) \\ &\quad = m_i + \rho_i(P, T, y_1) \cdot (V_{\mathrm{SV}} + V_{\mathrm{AV}} - V), \quad i = 1, 2. \end{aligned} \tag{4c}$$

Combining the Eqs. (3) and (4c) allows to calculate the unknown density of the mixed gas adsorptive in the equilibrium state $\rho = \rho(p, T, y_1)$ from the measured quantities:

$$\rho = \frac{V_{\mathrm{SV}} \cdot \{\rho_1(P^*, T^*, y_1^*) + \rho_2(P^*, T^*, y_1^*)\} - \Delta m}{V_{\mathrm{SV}} + V_{\mathrm{AV}}}. \tag{5}$$

Using the equation of state (EOS), $\rho = \rho(P, T, y_1)$ of the binary adsorptive with the measured quantities density ρ (cp. Eq. 5), pressure P, and temperature T, the molar concentration y_1 of the adsorptive in the equilibrium state of adsorption can be calculated:

$$y_1 \overset{\text{EOS}}{=} y_1(\rho, P, T) = 1 - y_2(\rho, P, T), \tag{6}$$

and from these quantities the partial densities of adsorptive's components $\rho_i(P, T, y_1)$ in the equilibrium state of adsorption. Above given Eqs. (3), (4c) and the EOS provide a set of four algebraic equations with the five unknown quantities m_1, m_2, y_1, y_2, and V. Thus, only the so-called reduced masses adsorbed of the components of the binary mixture can be determined, i.e., the quantities:

$$\begin{aligned}\Omega_i &\equiv m_i - \rho_i(P, T, y_1) \cdot V, \\ &= V_{\text{SV}} \cdot \rho_i(P^*, T^*, y_1^*) - \rho_i(P, T, y_1) \\ &\quad \cdot (V_{\text{SV}} + V_{\text{AV}}), \quad i = 1, 2,\end{aligned} \tag{7}$$

these being the difference between the mass of component i adsorbed m_i and the displaced gas mass of the same component. Note, that no concentration measurement of the adsorptive gas-mixture in adsorption equilibrium is needed to determine the reduced masses Ω_i. Note also, that even when concentrations y_i of the mixed gas-adsorptive are measured, there is no way to calculate the unknown quantity V from any of the equations mentioned above.

Ternary Gas Mixture Adsorption Measurements. The material balances of components $i = 1, 2, 3$ of the volumetric-chromatographic measurements of adsorption equilibria of the ternary gas-mixture yield the equations:

$$\begin{aligned}&V_{\text{SV}} \cdot \rho_i(P^*, T^*, y_i^*) \\ &\quad = m_i + \rho_i(P, T, y_i) \cdot (V_{\text{SV}} + V_{\text{AV}} - V), \\ &\qquad\qquad\qquad\qquad i = 1, 2, 3.\end{aligned} \tag{8}$$

Adsorptive's concentrations y_i, $i = 1, 2, 3$ in adsorption equilibrium are assumed to have been determined by gas chromatography (Fig. 1). These three equations contain the four unknown quantities m_1, m_2, m_3 and V and therefore again only allow to calculate the reduced masses of mixture's components adsorbed:

$$\begin{aligned}\Omega_i &\equiv m_i - \rho_i(P, T, y_1) \cdot V, \\ &= V_{\text{SV}} \cdot \rho_i(P^*, T^*, y_1^*) - \rho_i(P, T, y_1) \\ &\quad \cdot (V_{\text{SV}} + V_{\text{AV}}), \quad i = 1, 2, 3,\end{aligned} \tag{9}$$

i.e., the difference between the mass of component i being adsorbed m_i and the mass of gas of this component displaced by the adsorbent and the mixture adsorbate. Performing additionally microbalance measurements only would lead to values of the sum of all masses adsorbed with improved accuracy but not circumvent the necessity to introduce a model for the volume V.

Volume of Adsorbent and Adsorbate

Surface Excess Adsorbed. To calculate the molar surface excess amounts adsorbed n_i^{ex}, the void volume of the adsorptive has to be modeled. We here follow the traditional way and introduce the so-called Helium volume of the adsorbent, i.e., the volume obtained by adsorption isotherm measurements with Helium as adsorptive (Gregg and Sing, 1967; Young and Crowell, 1962). For the activated carbon Norit R1 Extra the specific He-volume was measured as,

$$\frac{V}{m^{\text{S}}} = \frac{V_{\text{He}}}{m^{\text{S}}} = 0.3511 \frac{\text{cm}^3}{\text{g}}.$$

Hence we get for the specific surface excess amounts adsorbed n_i^{ex} calculated from Eqs. (2), (7) and (9):

$$n_i^{\text{ex}} = \frac{\Omega_i + V_{\text{He}} \cdot \rho_i}{m^{\text{S}} \cdot M_i}, \tag{10}$$

$i = 1$ (pure gases), $i = 1, 2$ (binary mixtures), $i = 1, 2, 3$ (ternary mixture).

The specific total excess amount adsorbed is

$$n^{\text{ex}} = \sum_i n_i^{\text{ex}}. \tag{11}$$

Quantities m^{S} and M_i are the mass of adsorbent and the molar mass of component i.

Adsorbate's molar excess concentration of component i is determined as:

$$x_i^{\text{ex}} = \frac{n_i^{\text{ex}}}{n^{\text{ex}}}. \tag{12}$$

The excess properties n^{ex} and x_i^{ex} are given in Tables 2–7 below.

Absolute Adsorption. Because almost all analytical models and computer simulations of adsorption processes yield the absolute amounts adsorbed, the specific values of these quantities n_i and their concentrations

Table 1. Liquid densities of pure components of the adsorptive at their boiling points at ambient pressure (IUPAC, 1976, 1978, 1979).

