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Single and Mixed Gas Adsorption Equilibria of Carbon Dioxide/Methane on Activated Carbon

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Abstract. Single gas adsorption isotherms of methane and carbon dioxide on micro-porous Norit RB1 activated carbon were determined in a gravimetric analyser in the temperature range of 292 to 349 K and pressures to 0.8 Mpa. Furthermore binary isotherms of carbon dioxide and methane mixtures were determined at 292 K and pressures up to 0.65 MPa. Adsorbed phase compositions were determined from the gravimetric data by the rigorous thermodynamic method of Van Ness.

These experimental binary equilibrium data were compared with equilibrium data calculated by the Ideal Adsorbed Solution (IAS) model. Only moderate agreement could be obtained.

Finally, activity coefficients, accounting for the non-ideality of the adsorbate mixture, were calculated from the experimental data. The Wilson equation, derived for bulk solutions, was fitted on these activity data and the Wilson interaction parameters were determined. The Wilson equation proved to correlate the experimental data reasonably. However, the Wilson interaction parameters are not only completely different from those found for bulk solutions, but also the physical interpretation of these parameter values is completely lacking.

It is concluded that new solution models should be developed encompassing both non-ideal solution behaviour and surface heterogeneity.

Keywords: gas adsorption, activated carbon, theory, experimental data, activity coefficient, spreading pressure

Introduction

Mixed gas equilibrium adsorption data are essential for development and design of adsorptive gas separation processes. Since experimental determination of mixed gas adsorption data is elaborate and time-consuming, it is desirable to predict mixed gas adsorption equilibria from single gas adsorption isotherms. In the literature a number of models for these calculations can be found. Reviews have been given by, among others, Ruthven (1984), Yang (1987), Tien (1994), Hu and Do (1995) and Do (1998).

The adsorbed solution theory of Myers and Prausnitz (1965) provides an elegant method for calculation of mixed gas equilibrium data from single gas isotherms and was therefore adopted in the present study. In this theory the adsorbate mixture is visualised as a solution in equilibrium with the gas phase and adsorbate non-ideality is expressed in terms of activity coefficients of the adsorbate mixture.

The gravimetric technique is an efficient method to determine gas adsorption equilibria, since only the measurement of the total amount of adsorbate is required. The gravimetric technique, however, does not allow the calculation of mixed gas equilibria directly from the experimental data, since the composition of the mixed adsorbed phase can not be measured. Van Ness (1969) developed a rigorous thermodynamic method, using the Gibbs adsorption isotherm, for calculation of the adsorbate composition from the total

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amount of adsorbate. Although the powerful combination of gravimetric experimentation and Van Ness method leads to considerable savings in experimental equipment and time, the method has apparently caught little attention, since only a limited number of applications of this method has been reported in literature. In the following section a selected number of references is given to illustrate the application of the Van Ness method

Friederich and Mullins (1972) have applied the technique, using a commercial microbalance (gravimeter), to measure binary adsorption equilibria of ethylene-ethane, propene-propane and ethane-propane on carbon black at 25°C and 0.01–1 bar pressure. Equilibrium adsorption of benzene-cyclohexane gas mixtures on graphitised carbon and activated charcoal was studied by Myers et al. (1982). Kariavas and Myers (1992) applied the Bragg-Williams beta BWB) approximation for the adsorbent-adsorbate interaction and a beta distribution of adsorptive energies and calculated adsorbed phase compositions in agreement with experimental data and with Monte Carlo calculations. Buss (1995) studied adsorbed phase non-ideality for the adsorption of carbon dioxide-methane mixtures on activated carbon.

In the present study adsorption isotherms of methane and carbon dioxide and their binary mixtures on microporous Norit RB1 activated carbon were determined using a commercial gravoimetric analyser. Adsorbed phase compositions for binary mixtures are determined from the gravimetric data by the rigorous thermodynamic method of Van Ness.

These experimental binary equilibrium data are compared with equilibrium data calculated by the Ideal Adsorbed Solution (IAS) model.

Finally, activity coefficients, accounting for the non-ideality of the adsorbate mixture, are calculated. The Wilson equation, derived for bulk solutions, is fitted on these activity data and the Wilson interaction parameters are determined.

Theoretical Considerations

The Gibbs Adsorption Isotherm

The Van Ness method for calculation of the composition of adsorbed mixtures from gravimetric adsorption experiments is based on the Gibbs adsorption isotherm. The Gibbs adsorption isotherm for a two-dimensional adsorbate phase is:

$$A_{\mathrm{m}} d\pi + \sum_i x_i d\mu_{i,\mathrm{a}} = 0 \quad (\text{constant } T) \tag{1}$$

Here π [N m^{-1}] is the spreading pressure and $\mu_{i,\mathrm{a}}$ [J mol^{-1}] is the chemical potential of component i in the adsorbed phase. The molar surface area A_{m} [m^2 mol^{-1}], is given by:

$$A_{\mathrm{m}} = \frac{A}{q_{\mathrm{t}}} \tag{2}$$

where A is the specific surface area [m^2 kg^{-1}] of the adsorbent and q_{t} [mol kg^{-1}] is the total adsorbed amount. At equilibrium the chemical potential of the adsorbed phase $\mu_{i,\mathrm{a}}$ is equal to the chemical potential of the gas phase $\mu_{i,\mathrm{g}}$ [J mol^{-1}]:

$$\mu_{i,\mathrm{a}} = \mu_{i,\mathrm{g}} = \mu^0_{i,\mathrm{g}} + RT \ln \varphi_i y_i p \tag{3}$$

with φ_i is the fugacity coefficient of component i, y_i is the mole fraction of i in the gas phase and p is total gas phase pressure. Since gas pressures are moderate ($p < 0.7$ MPa) and the adsorbates are relatively light, the fugacity coefficients φ_i are set to unity in the remainder of this study. Substitution of Eq. (3) with $\varphi_i = 1$ into Eq. (1) gives an alternative expression for the Gibbs adsorption isotherm:

$$-\frac{1}{q_{\mathrm{t}}} d\pi^* + d\ln p + \sum_i x_i d\ln y_i = 0 \quad (\text{constant } T) \tag{4}$$

where x_i[-] is the composition of the adsorbed phase and π^* [mol kg^{-1}] the reduced spreading pressure of the adsorbed mixture:

$$\pi^* = \pi \frac{A}{RT} \tag{5}$$

The isotherm expression of Eq. (4) is used throughout the present study.

