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THE MAGNETIC SUSPENSION BALANCE IN HIGH PRESSURE MEASUREMENTS OF PURE GASES

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Abstract

In the present work the supercritical fluids argon, methane, nitrogen, carbon dioxide, ethane, ethylene and propane were picked out as examples, and the results of analysis concerning the adsorption of these fluids at activated carbon Norit R1 (Norit Company, Germany) and SCS-3 (ISPE, Kiev) at different temperatures up to a pressure of 50 MPa are presented and discussed in this paper. The principle of working of the measuring device is described in this context as well.

A three-parameter isothermal equation is used to represent the adsorption equilibrium. The isothermal equation is based on a physical model concept which has already been used for the modelling of adsorption processes with a pressure up to 15 MPa.

Keywords: activated carbon, excess adsorption, gravimetric measurement, high pressure, supercritical fluids

Introduction

Physical adsorption of fluids onto solids is of interest in the transportation and storage of fuel and radioactive gases, the separation and cleaning of materials, solid-phase extractions, adsorbent regenerations using supercritical fluids, supercritical fluid chromatography and critical-point drying. Although physical adsorption of pure gases on different porous solids has been extensively studied over a wide range of temperatures and pressures, the number of works related to adsorption at high pressures is limited.

In adsorption experiments the excess adsorption only can be measured, which is defined as the excess gas present in the pores and on the surface of the adsorbent and above it corresponding to the density of the gas in the bulk phase at the given temperature and pressure.

The aims of this research work are the measurement and the thermodynamic description of the excess in the adsorption of pure gases up to pressures of 50 MPa. Different adsorbents were tested to determine for example the influence of the structure of pores under high pressure to obtain specific characteristics of these materials.

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Used adsorbents

Two different adsorbents were tested: activated carbon Norit R1 (Norit Company, Germany) and activated carbon SCS-3 from the Institute of Sorption and Problems of Endoecology (Ukraine). Both adsorbents were exposed to high pressure up to 50 MPa during the adsorption process.

Table 1 Properties of adsorbents

	Norit R1	SCS-3
BET surface/m^2 g^{-1}	1339	1094
Internal surface (*t*-plot)/m^2 g^{-1}	1307	929
Volume of micro-pores/cm^3 g^{-1}	0.6446	0.4382
Total volume/cm^3 g^{-1}	0.7074	1.0534

The adsorbents were analyzed by nitrogen adsorption at 77 K using ASAP-2000M (Micromeritics Company, USA). The resulting data are summarized in Table 1.

Experiment

High pressure adsorption measurements 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 behaviour of fluids on adsorbents even in corrosive media without danger of pollution or destruction of the balance. In comparison to traditional balances the test substance is not directly connected with the balance, it hangs on a so-called suspension magnet. The weight to measure is transmitted by magnetic suspension coupling from a closed and pressure-proof metal container to an external

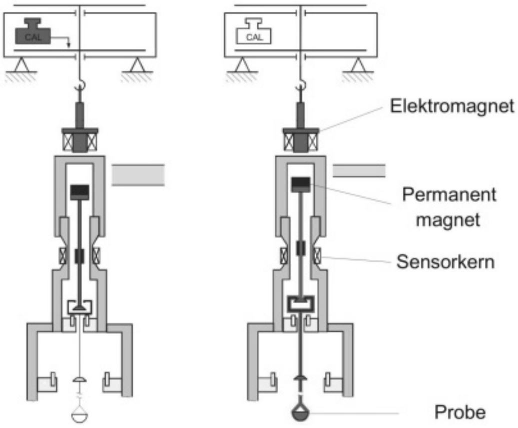

Fig. 1 Operating principle of magnetic suspension balance

microbalance. The suspension consists of a measuring load, a sensor core and a permanent magnet (Fig. 1). Regulation systems keep the electric magnet in free suspension and transmit the weight to measure to the external balance.