	CO_2	CH_4	N_2
ρ^L (kg/m^3)	1277.78	422.53	808.60
T (K)	194.67	111.63	77.35

x_i are quantities of interest (Myers, 1997). The difference between surface excess and absolute amounts adsorbed is proportional to the volume of the adsorbed phase (Keller et al., 1999). Assuming that the density of component i of the adsorbate is equal to the density of pure liquid i in saturated or boiling state at ambient pressure ρ_i^L, the volume of the adsorbed phase V^a (consisting of mass adsorbed $m = \sum_i m_i$) can be calculated neglecting the excess mixture volume as the sum:

$$\frac{V^a}{m^S} = \frac{1}{m^S} \cdot \sum_i V_i^a = \frac{1}{m^S} \cdot \sum_i \frac{m_i}{\rho_i^L}, \qquad (13)$$

$i = 1$ (pure gases), $i = 1, 2$ (binary mixtures), $i = 1, 2, 3$ (ternary mixture).

Numerical values of the pure liquid densities of CO_2, CH_4, N_2 in saturated boiling states at ambient pressure which are assumed to be the densities of the adsorbates are given in Table 1.

The specific absolute adsorption quantities, absolute amounts adsorbed $n = \sum_i n_i$ and molar concentrations of component i, $x_i = n_i/n$, are calculated by using the Eqs. (10), (11) and (12) with the new, adsorbate dependent displacing volume,

$$\frac{V}{m^S} = \frac{V_{He} + V^a}{m^S}, \qquad (14)$$

(V^a/m^S) calculated by Eq. (13).

This results in the equation for the specific absolute amount adsorbed of component i:

$$n_i = n_i^{ex} + \frac{V^a \cdot \rho_i}{m^S \cdot M_i}, \qquad (15)$$

$i = 1$ (pure gases), $i = 1, 2$ (binary mixtures), $i = 1, 2, 3$ (ternary mixture).

Numerical values of these quantities are given in the following tables. The mean relative uncertainties of the resulting quantities have been determined by a brief error calculation. Results are:

1. For gravimetric pure gas adsorption measurements we have:

$$\Delta n = \frac{1}{K} \sum_{i=1}^{K} \left| \frac{\Delta n_i}{n_i} \right| \leq 0.3\%,$$

   K ... number of measurements.
2. For volume-gravimetric measurements of binary coadsorption equilibria the analysis yields:

$$\Delta n \leq 0.6\%, \quad \Delta x \leq 3\%.$$

3. For volumetric-chromatographic measurements of ternary coadsorption equilibria the uncertainties are:

$$\Delta n \leq 0.6\%, \quad \Delta x_{CH_4} \leq 1\%,$$
$$\Delta x_{CO_2} \leq 0.7\%, \quad \Delta x_{N_2} \leq 3\%.$$

The integral thermodynamic consistency of the resulting binary adsorption data has been tested by methods acknowledged in the literature (Li and Talu, 1993; Talu and Myers, 1988). The integral spreading pressure difference of the binary adsorption data was found to be small (8% for CH_4/N_2, 14% for CH_4/CO_2 and 6% for CO_2/N_2) and to depend strongly on the pressure of the adsorptive. To give an example, we mention that the spreading pressure difference for all mixtures investigated has values below 2% for pressures of the adsorptive up to 1 MPa. At higher pressures the increase of the spreading pressure difference seems strongly to be related to the non-ideality of the adsorptive mixtures components and their interactions. Thus, the experimental binary mixture data are proven to be nearly thermodynamic consistent.

Measured Data

The experimental data for the pure gas adsorption isotherms of CH_4, N_2, and CO_2 on activated carbon (AC) Norit R1 Extra at $T = 298$ K are listed in Table 2. Here the pressure P is given in MPa and the specific surface excess amount adsorbed n^{ex} as well as the absolute amount adsorbed per unit mass of adsorbent n in mmol/g.

Table 2. Pressures P, surface excess amounts n^{ex}, and absolute amounts n adsorbed of pure gases CH_4, N_2, and CO_2 adsorbed on AC Norit R1 Extra at $T = 298$ K.

CH_4			N_2			CO_2		
P (MPa)	n^{ex} (mmol/g)	n (mmol/g)	P (MPa)	n^{ex} (mmol/g)	n (mmol/g)	P (MPa)	n^{ex} (mmol/g)	n (mmol/g)
0.010	0.165	0.165	0.031	0.116	0.116	0.008	0.320	0.320
0.037	0.501	0.501	0.071	0.260	0.260	0.015	0.538	0.538
0.052	0.663	0.663	0.111	0.389	0.390	0.026	0.883	0.883
0.077	0.877	0.878	0.499	1.265	1.274	0.051	1.417	1.418
0.101	1.076	1.078	0.981	1.952	1.979	0.099	2.229	2.232
0.504	2.889	2.912	1.971	2.819	2.899	0.497	5.650	5.690
0.966	3.955	4.016	2.918	3.324	3.466	0.995	7.548	7.660
1.989	5.168	5.337	3.984	3.692	3.910	1.991	9.323	9.621
2.692	5.629	5.883	4.679	3.860	4.132	2.994	10.024	10.552
3.930	6.089	6.508	5.980	4.066	4.438	3.989	10.247	11.051
4.912	6.278	6.838				4.987	10.041	11.183
5.753	6.364	7.049				6.000	9.590	11.270

For the binary gas-mixture experiments data are given in Tables 3–5. These include adsorptive's pressure P in MPa and concentration of one of the components, say component 1, y_1, the surface excess n^{ex}, the absolute amount adsorbed n in mmol/g, and the respective concentrations of component 1 in the adsorbate x_1^{ex} and x_1.

The Data of adsorption equilibria of the ternary gas-mixtures are given in Tables 6 and 7. In these tables the pressure of the adsorptive P in MPa and the concentrations of methane y_{CH_4} and carbon dioxide y_{CO_2} are given. Also the surface excess n^{ex}, the absolute amount adsorbed n in mmol/g, and the respective concentrations of methane and carbon dioxide in the adsorbate $x_{CH_4}^{ex}$, x_{CH_4}, $x_{CO_2}^{ex}$ and x_{CO_2} are depicted.

