



Experimental Determination and Analysis of High Pressure Adsorption Data of Pure Gases and Gas Mixtures

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Abstract. Adsorption data of the pure gases ethane, methane and their mixtures on zeolite 13X and the pure gases carbon dioxide, nitrogen and their mixtures on activated carbon Norit R1 were measured gravimetrically at a temperature of 298 K and pressures up to 15 MPa. From the total loads the partial loads were calculated by the modified van Ness approach. The calculated loads show a good agreement with the experimental data.

Keywords: adsorption, gas mixtures, high pressure, gravimetric measurements

Introduction

Adsorption represents an important procedure for separation and purification processes within many domains of the chemical industry. The separation effect based by selective adsorption of one species of a mixture (King, 1980). Thereby porous materials such as activated carbons or zeolites are used due to their large internal surface and their complex pore system. Important criteria for the selection of the adsorbents are a high adsorption capacity as well as a formed selectivity. The adsorption isotherms are the basic information of the adsorption systems. For pure components they can be determined relatively easily by experiment and can be described thermodynamically for different isotherm models: the Langmuir approach (1918); the Gibbs approach or the potential theory formalized by Polanyi (Adams, 1976).

But gas mixtures are involved in the most technical adsorption processes. Due to this fact it is necessary to know the mixture adsorption equilibrium. The composition of the adsorbate phase can be determined experimentally by using the volume-gravimetric method.

This method requires too much time and becomes increasingly inaccurate with rising pressure. Gravimetric analysis, on the other hand, represents an accurate measuring method. This experimental method gives only the total loads of the components included the adsorbate phase. Therefore it is necessary to create thermodynamic models, based on accurate total load measurements, to make statements about the coadsorption equilibrium and about the separation factors.

Danner and Choi (1978) investigated adsorption equilibria of the pure gases ethane, ethylene and their mixtures on 13X molecular sieves in the pressure range 0 – 0.15 MPa at 298 K and 328 K. Reich et al. (1980) published adsorption data of the gases CH₄, C₂H₆, C₂H₄, CO₂ and their binary and ternary mixtures on activated carbon up to 3.5 MPa in the temperature range of 212–301 K. Dreisbach et al. (1999) researched the coadsorption equilibria of the gases CH₄, CO₂, N₂, and their binary and ternary mixtures on activated carbon Norit R1 in the pressure range 0 – 6 MPa at 298 K. But for some technique processes it is necessary to know the adsorption equilibria for a large pressure range. Therefore in this work the adsorption equilibria were measured for two different binary gas mixtures up to 15 MPa.

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The well-known ISAT (ideal adsorbed solution theory) enables the prediction of separation factors from single component isotherms. Many theories describing mixed gas adsorption equilibria are developed the adsorbed solution theory on this basis (Myers and Prausnitz, 1965; Sievers and Mersmann, 1993).

In this paper we modified the well-known van Ness method (1969) for high pressure application. We measured high pressure adsorption data for two different adsorption systems to test the new method. For the calculations of the partial loads we used the experimentally determined total excess adsorbed amount. This is described below in more detail.

Absolute Adsorption–Excess Adsorption

Adsorption is the transition of molecules from the fluid phase near to the interface of a solid. The bulk phase represents the fluid phase and the solid the adsorbent. Through the adsorption a spatially limited range is formed at the surface (adsorbed phase). In this range the density is higher compare to the bulk density of the free fluid phase (Fig. 1).

The description of the adsorption equilibrium must principally distinguish between absolute adsorption and excess adsorption. This distinction has to be made especially at higher pressures. A short definition should clarify the difference. If all molecules are considered, which are in the adsorbate phase thus in the field of the adsorption potential, called absolute adsorption. The typical of the absolute adsorption isotherm is that it approaches with rising pressure a limiting value. This is achieved, if the total adsorption space is filled with gas molecules of highest packing. The value is called as saturation value or maximal loading. The excess adsorption represents only the molecules in the adsorbate phase, which are additionally in the adsorption layer due to the effect of the adsorption potential compare to the bulk density of gas phase (Myers, 1997; Do, 1998; Talu, 1998; Rouquerol et al., 1999). The excess isotherms pass through a maximum with rising pressure and approximate to zero for $p \rightarrow \infty$ (Herbst, 2001). The reason for this is that the difference in density between adsorbate phase and gas phase becomes small. The difference between absolute adsorption and excess adsorption is less at lower pressures. Therefore often no distinction is made at low pressures. The difference can't be neglected in high pressure adsorption. With increasing pressure

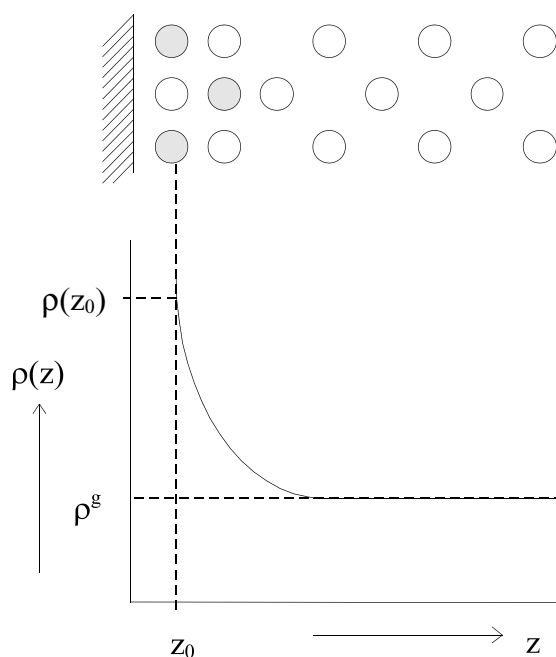


Figure 1. Schematic representation of a compressed gas near an adsorbing surface; surface excess molecules indicated by shading; Density profile $\rho(z)$ as a function of distance z from the surface; Gibbs dividing surface intersects z -axis at z_0 ; ρ^g is the bulk density of the gas.

the difference between absolute and excess adsorption amount increases. The absolute values can calculate principal from the experimental excess data. But therefore it is necessary to know the size of the adsorbate volume. The adsorbate volume can determine from the volume of the micro pores (Buss, 1997) or from the fluid density of the adsorptive (Dreisbach, 1999). These theories can use in the pressure range until the maximum of the excess isotherms. Up to high pressure the calculated absolute adsorption isotherms are not equivalent to the thermodynamically consistency requirement. In this work all calculations refer to the experimental determined excess values. The separation factor is defined by relation of the composition of the gas phase y_i and by relation of the composition of the excess in the adsorbate phase x_i^σ :

$$\alpha^\sigma = \frac{x_i^\sigma}{x_2^\sigma} \cdot \frac{y_2}{y_i} \quad (1)$$

Experiment

The experimental measurements have been made with a high-pressure ultra-microbalance (type S3D-P,

As adsorbents, activated carbon of the type Norit R1 and a zeolite “Zeosorb” 13X were selected. The characteristics of the adsorbents like BET-surface and pore volume are summarised in Table 1.