Since the spreading pressure adds an extra variable, the number of degrees of freedom, F, for gas/adsorbate equilibria is given by a modified version of the phase rule $F = N + 1$ ($N =$ number of components). Therefore, adsorption equilibria of binary gas mixtures have 3 degrees of freedom: 3 intensive variables can be chosen arbitrarily. In this paper two sets of 3 intensive variables are considered: T, p, y and T, π^*, x.

Calculation of Adsorbed Phase Composition from Gravimetric Experiments

To calculate the composition of the adsorbed phase from gravimetric adsorption experiments we adopt the approach of Van Ness (1969). His method is summarised below.

At constant composition of the gas phase the Gibbs isotherm (Eq. (4)) becomes:

$$\frac{\partial \pi^*}{\partial p} = \frac{q_t}{p} \quad \text{(constant } T \text{ and } y\text{)} \qquad (6)$$

which is integrated as:

$$\pi^* = \int_0^p \frac{w_t/M}{p} dp \quad \text{(constant } T \text{ and } y\text{)} \qquad (7)$$

with:

$$M = \sum_i x_i M_i \qquad (8)$$

where $w_t = Mq_t$ [kg kg^{-1}] is the total mass adsorbed per unit mass adsorbent, which is determined gravimetrically. M_i [kg mol^{-1}] is the molar mass of component i and M is the average molar mass of the mixture. The reduced spreading pressure is calculated from the experimental data at constant temperature and gas phase composition y with Eq. (7).

At constant pressure Eq. (4) reduces to:

$$-\frac{1}{q_t} d\pi^* + \sum \frac{x_i}{y_i} dy_i = 0 \quad \text{(constant } T \text{ and } p\text{)} \qquad (9)$$

Since the present study is limited to binary CO_2-CH_4 mixtures, Eq. (9) becomes:

$$x = y + \frac{y(1-y)}{w_t/M}\left(\frac{\partial \pi^*}{\partial y}\right)_{T,p} \quad \text{(constant } T \text{ and } p\text{)} \qquad (10)$$

Equations (7, 8 and 10) are solved simultaneously for the unknowns π^*, M and x by an iterative method, yielding the binary equilibrium relation at a given temperature and pressure.

Calculation of activity coefficients, as set out in the next section on the adsorbed solution theory, requires equilibrium data at constant temperature and *spreading pressure*. These equilibrium data were calculated by cubic spline interpolation of the equilibrium data at constant temperature and *pressure*.

The above method is a rigorous thermodynamic method for calculation of equilibrium adsorption data from gravimetric data, involving no other assumptions than those underlying the Gibbs adsorption isotherm.

The Adsorbed Solution Theory

The Adsorbed Solution theory (AS) (Myers and Prausnitz, 1965) provides an elegant way to calculate adsorption data of mixtures from their single gas isotherms. We adopt a (substantial) part of their theory to calculate the composition of binary adsorbed solutions. The single adsorbate reduced spreading pressure $\pi^*_{0,i}$ and equilibrium (saturation) vapour pressure p_i^0 are related through the single gas adsorption isotherm $q_i^0\,(p)$ in Eq. (6):

$$\pi^*_{0,i} = \int_0^{p_i^0} \frac{q_i^0(p)}{p} dp \quad \text{(constant } T\text{)} \qquad (11)$$

where p_i^0 is the equilibrium (saturation) vapour pressure for adsorption of single component i. Mixing at constant spreading pressure requires:

$$\pi^*_{0,i} = \pi^* \qquad (12)$$

and the requirement of equilibrium between gas and adsorbate phases leads to:

$$y_i\, p = \gamma_i x_i\, p_i^0 \quad \text{(constant } T \text{ and } \pi\text{)} \qquad (13)$$

at the same spreading pressure π and the same T as the adsorbate mixture, see Eq. (7). The saturation pressures p_i^0 at a chosen value of reduced spreading pressure are calculated from Eq. (11).

For binary adsorbed solutions Eq. (13) leads to:

$$yp = \gamma_1 x p_1^0 \quad \text{(constant } T \text{ and } \pi\text{)} \qquad (14)$$

$$(1-y)p = \gamma_2(1-x)p_0^2 \quad \text{(constant } T \text{ and } \pi\text{)} \qquad (15)$$

And after elimination of the total pressure p from Eqs. (14) and (15):

$$x_{\mathrm{AS}} = \frac{1}{1 + \frac{1-y}{y}\frac{\gamma_1 p_1^0}{\gamma_2 p_2^0}} \quad \text{(constant } T \text{ and } \pi\text{)} \qquad (16)$$

The activity coefficients γ_1 and γ_2 in Eqs. (14–16) are a function of temperature, spreading pressure and adsorbate composition.

If the binary adsorbate phase forms an Ideal Adsorbed Solution (IAS), then $\gamma_1 = 1$ and $\gamma_2 = 1$ In this case the composition of the adsorbed phase, x_{IAS}, can be derived directly as a function of y from the saturation pressures p_1^0 and p_2^0 of the single gases at a given temperature and spreading pressure:

$$x_{\mathrm{IAS}} = \frac{1}{1 + \frac{1-y}{y}\frac{p_1^0}{p_2^0}} \quad \text{(constant } T \text{ and } \pi) \quad (17)$$

In the appendix it will be shown that the thermodynamically consistent Langmuir equations for single gases lead directly to Eq. (17).

For (nonideal) binary adsorbed solutions (AS) $\gamma_1 \neq 1$ and $\gamma_2 \neq 1$. Substitution of the experimental values of y and x (Van Ness method) in Eqs. (14) and (15) yields the activity coefficients γ_1 and γ_2 at a given T, π and x.

The above calculation of activity coefficients does not require analytical expressions for the single gas isotherms. To evaluate the integral in Eq. (11), cubic spline interpolation through the sets of experimental single gas adsorption data was used.

