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Adsorption of Pure Gases and Mixtures on Porous Solids up to High Pressures*

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Abstract. Physisorption equilibria of multicomponent gases on microporous solids like zeolites or activated carbons are considered. An overview about adsorption measurements of pure gases H_2, He, O_2, N_2, Ar, CO_2, CO, CH_4, C_2H_4 and C_2H_6 and some of their mixtures in the pressure range vacuum $< p < 50\,\mathrm{MPa}$ at different temperatures 10°C–70°C were investigated. Also a thermodynamic formalism based on a modified *van Ness* method and on a new 3 parameter Isotherm equation (3-PIG) to describe the excess amount adsorbed was developed. Results are shown and discussed.

Keywords: excess adsorption, mixed gas adsorption, gravimetric measurement, van Ness method

Introduction

Physisorption phenomena of gas mixtures on inert porous solids like zeolites and activated carbons provide the basis for a variety of gas separation processes including the purification of exhaust air from technical processes (often hazardous compounds like VOCs, FCHCs, HCl, Cl_2 etc. in view of increasing environmental regulations and requirements), the separation of air into nitrogen and oxygen enriched components at ambient temperature, the purification of natural gas from chemically aggressive or toxic components like H_2S etc. and the regain and / or concentration of valuable components of low BTU-gases like hydrogen from blast-furnace gases or methane from garbage deposit gases (Suzuki, 1993; LeVan 1998).

Pure component isotherms are the simplest measurement of adsorption equilibria (Talu, 1998; Keller et al., 1999). Isotherm measurements for low pressures are so common that commercial “push-button” measurement systems have been available for many years. On the other hand applications of adsorption almost always involve mixtures. Although several models can predict mixture equilibria from pure component information in the low pressure range, where the adsorption behavior can be assumed to be ideal. The accuracy of predictions are, in general, less than desirable to an application engineer, i. e. the Ideal Adsorbed Solution Theory or the Mixed-Langmuir model (Myers and Prausnitz, 1965; Markham and Benton, 1931). Hence, there is need for direct measurements of mixture equilibria. Most of models can predict multicomponent equilibria with good accuracy once the binary data are available. Therefore the majority of experimental effort in mixture equilibria has been devoted to binary systems.

It is the purpose of this paper to contribute to this field by new methods to measure adsorption equilibria of pure components and mixtures using only the gravimetric method.

Surface Excess Amount Adsorbed

In this section we briefly will discuss some of the basic concepts of gas-adsorption-systems, namely the absolute mass and the excess mass of an adsorbed phase and related quantities like its volume and density. Reference is made to the respective literature (Gibbs, 1878;

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*Dedication to the memory of W. Schirmer

Myers et al., 1997; Rouquerol et al., 1999; Do, 1999) where also working formulae for these quantities are given.

Adsorption occurs at the interface between bulk phases, a solid and a fluid phase, where the density of fluid molecules is higher than the bulk density due to intermolecular interactions (dispersion, electrostatic and induced electrostatic forces). The interfacial region is in dynamic equilibrium with the fluid phase and there is a constant exchange of molecules between the interfacial region and the bulk fluid phase. The density close to the solid interface is not uniform and it is not possible to determine this density profile. Without any independent information concerning the structure of the adsorbed layer, the void volume of the porous solid and pore size distribution it is not possible to determine the absolute amount adsorbed. To overcome these problems, J.W. Gibbs proposed an alternative approach, the concept of the so-called "Gibbs surface excess" to quantify the amount adsorbed (Talu, 1998; Markham and Benton, 1931; Rouquerol et al., 1999). But the Gibbs definition possesses a practical problem for adsorption measurements in porous solids, the determination of the void volume. The quantity most often used today to approximate the void volume of a porous solid is the so-called helium volume. It is simply measured by exerting the (activated) adsorbent to a helium atmosphere at known pressure and temperature. Assuming helium neither to be adsorbed nor absorbed in the sorbent the void volume can be determine (Talu, 1998; Keller et al., 1999; Rouqerol et al. 1999; Staud et al., 1997).

Experiment

The gravimetric method was used to measure adsorption equilibria of pure gases and the total load of gas mixtures on porous solids (Staudt et al., 1993 and 1994; Dreisbach et al., 1999). In this method the change of the weight of a sorbent sample in the gravity field of earth due to adsorption of molecules from a gas is observed. Figure 1 presents a schematic diagram of the gravimetric setup.