The measuring cell 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). The gases used were ultra-high purity grade supplied by Air Liquid. A known amount of active carbon (~4 g), which was outgassed at 423 K, was placed into the sample pan of the balance. Before the measurements the system was evacuated at $2\cdot10^{-3}$ hPa. Equilibrium weights were achieved in 20–30 min.

Table 2 Systems already measured

Adsorbent	298 K	313 K	328 K	343 K	373 K	398 K	403 K
Norit R1	He, N_2, Ar, CH_4, C_2H_6, C_2H_4, CO_2	He, N_2, Ar, CH_4, C_2H_6, C_2H_4, CO_2	He, N_2, Ar, CH_4, C_2H_6, C_2H_4, CO_2	He, N_2, Ar, CH_4, C_2H_6, C_2H_4, CO_2	He, C_3H_8	C_3H_8	C_3H_8
SCS-3	He, N_2, Ar, CH_4	N_2, Ar, CH_4, CO_2					

The measurements of excess adsorption isotherms of the pure gases methane, argon and nitrogen on the both adsorbents were carried out at different temperatures from 298 up to 403 K over a wide pressure range from 0 to 50 MPa (Table 2). These adsorption isotherms are typical excess isotherms with a distinct maximum.

Analysis of row gravimetric adsorption measurement data

Row gravimetric adsorption measurement data m^s include also quantities concerning experimental equipment, for example the container which contains the sample. The parameter V_{cont} represent the volume of the container. It can be determined separately by buoyancy measurements with the empty balance and with the sample container without adsorbents. The resulting values for all measured systems are summarized in Table 3.

First the row data must corrected by the equipment quantities to come to equipment independent data, to the so-called reduced mass Ω in the sense of Staudt *et al.* [10].

$$\Omega = m^s + \rho_{\mathrm{fl}} V_{\mathrm{cont}} \tag{1}$$

With the gravimetric adsorption measurements only the sum of excess Γ and buoyancy $\rho_{\mathrm{fl}} V_{\mathrm{ads}}$ can be obtained [10, 11]. The results for the specific excess $\overline{\Gamma}$ are as follows:

$$\overline{\Gamma} = \frac{\Omega + \rho_{\mathrm{fl}} V_{\mathrm{ads}}}{m} \tag{2}$$

with $\overline{\Gamma}$ – specific excess adsorption, ρ_{fl} – density of the fluid, V_{ads} – volume of the empty adsorbent, m – mass of adsorbent at microbalance.

Table 3 The resulting values for all measured systems

Norit R1	298 K	313 K	328 K	343 K	V_{cont}/cm^3
m/g, N_2	4.08325		4.12680	4.14252	0.70492
m/g, Ar	4.08325			4.14252	0.70492
m/g, CH_4	4.37217				1.97883
m/g, CO_2	4.12680		4.08325	4.04692	0.70492
m/g, C_2H_6	4.15962				0.70492
m/g, C_2H_4	4.16065				1.97883
$\overline{V}_{as, He}$/cm^3 g^{-1}	0.46161	0.46898	0.47335	0.47768	–

	373 K	388 K	403 K	V_{cont}/cm^3
m/g, C_3H_8		4.16065		1.97883
$\overline{V}_{as, He}$/cm^3 g^{-1}		0.48090		–

	SCS-3		
	298 K	313 K	V_{cont}/cm^3
m/g, N_2	2.54388		0.69622
m/g, Ar	2.76762		0.69622
m/g, CH_4	2.72348		0.69622
m/g, CO_2	–	2.76762	0.69622
$\overline{V}_{as, He}$/cm^3 g^{-1}	0.49019		–