Correlation of Activity Coefficients

Presently no models are available for prediction of activity coefficients in adsorbate mixtures. Attempts have been made to use bulk solution theories to calculate activity coefficients in adsorbate mixtures. Costa et al. (1981) used the Wilson and UNIQUAC equations to correlate their data on binary- and ternary-mixture adsorbates, while Talu (1984) applied an equation similar to the UNIQUAC equation. Although these correlations were reasonably successful, the empirical binary constants in these equations differed considerably from those reported for bulk solutions. This point will be discussed later in more detail.

In this work the (thermodynamically consistent) Wilson equation is used to correlate activity data. For a binary mixture the Wilson equation is given by Eq. (18), involving two interaction parameters, $\Lambda_{1,2}$ and $\Lambda_{2,1}$:

$$\begin{aligned} \ln\gamma_1 &= 1 - \ln(x_1 + \Lambda_{1,2}x_2) - \frac{x_1}{x_1 + \Lambda_{1,2}x_2} \\ &\quad - \frac{\Lambda_{2,1}x_2}{x_2 + \Lambda_{2,1}x_1} \\ &\qquad\qquad \text{(constant } T \text{ and } \pi) \quad (18) \\ \ln\gamma_2 &= 1 - \ln(x_2 + \Lambda_{2,1}x_1) - \frac{x_2}{x_2 + \Lambda_{2,1}x_1} \\ &\quad - \frac{\Lambda_{1,2}x_1}{x_1 + \Lambda_{1,2}x_2} \end{aligned}$$

While activity coefficients in bulk mixtures are correlated at constant p, activity coefficients in adsorbate mixtures should be correlated at constant T and constant spreading pressures π (Myers, 1983).

Calculational and Fitting Procedures

Van Ness Method

Binary mixture equilibria at constant T and p were calculated from gravimetric data by solving Eqs. (7, 8 and 10) by an iterative method. Cubic spline interpolation was applied to evaluate the integral in Eq. (11). A 3rd order polynomial was then passed through the resulting set of (y, π^*). To obtain accurate values of the $\partial\pi^*/\partial y$ derivative in Eq. (9), experimental data at (at least) five different gas phase compositions is needed. The iteration scheme was programmed in MathCad Plus 6.0 (Van der Vaart, 1997). The algorithm was tested successfully on data presented by Buss (1995). Finally binary mixture equilibria at constant temperature and spreading pressure were calculated by cubic spline interpolation of the above equilibrium data.

Adsorption Solution Theory

The binary mixture equilibria and activity coefficients were calculated from Eqs. (11), (12), (14) and (15). A scheme of nested iterations was programmed in MathCad Plus 6.0 (Van der Vaart, 1997). The experimental single gas isotherms were represented by a cubic spline. The curve fitting procedures were based on the criterium of the least absolute mean squared errors between calculated and experimental values.

Experimental Details

Apparatus and Materials

Gravimetric adsorption measurements were performed with a fully automated Intelligent Gravimetric Analyser (IGA) of Hiden Analytical (UK), see Fig. 1. This system, the prototype of the IGA model 3, allows measurement of total adsorbate amounts at different pressures at constant gas phase composition. It can be operated from vacuum (10^{-4} mbar) up to 20 bar in a static or flowing mode to enable single and mixed gas adsorption experiments at varying pressure and composition. The resolution of the mass reading is 1 μg in static operation and 5–10 μg in flowing operation. The system is completely symmetric: the gas flow rate and composition are equal at the reference and the sample side due to a set of diffuser and collector rings which guide the gas stream from the sample side to the

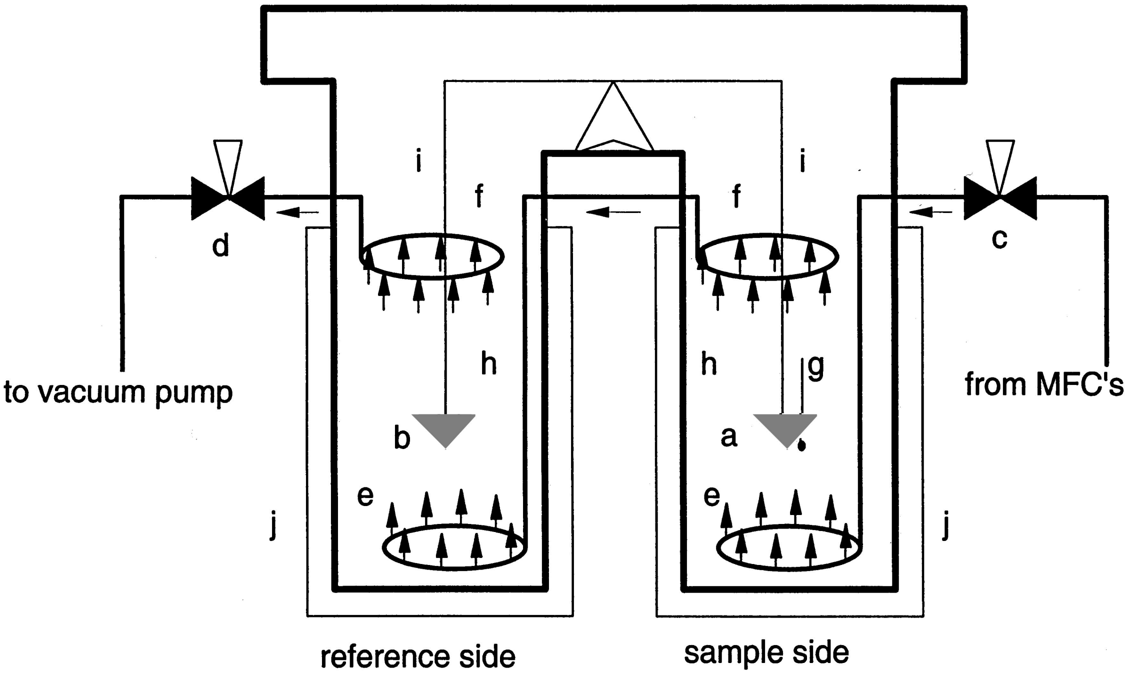

Figure 1. Schematic representation of the gas handling in the IGA system 3 (Hiden Analytical, UK) gravimetric analyser; (a) sample, (b) reference weight, (c) computer controlled inlet needle valve, (d) computer controlled outlet needle valve, (e) inlet diffuser ring, (f) collector ring, (g) thermocouple, (h) stainless steel tubes, (i) gold chain hang-down, (j) water-jacket.

reference side. Buoyancy and drag-force influences are minimised in this way. To enable exact correction for the remaining buoyancy, the volumes at the sample side (the sample and sample suspension) and the reference side (counter weight and counter weight suspension) were determined using a Micromeritics Accupic 1330 Helium Picnometer (using 5.0 purity Helium, Praxair). The IGA was equipped with a turbopump (Balzers TCP121), water bath (Neslab RTE-100), oven (SFL TF1042) and 2 mass flow controllers (Brooks 5850E).