Data Correlation

The experimental data of adsorption equilibria of the pure gases on AC Norit R1 at $T = 298$ K (absolute amounts adsorbed n, cp. Table 2) were correlated with a dual-site Langmuir isotherm, i.e., a linear superposition of two Langmuir isotherms reflecting geometric (and energetic) heterogenity of the adsorbent. The model used is developed by generalizing the well known dual-site Langmuir model (Keller et al., 1998; Mathias et al., 1996; Sircar and Myers, 1984) introducing Freundlich type exponents α describing the fractal dimension of the adsorbate as has been formulated for the first time in (Keller, 1990):

$$\begin{aligned} n(P,T) &= n_\infty^P(T)\cdot\alpha_\infty^P(T)\cdot\frac{(b^P(T)\cdot P)^{\alpha^P(P,T)}}{1+(b^P(T)\cdot P)^{\alpha^P(P,T)}} \\ &\quad + n_\infty^S(T)\cdot\alpha_\infty^S(T)\cdot\frac{(b^S(T)\cdot P)^{\alpha^S(P,T)}}{1+(b^S(T)\cdot P)^{\alpha^S(P,T)}}. \end{aligned} \tag{16}$$

Here the upper indices "P" and "S" indicate primary and secondary adsorption sites (Keller et al., 1998). The exponents $\alpha^P(P,T)$, $\alpha^S(P,T)$ are related to the fractal dimension of the adsorbate and can be chosen to be pressure dependent (Staudt et al., 1996):

$$\alpha^P(P,T) = \frac{1+\alpha_\infty^P(T)\cdot P/a^P}{1+P/a^P}, \tag{17a}$$

$$\alpha^S(P,T) = \frac{1+\alpha_\infty^S(T)\cdot P/a^S}{1+P/a^S} \tag{17b}$$

The parameters of the generalized dual-site Langmuir isotherm describing the adsorption of the three pure gases on the AC are determined numerically by using a regression procedure simultaneous for all pure gas isotherms. The two parameters $n_\infty^P(T)$ and $n_\infty^S(T)$ are the number of adsorption sites for the primary and the secondary class of adsorption places defined by the dual-site model and are independent of the adsorptive.

Table 3. Binary co-adsorption equilibria of gas-mixtures CH_4/N_2 on AC Norit R1 Extra at $T = 298\,K$. *Adsorptive*: P: pressure in MPa. Methane concentration: y_{CH_4}; *Adsorbate*: n^{ex}: surface excess adsorbed with concentration of methane $x^{ex}_{CH_4}$; n: absolute amount adsorbed with concentration of methane x_{CH_4}.

P (MPa)	y_{CH_4}	n^{ex} (mmol/g)	$x^{ex}_{CH_4}$	n (mmol/g)	x_{CH_4}
0.151	0.089	0.658	0.344	0.660	0.343
0.522	0.059	1.483	0.241	1.495	0.240
0.974	0.095	2.200	0.322	2.232	0.318
1.925	0.095	3.115	0.330	3.204	0.324
2.970	0.095	3.739	0.346	3.908	0.335
3.930	0.088	4.074	0.319	4.320	0.306
5.056	0.091	4.368	0.337	4.715	0.319
6.035	0.090	4.518	0.345	4.953	0.322
0.111	0.377	0.851	0.754	0.852	0.753
0.533	0.384	2.290	0.750	2.309	0.747
1.038	0.439	3.296	0.793	3.349	0.788
2.285	0.428	4.579	0.787	4.745	0.777
2.764	0.427	4.870	0.801	5.085	0.787
3.979	0.403	5.480	0.793	5.837	0.769
4.989	0.449	5.734	0.818	6.216	0.789
5.980	0.425	5.851	0.823	6.452	0.786
0.108	0.731	1.120	0.932	1.122	0.932
0.518	0.668	2.679	0.909	2.701	0.907
1.091	0.735	3.829	0.935	3.894	0.932
2.022	0.733	4.818	0.937	4.975	0.931
2.978	0.731	5.451	0.938	5.719	0.928
3.972	0.726	5.714	0.942	6.100	0.929
4.986	0.727	5.931	0.946	6.449	0.928
5.975	0.733	6.098	0.951	6.755	0.929

Table 4. Binary coadsorption equilibria of gas-mixtures CH_4/CO_2 on AC Norit R1 Extra at $T = 298$ K. *Adsorptive*: P: pressure in MPa. Methane concentration: y_{CH_4}; *Adsorbate*: n^{ex}: surface excess adsorbed with concentration of methane $x^{ex}_{CH_4}$; n: absolute amount adsorbed with concentration of methane x_{CH_4}.

P (MPa)	y_{CH_4}	n^{ex} (mmol/g)	$x^{ex}_{CH_4}$	n (mmol/g)	x_{CH_4}
0.098	0.253	1.972	0.138	1.975	0.138
0.557	0.239	5.456	0.089	5.500	0.090
1.140	0.214	7.475	0.066	7.603	0.068
2.088	0.211	9.058	0.064	9.358	0.068
3.082	0.198	9.976	0.062	10.502	0.069
3.861	0.220	10.233	0.052	10.948	0.063
5.230	0.196	10.352	0.046	11.475	0.061
6.023	0.201	10.236	0.048	11.635	0.066
0.102	0.574	1.704	0.357	1.706	0.357
0.502	0.542	4.387	0.308	4.420	0.310
1.014	0.536	6.041	0.294	6.133	0.298
2.042	0.527	7.702	0.264	7.948	0.273
3.096	0.524	8.769	0.260	9.218	0.273
3.887	0.541	9.107	0.255	9.714	0.273
5.026	0.506	9.432	0.243	10.309	0.265
5.877	0.534	9.367	0.250	10.425	0.279
0.100	0.954	1.207	0.908	1.209	0.908
0.500	0.957	3.199	0.916	3.224	0.916
1.025	0.948	4.474	0.892	4.546	0.892
2.149	0.941	5.833	0.886	6.038	0.888
3.097	0.948	6.300	0.893	6.640	0.898
3.887	0.939	6.417	0.891	6.851	0.894
5.100	0.940	6.417	0.893	7.013	0.897
5.916	0.947	6.386	0.900	7.097	0.905

Six parameters $\alpha^{P}_{\infty}(T)$, $b^{P}(T)$, a^{P} and $\alpha^{S}_{\infty}(T)$, $b^{S}(T)$, a^{S} are describing the adsorptive dependent behavior of the isotherm. Thus, there are 20 parameters determined by the parameter optimization procedure for the three pure gas adsorption isotherms. The resulting parameters are given in Table 8.