High pressure adsorption measurements of the pure gases were performed on a magnetic suspension balance, Rubotherm (Bochum, Germany). The balance working up to 50 MPa, allows the determination of specific quantities, e.g. solubility of substances in fluids, density of fluids and adsorption behavior of fluids on adsorbents even in corrosive media without danger

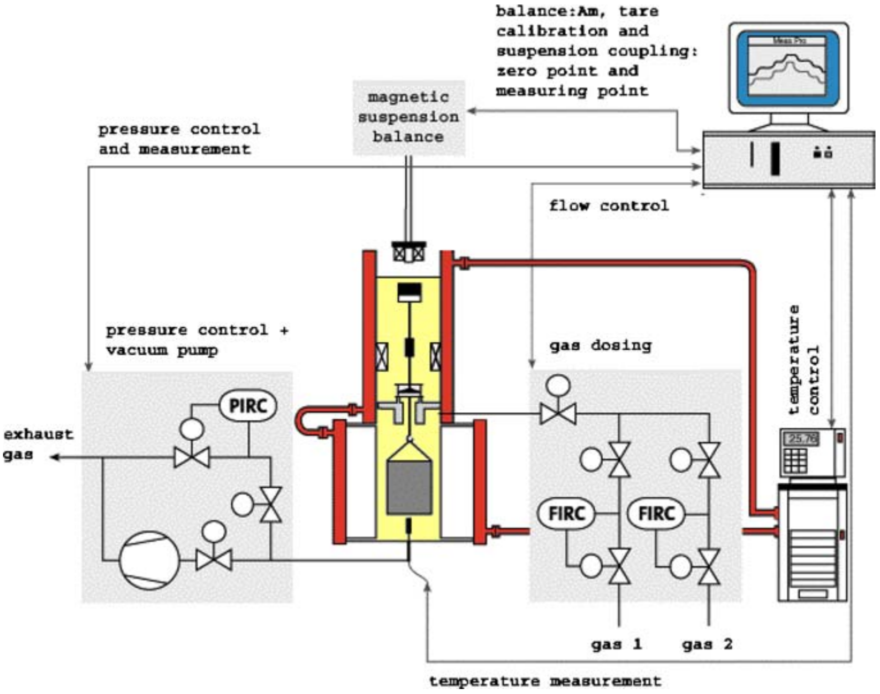

Figure 1. Experimetal setup for gravimetric measurements of adsorption equilibria (Beutekamp, 2002).

of pollution or destruction of the balance. The unit consists of a conventional high-pressure stainless steel sample cell, which was connected to a gas reservoir via an air driven gas booster (Haskel, USA). A known amount of active carbon was placed into the sample pan of the balance and than out gassed at 423 K. Before starting the measurements the system was evacuated to 10^{-3} Torr. Equilibrium weights were achieved in 20–30 min.

Identifying again the void volumes with the so-called helium volume, i.e. assuming, the excess amount adsorbed can be determined. Advantages of the gravimetric method are its sensitivity and relative accuracy of up to 10^{-7}, the possibility to check (in vacuum) the state of activation of a sorbent sample and also the approach to equilibrium of a adsorption process-even in gas mixtures (Keller et al., 1999; Staudt et al., 1993 and 1994; Dreisbach et al., 1999).

The measurements of excess adsorption isotherms of the pure gases He, CH_4, N_2, Ar, CO_2, C_2H_4 and C_2H_6 and some of their binary mixtures on different adsorbents were carried out at different temperatures from 10 to 70°C over a wide pressure range from 0 to 50 MPa.

Different adsorbents were tested: activated carbon (AC) Norit R1 (Norit, Germany), activated carbon SCS-3 (Institute of Sorption and Problems of Endoecology, Ukraine), zeolite type 13X (Wolfen Zeosorb, Germany) and Envisorb B+ (Engelhard, Germany). The adsorbents were analyzed also by nitrogen adsorption at 77 K using ASAP–2000 M, (Micrometrics, USA).

Theory

The primary purpose of binary gas adsorption measurements is to measure the partial amount adsorbed (or total amount adsorbed and selectivity) as a function of gas composition, pressure and temperature. This constitutes a full measurement of equilibrium (Talu, 1998). The so-called partial measurements make use of thermodynamic relations (Gibbs-Duhem relation for the surface phase, so-called van Ness method (van Ness, 1969)) to calculate one property which may not be direct measured. This includes two disadvantages: (1) A thermodynamic consistency check cannot be utilized and (2) large amounts of data are necessary to come to a satisfying result since the Gibbs-Duhem relation is a differential equation which is integrated using data.