The adsorbent material consisted of Norit RB1 microporous activated carbon extrudates. High purity carbon dioxide (Hoek Loos, 99.995%) and methane (Hoek Loos, 99.995%) were used as feed gases without additional purification.

Adsorption Procedure

Prior to the adsorption experiments, the sample was degassed at 200°C at 10^{-4} mbar for 4 hours. After each adsorption run the sample was regenerated by over night evacuation to constant weight at 10^{-4} mbar, before using it in the followung run. Adsorption runs were automatically terminated when the adsorbed amount reached a value of 99% of the final equilibrium value. The final equilibrium value was estimated by a built-in real-time extrapolation function. The next pressure setpoint was entered after reaching the 99% value.

Single gas adsorption experiments were carried out in the static mode, while mixed gas experiments were executed in the flowing mode. In the flowing mode a total flow rate of 0.14 mol s^{-1} was used in the case of carbon dioxide mole fractions of 0.06 and 0.10. At higher mole fractions a total flow rate of 0.07 mmol s^{-1} was used. Before the next pressure set-point was entered the flow was stopped temporarily. The difference in read-out was used as drag-force correction. The composition of the gas mixture was determined by gas chromatography (Varian 3400 with porapack column).

During the gravimetric experiments the temperature of the gas near the sample deviated slightly from the controlled wall temperature. The thermodynamically non-consistent extended Langmuir isotherm was used to correct for the effect of these temperature deviations:

$$q_i = \frac{q_{\mathrm{m},i} b_i y_i p}{1 + \sum_i b_i y_i p} \quad \text{(constant } T \text{ and } p) \qquad (19)$$

with

$$b_i = b_{0,i} \exp - \frac{\Delta H_{a,i}}{RT} \qquad (20)$$

In case of single component adsorption, the single component form of Eq. (19) was used. In Eqs. (19) and (20) q_i [mol kg^{-1}] is the equilibrium amount adsorbed, $q_{m,i}$ [mol kg^{-1}] the adsorbate monolayer capacity, $b_{0,i}$ [Pa^{-1}] the Langmuir constant and $\Delta H_{a,i}$ [J mol^{-1}] the heat of adsorption of component i.

All experimental single gas CO_2 and CH_4 adsorption isotherms were fitted to Eqs. (19 and 20) to obtain the three Langmuir parameters $q_{m,1}$, $b_{0,1}$ and $\Delta H_{a,1}$, resp. $q_{m,2}$, $b_{0,2}$ and $\Delta H_{a,2}$. These results were used to correct the *mixed* gas adsorption data to the same temperature of 302.9 K. The corrections were typically smaller than 1% but occasionally up to 3% of the adsorbed amount.

Results

Single Component Gas Adsorption

The single component gas adsorption isotherms for carbon dioxide and methane on the activated carbon extrudates obtained at temperatures in the range of 292–350 K are presented in Figs. 2 and 3 and Tables 1 and 2, respectively. Each of both adsorption series was fitted simultaneously for all temperatures to the single component Langmuir Eq. (19) to get monolayer capacities $q_{m,i}$, Langmuir constants $b_{0,i}$ and heats of adsorption $\Delta H_{a,i}$. The resulting parameters are shown in Table 3, the solid lines in Figs. 2 and 3 are calculated with these parameters.

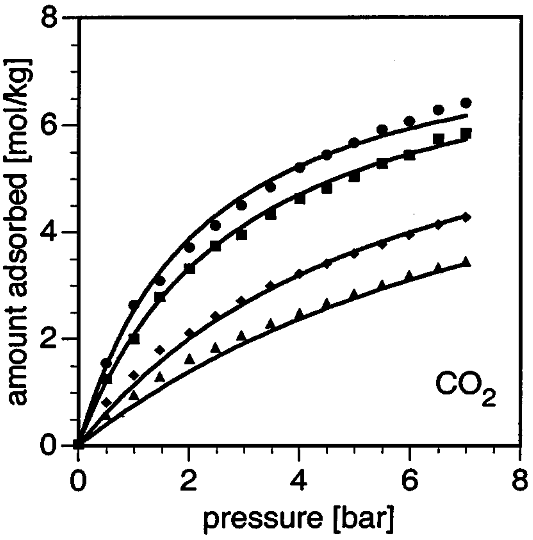

Figure 2. Single carbon dioxide adsorption isotherms and their Langmuir fits. ● 294.5 K; ■ 303.1 K; ◆ 329.9 K; ▲ 348.3 K.

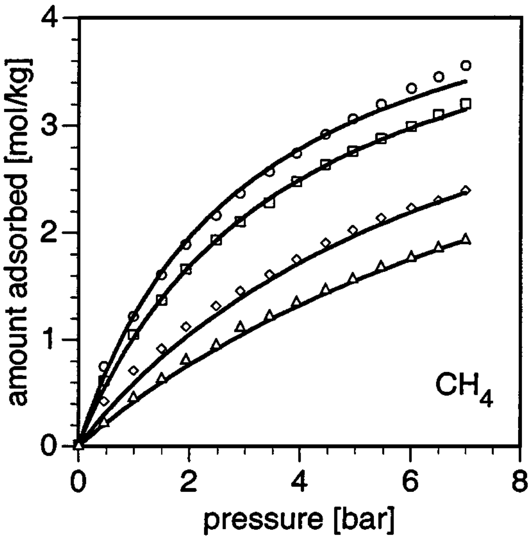

Figure 3. Single methane adsorption isotherms and their Langmuir fits. ○ 293.8 K; □ 303.0 K; ◇ 331.3 K; △ 350.6 K.

