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MEASUREMENT OF GAS-ADSORPTION EQUILIBRIA VIA ROTATIONAL OSCILLATIONS

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Abstract

By using slow damped oscillations of a torsional pendulum, it is possible to determine the mass adsorbed on the surface of a porous sorbent without buoyancy effects from the frequency and the logarithmic decrement of the pendulum motion. In principle, it is then possible to determine directly the buoyancy-related volume V^{as} of the sorbent/sorbate system by combining the results with gravimetric measurements.

Measurements with a preliminary testing pendulum are presented for N_2 and CH_4 on the activated carbon Norit R1 Extra at ambient temperature in the pressure range $0<p<0.5$ MPa. Values for V^{as} calculated from these measurements and gravimetrically determined data are presented and discussed to a certain extent.

Keywords: gas-adsorption system, gravimetric adsorption measurements, rotational pendulum

Introduction

Either gravimetric or volumetric measurements of gas-adsorption equilibria allow only determination of the difference

$$\Omega = m - \rho^{f} V^{as} \tag{1}$$

between the net mass adsorbed m and the buoyancy-related product of the volume V^{as} of the adsorbent/adsorbate system and the density ρ^{f} of the fluid (adsorptive). In the case of the gravimetric method, this is due to the buoyancy exerted by the adsorptive on the adsorbent/adsorbate system. For volumetric measurements, the dead space must be determined, i.e. the volume V^{as} of the adsorbent/adsorbate system is needed. This quantity is generally unknown and still poses an obstacle when porous sorbents are used. To provide a phenomenological definition, we assume it to be the sum of a certain volume V^{s} of the sorbent,

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which in principle, i.e. even at very high pressures, is not accessible to sorptive molecules, and a ficticious volume calculated from the sorbate mass m by dividing it by the density of the sorptive in a liquid reference state ρ_o^f, which in principle can be chosen arbitrarily:

$$V^{as} = V^s + \frac{m}{\rho_0^f} \tag{2}$$

For the sake of simplicity, we have chosen ρ_o^f here to be the density of the sorptive in its liquid state at ambient pressure, assuming thus that the sorbate is a kind of two-dimensional liquid layer at this density. Also, the void volume V^s is sometimes simply assumed to be a constant quantity, which can be approximated reasonable well by its helium-volume (V_{He}^s), i.e. the internal volume of a porous structure inaccessible to helium atoms, which at ambient temperature (298 K) and moderate pressure (p<1 atm) are assumed not to be adsorbed at all. However, it should be taken into account that in principle the volume V^s may very well depend on both the size of the sorptive molecules and the external pressure exerted by them on the sorbent. Indeed, any solid sorbent structure may likewise be squeezed by the external sorptive molecules or swelled by those molecules of the sorptive which have already intruded into the inner pore system of the sorbent. These effects, though normally very small, have been investigated for clay minerals among others by Tvardovski *et al.* [1].

As a result of this discussion, we should bear in mind that the volume V^{as} will normally depend on the sorptive used and the pressure exerted by the sorptive on the sorbent system. Therefore, Eq. (2) serves only as an approximation of the as yet unknown volume V^{as} of the adsorbate/adsorbent system.

It is sometimes argued that the volume V^{as} can simply be approximated by the helium-volume mentioned above, i.e. instead of Eq. (2) one assumes

$$V^{as} \cong V^s \cong V_{He}^s \tag{3}$$

However, this model of a constant, pressure-independent volume may lead to thermodynamic inconsistencies [2], which basically result in a violation of the Second Law. Hence, the use of Eq. (3) should be avoided.

By using slow damped oscillations of a torsional pendulum, it is possible in principle to determine the adsorbed mass without buoyancy effects [3]. By using the inertia of mass and not its gravity, no assumption concerning the volume V^{as} of the adsorbent/adsorbate system should be needed. Indeed, as has been shown in [3], the relative increase in mass of the adsorbent due to gas adsorption can be calculated from the frequency and the logarithmic decrement of the slow damped rotational oscillations of the pendulum in the gaseous atmosphere and in vacuum, respectively.

Experimental set-up

Figure 1 shows a sketch of the principle of the torsional pendulum. The actual design of the pendulum follows the design of an oscillating disk viscometer as given by Kestin *et al.* [4]. The pendulum consists of an aluminum disk (radius R_a=75 mm, thickness d=11 mm) suspended on a thin torsional wire (radius r_w=0.0625 mm) made of a platinum alloy. The disk is stabilized by a stem bearing a mirror. Above and below the oscillating disk, fixed plates are attached to avoid secondary flows. The gap b between the oscillating disk and each plate is 5 mm. The outer ring of the disk is entirely filled with preferably pulverous adsorbent of mass m^s and specific bulk volume V^*. The whole oscillating disk system is included in a pressure vessel withstanding pressures up to 5 MPa at ambient temperature.