Henry's law constant H_i,

$$H_i = \lim_{P \to 0} \frac{n(P)}{P}, \quad i = CH_4, CO_2, N_2,$$

has been determined by the data fit, too. Values are given in the Table 8 together with the parameters of the isotherm.

For the pure gases CH_4, CO_2, N_2 the mean relative deviations between experimentally measured amounts adsorbed n and their values calculated with the model, $\bar{\Delta}n$ (cp. Eq. (20)) are also given in Table 8. These quantities can be compared with the mean relative experimental uncertainty Δ_{exp} of the measured isotherms. Obviously, the deviations between measured and calculated values ($\bar{\Delta}n < 1\%$) is greater than the (small) uncertainty of the experimental data. The resulting fits and the experimental data are shown in Fig. 2.

Prediction of Mixture Adsorption

Using the parameters given in Table 8 the mixture data can be predicted by using Markham and Benton's formalism with the generalized dual-site Langmuir isotherm (Markham and Benton, 1931). Thus, the

Table 5. Binary co-adsorption equilibria of gas-mixtures CO_2/N_2 on AC Norit R1 Extra at $T = 298$ K. *Adsorptive*: P: pressure in MPa. Carbon dioxide concentration: y_{CO_2}; *Adsorbate*: n^{ex}: surface excess adsorbed with concentration of carbon dioxide $x^{ex}_{CO_2}$; n: absolute amount adsorbed with concentration of carbon dioxide x_{CO_2}.

P (MPa)	y_{CO_2}	n^{ex} (mmol/g)	$x^{ex}_{CO_2}$	n (mmol/g)	x_{CO_2}
0.108	0.189	0.962	0.759	0.964	0.758
0.535	0.202	2.836	0.777	2.857	0.772
1.058	0.216	4.057	0.783	4.119	0.774
1.875	0.216	5.622	0.806	5.786	0.789
3.078	0.217	6.169	0.825	6.452	0.799
4.102	0.211	6.634	0.811	7.050	0.776
5.066	0.180	6.871	0.807	7.411	0.761
6.077	0.203	7.055	0.841	7.739	0.785
0.109	0.489	1.528	0.916	1.530	0.915
0.531	0.504	4.170	0.934	4.201	0.931
1.048	0.488	5.576	0.943	5.661	0.936
2.122	0.490	7.254	0.934	7.476	0.921
3.061	0.487	7.976	0.948	8.344	0.927
4.156	0.487	8.647	0.960	9.217	0.931
5.015	0.480	9.137	0.971	9.904	0.933
6.055	0.475	9.128	0.977	10.091	0.929
0.116	0.794	2.203	0.978	2.206	0.978
0.522	0.834	5.438	0.985	5.478	0.983
1.000	0.883	7.172	0.991	7.278	0.989
1.972	0.861	9.016	0.990	9.295	0.986
2.901	0.895	9.917	0.995	10.403	0.990
3.940	0.856	10.482	0.995	11.231	0.986
5.023	0.874	10.554	0.999	11.633	0.988
5.634	0.847	10.713	0.999	11.997	0.984

amount adsorbed of component i n_i of a mixture is given by:

$$\begin{aligned} n_i(p,T) = {} & n^{P}_{\infty}(T)\cdot\alpha^{P}_{i,\infty}(T) \\ & \cdot \frac{\left[b^{P}_i(T)\cdot P_i\right]^{\alpha^{P}_i(P_i,T)}}{1+\sum_{k=1}^{N}\left[b^{P}_k(T)\cdot P_k\right]^{\alpha^{P}_k(P_k,T)}} \\ & + n^{S}_{\infty}(T)\cdot\alpha^{S}_{i,\infty}(T) \\ & \cdot \frac{\left[b^{S}_i(T)\cdot P_i\right]^{\alpha^{S}_i(P_i,T)}}{1+\sum_{k=1}^{N}\left[b^{S}_k(T)\cdot P_k\right]^{\alpha^{S}_k(P_k,T)}}, \end{aligned} \tag{18}$$

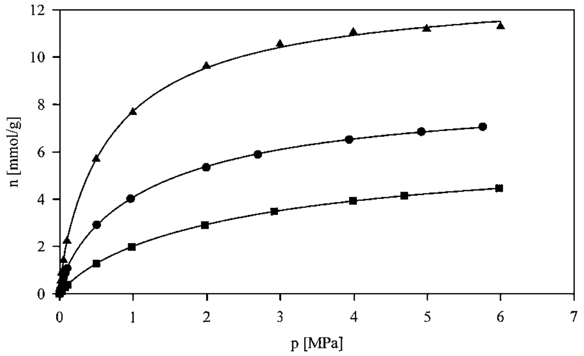

Figure 2. Measured amounts adsorbed of the pure gases CH_4 (●), CO_2 (▲), and N_2 (■) on AC Norit R1 at $T = 298$ K. Simultaneous fit of all data with the generalized dual-site Langmuir isotherm (—) (Eqs. (16)–(17b)); parameter values are given in Table 8.

with the pressure dependent exponents:

$$\alpha^{P}_i(P_i,T) = \frac{1+\alpha^{P}_{i,\infty}(T)\cdot P_i/a^{P}_i}{1+P_i/a^{P}_i}, \tag{19a}$$

$$\alpha^{S}_i(P_i,T) = \frac{1+\alpha^{S}_{i,\infty}(T)\cdot P_i/a^{S}_i}{1+P_i/a^{S}_i}, \tag{19b}$$

$i,k = 1,2$ (binary mixtures), $i,k = 1,2,3$ (ternary mixture).