Mixed Gas Adsorption

The total amount adsorbed was measured at several gas compositions at temperatures around 302.9 K. These experimental data were corrected to 302.9 K according to the procedure described above. The corrected data is presented in Fig. 4 and is tabulated in Table 4. The composition of the adsorbate was calculated from the experimental mixed gas data by the Van Ness method as defined by Eqs. (7, 8 and 10). The results are shown in Figs. 5 and 6 and in Table 5. Figure 5 shows the reduced spreading pressure π^* as function of the gas composition y at total pressures up to 6 bar. The lines in this figure represent the 3rd order polynomial fits to the experimental points. The quality of this fit is essential for obtaining reliable values of the $\partial \pi^* / \partial y$ derivative, see Eq. (10).

The equilibrium data calculated from the experimental gravimetric data by the van Ness method are compared with the equilibrium data predicted by the ideal adsorbed solution (IAS) theory in Fig. 6. The IAS equilibrium lines at $\pi^* = 2.0, 3.0, 4.0$ and 5.0 mol kg^{-1},

Table 1. CO_2 adsorption isotherm data at several temperatures.

	q_t (mol kg^{-1})			
p (Mpa)	$T = 294.2$ K	$T = 311.2$ K	$T = 329.6$ K	$T = 348.3$ K
0	0	0	0	0
0.050	1.632	1.132	0.773	0.535
0.100	2.456	1.759	1.263	0.911
0.150	3.052	2.243	1.652	1.214
0.200	3.532	2.642	1.979	1.488
0.250	3.923	2.972	2.258	1.713
0.300	4.249	3.267	2.506	1.916
0.349	4.530	3.522	2.721	2.103
0.400	4.781	3.747	2.919	2.273
0.450	4.997	3.946	3.103	2.432
0.500	5.189	4.130	3.274	2.571
0.550	5.365	4.297	3.424	2.712
0.600	5.522	4.452	3.567	2.836
0.650	5.665	4.591	3.696	2.951
0.699	5.796	4.722	3.816	3.063
0.750	5.916	4.845	3.938	3.178
0.800	6.027	4.956	4.043	3.280

Table 2. CH_4 adsorption isotherm data at several temperatures.

	q_t (mol kg^{-1})			
p (Mpa)	$T = 293.8$ K	$T = 311.5$ K	$T = 331.3$ K	$T = 350.6$ K
0	0	0	0	0
0.050	0.772	0.528	0.373	0.265
0.100	1.206	0.870	0.633	0.468
0.150	1.532	1.139	0.855	0.647
0.200	1.801	1.366	1.052	0.797
0.250	2.025	1.560	1.209	0.934
0.300	2.221	1.731	1.350	1.066
0.350	2.394	1.885	1.485	1.180
0.400	2.549	2.028	1.618	1.295
0.450	2.689	2.152	1.731	1.400
0.500	2.817	2.269	1.838	1.503
0.550	2.935	2.381	1.948	1.579
0.600	3.043	2.484	2.038	1.686
0.650	3.142	2.574	2.124	1.752
0.700	3.236	2.662	2.207	1.822
0.750	3.324	2.747	2.282	1.896
0.800	3.406	2.827	2.354	1.959

Table 3. Langmuir parameters of CO_2 and CH_4.

	$q_{m,i}$ (mol kg^{-1})	$b_{i,0}$ (10^{-10} Pa^{-1})	$\Delta H_{a,i}$ (10^4 J mol^{-1})	Mean squared error (mol kg^{-1})
CO_2	7.94	3.22	−2.35	0.013
CH_4	4.81	11.7	−1.95	0.002

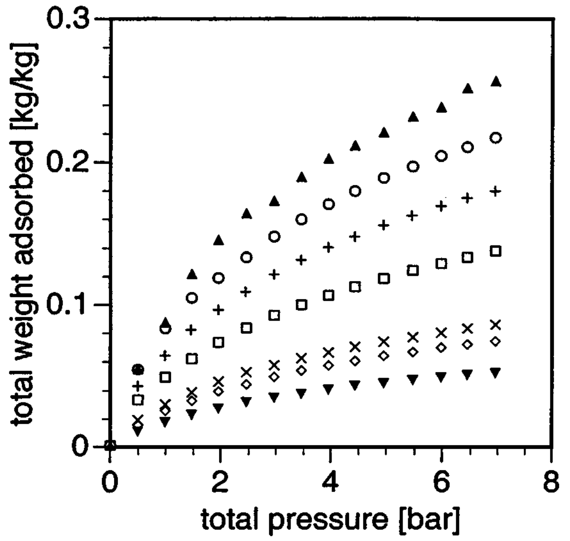

Figure 4. Adsorbed weights of CO_2-CH_4 adsorbate mixtures w_t as function of pressure and gas phase composition at 302.9 K. ▲ $y = 0$ (CH_4); ○ $y = 0.06$; + 0.10; □ $y = 0.32$; × $y = 0.52$; ◇ $y = 0.72$; ▼ $y = 1.0$ (CO_2).

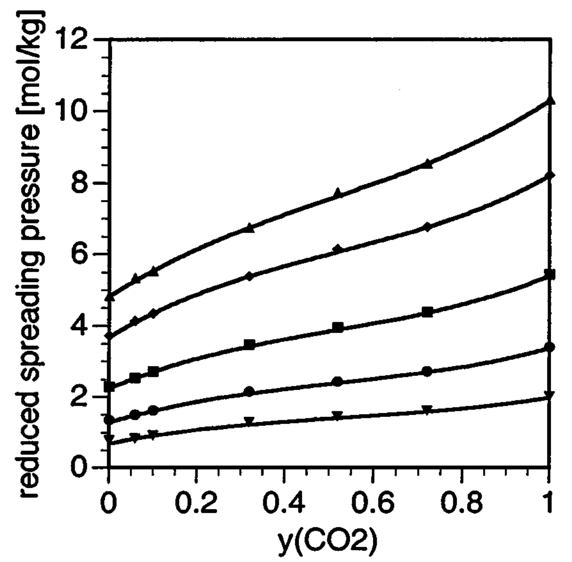

Figure 5. Reduced spreading pressure as function of adsorbate phase composition and pressure. ▼ $p = 0.050$ MPa; ● $p = 0.100$ MPa; ■ $p = 0.200$ MPa; ◆ $p = 0.400$ MPa r; ▲ $p = 0.600$ MPa.

differing only marginally, coincide in the solid line in Fig. 6. At gas phase compositions below 0.2 and above 0.8 the composition of the adsorbed phase follows the IAS theory. For values in between, significant, though not very large, deviations from the IAS-model are observed, indicating non-ideality of the adsorbate.