The gravimetric determined data of the adsorption equilibria of the pure gases and gas mixtures have to be corrected by the void volume. The adsorbed mass can be calculated from the microbalance signal $\Delta m_{\text{balance}}$

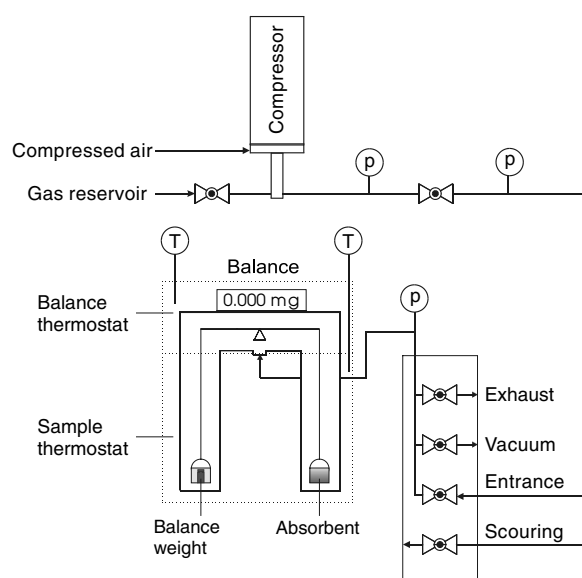


Figure 2. Operating principle of the high-pressure ultra microbalance.

Table 1. Characteristic of the adsorbents.

Adsorbent	BET-surface (m ² /g)	Micro pore volume (cm ³ /g)	Total pore volume (cm ³ /g)
Norit R1	1262	0.59	0.64
Zeolite 13X	383	0.21	0.26

and the product of the volume V^{as} of the adsorbent and the gas density ρ^f (Staudt, 1993; Talu, 1998).

$$\Gamma^\sigma = \Delta m_{\text{balance}} + V^{as} \rho^f \quad (2)$$

The adsorption isotherms of the pure gas methane on zeolite 13X was determined in the pressure range vacuum $< p < 15$ MPa at 298 K. Ethane on zeolite 13X was measured from vacuum until the critical pressure and at 298 K. The buoyancy corrected adsorption data (excess amount adsorbed) for the both pure gases as a function of pressure are given in Table 2 (Salem, 1995). The adsorption equilibria of the pure gas nitrogen on activated carbon Norit R1 was measured

Table 2. Pressure p and excess amount adsorbed Γ^{σ} of the pure gases C_2H_6 and CH_4 on zeolith 13X at $T = 298$ K.

C ₂ H ₆		CH ₄	
p (MPa)	Γ^σ (mg/g)	p (MPa)	Γ^σ (mg/g)
0.140	66.263	0.148	7.245
0.222	70.915	0.228	10.710
0.337	74.355	0.350	15.234
0.515	77.270	0.526	20.404
1.036	80.854	1.061	29.856
1.523	82.132	2.148	37.692
2.021	82.559	3.275	40.857
2.524	82.458	4.075	41.359
3.037	81.882	5.102	41.943
3.508	80.966	6.171	41.953
3.948	78.990	7.152	41.630
		8.144	41.079
		9.146	40.346
		10.136	39.475
		12.028	37.551
		13.130	36.344
		14.095	35.261
		15.022	34.239

Table 3. Pressure p and excess amount adsorbed Γ^σ of the pure gases CO₂ and N₂ on AC Norit R1 at $T = 298$ K.

CO ₂		N ₂	
p (MPa)	Γ^σ (mg/g)	p (MPa)	Γ^σ (mg/g)
0.034	46.197	0.03371	3.8727
0.0634	72.010	0.0626	6.9607
0.0915	93.236	0.0910	9.6987
0.0990	98.488	0.1014	10.6815
0.130	117.098	0.105	10.8468
0.218	160.245	0.221	20.2785
0.348	208.516	0.341	28.3487
0.464	241.659	0.465	35.4248
0.580	268.896	0.596	42.0466
0.685	289.525	0.714	47.3421
0.804	309.735	0.878	53.7920
0.913	328.649	1.030	59.2846
1.044	343.366	1.201	64.7461
1.184	359.322	1.353	69.1705
1.306	372.086	1.493	71.0977
1.408	381.615	1.524	73.6973
1.519	391.181	1.699	77.8978
1.527	393.716	2.503	91.3588
1.600	397.641	3.510	103.5191
1.703	405.284	4.509	113.4330
2.011	426.991	5.497	119.720
2.510	450.205	5.827	121.519
3.012	465.402	6.573	124.489
3.512	473.925	7.538	127.047
4.012	477.195	8.564	129.023
4.519	476.035	9.490	129.974
5.010	471.012	10.550	130.336
5.511	461.411	11.548	130.150
6.036	443.973	12.537	129.515
		13.528	128.550
		14.565	127.160

from vacuum to 15 MPa at 298 K and of Carbon dioxide on activated carbon Norit R1 was determined from vacuum up to the critical pressure at 298 K. Table 3 shows the excess amount adsorbed in dependence of pressure (Beutekamp, 2001).

The adsorption equilibria of the total load of both components of the mixture ethane-methane at different gas compositions was measured in the pressure range

Table 4. Total excess amount adsorbed of gas mixtures C₂H₆/CH₄ ($y_{C_2H_6} = 0.8$) on zeolite 13X at $T = 298$ K.

p (MPa)	$y_{C_2H_6}$	Γ^σ (mg/g)
0.121	0.8	58.947
0.217	0.8	66.356
0.317	0.8	69.937
0.527	0.8	73.814
1.030	0.8	77.667
2.303	0.8	79.433
3.021	0.8	79.284
4.031	0.8	77.440
5.014	0.8	73.398
6.020	0.8	61.985
7.023	0.8	35.139
7.970	0.8	30.633
8.992	0.8	26.961
10.160	0.8	24.060
11.134	0.8	21.954
12.129	0.8	20.321
13.305	0.8	18.840
14.170	0.8	17.824
15.153	0.8	16.914

vacuum $< p < 15$ MPa at 298 K. The experimental data of the adsorption excesses as function of pressure are summarized in Tables 4 – 9 (Salem, 1995). For the gas mixture carbon dioxide-nitrogen at different gas compositions the adsorption equilibria was determined from vacuum to 15 MPa at 298 K. The Tables 10 – 16 shows all experimental determined excess amounts adsorbed as function of pressure (Beutekamp, 2001).

The measuring accuracy of the gravimetric determined data of the pure components and the mixtures is $< 1\%$ in the total pressure range.

The typical adsorption isotherms of the excess are shown in Fig. 3 for the gases ethane, methane and their mixtures on zeolite 13X. Figure 4 shows experimental adsorption data for the gases carbon dioxide, nitrogen and their mixtures on activated carbon Norit R1.