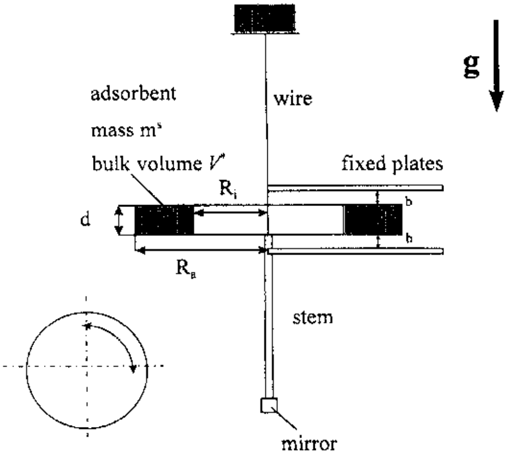

Fig. 1 Sketch of principle of rotational pendulum

The temperature within the pressure vessel is measured by using two Pt 100 resistance thermometers obtained from Philips Thermocoax. Pressure measurements are made with a pressure gauge (range<65 bar) obtained from Burster Präzisionsmeβtechnik, with a relative uncertainty of 0.1%.

The rotational motion of the disk suspended on the torsional wire is initiated through manual turning of the entire pressure vessel containing the oscillating disk system. Of course, this should be done cautiously in order to avoid uncontrolled and/or irregular oscillations of the pendulum. Given this, we could not observe any influence of the experimenter on the resulting oscillation during our experiments. After initialization, the free motion of the system can be described by a damped harmonic oscillation:

$$\alpha(t) = \alpha_0 e^{-\Delta\omega t}[\cos(\omega t) + \Delta\sin(\omega t)] \tag{4}$$

Here, $\alpha(t)$ is (time-dependent) angular deflection of the pendulum, α_o is the initial amplitude, ω is the angular frequency and Δ is the logarithmic decrement related to the damping of the motion. It should be noted that the angular frequency ω and the logarithmic decrement Δ are (within the limits valid for damped harmonic oscillations) parameters that are independent of the motion and thus independent of the initial amplitude α_o. The mirror attached to the stem reflects a laser beam to allow observation of the motion of the pendulum, as shown in Fig. 2.

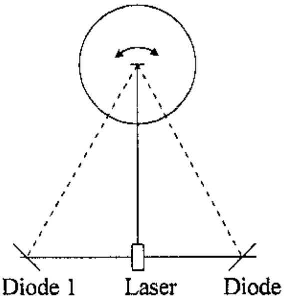

Fig. 2 Data acquisition for observing the motion of a pendulum

The angular frequency ω and logarithmic decrement Δ of the slow damped oscillation of the pendulum disk are then calculated by fitting the parameters of the damped harmonic oscillation in Eq. (4) to measurements of times (t_i) at which the reflected laser beam passes through diodes 1 and 2, respectively. The procedure is described by Vogel *et al.* [5] for an oscillating disk viscometer. It should be mentioned that the angles indicating the positions of the diodes need not be known, but they do have to be fixed through the period of measurement. Assuming the pendulum to be rotional symmetric, the mass m of gas adsorbed in the mass m^s of a porous solid placed on the pendulum is then determined from the motion of the empty disk in vacuum (*), the disk loaded with adsorbent in vacuum (0) and the loaded disk in the gaseous atmosphere (E) through the following relation [3]:

$$\frac{m}{m^s}=\frac{\dfrac{1+\Delta_0^2}{1+\Delta_E^2}\left(\dfrac{\omega_0}{\omega_E}\right)^2-1}{1-\dfrac{\Delta_0\omega_0}{\Delta^*\omega^*}} \tag{5}$$

This relation holds for small angular deflections and slow motions of the pendulum, i.e. low Reynolds numbers for the flow induced by the motion. Further, secondary flows, prevented by the two fixed plates above and below the disk, are excluded. Additionally, it should be noted that in order to apply Eq. (5) it is not necessary to know the exact geometric form or structure of the pendulum as long as it can be assumed to be rotational symmetric. That is, Eq. (5) holds for any rotational pendulum as long as it is rotational symmetric and secondary flows of the adsorptive can be neglected (cf. the fixed plates in Fig. 1).