Table 4. Adsorption data of CO_2-CH_4 gas mixtures at $T = 302.9$ K.

	w_t (kg/kg)						
p (Mpa)	$y = 0$	$y = 0.060$	$y = 0.10$	$y = 0.32$	$y = 0.52$	$y = 0.72$	$y = 1.0$
0.050	0.01027	0.01564	0.01909	0.03230	0.04195	0.05339	0.07200
0.100	0.01697	0.02604	0.03050	0.04843	0.06369	0.08225	0.1070
0.150	0.02254	0.03356	0.03911	0.06274	0.08192	0.1040	0.1330
0.200	0.02677	0.03966	0.04620	0.07405	0.09766	0.1196	0.1500
0.250	0.03104	0.04494	0.05200	0.08375	0.1102	0.1350	0.1670
0.300	0.03395	0.04993	0.05780	0.09189	0.1210	0.1477	0.1830
0.350	0.03720	0.05416	0.06252	0.09988	0.1310	0.1597	0.1958
0.400	0.03984	0.05791	0.06670	0.1066	0.1400	0.1709	0.2082
0.450	0.04200	0.06101	0.07049	0.1128	0.1483	0.1803	0.2190
0.500	0.04500	0.06417	0.07398	0.1185	0.1552	0.1885	0.2287
0.550	0.04594	0.06716	0.07723	0.1235	0.1624	0.1968	0.2388
0.600	0.04785	0.06986	0.08028	0.1284	0.1684	0.2039	0.2460
0.650	0.04963	0.07244	0.08328	0.1330	0.1745	0.2107	0.2553

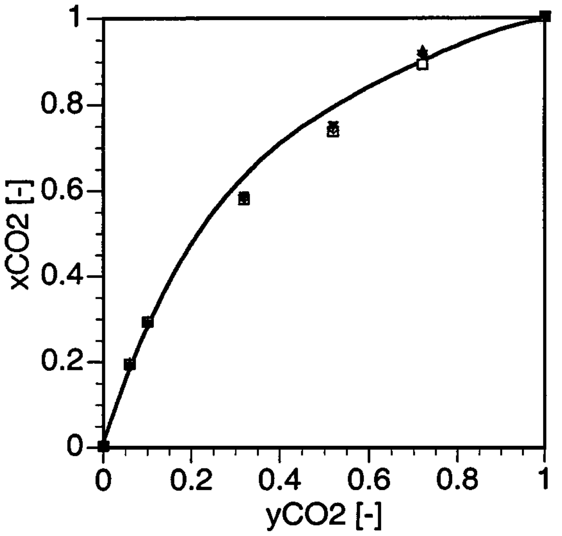

Figure 6. Binary adsorption equilibria of CO_2-CH_4 mixtures at 302.9 K. Symbols represent equilibria calculated by method of Van Ness: △ at $\pi^* = 5.0$ mol kg^{-1}, □ at $\pi^* = 3.0$ mol kg^{-1}, ◇ at $\pi^* = 4.0$ mol kg^{-1}, ▼ at $\pi^* = 5.0$ mol kg^{-1}; solid line: x_{IAS} according Eq. (17).

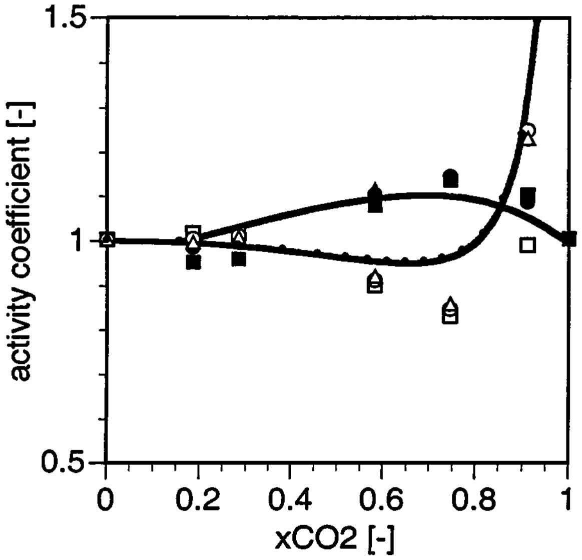

Figure 7. Experimental and fitted Wilson activity coefficients for CO_2-CH_4 adsorbare mixtures at $T = 302.9$ K. Solid symbols: γ_1 for CO_2; open symbols: γ_2 for CH_4. Squares: $\pi^* = 3.0$ mol kg^{-1}; circles: $\pi^* = 4.0$ mol kg^{-1}; triangles: $\pi^* = 5.0$ mol kg^{-1}.

Calculation of Activity Coefficients in the Adsorbed Phase

The observed deviations from ideal behaviour can be accounted for by activit coefficients γ_i, calculated from Eqs. (14–15). These activity coefficients are plotted as a function of adsorbed phase composition x in Fig. 7 at 302.9 K and reduced spreading pressures $\pi^* = 3.0$, 4.0 and 5.0 mol kg^{-1} (Myers, 1983). The size of the symbols reflects the experimental error. The solid and dotted solid line represent the fitted Wilson equations, Eq. (18). The calculated interaction parameters, $\Lambda_{1,2}$ and $\Lambda_{2,1}$, are given in Table 6.