The mean relative deviations between the predicted ($n = n_1 + n_2$) and the experimental (n_{exp}) total amounts adsorbed as well as between the predicted ($x_1 = n_1/(n_1+n_2)$) and measured concentration ($x_{1,exp}$) of component 1 in the binary mixture are calculated as:

$$\bar{\Delta} n = \frac{1}{N}\sum_{i=1}^{N}\sqrt{\left(\frac{n_{exp,i}-n_i}{n_{exp,i}}\right)^2}, \tag{20}$$

$$\bar{\Delta} x_1 = \frac{1}{N}\sum_{i=1}^{N}\sqrt{\left(\frac{x_{1,exp,i}-x_{1,i}}{x_{1,exp,i}}\right)^2}, \tag{21}$$

with N being the total number of measurements. The resulting deviations are given in Table 9 for the three binary systems investigated. Together with these data in the same table the deviations of the the binary adsorption equilibria data from the data calculated with the ideal adsorbed solution theory (IAST) (Myers and Prausnitz, 1965) are given. Examples of the predictions with the generalized dual site Langmuir model for the three binary systems are shown in Figs. 3–5 together with the measured co-adsorption equilibria. Agreement

Table 6. Ternary co-adsorption equilibria of gas-mixtures $CH_4/CO_2/N_2$ on AC Norit R1 Extra at $T = 298$ K. *Adsorptive*: P: pressure in MPa. Methane concentration: y_{CH_4}. Carbon dioxide concentration: y_{CO_2}; *Adsorbate*: n^{ex}: surface excess adsorbed with concentrations of methane $x^{ex}_{CH_4}$ and of carbon dioxide $x^{ex}_{CO_2}$; n: absolute amount adsorbed with concentrations of methane x_{CH_4} and of carbon dioxide x_{CO_2}.

P (MPa)	y_{CH_4}	y_{CO_2}	n^{ex} (mmol/g)	$x^{ex}_{CH_4}$	$x^{ex}_{CO_2}$	n (mmol/g)	x_{CH_4}	x_{CO_2}
0.102	0.309	0.220	1.116	0.352	0.579	1.117	0.352	0.579
0.467	0.349	0.248	3.139	0.297	0.632	3.160	0.298	0.630
1.017	0.329	0.283	5.296	0.366	0.530	5.376	0.366	0.526
2.009	0.340	0.304	7.373	0.344	0.503	7.599	0.344	0.497
3.011	0.342	0.281	8.337	0.341	0.495	8.726	0.341	0.485
4.000	0.342	0.286	9.127	0.334	0.499	9.674	0.334	0.487
5.017	0.331	0.297	9.740	0.334	0.508	10.492	0.334	0.493
6.013	0.342	0.307	9.968	0.322	0.520	10.919	0.324	0.502
0.107	0.564	0.289	1.360	0.404	0.577	1.362	0.405	0.577
0.433	0.535	0.340	3.517	0.414	0.569	3.540	0.415	0.568
1.054	0.538	0.347	5.439	0.359	0.629	5.524	0.361	0.625
1.996	0.535	0.359	7.036	0.323	0.650	0.254	0.329	0.641
3.020	0.524	0.373	8.200	0.330	0.638	8.601	0.339	0.625
4.025	0.522	0.377	8.910	0.334	0.632	9.518	0.346	0.615
5.034	0.518	0.382	9.495	0.352	0.609	10.346	0.366	0.591
5.861	0.522	0.377	9.734	0.357	0.606	10.770	0.372	0.584
0.113	0.445	0.051	0.923	0.553	0.232	0.924	0.553	0.232
0.525	0.474	0.070	2.648	0.563	0.228	2.668	0.563	0.227
1.111	0.486	0.073	3.849	0.528	0.250	3.914	0.527	0.247
1.986	0.484	0.078	4.965	0.528	0.252	5.117	0.526	0.247
3.011	0.485	0.082	5.738	0.523	0.248	6.011	0.521	0.240
4.011	0.486	0.084	6.249	0.519	0.235	6.654	0.517	0.226
4.964	0.485	0.085	6.665	0.540	0.229	7.215	0.535	0.218
5.798	0.487	0.087	6.859	0.554	0.216	7.532	0.548	0.205

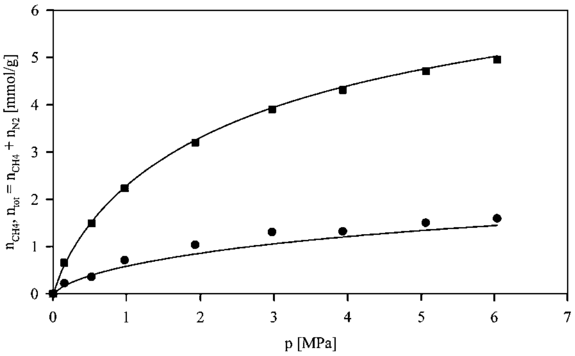

Figure 3. Measured total amount adsorbed of the binary gas mixture CH_4/N_2 ($\bar{y}_{CH_4} \approx 0.09$) n_{tot} (■) and measured partial amount of CH_4 adsorbed (●). Prediction of the data with the generalized dual-site Langmuir isotherm (—) (Eqs. (18)–(19b)) with parameter values given in Table 8.