Three Parameter Isotherm

To describe adsorption equilibria in a wide pressure range a three parameter isotherm was developed (Honigberg, 1969; Harting et al., 1998; Beutekamp, 2002). The resulting three parameter isotherm equation "3-PIG" is:

$$\Gamma^{\sigma}(p, T) = \frac{f}{f + k_0 \exp\left(\frac{v_0 \cdot p}{R \cdot T}\right)} \cdot I_0 \qquad (1)$$

with

I_0	maximum load [mg/g],
k_0	Henry's law constant [MPa],
v_0	molar volume of the adsorbed phase [cm^3/mol],
f	fugacity [MPa],
R	gas constant [J/mol*K],
T	temperature [K].

The 3 parameters are maximum load I_0, the Henry's law constant k_0 and the molar volume of the adsorbed phase v_0. This isotherm of pure components adsorbed in the porous solids should be obey the chemical equilibria and phase equilibria between the fluid phase and the adsorbed phase (Beutekamp, 2002). This 3-PIG can describe the increase at low pressures as well as the decrease at high pressures of the excess amount adsorbed (cp. Figs. 2 and 3).

Modified van Ness Method

Using the *van Ness* formalism (Harting et al., 1998; Beutekamp, 2002) partial loads of mixed gas

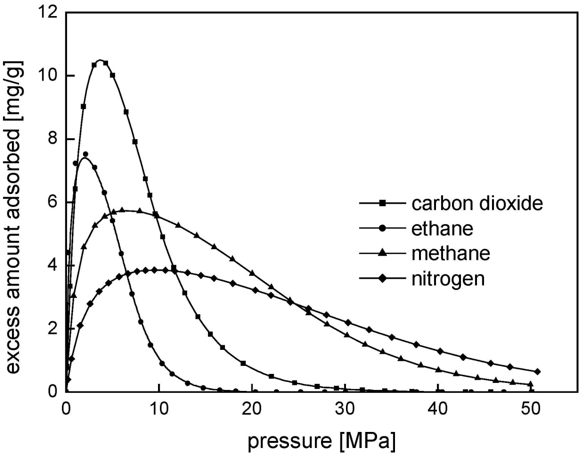

Figure 2. Excess adsorption of C_2H_6, CO_2, CH_4 and N_2 on AC Norit R1 at 40°C (Herbst and Harting, 2002).

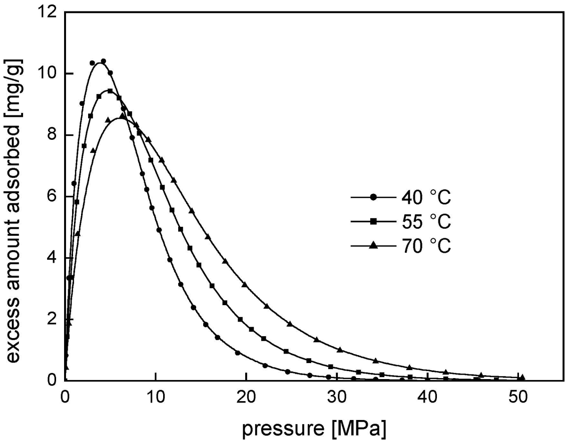

Figure 3. Excess adsorption of carbon dioxide on Norit R1 at 40, 55 and 70°C (Herbst and Harting, 2002).

adsorption equilibria can be calculated from pure component adsorption isotherms and total loads of mixtures measured in gravimetric experiments. The used adsorption isotherm is the 3-PIG isotherm.

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 of the entire pressure range.