Table 5. Adsorbed phase compositions of CO_2-CH_4 mixed gas adsorption at 302.9 K, calculated from the data in Table 4 by the method of Van Ness.

	x [-]						
p (Mpa)	$y = 0$	$y = 0.060$	$y = 0.10$	$y = 0.32$	$y = 0.52$	$y = 0.72$	$y = 1.0$
0.050	0	0.2092	0.3074	0.5439	0.6884	0.8586	1
0.100	0	0.1957	0.2986	0.5613	0.7127	0.8855	1
0.150	0	0.1919	0.2946	0.5593	0.7175	0.8938	1
0.200	0	0.1909	0.2937	0.5620	0.7183	0.8998	1
0.250	0	0.1878	0.2915	0.5648	0.7230	0.9002	1
0.300	0	0.1849	0.2874	0.5671	0.7258	0.9015	1
0.350	0	0.1837	0.2866	0.5681	0.7282	0.9016	1
0.400	0	0.1819	0.2850	0.5703	0.7312	0.9019	1
0.450	0	0.1816	0.2842	0.5724	0.7337	0.9033	1
0.500	0	0.1808	0.2838	0.5736	0.7364	0.9049	1
0.550	0	0.1795	0.2827	0.5757	0.7383	0.9059	1
0.600	0	0.1792	0.2826	0.5771	0.7405	0.9072	1
0.650	0	0.1788	0.2821	0.5784	0.7419	0.9082	1

Table 6. Wilson interaction parameters for CO_2-CH_4.

	in adsorbate mixture[a]	in bulk-liquid mixture[b]
$\triangle_{1,2}$	2.8	0.02
$\triangle_{2,1}$	0.018	0.4

[a] Calculated in this work.
[b] Calculated from data given by Mraw et al. (1978).

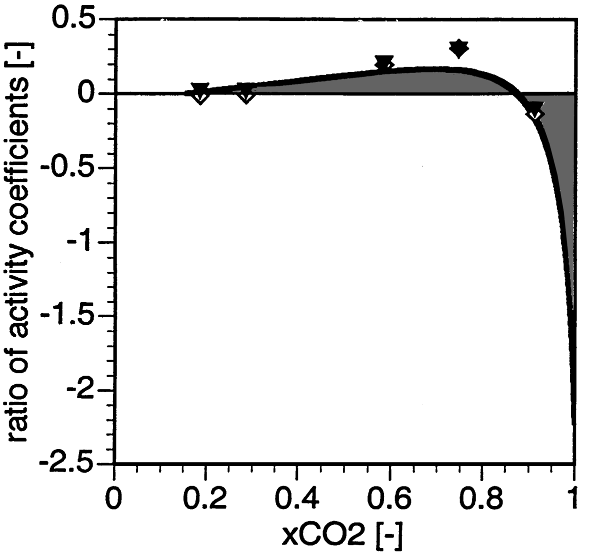

Figure 8. Thermodynamic consistency of experimental activity coefficients for CO_2-CH_4 adsorbate mixtures ar $T = 302.9$ K. ◇: $\pi^* = 4.0$ mol kg^{-1}; ▼: $\pi^* = 5.0$ mol kg^{-1}.

The fitted Wilson equation as shown in Fig. 7 satisfies the thermodynamic consistency test (Herington, 1947; Redlich and Kister, 1948):

$$\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx = 0 \quad (\text{constant } T \text{ and } \pi^*) \quad (21)$$

The activity coefficients calculated from the experimental data should also satisfy this consistency test. Figure 8 shows the ratio of the activity coefficients as a function of adsorbed phase composition. Both Figs. 7 and 8 suggest that the experimental mixed gas data are thermo-dynamically consistent.

Discussion

Activity coefficients of CO_2-CH_4 bulk solutions are larger than unity over the whole compostion range, while adsorbed solutions show a variation around unity, see Fig. 7. Comparable results were reported by Nakahara et al. (1981) for the adsorption of mixtures of ethane and propane on a carbon molecular sieve. However, the results of the present study are not in agreement with those reported by Buss (1995) in a similar study on equilibrium adsorption of carbon dioxide-methane mixtures on a large pore activated carbon with low energetic heterogeneity. He found activity coefficients larger than unity over the whole adsorbed phase composition range for both components. Activity coefficients larger than unity were also reported for adsorption of various gas mixtures on energetic homogeneous low-surface area graphite or highly graphitised carbons (Sloan Jr. and Mullins, 1975; Myers et al., 1982). On the other hand, Costa et al. (1981, 1989) found activity coefficients smaller than unity for both components in methane-ethane mixtures adsorbed on relatively low-surface area activated carbon.

The variation of the activity coefficients with the adsorbed phase composition, as shown in Fig. 7, deviates from the behaviour one would expect for a simple bulk mixture as carbon dioxide-methane, where strong interactions are absent. This is illustrated by the value of the Wilson interaction parameters. Application of the Wilson equation, which is derived for bulk solutions, by Mraw et al. (1978) to bulk liquid mixtures of carbon dioxide and methane results in low values of $\Lambda_{1,2}$ and $\Lambda_{2,1}$, see Table 6, indicating that no strong interactions between the two species exists.

Application of the Wilson equation to the adsorbed phase, on the other hand, results in a relative high value of $\Lambda_{1,2}$ (2.8 in Table 6), indicating a large influence of carbon dioxide on methane. This suggests that solid-adsorbate interactions in the adsorbate on the solid surface are of major importance.

The above considerations show that bulk solution models cannot be used for calculation of activity coefficients in adsorbate mixtures. The adsorbed solution theory, which is based on the assumption of surface homogeneity, is not approriate for heterogeneous surfaces. Myers (1983) showed that application of the adsorbed solution theory to adsorbates on heterogeneous surfaces may result in a *pseudo* adsorbate nonideality, reflecting to a large extent the effect of surface heterogeneity.

New models should be developed encompassing both nonideal adsorbed solution behaviour and surface heterogeneity.