Analysis of Adsorption Data

All experimental determined adsorption data was checked by thermodynamic condition (Talu, 1998).

Table 5. Total excess amount adsorbed of gas mixtures C_2H_6/CH_4 ($y_{C_2H_6} = 0.6$) on zeolite 13X at $T = 298$ K.

p (MPa)	$y_{C_2H_6}$	Γ^σ (mg/g)
0.146	0.6	56.643
0.229	0.6	62.658
0.334	0.6	66.296
0.576	0.6	70.612
1.124	0.6	74.322
2.187	0.6	76.065
3.280	0.6	75.539
4.357	0.6	73.765
5.047	0.6	71.163
6.074	0.6	67.415
7.024	0.6	62.529
8.100	0.6	55.626
9.130	0.6	48.840
10.056	0.6	43.616
11.092	0.6	38.474
12.151	0.6	34.401
13.135	0.6	32.183
14.283	0.6	29.376
15.177	0.6	27.612

Table 6. Total excess amount adsorbed of gas mixtures C_2H_6/CH_4 ($y_{C_2H_6} = 0.4$) on zeolite 13X at $T = 298$ K.

p (MPa)	$y_{C_2H_6}$	Γ^σ (mg/g)
0.153	0.4	45.335
0.225	0.4	52.149
0.353	0.4	58.215
0.524	0.4	62.283
1.134	0.4	67.733
2.204	0.4	70.122
3.372	0.4	70.073
4.232	0.4	69.199
5.288	0.4	67.491
6.307	0.4	65.306
7.171	0.4	63.063
8.227	0.4	59.814
9.182	0.4	56.579
10.260	0.4	52.818
11.113	0.4	49.509
12.335	0.4	45.502
13.257	0.4	43.300
14.096	0.4	40.721
15.261	0.4	38.120

Table 7. Total excess amount adsorbed of gas mixtures C_2H_6/CH_4 ($y_{C_2H_6} = 0.25$) on zeolite 13X at $T = 298$ K.

p (MPa)	$y_{C_2H_6}$	Γ^σ (mg/g)
0.127	0.25	34.763
0.222	0.25	44.880
0.350	0.25	52.311
0.521	0.25	57.391
1.044	0.25	63.696
2.054	0.25	67.165
3.048	0.25	67.927
4.066	0.25	67.529
5.065	0.25	66.495
6.010	0.25	65.143
7.044	0.25	63.355
8.043	0.25	61.247
9.099	0.25	58.782
10.015	0.25	56.469
11.055	0.25	53.659
11.996	0.25	51.182
13.211	0.25	48.332
13.990	0.25	46.330
15.396	0.25	43.401

Table 8. Total excess amount adsorbed of gas mixtures C_2H_6/CH_4 ($y_{C_2H_6} = 0.2$) on zeolite 13X at $T = 298$ K.

p (MPa)	$y_{C_2H_6}$	Γ^σ (mg/g)
0.135	0.2	27.699
0.235	0.2	39.621
0.335	0.2	46.567
0.563	0.2	54.579
1.109	0.2	61.275
2.091	0.2	64.801
3.144	0.2	65.594
4.110	0.2	65.298
5.094	0.2	64.382
6.226	0.2	62.847
7.154	0.2	61.286
8.241	0.2	59.205
9.151	0.2	57.261
10.224	0.2	54.861
11.158	0.2	52.611
12.136	0.2	50.330
13.190	0.2	47.971
14.145	0.2	45.733
15.320	0.2	43.389

Table 9. Total excess amount adsorbed of gas mixtures C₂H₆/CH₄ ($y_{\text{C}_2\text{H}_6} = 0.1$) on zeolite 13X at $T = 298$ K.

p (MPa)	$y_{\text{C}_2\text{H}_6}$	Γ^σ (mg/g)
0.127	0.1	18.734
0.221	0.1	27.303
0.326	0.1	34.552
0.545	0.1	43.488
1.048	0.1	52.129
2.043	0.1	57.438
3.064	0.1	59.003
4.014	0.1	59.181
5.062	0.1	58.728
6.075	0.1	57.800
7.010	0.1	56.670
8.021	0.1	55.236
9.033	0.1	53.572
10.039	0.1	51.850
11.052	0.1	49.958
12.055	0.1	48.090
13.036	0.1	46.277
14.042	0.1	44.425
15.166	0.1	42.412

Calculation of the Partial Loads

For the thermodynamic considerations the condition must be fulfilled that the composition of the gas phase does not change during the measurements of the equilibrium. Accordingly the measuring device was designed. The volume of the balance is related to volume of the adsorbed phase large enough so that the gas composition can be regarded as constant over the total pressure range.

Starting from the condition of the thermodynamic equilibrium of the chemical potential of each species between adsorbate phase and gas phase:

$$\mu_i^{\text{Ad}} = \mu_i^{\text{G}} \quad (3)$$

we can write for the chemical potential of the gas phase:

$$\mu_i^{\text{G}} = RT \ln y_i f \quad (4)$$

in the consideration of the imperfect gases at high pressures the pressure p was replaced by the fugacity f (Myers and Prausnitz, 1965).

Table 10. Total excess amount adsorbed of gas mixtures CO₂/N₂ ($y_{\text{CO}_2} = 0.95$) on AC Norit R1 at $T = 298$ K.

p (MPa)	y_{CO_2}	Γ^σ (mg/g)
0.0382	0.95	48.181
0.0625	0.95	69.013
0.0921	0.95	89.716
0.1013	0.95	95.556
0.2250	0.95	158.791
0.330	0.95	197.358
0.440	0.95	229.071
0.556	0.95	256.667
0.678	0.95	280.946
0.789	0.95	299.519
0.919	0.95	318.757
1.035	0.95	333.882
1.190	0.95	351.543
1.307	0.95	361.841
1.406	0.95	372.652
1.514	0.95	381.928
1.602	0.95	388.904
1.708	0.95	396.779
2.107	0.95	424.483
3.016	0.95	459.847
4.089	0.95	474.257
5.027	0.95	474.095
6.077	0.95	450.449
7.110	0.95	400.034
7.912	0.95	178.795
8.989	0.95	133.287
10.047	0.95	114.410
11.015	0.95	101.151
11.925	0.95	91.764

Analogous to the Gibbs formalism we can write for the *Gibbs* adsorption isotherm for high pressure:

$$-Ad\pi + \sum n(x_i d\mu_i^{\text{G}}) = 0 \quad (T = \text{const.}) \quad (5)$$

According to Cracknell and Nicholson (1995) the Eq. (5) is to extend with the term $V \cdot dp$.

$$-Ad\pi + \sum n(x_i d\mu_i^{\text{G}}) - V \cdot dp = 0 \quad (T = \text{const.}) \quad (6)$$