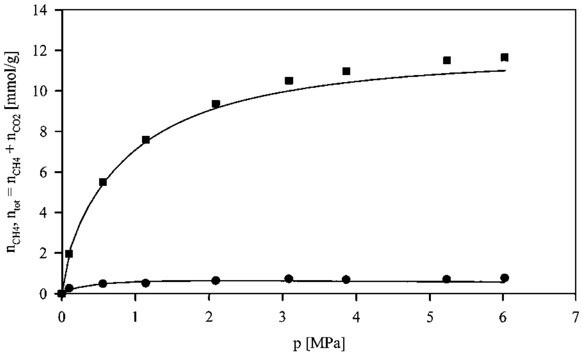

Figure 4. Measured total amount adsorbed of the binary gas mixture CH_4/CO_2 ($\bar{y}_{CH_4} \approx 0.21$) n_{tot} (■) and measured partial amount of CH_4 adsorbed (●). Prediction of the data with the generalized dual-site Langmuir isotherm (—) (Eqs. (18)–(19b)) with parameter values given in Table 8.

Table 7. Ternary co-adsorption equilibria of gas-mixtures $CH_4/CO_2/N_2$ on AC Norit R1 Extra at $T = 298\,K$. *Adsorptive*: P: pressure in MPa. Methane concentration: y_{CH_4}. Carbon dioxide concentration: y_{CO_2}; *Adsorbate*: n^{ex}: surface excess adsorbed with concentrations of methane $x^{ex}_{CH_4}$ and of carbon dioxide $x^{ex}_{CO_2}$; n: absolute amount adsorbed with concentrations of methane x_{CH_4} and of carbon dioxide x_{CO_2}.

P (MPa)	y_{CH_4}	y_{CO_2}	n^{ex} (mmol/g)	$x^{ex}_{CH_4}$	$x^{ex}_{CO_2}$	n (mmol/g)	x_{CH_4}	x_{CO_2}
0.103	0.500	0.157	1.153	0.496	0.426	1.155	0.496	0.426
0.485	0.510	0.182	3.158	0.460	0.474	3.181	0.461	0.472
1.073	0.509	0.201	4.909	0.457	0.464	0.988	0.458	0.460
1.999	0.512	0.210	6.363	0.439	0.481	6.559	0.442	0.473
3.008	0.512	0.218	7.315	0.428	0.486	7.665	0.432	0.474
4.016	0.511	0.223	8.000	0.423	0.481	8.527	0.429	0.465
4.957	0.510	0.227	8.601	0.438	0.444	9.323	0.443	0.427
5.991	0.508	0.230	8.950	0.442	0.431	9.890	0.448	0.412
0.093	0.707	0.113	1.082	0.705	0.218	1.084	0.705	0.218
0.478	0.707	0.113	3.086	0.679	0.268	3.108	0.680	0.267
1.030	0.740	0.096	4.306	0.609	0.313	4.369	0.611	0.310
2.004	0.720	0.126	5.749	0.614	0.306	5.930	0.617	0.301
3.022	0.712	0.132	6.605	0.614	0.305	6.930	0.619	0.297
3.834	0.730	0.131	6.987	0.649	0.287	7.437	0.654	0.277
4.937	0.726	0.130	7.442	0.637	0.281	8.082	0.644	0.269
5.837	0.718	0.134	7.643	0.631	0.273	8.450	0.639	0.260

between measured and predicted data is fairly good for all three investigated binary mixtures. Especially the total amounts adsorbed of the binary mixtures can be predicted with deviations below 4%. The mean relative deviation in the concentration of mixture's components in the adsorbate are in the range between 2.7% and 8.8%. This may be acceptable for the design and development of adsorption processes and/or equipments. The mean deviations between measured and predicted adsorption equilibria data of the investigated

Table 8. Parameters of the generalized dual-site Langmuir isotherm (Eqs. (16)–(17b)) determined by a regression of the experimental data of three pure gas adsorption isotherms (CH_4, CO_2, N_2) and Henry's law constant (H).

Parameter	Unit	CH_4	CO_2	N_2
n^P_∞	mmol/g		1.083	
n^S_∞	mmol/g		8.138	
b^P	1/MPa	10.378	18.215	2.773
α^P_∞		1.110	1.508	0.823
a^P	MPa	0.111	1.080	1.071
b^S	1/MPa	0.631	1.368	0.234
α^S_∞		0.932	1.282	0.787
a^S	MPa	1.033	0.705	1.093
H	mmol/g · MPa	17.240	47.370	4.040
$\bar{\Delta}n$	%	0.207	0.655	0.227
Δ_{exp}	%	0.082	0.065	0.154

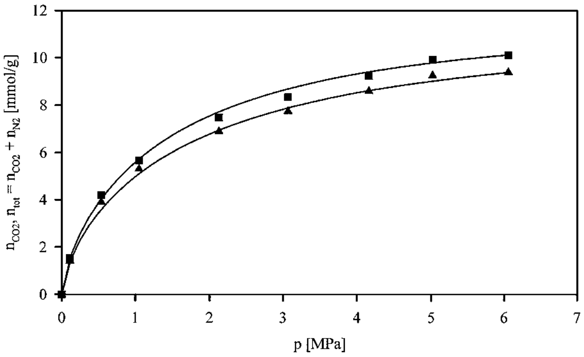

Figure 5. Measured total amount adsorbed of the binary gas mixture CO_2/N_2 ($\bar{y}_{CO_2} \approx 0.47$) n_{tot} (■) and measured partial amount of CO_2 adsorbed (▲). Prediction of the data with the generalized dual-site Langmuir isotherm (—) (Eqs. (18)–(19b)) with parameter values given in Table 8.

Table 9. Mean relative deviations between predicted and measured binary gas mixture adsorption equilibria on AC Norit R1 at $T = 298\,\text{K}$.

Binary system comp. 1/2	Generalized dual-site Langmuir		IAST	
	$\bar{\Delta}n$ (%)	$\bar{\Delta}x_1$ (%)	$\bar{\Delta}n$ (%)	$\bar{\Delta}x_1$ (%)
CH_4/CO_2	3.17	8.79	2.98	15.82
CH_4/N_2	3.41	7.50	3.82	5.20
CO_2/N_2	2.56	2.70	2.38	1.72

Table 10. Mean relative deviations between predicted and measured ternary gas mixture adsorption equilibria on the AC Norit R1 at $T = 298\,\text{K}$.