Sum-Isotherm-Method (SIM)

In this method the total load of mixed gas adsorption equilibria $\Gamma^{\sigma}_{tot}(p, T, y_i)$ can be described as a sum of 3-PIG isotherms for each component i in the mixture. The parameters can be determine by fitting the mixed gas adsorption isotherms to the total load measured in gravimetric experiments. The optimized parameters characterize the isotherm of each component in the mixture. This leads to the partial loads for each component adsorbed in the mixture (Beutekamp, 2002).

$$\Gamma^{\sigma}_{\text{tot}}(p, T, y_i) = \sum_{i=1}^{N} \frac{f_i}{f_i + k_{0,i} * \exp\left(\frac{v_0 \cdot p_i}{R \cdot T}\right)} \cdot I_{0,i} \quad (2)$$

Results and Discussion

Pure Adsorption Isotherms

Adsorption equilibria of the gases He, CH_4, N_2, Ar, CO_2, C_2H_4 and C_2H_6 were carried out at 25, 40, 55 and 70°C on different adsorbents (Herbst and Harting, 2002; Beutekamp, 2002) and the pure gas adsorption equilibria were measured gravimetrically. The void volume of the adsorbent can be determined by buoyancy measurements with helium as fluid. It based on the assumption that helium is not adsorbed ($\Gamma^{\sigma} = 0$) but fills out the pore volume without changing the pore structure of the adsorbent.

Figure 2 shows the pure adsorption isotherms of C_2H_6, CO_2, CH_4 and N_2 on activated carbon Norit R1 at 318 K in the pressure range up to 50 MPa (Herbst and Harting, 2002). The symbols are the experimental data and the lines are the best fit using the 3-PIG isotherm. The agreement between experiment and fit is very good. All excess isotherms show a maximum which is characterized by the parameter v_0, i.e. molar volume of the adsorbed phase. At this point the difference between the fluid density and the density of the adsorbed phase shows also a maximum. For high pressures the excess amount adsorbed approaches to zero, i.e. there is no difference in the densities of both phases.

Figure 3 shows the temperature dependency of the adsorption isotherm of CO_2 on Norit R1. Again, symbols are experimental data and lines the best fit using the 3-PIG (Herbst and Harting, 2002). With increasing temperature the Henry's law constant decrease and the excess isotherm maximum is shifted to higher pressures (fugacities). After passing through the isotherm maximum the amount adsorbed increase with increasing temperature. This can be explained by the strong decrease of the fluid density compare to the density in the adsorbed phase. At high pressures the excess amount adsorbed goes to zero.

This Figures 2 and 3 show also that the 3-PIG is able to describe the excess amount adsorbed in a very wide pressure and temperature range with high accuracy. Experimental data, detailed results (values of parameters) and an extensive discussion of this pure isotherm measurements are in Herbst and Harting (2002).

Mixed Gas Adsorption Isotherms

Adsorption equilibria of the mixed gases CH_4/N_2, CO_2/CH_4, CO_2/N_2, CH_4/C_2H_6, O_2/N_2 and CO/H_2

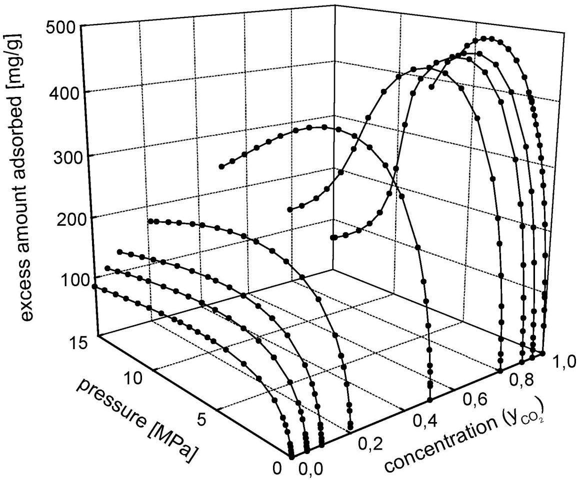

Figure 4. Excess adsorption isotherms (total load) of mixtures CO_2/CH_4 on AC Norit R1 at 25°C (Beutekamp 2002).

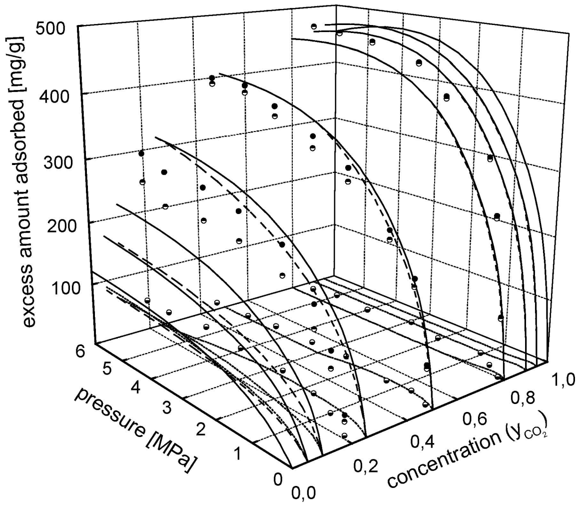

Figure 5. Total and partial loads of system CO_2/N_2 on AC Norit R1 at 25°C (Beutakamp, 2002).

were investigated at different temperatures (10–70°C) on different adsorbents (Herbst and Harting 2002; Beutekamp, 2002) and the total amount adsorbed was determined gravimetrically. The partial loads were calculated using the modified *van Ness* method and the SIM.