Table 11. Total excess amount adsorbed of gas mixtures CO₂/N₂ (y_{CO₂} = 0.9) on AC Norit R1 at T = 298 K.

p (MPa)	y _{CO₂}	Γ ^σ (mg/g)
0.0335	0.90	42.828
0.0629	0.90	67.292
0.0927	0.90	87.201
0.1020	0.90	92.977
0.1222	0.90	104.615
0.225	0.90	152.227
0.330	0.90	188.825
0.440	0.90	219.697
0.550	0.90	245.697
0.663	0.90	268.104
0.776	0.90	287.643
0.914	0.90	308.230
1.029	0.90	323.209
1.174	0.90	339.989
1.302	0.90	353.182
1.408	0.90	363.071
1.509	0.90	371.812
1.587	0.90	377.843
1.600	0.90	379.088
1.701	0.90	386.634
2.544	0.90	431.742
3.630	0.90	462.860
4.544	0.90	472.922
5.597	0.90	462.274
6.592	0.90	440.858
7.706	0.90	399.300
8.444	0.90	344.779
9.364	0.90	262.877
10.526	0.90	206.155
11.503	0.90	177.227
12.568	0.90	155.452
13.448	0.90	142.370
14.558	0.90	129.720

Table 12. Total excess amount adsorbed of gas mixtures CO₂/N₂ (y_{CO₂} = 0.8) on AC Norit R1 at T = 298 K.

p (MPa)	y _{CO₂}	Γ ^σ (mg/g)
0.0337	0.80	39.271
0.0623	0.80	60.590
0.0921	0.80	79.624
0.1030	0.80	86.992
0.103	0.80	90.798
0.201	0.80	140.516
0.341	0.80	178.834
0.446	0.80	206.340
0.552	0.80	229.777
0.660	0.80	250.518
0.776	0.80	270.183
0.914	0.80	290.282
1.033	0.80	305.488
1.170	0.80	321.051
1.316	0.80	335.678
1.407	0.80	344.033
1.503	0.80	351.971
1.504	0.80	352.241
1.605	0.80	360.197
1.708	0.80	367.828
2.499	0.80	411.310
3.515	0.80	442.154
4.517	0.80	454.724
5.504	0.80	455.062
6.517	0.80	446.484
7.509	0.80	430.666
8.555	0.80	405.737
9.513	0.80	375.268
10.352	0.80	343.920
11.497	0.80	300.837
12.548	0.80	266.830
13.622	0.80	240.534
14.462	0.80	223.281

The size n in Eq. (6) characterizes the total number of moles in the adsorbate phase. This leads to:

$$n = n^{na} + n^{\sigma} \quad (7)$$

with n^{na} , as the number of moles which would be present in the adsorbate phase without adsorption forces and n^{σ} the number of moles of the excess. On the

assumption that the gas phase would be ideal, results:

$$V = \frac{n^{na} \cdot RT}{p} \quad (8)$$

We can write for the *Gibbs* adsorption isotherm with the moles of the surface excess n^{σ} :

$$Ad\pi = n^{\sigma} RT d \ln p \quad (9)$$

Table 13. Total excess amount adsorbed of gas mixtures CO₂/N₂ ($y_{\text{CO}_2} = 0.5$) on AC Norit R1 at $T = 298$ K.

p (MPa)	y_{CO_2}	Γ^σ (mg/g)
0.0341	0.50	28.559
0.0633	0.50	45.335
0.0921	0.50	59.215
0.1120	0.50	69.588
0.1307	0.50	75.347
0.216	0.50	105.158
0.347	0.50	139.501
0.450	0.50	161.384
0.507	0.50	173.748
0.710	0.50	205.814
0.866	0.50	226.635
0.931	0.50	234.945
1.056	0.50	248.768
1.162	0.50	259.995
1.283	0.50	270.332
1.374	0.50	278.078
1.453	0.50	283.409
1.496	0.50	285.902
1.609	0.50	294.334
1.717	0.50	301.330
2.476	0.50	342.191
3.516	0.50	375.114
4.480	0.50	393.960
5.508	0.50	405.115
6.492	0.50	409.439
7.507	0.50	409.144
8.501	0.50	405.395
9.510	0.50	398.797
10.558	0.50	389.759
11.526	0.50	379.856
12.512	0.50	368.809
13.501	0.50	357.260
14.525	0.50	344.728

Table 14. Total excess amount adsorbed of gas mixtures CO₂/N₂ ($y_{\text{CO}_2} = 0.25$) on AC Norit R1 at $T = 298$ K.

p (MPa)	y_{CO_2}	Γ^σ (mg/g)
0.0348	0.25	18.120
0.0629	0.25	28.757
0.0925	0.25	38.527
0.1307	0.25	49.404
0.144	0.25	52.360
0.233	0.25	75.411
0.365	0.25	99.546
0.472	0.25	118.095
0.555	0.25	128.906
0.712	0.25	146.964
0.877	0.25	162.820
0.942	0.25	168.988
1.058	0.25	178.743
1.192	0.25	190.128
1.300	0.25	197.448
1.450	0.25	206.979
1.510	0.25	209.228
1.584	0.25	214.389
1.711	0.25	220.923
2.604	0.25	258.267
3.526	0.25	282.646
4.528	0.25	301.032
5.528	0.25	312.584
6.524	0.25	319.879
7.515	0.25	323.938
8.530	0.25	325.620
9.516	0.25	325.326
10.463	0.25	323.855
11.511	0.25	320.665
12.534	0.25	316.583
13.530	0.25	311.861
14.531	0.25	306.567

If the concentration of the gas phase does not change during adsorption we can calculate the reduced spreading pressure $\frac{\pi}{RT}$ according to van Ness method under the conditions of constant concentration and constant temperature (van Ness, 1969):

$$\frac{\pi}{R \cdot T} = \int_0^p \frac{n^{\text{Ex}}}{A} d \ln(f_i) \quad (T; y = \text{const.}) \quad (10)$$

Assuming:

$$\frac{n^{\text{Ex}}}{A} \equiv \frac{\Gamma^\sigma}{\bar{M}} \quad \text{with } \bar{M} = x_1 M_1 + x_2 M_2$$

π can be determined from the experimental excess data. Into the calculation of the average mol mass \bar{M} the composition of the adsorbate phase x_i is included. Since the partial loading at the start of the calculation is unknown,

Table 15. Total excess amount adsorbed of gas mixtures CO₂/N₂ ($y_{\text{CO}_2} = 0.1$) on AC Norit R1 at $T = 298$ K.