The skeletal volume of the adsorbent V_{ads} can be determined by means of buoyancy measurements with helium as fluid [7, 10, 11]. It is based on the assumption that helium is not adsorbed (Γ=0) but fills out the pore volume without changing the pore structure of the adsorbent. The resulting, so-called helium volume of porous solids $\overline{V}_{ads, He}$ can be calculated from the microbalance signal m^s and knowing V_{cont} as

$$V_{ads, He} = \frac{-(\rho_{He} V_{cont} + m^s)}{\rho_{He}} \tag{3}$$

Helium on activated carbon Norit R1

The skeletal volume of the adsorbent can be determined by means of buoyancy measurements with helium as fluid [3–6]. The values of the volume of the adsorbent in Fig. 2 were calculated for each experimental point at pressure p. Assuming helium not be adsorbed and only buoyancy occur, the buoyancy related volume of adsorbent can be calculated using the experimental point at pressure p and vacuum (p=0).

$$V_{\mathrm{ads}}(p)=-\frac{\Omega(p)-\Omega(p=0)}{\rho_{\mathrm{He}}(p)-\rho_{\mathrm{He}}(p=0)} \quad (4)$$

The experimental determination of the volume of the activated carbons by means of this method shows at low pressures a decrease of the volume. At a certain pressure the volume increase again with increasing pressure (Fig. 2 by example of Norit R1). This behavior can be explained by the pressure dependence of the volume of porous solids. First, with increasing pressure the adsorbent will be compressed by the surrounding fluid. The increase of the volume is caused by penetration of helium into the adsorbent combined with swelling of the crystal structure. Additionally, a temperature dependence can be observed here.

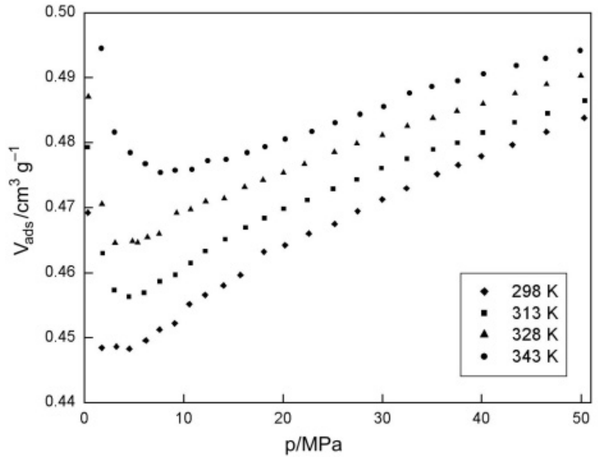

Fig. 2 Measurements of the buoyancy with helium on activated carbon Norit R1 at 298, 313, 328 and 343 K

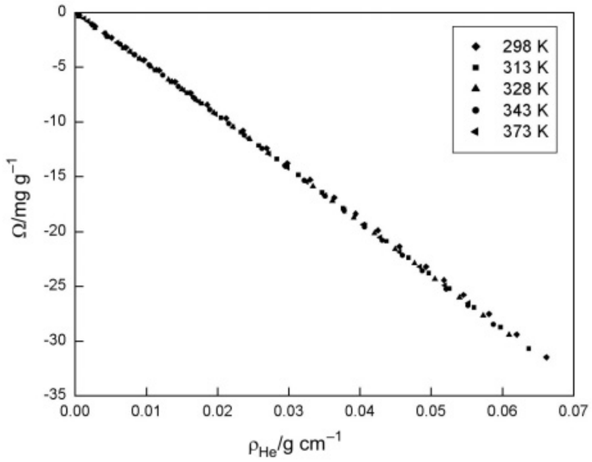

Fig. 3 Determination of helium-volume of Norit R1 at 298, 313, 328, 343 and 373 K

The classical method for determination of the volume of adsorbent is described in [4, 10, 11]. The results using this method are shown in Fig. 3, where the specific mass of the sample of adsorbent at the microbalance were plotted in dependence of the density of fluid [7, 8]. The slope of this isotherm is volume $\overline{V}_{\mathrm{ads,\,He}}$. On the basis of the temperature dependence of volume of adsorbent, $\overline{V}_{\mathrm{ads,\,He}}$ were determined for all measurement temperatures (Fig. 3). With increasing temperature an increase of the volume of porous solids can be observed (Table 3).