Conclusion

Accurate calculation of mixed gas adsorption data from single component adsorption isotherms requires nonideality in the adsorbed phase to be taken into account. A semi-emperical approach involving the calculation of activity coefficients of the components in the adsorbed phase from the Wilson equation leads to a good fit with the experimental data. However, the Wilson interaction parameters cannot be obtained from the values for bulk mixtures. Therefore, new models should be developed encompassing both nonideal adsorbed solution behaviour and surface heterogeneity

Appendix

Langmuir and Ideal Adsorbed Solutions

For binary gas mixtures it will be shown below, that adsorption equilibria calculated from thermodynamically consistent extended Langmuir isotherms are equal to equilibria calculated from the Langmuir single gas isotherms by the ideal adsorption solution theory. For the sake of convenience the expression for the extended Langmuir isotherm is repeated here:

$$q_i = \frac{q_{\mathrm{m},i} b_i y_i p}{1 + \sum_i b_i y_i p} \quad (\text{constant } T \text{ and } p) \quad (19)$$

with

$$b_i = b_{0,i} \exp\left(-\frac{\Delta H_{\mathrm{a},i}}{RT}\right) \quad (20)$$

By definition, the composition of an adsorbed solution is given by

$$x_i = \frac{q_i}{\sum_i q_i} = \frac{q_i}{q_\mathrm{t}} \quad (22)$$

In the thermodynamic consistent form of the Langmuir equation the monolayer adsorption capacities $q_{\mathrm{m},i}$ are equal for all components. For binary gas mixtures: $q_\mathrm{m} = q_{\mathrm{m},1} = q_{\mathrm{m},2}$. The equilibrium composition of the adsorbed phase, x_EL, now follows from Eqs. (19) and (22):

$$\boxed{x_\mathrm{EL} = \frac{1}{1 + \frac{1-y}{y} \cdot \frac{b_2}{b_1}}} \quad (\text{constant } T) \quad (23)$$

The expression of Eq. (23) is now compared with the binary equilibria composition predicted by the ideal adsorbed solution theory using the two single gas isotherms:

$$x_\mathrm{IAS} = \frac{1}{1 + \frac{1-y}{y} \cdot \frac{p_1^0}{p_2^0}} \quad (\text{for constant } T \text{ and } \pi) \quad (17)$$

LeVan and Vermeulen (1981) derived explicit binary isotherms based on single component Langmuir isotherms and showed the equality of the latter two equations for equal Langmuir monolayer capacities. The analysis below, similar to the approach of Do (1998), shows that this result is a consequence of applying the requirement of mixing at constant spreading pressure to single components obeying the Langmuir equation with equal monolayer capacities. Calculation of the spreading pressures of the adsorbed mixture from Eqs. (11–12) and the single component form of Eq. (19) gives:

$$\pi^* = q_\mathrm{m} \ln\left(1 + b_1 p_1^0\right) = q_\mathrm{m} \ln\left(1 + b_2 p_2^0\right) \quad (\text{constant} T \text{ and } \pi) \quad (24)$$

leading to the conclusion that at equal spreading pressure and equal monolayer capacities the ratio of the saturation pressures is given by:

$$\frac{p_1^0}{p_2^0} = \frac{b_2}{b_1} \quad (25)$$

Combination of Eqs. (17) and (25) leads to the following expression for x_IAS:

$$x_\mathrm{IAS} = \frac{1}{1 + \frac{1-y}{y} \cdot \frac{b_2}{b_1}} \quad (\text{constant } T) \quad (26)$$

which appears to be identical with that for x_EL in Eq. (23). Moreover, this results shows that, under the restrictions mentioned above, the composition of the adsorbed phase is a function of gas composition and temperature only, not of pressure or spreading pressure.

Nomenclature

Latin Symbols

A	specific surface area of adsorbent ($\mathrm{m^2\ kg^{-1}}$)
A_m	molar surface area ($\mathrm{m^2\ mol^{-1}}$)

b_i	Langmuir parameter of component i (Pa^{-1})
$b_{0,i}$	Langmuir constant of component i (Pa^{-1})
F	number of degrees of freedom -
ΔH_m	heat of adsorption ($\mathrm{J\ mol}^{-1}$)
M	average molecular mass of adsorbate mixture ($\mathrm{kg\ mol}^{-1}$)
M_i	molecular mass of component i in adsorbate mixture ($\mathrm{kg\ mol}^{-1}$)
N	number of components -
p	total gas pressure (Pa)
p_i^0	equilibrium vapour pressure of component i (Pa)
q_t	total equilibrium amount adsorbed ($\mathrm{mol\ kg}^{-1}$)
q_i^0	equilibrium amount adsorbed of single component i ($\mathrm{mol\ kg}^{-1}$)
q_i	equilibrium amount adsorbed of component i in mixture ($\mathrm{mol\ kg}^{-1}$)
$q_{\mathrm{m},i}$	monolayer capacity of component i ($\mathrm{mol\ kg}^{-1}$)
R	gas constant ($\mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$)
T	temperature (K)
w_t	total mass adsorbed per unit mass adsorbent ($\mathrm{kg\ kg}^{-1}$)
x	mol fraction of CO_2 in CO_2-CH_4 adsorbate mixture -
x_i	mol fraction of component i in adsorbate mixture -
x_EL	mol fraction of component 1 in adsorbate mixture in Eq. (23) -
x_IAS	mol fraction of component 1 in adsorbate mixture in Eq. (17) -
y	mol fraction of CO_2 in CO_2-CH_4 gas mixture -
y_i	mol fraction of component i in gas mixture -

Greek Symbols

γ_i	activity coefficient of component i in adsorbate mixture -
ϕ_i	fugacity coefficient of component i in gas phase -
$\Lambda_{1,2}$	CO_2-CH_4 interaction coefficient in Wilson equation -
$\Lambda_{2,1}$	CH_4-CO_2 interaction coefficient in Wilson equation -
$\mu_{i,\mathrm{a}}$	chemical potential of component i in adsorbate mixture ($\mathrm{J\ mol}^{-1}$)
$\mu_{i,\mathrm{g}}$	chemical potential of component i in the gas phase ($\mathrm{J\ mol}^{-1}$)
π	spreading pressure in adsorbate mixture ($\mathrm{N\ m}^{-1}$)
π^*	reduced spreading pressure of adsorbed mixture ($\mathrm{mol\ kg}^{-1}$)
$\pi^*_{0,i}$	reduced spreading pressure of single adsorbate i ($\mathrm{mol\ kg}^{-1}$)

Subscripts

i	component number
1	CO_2
2	CH_4

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