p (MPa)	y_{CO_2}	Γ^σ (mg/g)
0.0347	0.10	10.684
0.0628	0.10	17.488
0.0923	0.10	23.446
0.1290	0.10	32.146
0.1305	0.10	30.447
0.2440	0.10	51.295
0.3610	0.10	64.653
0.4710	0.10	75.266
0.5740	0.10	84.352
0.7130	0.10	94.856
0.8450	0.10	103.998
0.9550	0.10	110.793
1.0640	0.10	117.257
1.1920	0.10	124.021
1.3030	0.10	130.687
1.4410	0.10	136.845
1.5620	0.10	141.785
1.7110	0.10	147.373
1.7110	0.10	148.349
2.5440	0.10	173.101
3.5770	0.10	194.309
4.5220	0.10	207.101
5.5140	0.10	216.777
6.5390	0.10	223.241
7.5330	0.10	227.225
8.7820	0.10	229.919
9.5320	0.10	230.531
10.4890	0.10	230.580
11.5120	0.10	229.585
12.5610	0.10	227.827
13.5330	0.10	225.635
14.5470	0.10	222.935

the composition of the gas phase y_i is used as starting value. The following differentiation of dy_1 at fixed temperature and constant pressure gives the size

$$\left. \frac{d\pi}{R \cdot T \cdot dy_1} \right|_{T,p}.$$

The composition of the adsorbate phase can be determined iteratively for binary gas mixtures directly from

Table 16. Total excess amount adsorbed of gas mixtures CO₂/N₂ ($y_{\text{CO}_2} = 0.05$) on AC Norit R1 at $T = 298$ K.

p (MPa)	y_{CO_2}	Γ^σ (mg/g)
0.0341	0.05	6.804
0.0635	0.05	12.005
0.0923	0.05	17.028
0.1140	0.05	20.693
0.1302	0.05	22.305
0.218	0.05	33.347
0.352	0.05	46.356
0.459	0.05	54.675
0.538	0.05	61.417
0.700	0.05	71.098
0.830	0.05	78.698
0.930	0.05	84.254
1.043	0.05	89.835
1.139	0.05	94.057
1.284	0.05	101.156
1.430	0.05	106.633
1.510	0.05	109.666
1.580	0.05	104.230
1.597	0.05	112.779
1.705	0.05	116.031
2.504	0.05	129.862
3.502	0.05	148.149
4.540	0.05	160.583
5.500	0.05	169.259
6.522	0.05	175.432
7.440	0.05	179.848
8.507	0.05	182.416
9.501	0.05	183.677
10.565	0.05	183.993
11.523	0.05	183.501
12.497	0.05	182.556
13.654	0.05	180.823
14.532	0.05	179.131

experimental data according to the following working equation.

$$x_1 = y_1 \cdot \frac{\Gamma^\sigma + (1 - y_1) \cdot M_1 \cdot \left. \frac{d\pi}{R \cdot T \cdot dy_1} \right|_{T,p}}{\Gamma^\sigma - y_1 \cdot (1 - y_1) \cdot (M_1 - M_2) \cdot \left. \frac{d\pi}{R \cdot T \cdot dy_1} \right|_{T,p}} \quad (11)$$

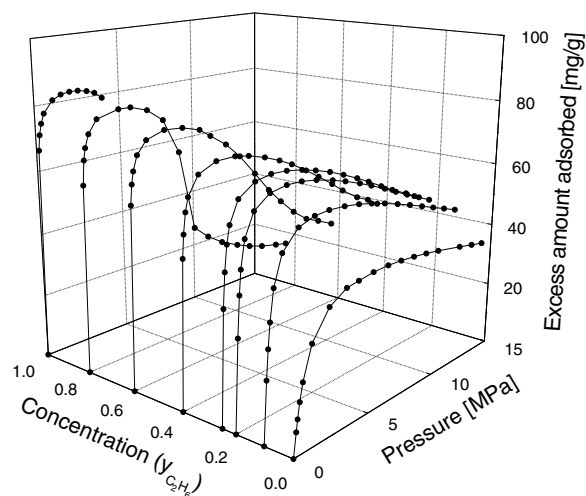


Figure 3. Experimental data connected by spline of the system ethane-methane on zeolite 13X at 298 K for the different gas mixtures $y_{C_2H_6}$.

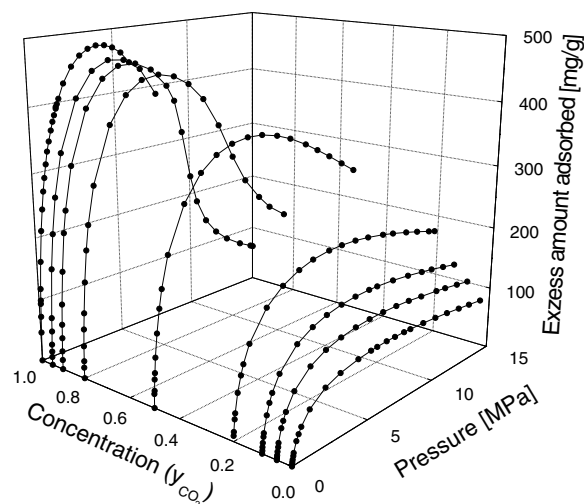


Figure 4. Experimental data connected by spline of the system carbon dioxide-nitrogen on AC Norit R1 at 298 K for the different gas mixtures y_{CO_2} .

The buoyancy corrected experimental data Γ^σ was described by a 3-Parameter-Isotherm-Equation dependent on pressure.

3-Parameter-Isotherm-Equation

A 3-Parameter-Isotherm-Equation was used for the description of the trend of the excess adsorption data as a function of the pressure. This equation was devel-

oped for pure gases and can also be transferred to gas mixtures (i.e. total load) (Harting et al., 1998). The fugacity f of the used gas mixtures was determined by the Bender-EOS (Bender, 1970).

$$\Gamma^\sigma(p, T) = \frac{f}{f + k_0 \exp\left(\frac{v_0 \cdot p}{R \cdot T}\right)} \cdot I_0 \quad (12)$$

The parameters of the 3-Parameter-Isotherm-Equation are I_0 maximal loading, k_0 Henry constant and v_0 molar volume of the adsorbed phase. In the description of the adsorption excess with the isotherm equation (Eq. (7)) there are deviations from the experimental values with increasing carbon dioxide concentration for the system of carbon dioxide-nitrogen within the lower pressure range. The reason for this phenomenon is the occurrence of capillary condensation. It results from the large micro pore proportion of the activated carbon and the approximation to the critical temperature with increasing concentration of carbon dioxide of the gas mixtures. For the pure gas carbon dioxide the effect of the capillary condensation is highest. Equation (7) is extended empirically with the condensation term:

$$C \cdot \exp\left(1 - \frac{p}{p_c} \left(\frac{T}{T_c}\right)^2 \cdot L\right)$$

for the description of this effect as additive link for the parameter maximal loading I_0 . The size C is analogous to I_0 the maximal loading of the condensation term and L characterize the interactions between solid and adsorbed molecules. The results of the extension of the 3-Parameter-Isotherm-Equation are represented in Fig. 5 for carbon dioxide. The values of the parameter of the 3-Parameter-Isotherm-Equation are summarized in Tables 17 and 18.