The Three-Parameter isothermal equation

The thermodynamic description of the excess is possible with the following three-parameter isothermal equation of the form:

$$\overline{\Gamma}(p,T)=\frac{f}{f+k_0\exp\left(\frac{v_0 p}{RT}\right)}I_0 \tag{5}$$

with I_0 – maximal loading/mg g^{-1}, k_0 – Henry-constant/MPa, v_0 – molar volume/cm^3 mol^{-1}, f – fugacity/MPa, p – pressure/MPa, R – gas constant/cm^{3}MPa mol^{-1} K^{-1}, T – temperature/K.

The equation was derived with a physical model based on the equality of the chemical potentials of the adsorbed and the fluid phase [1]. Until now this equation was applied for pressures up to about 15 MPa [2]. However, the first applications of the three-parameter isothermal equation on the gases methane, argon and nitrogen over the entire pressure range of up to 50 MPa showed significant deviation values (Fig. 4 by the example of methane at 298 K). These deviations become still larger in the all other cases. This was caused primarily by the necessary buoyancy correction, which was carried out with helium as reference gas. Therefore, this aspect requires more attention.

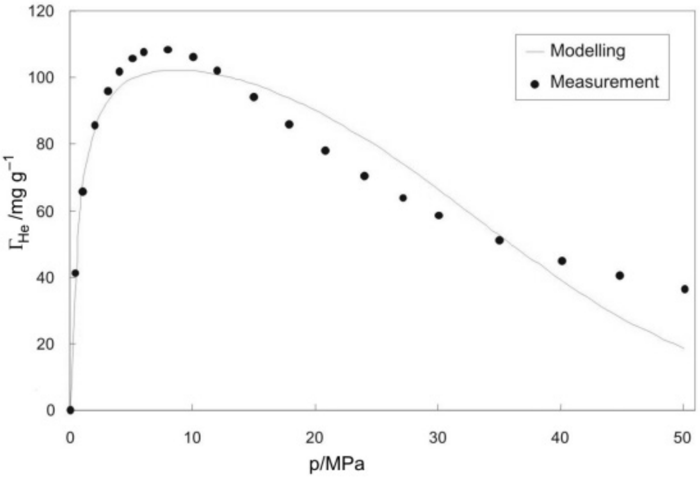

Fig. 4 The first modelling of the excess adsorption of methane on Norit R1 at 298 K

Extension of the Three-Parameter isothermal equation

The Eq. (5) results from Eqs (1), (2) and (5). Equation (6) allows the modelling of the specific reduced (equipment independent) mass $\overline{\Omega}$ with $\overline{V}_{\mathrm{ads}}$ as an additional fitting parameter:

$$\overline{\Omega}=\frac{f}{f+k_0\exp\left(\frac{v_0 p}{RT}\right)}I_0-\rho_{\mathrm{fl}}\overline{V}_{\mathrm{ads}} \tag{6}$$

with $\overline{\Omega}$ – specific reduced mass, $\overline{V}_{\mathrm{ads}}$ – specific volume of the adsorbent.

Therefore, it is proposed to use the precisely measured values of adsorption for the thermodynamic modelling without additional information (volume of the adsorbents). The parameters I_0, k_0, v_0 and $\overline{V}_{\mathrm{ads}}$ of Eq. (6) are fitted to the specific reduced mass measured directly at the microbalance. The fit was successful for all measured gases up to 50 MPa at different temperatures. Modellings for both adsorbents used were made. The results show (by the example of carbon dioxide on Norit R1, Fig. 5) that the Three-Parameter Isothermal Equation for the description of the adsorption isotherms for both different adsorbents are suitable (Norit R1 is a microporous adsorbent, and SCS-3 indicates a large proportion of meso- and macropores). The results of the modellings of methane, argon, nitrogen, carbon dioxide, ethane, ethylene and propane are summarized for Norit R1 at four different temperatures in Table 5 and for SCS-3 at two temperatures in Table 4, respectively.