Generalized dual-site Langmuir				IAST			
$\bar{\Delta}n$ (%)	$\bar{\Delta}x_{CH_4}$ (%)	$\bar{\Delta}x_{CO_2}$ (%)	$\bar{\Delta}x_{N_2}$ (%)	$\bar{\Delta}n$ (%)	$\bar{\Delta}x_{CH_4}$ (%)	$\bar{\Delta}x_{CO_2}$ (%)	$\bar{\Delta}x_{N_2}$ (%)
4.88	10.79	15.11	35.53	4.29	14.85	27.21	47.19

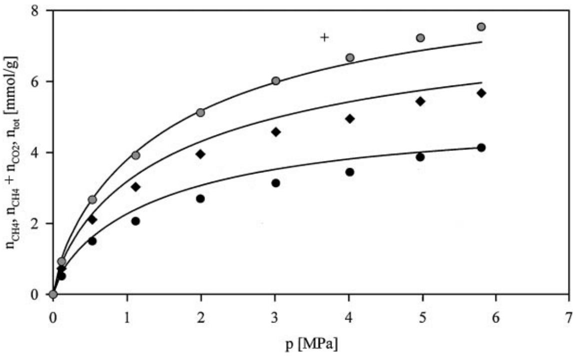

Figure 6. Measured total amount adsorbed of the ternary gas mixture $CH_4/CO_2/N_2$ n_{tot} (◉), measured partial amount of CH_4 adsorbed n_{CH_4} (●) and measured partial amounts of $CH_4{+}CO_2$ $n_{CH_4} + n_{CO_2}$ (◆) adsorbed. Prediction of the data with the generalized dual-site Langmuir isotherm (—) (Eqs. (18)–(19b)) with the parameter values given in Table 8.

ternary mixture are calculated according to Eqs. (20) and (21) and are given in Table 10, again for the dual-site Langmuir model and for the ideal adsorbed solution theory (IAST). As an example for the prediction, the measured and predicted co-adsorption data of the ternary mixture isotherm with the mean concentrations ($\bar{y}_{CH_4} \approx 0.48/\bar{y}_{CO_2} \approx 0.08/\bar{y}_{N_2} \approx 0.44$) on AC Norit R1 at $T = 298\,\text{K}$ is given in Fig. 6.

The total amount adsorbed could be predicted with deviations of about 5%. The concentrations of the strongly adsorbed components in the adsorbate (CH_4 and CO_2) could be calculated with deviations below 15%. The concentration of the weakly adsorbed component N_2 could not be predicted. Its deviations from experimental values are about 35%. To improve this situation it seems to be necessary to use isotherms which basically take into account molecular interactions (Keller et al. 1998).

Conclusion

In this study adsorption equilibria of the pure gases CH_4, CO_2, and N_2 on activated carbon (AC) Norit R1 Extra have been measured in the pressure range $0 \leq P \leq 6$ MPa at $T = 298\,\text{K}$ using the gravimetric method. Co-adsorption equilibria of the binary mixtures CH_4/N_2, CH_4/CO_2, and CO_2/N_2 on the same AC in the same range of pressure and at the same temperature have been measured using the volume-gravimetric method for three almost constant adsorptive concentrations for every binary system. Using this method no measurement of the concentration of the gas or the adsorbed phase is necessary. Five coadsorption isotherms of the ternary mixture $CH_4/N_2/CO_2$ have been measured under the same pressure and temperature conditions with the volume-chromatographic method for almost constant concentrations of the adsorptive.

For the necessary (buoyancy or displacement related) correction of data measured in volumetric and/or gravimetric experiments the so-called helium volume of the AC was used to get the surface excess amounts adsorbed. A new model to determine the absolute amounts adsorbed is described and used. The measurement procedure and data handling is described in detail and the results of an error calculation are given in brief.

The binary co-adsorption data have been checked for thermodynamic consistency.

The pure gas adsorption equilibria have been correlated with a generalized adsorption model of Langmuir-type taking into account the heterogeneity of the adsorbent as well as the fractal character of its internal microporous structure. Prediction of binary and ternary co-adsorption data has been performed using this model with the resulting pure gas adsorption parameters. Agreement between predicted and experimental data was fairly good:

(i) The total amounts adsorbed could be predicted with deviations below 5%.
(ii) The concentrations of the adsorbate of the binary mixtures could be calculated fairly well (mean relative deviation below 9%).
(iii) The concentrations of the strongly adsorbed components of the ternary mixture in the adsorbate could be predicted from pure gas data with deviation below 15%.

Only the deviations between measured concentrations of the weakly adsorbed component (N_2) of the ternary mixture $CH_4/CO_2/N_2$ and their calculated values was unacceptable high (35%). In general, predictions with the generalized dual-site Langmuir model for the binary mixtures are of the same quality as those made with the Ideal Adsorbed Solution Theory (Myers and Prausnitz, 1965). For the ternary mixtures the predictions with the generalized dual-site Langmuir model are better than those made with the IAS theory.

Nomenclature

Latin letters

a^{P}	constant in the pressure dependent exponent of the primary class of adsorption sites (Eqs. (17a) and (19a))	MPa
a^{S}	constant in the pressure dependent exponent of the secondary class of adsorption sites (Eqs. (17a) and (19a))	MPa
b^{P}	Langmuir's constant for the primary class of adsorption sites	1/MPa
b^{S}	Langmuir's constant for the secondary class of adsorption sites	1/MPa
m	adsorbed mass	mg
m^{f}	mass of adsorptive after adsorption	mg
m^{S}	mass of adsorbent connected to the microbalance	g
m^{*}	mass of adsorptive prepared for adsorption	mg
M_i	molar mass of component *i*	g/mol
n	adsorbed amount	mmol/g
n^{ex}	surface excess amount adsorbed	mmol/g
n^{P}_{∞}	number of adsorption sites in the primary class of adsorption places (Eqs. (16) and (18))	mmol/g
n^{S}_{∞}	number of adsorption sites in the secondary class of adsorption places (Eqs. (16) and (18))	mmol/g
P	pressure	MPa
P^{*}	pressure in the storage vessel during preparation of the adsorptive	MPa
T	temperature	K
T^{*}	temperature in the storage vessel during preparation of the adsorptive	K
V	volume of the adsorbent-adsorbate system	cm^3
V^{a}	volume of the adsorbate	cm^3
V_{AV}	volume of the adsorption vessel	dm^3
V_{He}	helium-volume of the adsorbent	cm^3
V_{SV}	volume of the storage vessel	dm^3
x_i	molar concentration of component *i* in the adsorbate	1
x_i^{ex}	excess molar concentration of component *i* in the adsorbate	1
y	molar concentration of component *i* in the adsorptive	1
y_i^{*}	molar concentration of component *i* during preparation of the adsorptive	1