Table 17. Parameter of the 3-Parameter-Isotherm-Equation of the system C_2H_6/CH_4 on zeolite 13X at $T = 298$ K.

$y_{C_2H_4}$	I_0 (mg/g)	k_0 (MPa)	v_0 (cm ³ /mol)
0.00	87.77	0.048	1084.49
0.10	84.69	0.056	1069.61
0.20	82.09	0.069	1006.94
0.25	77.50	0.099	876.05
0.40	77.28	0.155	727.91
0.60	75.27	0.191	670.08
0.80	72.77	0.349	545.12
1.00	63.54	1.000	413.14

Table 18. Parameter of the 3-Parameter-Isotherm-Equation of the system CO_2/N_2 on AC Norit R1 at $T = 298 \text{ K}$.

y_{CO_2}	$I_0 \text{ (mg/g)}$	$k_0 \text{ (MPa)}$	$v_0 \text{ (cm}^3\text{/mol)}$	$C \text{ (mg/g)}$	L
0.00	202.15	2.261	229.19	—	—
0.05	352.84	3.458	237.66	94.92	0.93
0.10	361.36	2.101	240.40	95.92	2.40
0.25	517.97	1.916	263.19	132.77	3.78
0.50	662.83	1.602	310.63	198.32	9.34
0.80	781.30	1.362	390.36	282.77	22.55
0.90	884.27	1.532	417.51	310.61	21.82
0.95	890.00	1.496	402.68	309.05	22.27
1.00	895.55	1.379	451.04	300.50	27.51

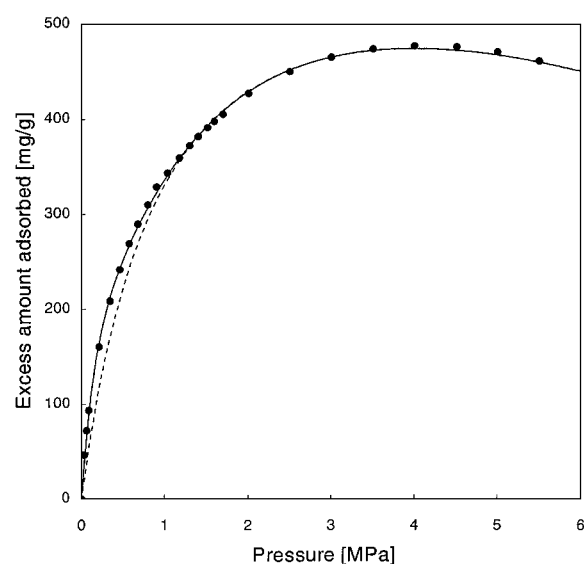


Figure 5. Correlation of the carbon dioxide 3-Parameters-Isotherm-Equation; ---- without condensation term, — with condensation term.

In the Figs. 6 and 7 the correlation of the extended 3-Parameter-Isotherm-Equation to the experimentally determined isotherms are plotted for different adsorption systems. The correlations were made up to the critical pressure of the subcritical components carbon dioxide and ethane. The correlations of the gas mixtures can be made up to the experimental pressure range with use of the 3-Parameter-Isotherm-Equation (Harting et al., 1998). But in this paper the correlations of the mixture were made also only up to critical pressures of the subcritical components.

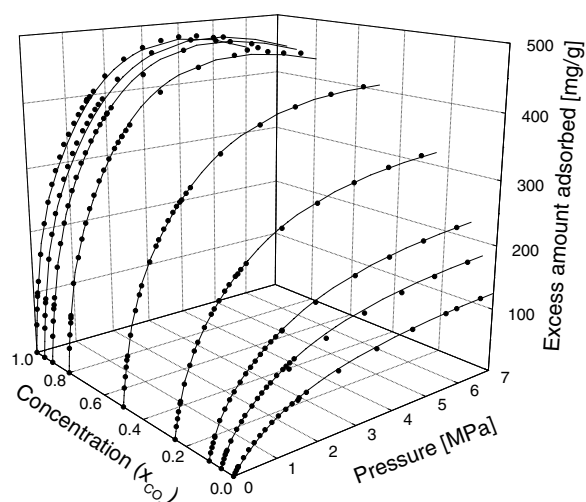


Figure 6. Correlation of the 3-Parameters-Isotherm-Equation at the experimental measuring data of the gas mixtures carbon dioxide-nitrogen on AC Norit R1 at 298 K; • gravimetric measurements, — 3-Parameter-Isotherm-Equation.

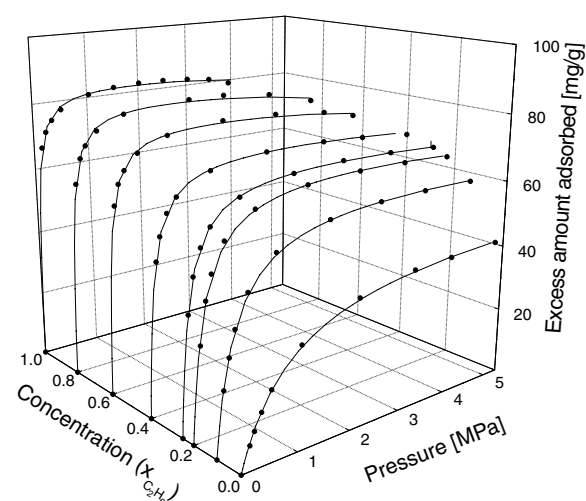


Figure 7. Correlation of the 3-Parameters-Isotherm-Equation at the experimental measuring data of the gas mixtures ethane-methane on zeolite at 298 K; • gravimetric measurements, — 3-Parameter-Isotherm-Equation.

The results of the correlations using the 3-Parameter-Isotherm-Equation are in good agreement with the experimental data in the respective pressure range (cp. Figs. 6 and 7). Thus two homogeneous data sets are given, at which the model for the calculation of the partial loads was tested.

Results and Discussion

The adsorption equilibria of the two different adsorption systems (pure gases and mixtures) were measured gravimetrically up to 15 MPa and at 298 K. The systems are ethane-methane on zeolite 13X and carbon dioxide-nitrogen on activated carbon Norit R1. The isotherms of the pure gases and of the gas mixtures show isotherm type I (classification by IUPAC). For the excess isotherms as a function of the system pressure a monotonous rise is distorted at the beginning. The isotherms show a maximum. After the maximum they drop with increasing pressure due to the stronger increase of the gas phase density compare to the adsorbed phase density. Ethane is preferentially adsorbed compare to methane of the system ethane-methane on zeolite 13X. Carbon dioxide is also preferentially adsorbed compare to nitrogen of the system carbon dioxide-nitrogen on Norit R1.

According to the method described the partial loads were calculated from the gravimetric measurements of the total loads. The obtained results of the calculations of the composition of the adsorbed phase are represented for the gas mixture ethane-methane on zeolite 13X in the Figs. 8 and 9 for example for two gas compositions.