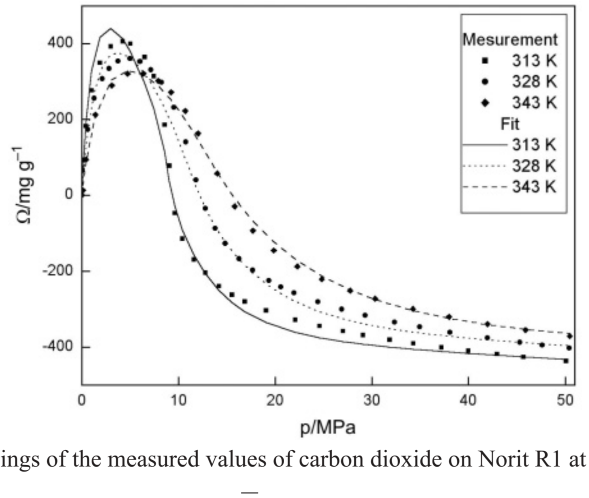

Fig. 5 Modellings of the measured values of carbon dioxide on Norit R1 at 313, 328 and 343 K

The volume of the adsorbent $\overline{V}_{\mathrm{ads}}$, determined from the respective modelling is, as expected, approximately identical. This proves the plausibility of the description.

The maximal loading I_0, which corresponds to the maximal quantity of adsorbate in the adsorption space, was, as expected, temperature-independent. The comparison of the maximal loading between both the measured activated carbons shows that the value I_0

depends directly on the micro-pore volumes of the adsorbents. Especially Norit R1, with a larger micropore volume has the larger I_0 for all gases presented. This corresponds to the reality and proves, therefore, the plausibility of the modelling.

Table 4 Thermodynamic quantities I_0, k_0, v_0 and $\overline{V}_{ads}$ for the different temperatures by measurements on SCS-3

SCS-3/Gas	T/K	I_0/mg g^{-1}	k_0/MPa	v_0/cm^3 mol^{-1}	$\overline{V}_{as}$/cm^3 g^{-1}
Argon	298	361.04	3.41	242.94	0.35
	313	360.77	4.50	225.33	0.36
Nitrogen	298	172.23	2.00	280.23	0.36
	313	184.83	2.74	267.32	0.36
Methane	298	121.75	1.14	379.94	0.33
	313	127.71	1.70	356.18	0.32
Carbon dioxide	313	1983.75	5.82	534.23	0.43

Table 5 Thermodynamic quantities I_0, k_0, v_0 and $\overline{V}_{ads}$ for the different temperatures by measurements on Norit R1

Norit R1/Gas	T/K	I_0/mg g^{-1}	k_0/MPa	v_0/cm^3 mol^{-1}	$\overline{V}_{ads}$/cm^3 g^{-1}
Argon	289	454.97	4.24	228.93	0.33
	313	452.24	5.33	221.61	0.34
	328	474.06	7.50	207.33	0.35
	343	463.09	9.14	197.93	0.36
Nitrogen	298	190.41	2.03	292.49	0.29
	313	192.93	2.76	282.27	0.30
	328	196.05	3.66	272.02	0.31
	343	197.64	4.86	259.98	0.31
Methane	298	144.45	0.95	414.23	0.27
	313	147.01	1.42	380.07	0.27
	328	140.97	1.74	353.92	0.30
	343	140.67	2.22	330.03	0.31
Carbondioxide	313	1286.58	2.07	697.53	0.44
	328	1319.93	3.56	524.16	0.40
	343	1300.95	5.52	384.45	0.44
Ethane	313	383.00	0.39	1404.74	0.37
	328	374.33	0.58	1064.82	0.37
	343	343.91	0.72	882.26	0.37
Ethylene	298	293.47	0.22	1165.73	0.35
	313	277.03	0.28	925.96	0.34
	328	246.41	0.33	836.97	0.33
	343	236.91	0.40	756.89	0.32
Propane	373	327.51	0.18	1987.85	0.39
	388	311.42	0.24	1542.09	0.38
	403	298.86	0.30	1418.68	0.37