Results

Measurements were carried out oscillometrically for the pure gases N_2 and CH_4 on the activated carbon Norit R1 Extra with preliminary testing equipment in the pressure range $0<p<0.5$ MPa at ambient temperature. The disk was filled

Table 1 CH_4 on Norit R1 Extra

p [bar]	Oscill. m/m^s [mg/g]	Grav. m/m^s [mg/g]	V^{as} [cm^3/g]
0.21	–	5.17	–
0.37	–	7.96	–
0.52	–	10.51	–
0.77	–	13.89	–
1.01	–	17.04	3.05
1.19	21.96	–	2.58
3.03	–	36.77	1.34
3.11	39.19	–	1.33
4.11	45.37	–	1.31
5.04	–	45.20	1.33

Table 2 N_2 on Norit R1 Extra

p [bar]	Oscill. m/m^s [mg/g]	Grav. m/m^s [mg/g]	V^{as} [cm^3/g]
0.77	–	7.83	5.78
1.04	–	10.72	5.30
1.21	19.17	–	5.06
2.22	–	19.87	4.29
2.22	31.05	–	4.29
3.10	40.33	–	3.95
3.20	–	26.76	3.93
4.10	49.69	–	3.73
4.16	–	32.17	3.72
5.32	59.90	–	3.55

with pellets of activated carbon with a specific bulk volume of 2.2 cm^3/g. A Langmuir-type adsorption isotherm was used to correlate the data.

The maximum error in determining the ratio m/m^S for the preliminary testing equipment was found to be 0.6%. This fairly high inaccuracy is due to the still insufficient method used for evaluation of the parameters ω and Δ of the slow damped oscillation of this preliminary testing device.

The isotherms obtained oscillometrically were compared with isotherms for the reduced mass Ω determined gravimetrically. The apparent volume V^{as} of the adsorbent/adsorbate system for each gas was calculated from these measurements by inverting Eq. (1), i.e.

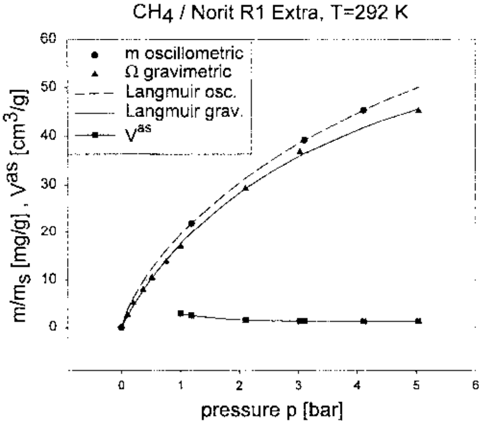

Fig. 3 Comparison of oscillometric/gravimetric isotherms and volume of adsorbent/adsorbate system of CH$_4$ on Norit R1 Extra

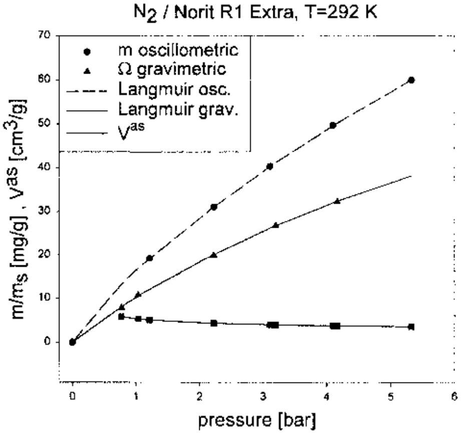

Fig. 4 Comparison of oscillometric/gravimetric isotherms and volume of adsorbent/adsorbate system of N$_2$ on Norit R1 Extra

$$V^{\mathrm{as}} = \frac{(m - \Omega)}{\rho^{\mathrm{f}}} \tag{6}$$

The experimental results for CH_4 on the activated carbon Norit R1 Extra are shown in Table 1. Table 2 presents the corresponding results for N_2. Figures 3 and 4 depict the same results in graphical form.

Conclusions

As expected, for both gases, CH_4 and N_2, the isotherms obtained oscillometrically exhibit higher values than the reduced masses Ω determined gravimetrically. The calculated volumes V^{as} display the same trend for both gases. In the low-pressure range covered by these preliminary experiments, they decrease with increasing pressure, approaching what seems to be a constant value at more elevated pressures. However, at very low pressures the values calculated for V^{as} seem to tend to infinity. From theory, one would expect a linear increase in volume of the adsorbent/adsorbate system with increasing pressure, due to the number of molecules adsorbed. At least, the results for CH_4 indicate that the values calculated for V^{as} may increase again at pressures p>5 bar.

The values for V^{as} calculated from measurements with N_2 are larger than the bulk volume of the adsorbent used. However, the values calculated for V^{as} from measurements with CH_4 at pressures p>3 bar are of the correct order of magnitude.

To investigate the discrepancies between theory and these preliminary results, further measurements need to be carried out. For example, the results of oscillometric measurements might include the mass accelerated in a boundary layer of the flow around the pendulum disk, which theory does not account for. This can be checked by performing oscillometric measurements with an inert filling of the disk (e.g. glass beads) which allows any increase in mass due to adsorption to be neglected. More accurate measurements in the low-pressure region and an extended pressure range of the measurements are also necessary. Such measurements are currently under way in our laboratory and will be reported elsewhere [6].

* * *

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