Figure 4 shows the total excess amount adsorbed of gas mixtures CO_2/CH_4 on AC Norit R1 for different concentrations (Beutekamp, 2002). The symbols are experimental data and the lines show the best fit using the 3-PIG isotherm. The agreement between experimental data and fit is very good in the whole pressure and concentration range. The AC Norit R1 prefers to adsorb CO_2. This leads to a high selectivity of CO_2 compare to CH_4. Using a concentration dependency of the 3-PIG isotherm parameters, we can describe the whole concentration field between the 2 pure isotherms.

Figure 5 shows the total excess and the partial excess amount adsorbed of gas mixtures CO_2/N_2 on AC Norit R1 for different concentrations (Beutekamp, 2002). The symbols are experimental data (Dreisbach et al. 1999). The lines show the results of the modified *van Ness* method. The partial loads are calculated from excess amount of the pure components and the total excess amount adsorbed in mixture. For this mixture the agreement between experiment and calculation is satisfied. Deviations are results of the high selectivity of the AC and the non-ideal gas behavior of CO_2.

Using the so-called SIM, partial loads can be calculated from the total load of the mixture and the pure adsorption isotherms. Figure 6 shows the results for the gas mixture CO_2/CH_4 ($yCO_2 = 0.05$) on AC Norit R1. The symbols are experimental results (Dreisbach et al., 1999) and the lines the fitted total amount adsorbed and calculated partial amount adsorbed. The difference between experimentally determined and calculated amount adsorbed is a result of different equilibrium concentrations in the experiments.

The experimental data, detailed results of calculations and an extensive discussion of pure and binary adsorption equilibria are in Herbst and Harting (2002).

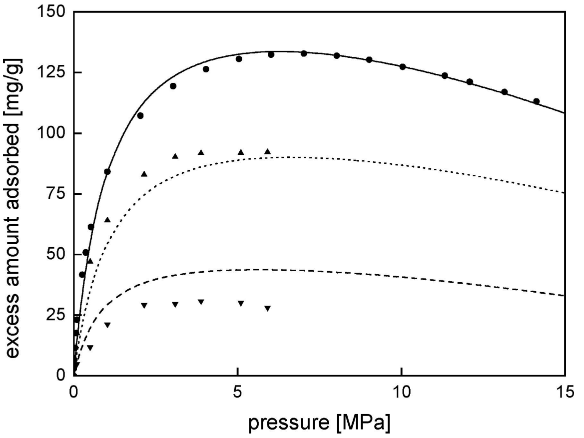

Figure 6. Total and partial amount adsorbed of gas mixture CO_2/CH_4 ($Y_{CO2} = 0.05$) on AC Norit R1 at 25°C (Beutekamp, 2002).

Conclusion

Adsorption equilibria of the gases He, CH_4, N_2, Ar, CO_2, C_2H_4 and C_2H_6 and some of their binary mixtures were carried out on different adsorbents at different temperatures (10°C < T < 70°C) in the pressure range Vacuum < p < 50 MPa. The pure gas isotherms and the total load of mixed gas adsorption equilibria were measured gravimetrically. The pure data can be described very well by the 3-PIG isotherm.

For the calculations of the concentration in the adsorbate phase two models were used, the modified *van Ness* method and the Sum Isotherm Method (SIM) based on the 3-PIG adsorption isotherm. The modified van Ness method can calculate partial loads of mixed gas adsorption equilibria in good agreement with experiments. With increasing real gas behavior of one ore more components the deviation between experiment and calculation increase. The handling of SIM is relatively simple and leads to smaller deviations between experiment and calculation compare to modified *van Ness* method.

Nomenclature

p	pressure MPa
Γ	excess adsorption calculated from 3-PIG mg/g
I_0	maximal loading mg/g
k_0	Henry-constant MPa
v_0	molar volume cm^3/mol
f	fugacity MPa
R	gas constant J/mol*K
T	temperature K

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