Greek letters

$\alpha^{\mathrm{P}}_{\infty}$	value of the fractal exponent of the primary class of adsorption places at infinite pressure (Eqs. (16)–(19))	1
$\alpha^{\mathrm{S}}_{\infty}$	value of the fractal exponent of the secondary class of	1

	adsorption places at infinite pressure (Eqs. (16)–(19))	
$\alpha^{\mathrm{P}}(P)$	value of the fractal exponent of the primary class of adsorption places at pressure P (Eqs. (16)–(19))	1
$\alpha^{\mathrm{S}}(P)$	value of the fractal exponent of the secondary class of adsorption places at pressure P (Eqs. (16)–(19))	1
Δm	microbalance signal	mg
ΔP	uncertainty of pressure measurement	MPa
ΔT	uncertainty of temperature measurement	K
Δn	relative uncertainty in the experimental determined amounts adsorbed	
Δx_i	relative uncertainty in the experimental determined concentration of component i in the adsorbate	1
$\bar{\Delta} n$	mean relative deviation between predicted and experimental amounts adsorbed	
$\bar{\Delta} x_i$	mean relative deviation between predicted and experimental concentration of component i in the adsorbate	
Ω	reduced mass of adsorbate	mg
ρ	density of the adsorptive	g/l
ρ^{L}	liquid density of the adsorptive in a reference state	g/l

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References

Gregg, S.J. and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1967.

IUPAC, *Chemical Data Series: International Thermodynamic Tables of the Fluid State-3 Carbon Dioxide*, Pergamon Press, Oxford, 1976.

IUPAC, *Chemical Data Series: International Thermodynamic Tables of the Fluid State-5 Methane*, Pergamon Press, Oxford, 1978.

IUPAC, *Chemical Data Series: International Thermodynamic Tables of the Fluid State-6 Nitrogen*, Pergamon Press, Oxford, 1979.

Jaeschke, M. et al. (Eds.), *GERG Technical Monograph: High Accuracy Compressibility Factor Calculation for Natural Gases and Similar Mixtures by Use of a Truncated Virial Equation*, Verlag des Vereins Deutscher Ingenieure, Düsseldorf, 1988.

Keller, J.U., "Equations of State of Adsorbates with Fractal Dimension," *Physica A*, **166**, 180–192 (1990).

Keller, J.U., R. Staudt, and M. Tomalla, "Volume-Gravimetric Measurements of Binary Gas Adsorption Equilibria," *Ber. Bunsenges. Phys. Chem.*, **96**, 28–32 (1992).

Keller, J.U., F. Dreisbach, H. Rave, R. Staudt, and M. Tomalla, "Measurement and Correlation of Gas Mixture Adsorption Equilibria of Natural Gas Compounds on Microporous Sorbens," *Adsorption*, *5*, 199–215.

Keller, J.U. et al., "Generalization of Langmuir's Adsorption Isotherms to Heterogeneous Microporous Solids," Institute of Fluid- & Thermodynamics, University of Siegen (1998), in preparation.

Li, J. and O. Talu, "Evaluation of Multicomponent Adsorption Data," *Presentation AIChE Annual Meeting*, St. Louis, 1993.

Mathias, P.M. et al., "Correlation of Multicomponent Gas Adsorption by the Dual-Site Langmuir Model. Application to Nitrogen/Oxygen Adsorption on 5A-Zeolite," *Ind. Eng. Chem. Res.*, **35**, 1477–1483 (1996).

Markham, E.C. and A.F. Benton, "The Adsorption of Gas Mixtures by Silica," *J. Am. Chem. Soc.*, **53**, 497–507 (1931).

Myers, A.L. and J.M. Prausnitz, "Thermodynamics of Mixed Gas Adsorption," *AIChE Journal*, **11**, 121–127 (1965).

Myers, A.L, "Comparison of Molecular Simulation of Adsorption with Experiment," *Adsorption*, **3**, 107–115 (1997).

Sircar, S. and A.L. Myers, "Energy Distributions for Adsorption of Gases on Heterogeneous Surfaces," *AIChE Symp. Ser.*, **233**, 55–61 (1984).

Staudt, R., G. Saller, M. Tomalla, and J.U. Keller, "A Note on Gravimetric of Gas Adsorption Equilibria," *Ber. Bunsenges. Phys. Chem.*, **97**, 98–105 (1993).

Staudt, R., F. Dreisbach, and J.U. Keller, "Generalized Isotherms for Mono- and Multicomponent Adsorption," *Fundamentals of Adsorption*, M.D. LeVan (Ed.), pp. 865–872, Kluwer, Boston, 1996.

Talu, O. and A.L. Myers, "Rigorous Thermodynamic Treatment of Gas Adsorption," *AIChE Journal*, **34**, 1887–1893 (1988).

Tomalla, M., R. Staudt, and J.U. Keller, "Determination of Binary Gas Adsorption Equilibria by Volume-Gravimetric Measurements," *Microbalance Techniques*, J.U. Keller and E. Robens (Eds.), 193–204, Multi-Science, Brentwood, 1994.

Young, D.M. and A.D. Crowell, *Physical Adsorption of Gases*, Butterworth, London, 1962.