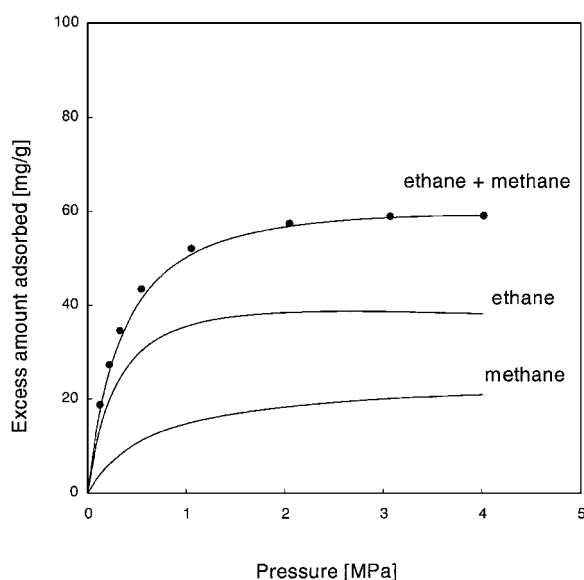


Figure 8. Results of the partial loadings of the gas mixture ethane-methane on zeolite 13X; $y_{\text{C}_2\text{H}_6} = 0.1$ ($T = 298$ K); • gravimetric measurements.

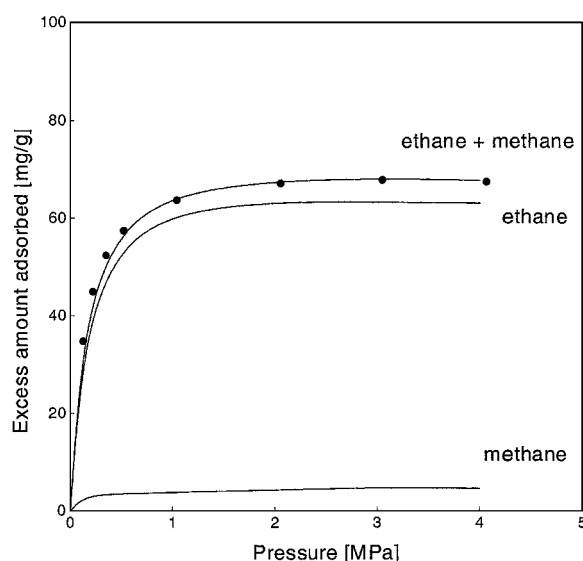


Figure 9. Results of the partial loadings of the gas mixture ethane-methane on zeolite 13X; $y_{\text{C}_2\text{H}_6} = 0.25$ ($T = 298$ K); • gravimetric measurements.

The partial loads could be calculated up to the critical pressure of the pure ethane. It is recognizable that, as expected, ethane is adsorbed more strongly than methane. Furthermore the amount adsorbed of ethane increase with rising ethane concentration in the adsorbate phase. The separation factors calculated from excess values increase with rising concentration of ethane (cp. Fig. 10).

The pressure dependence is illustrated in Fig. 11. Within the lower concentration range (up to $y_{\text{C}_2\text{H}_6} = 0.3$) the separation factors shift contrary to the pressure, i.e. the adsorbed amount of the partial load methane increase with rising pressure. The pressure-dependent behaviour of the separation factors reverses for the upper concentration range. Rising pressure causes a better adsorption of the component ethane.

The calculated partial loads for the gas mixture carbon dioxide-nitrogen on activated carbon Norit R1 are specified for example for two mixtures in the Figs. 12 and 13. The points are volume-gravimetrically determined partial loads (Dreisbach et al., 1999). It is recognizable that the calculations agree well with the experimental data. The model shows very good results for the system carbon dioxide-nitrogen up to pressures of 1.7 MPa.

The algorithm in this model is not usable at higher pressures ($p > 1.7$ MPa) for this gas mixture. The reason is the real behaviour of the gas mixtures at higher

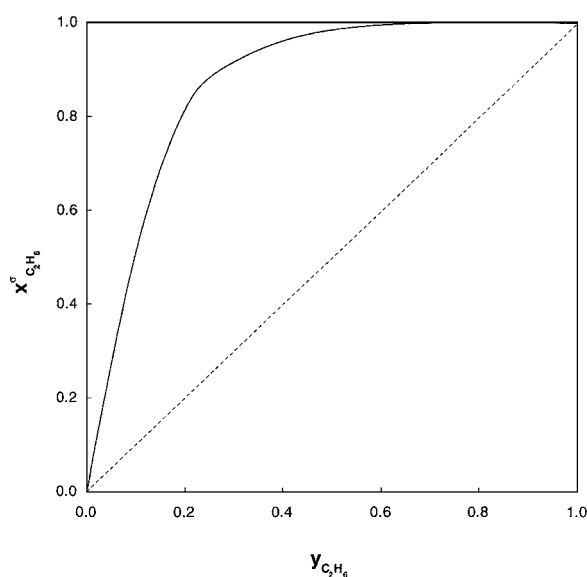


Figure 10. Separation diagram of the gas mixture ethane-methane on zeolite 13X; $p = 1$ MPa, $T = 298$ K calculated from excess data.

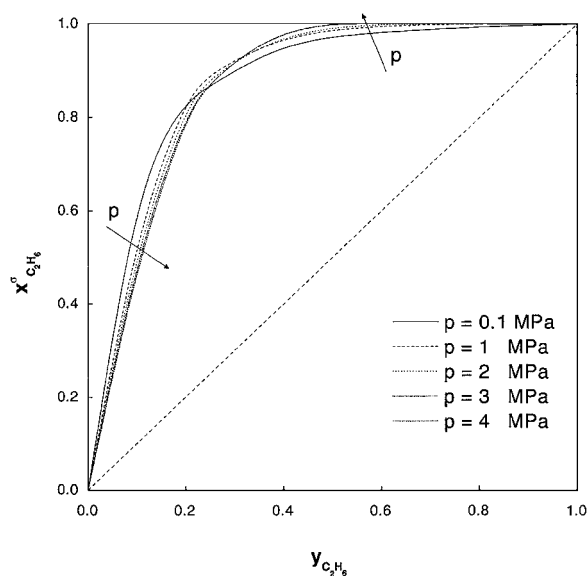


Figure 11. Separation diagram in pressure dependence of the gas mixture ethane-methane on zeolite 13X calculated from excess data.

pressures, especially CO_2 . Furthermore it can be assumed that the real gas behaviour increases with rising carbon dioxide content in the mixture. On the other hand if the selectivity is very high, most models can not described the real adsorption behaviour with high accuracy (Talu, 1998; Dreisbach et al., 1999). The separation effect resulting from the partial loads is represented