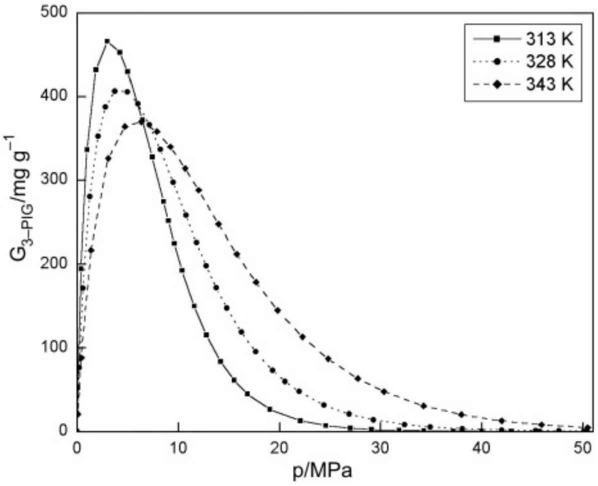

Fig. 6 Calculated adsorption excess of carbon dioxide on Norit R1 at 313, 328 and 343 K

The molar volume v_0 is a characteristic of the adsorbate phase. It is independent of the type of the adsorbent, which is acknowledged by the results of the fits. Consequently the molar volumes are identical for both adsorbents with the same gas.

From the dependence of the logarithm of the Henry-constant k_0 on the reciprocal temperature for the gases methane, argon and nitrogen the adsorption heats were calculated. The values of the adsorption heats are in an acceptable range.

From the calculated parameters the excess can be calculated. For all gases a common intersection results in the isotherms (for example Fig. 6 for carbon dioxide on Norit R1).

Gibbs surface excess

According to the Gibbsian thermodynamics the Gibbs excess amount adsorbed $\overline{\Gamma}_{\mathrm{He}}$ was also calculated using the so-called helium volume of porous solids $\overline{V}_{\mathrm{ads,\,He}}$ [9].

Conclusions

In the course of this project thermodynamically consistent sets of data of adsorption equilibria were measured and analyzed highly precisely by the use of a magnetic suspension balance at pressures of up to 50 MPa. Gravimetric measurements of adsorption with the pure gases methane, argon, nitrogen, carbon dioxide, ethane, ethylene and propane were carried out at 298 up to 403 K on two different adsorbents. The activated carbons were characterized with regard to their volume of pores and their internal surface.

The description of the excess by means of the original three-parameter isothermal equation, which was applied in the pressure range of up to 15 MPa is not possible due to the ‘unknown’ or inaccurate volume of the adsorbent. Therefore, it was proposed to use the precisely measured values of adsorption directly for the thermodynamic modelling without additional information (volume of the adsorbents). The excess is determined thereby subsequently from the parameters of the extended three-parameter isothermal equation.

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Notation

p	pressure	MPa
$\overline{\Gamma}_{\mathrm{He}}$	excess adsorption with buoyancy correction	mg g^{-1}
$\overline{\Gamma}_{3-\mathrm{PIG}}$	excess adsorption calculated from 3–PIG	mg g^{-1}
I_0	maximal loading	mg g^{-1}
k_0	Henry-constant	MPa
v_0	molar volume	cm^3 mol^{-1}
f	fugacity	MPa
R	gas constant	cm^3 MPa mol^{-1} K^{-1}
T	temperature	K
m^{s}	microbalance signal	mg
m	mass of adsorbent	g
$\overline{\Omega}$	specific mass of the sample of adsorbent at the micro-balance	mg g^{-1}
ρ_{fluid}	density of the fluid	g cm^{-3}
ρ_{He}	density of Helium	g cm^{-3}
V_{ads}	volume of the adsorbent	cm^3
$\overline{V}_{\mathrm{ads}}$	specific volume of the adsorbent	cm^3 g^{-1}
V_{cont}	volumen of container	cm^3
V_{cont}	volumen of container	cm^3

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