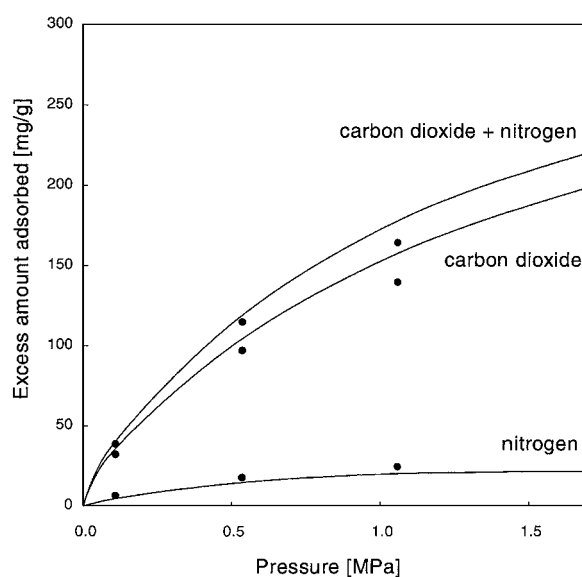


Figure 12. Results of the partial loadings of the gas mixture carbon dioxide-nitrogen on AC Norit R1; $y_{\text{CO}_2} = 0.25$ ($T = 298$ K); ● volume-gravimetric measurements (Dreisbach et al., 1999).

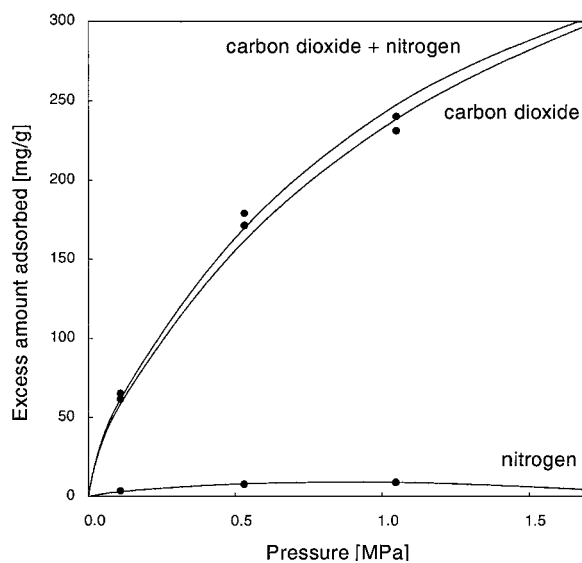


Figure 13. Results of the partial loadings of the gas mixture carbon dioxide-nitrogen on AC Norit R1; $y_{\text{CO}_2} = 0.5$ ($T = 298$ K); ● volume-gravimetric measurements (Dreisbach et al., 1999).

in Fig. 14. For this system it was found that the separation factor increases with rising pressure and increasing carbon dioxide concentration in the gas mixture.

The presented model for the calculation of the partial loadings requires high accuracy for the data set

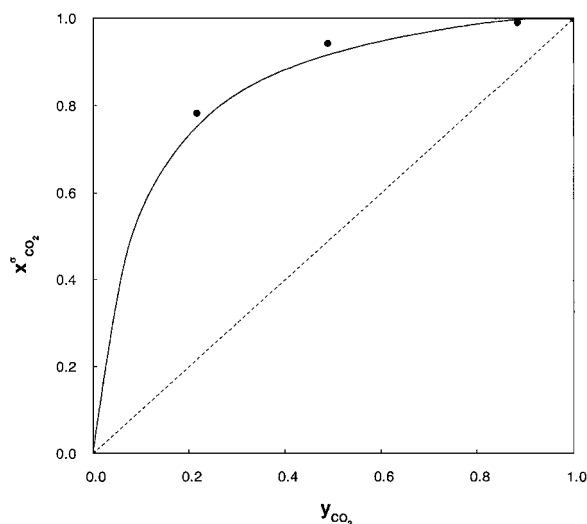


Figure 14. Separation diagram of the gas mixture carbon dioxide-nitrogen on AC Norit R1, $p = 1$ MPa, $T = 298$ K calculated from excess data, ● volume-gravimetric measurements (Dreisbach et al., 1999).

used. The uncertainty of the calculations is seen in the numerical integration of the isotherm equation for the evaluation of the spreading pressure. The average mol mass (the mole fraction of the adsorbate phase) is involved in this part of the calculation. Thus the calculations are iterative. Although a large quantity of data were present, the technique for the system failed starting from 1.7 MPa.

To get an accurate evaluation of the spreading pressure it is necessary to improve the calculation at higher pressure. The research indicates the dependence of the separation factor on pressure. This dependence must be recognised in calculations of the concentration of the adsorbate phase. Future investigations should be made to solve this problem.

Conclusions

Experimental determined adsorption data of the pure gases ethane, methane and their mixtures on zeolite 13X and of the pure gases carbon dioxide, nitrogen and their mixtures are represented. The adsorption equilibria were measured gravimetrically at 298 K and up to 15 MPa.

A method to calculate the composition of the adsorbate phase from gravimetrically determined adsorption data of pure gases and their binary mixtures was developed. The model based on the approach by

van Ness (1969). The proposal was extended by an accurate description of the gas phase in particular by using of the fugacity in place of the pressure. Thus the real behaviour of gases and of gas mixtures can be better described for a larger pressure range. Furthermore the calculation of the compositions of the adsorbate phase was made using the adsorption excess data. The calculations were accomplished for two gas mixtures with a sub- and a supercritical component on an activated carbon and on zeolite.

For two different adsorption systems it is possible to calculate the concentration of the adsorbate phase up to higher pressures directly from the gravimetric determined total loads with the modified van Ness model. The calculated loads are in good agreement with volume-gravimetric determined partial loads.

Nomenclature

A	Surface area (m^2/g)
f	Fugacity of a gas mixture (MPa)
m	Mass (mg, g)
Δm	Balance signal
M	Molecular weight (g/mol)
\bar{M}	Average molecular weight (mol/g)
n	Number of mole (mol)
p	System pressure (MPa)
R	Universal gas constant ($\text{J}/(\text{mol K})$)
T	Temperature (K)
V	Volume (cm^3)
x	Molar fraction in the adsorbed phase
y	Molar fraction in the gas phase

Parameter of the 3-Parameter-Isotherm-Equation

I_0	Maximal loading (mg/g)
k_0	Henry constant (MPa)
v_0	Molar volume of the adsorbed phase (cm^3/mol)
C	Constant (mg/g)
L	Constant

Greek Letters

α	Separation factor
Γ^σ	Excess amount adsorbed (mg/g)
μ	Chemistry potential (J/mol)
π	Spreading pressure ($\text{N}/(\text{kg} \cdot \text{m})$)

Superscript

<i>Ad</i>	Adsorbate phase
<i>as</i>	Adsorbent
<i>G</i>	Gas phase
<i>na</i>	Non adsorbed
σ	Excess

Subscripts

<i>c</i>	Critical
<i>i</i>	Component
1	More strongly adsorbed component
2	Less strongly adsorbed component

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