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# How to determine the correct sample volume by gravimetric sorption measurements

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**Abstract** Determining sample volumes for gas sorption measurements by pycnometry is often considered to be trivial, as it is assumed that helium does not sorb to the sample material. The aim of this study is to show the contrary, i.e., helium may sorb to certain polymers and to introduce the proposed helium-sorption correction algorithm for compensating for such helium sorption. By using a Rubotherm magnetic suspension balance, the volume of a commercial polyether block amide (Pebax© MH 1657) was analyzed with the new algorithm based on kinetic data. Helium was found to sorb to all tested Pebax© MH 1657 samples. Compared to the conventional calculations, the proposed algorithm yielded more precise sample volumes. To ensure accurate sorption measurements of any gas, it is important to take into account possible helium sorption.

**Keywords** Gravimetric sorption · Helium sorption · Volume determination · Buoyancy correction · Gas sorption

## 1 Introduction

Adsorption is a well-established method for gas separation in industry and laboratory-scale studies. To find the optimal adsorbent for any given separation process, sorption and desorption properties of the adsorbent are first tested at various pressures and temperatures. A fast and simple testing method to estimate the sorption capacity of an adsorbent is to measure the breakthrough curve using a packed-bed column. In this case, the adsorbent is characterized by its weight and packing density; its real volume is unimportant.

Adsorption capacity can be measured more accurately using volumetric or gravimetric methods. Whereas volumetry is the conventional means to indirectly determine the weight of a sorbed gas, gravimetry is the more precise method to directly measure it.

For both volumetric and gravimetric measurements, certain calibration measurements are necessary before beginning gas sorption experiments. For volumetry, it is important to calibrate all relevant volumes. In gravimetry, it is important to first weigh the empty balance and the empty sample holder as well as to measure the volume of the empty sample holder. More detailed descriptions of both methods can be found in the literature (Belmabkhout et al. 2006; Condon 2006; Keller and Robens 2003; Keller and Staudt 2005).

In both techniques only the so-called ‘reduced mass’ $\Omega$ is actually measured, because the actual volume of the sample inherently leads to a displacement of the surrounding gas:

$$\Omega = m_{\mathrm{sorbent}} - \rho \times V_{\mathrm{sorbent}}, \tag{1}$$

whereby $\rho$ is the density of the surrounding gas.

This displacement of the gas causes either a difference in pressure (volumetry) or affects buoyancy and, thus, causes a change in weight of the sample (gravimetry). Consequently, without knowing the precise sample volume, sorption data would be incorrect.

The most common volumetric method to determine sample volume is to use a gas pycnometer. The pycnometer consists of two calibrated vessels connected by a valve, whereby one of the vessels contains the sample and the other is filled with a defined amount of helium. Once the

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valve is opened, the helium flows into the sample vessel. Using a gas equation of state, the sample volume can then be calculated from the measured changes in temperature and pressure of the helium.

Unlike the volumetric method which requires at least two devices, gravimetry applying a magnetic suspension balance (MSB) (see Fig. 1) only requires one device to determine volume and mass of a given sample. With the latter technique, the weight of the sample as well as the pressure and temperature of the gas in the vessel are continuously recorded. Due to buoyancy effects, the weight of the sample decreases with increasing gas pressure. After several pressure increments, the weight of the sample at the end of each increment is plotted as a function of the density of the surrounding gas (see Fig. 3). As a result, the volume of the sample as well as the sample mass at zero pressure ('vacuum mass') can be calculated (Keller and Robens 2003; Keller and Staudt 2005). All the equations relevant for the current study are given in the Sect. 2.2.

For both volumetry and gravimetry, the following is assumed: Being an ideal gas, helium at room temperature and pressures of about 1 bar does not interact with the sample. Even though the sorption of helium can often be neglected in volume-determination experiments, this is not always true; helium may sorb to particular materials. Since it is very relevant to proof this sorption experimentally, one aim of this paper is to show that helium may sorb to particular polymers such as the polyether block amide Pebax® MH 1657 used for gas separation membranes. Another aim is to introduce the proposed helium-sorption correction (HSC) algorithm. The current paper will first present a summary of helium sorption studies on porous media. Then, it will present the proposed HSC algorithm used to analyze the raw, sample weight data.

### 1.1 Helium sorption on porous media

To our knowledge, no systematic study of helium sorption in polymers has been published. Therefore taking a closer look at helium sorption studies on porous, inorganic material is a good starting point, to learn, if these methods are applicable for polymers as well.

Since the 1950s, several different helium sorption studies, most of which involved volumetry, have been applied on porous materials at low temperatures (Aston and Mastrangelo 1951; Aston et al. 1955; Mastrangelo and Aston 1951; Steele and Halsey 1954; Springer et al. 1969). Here, both sample volume and sample surface area are used as reference parameters.

An example of this combined sample volume and surface area approach on porous media was described by Springer et al. (1969). This study applied a combination of a sample volume, determined via the buoyancy effect occurring during immersion in liquid nitrogen, and of a correction based on surface-area considerations. Surface areas were determined using liquid nitrogen adsorption, as it is most common until today. As nitrogen was applied here as an inert gas as well as an adsorbent, the validity of this work is questionable.

Nowadays, however, helium is the inert gas of choice for such sample volume studies. In this regard, one relevant study by Maggs et al. (1960) concerns volumetric experiments with helium on different types of carbon subjected to a broad temperature range (77–580 K). This publication focuses on the effect of helium adsorption on the determination of sample densities. The authors state, that an adsorption isotherm of helium over a limited pressure regime might be linear and therefore would stay undetected during the assessment of the apparent dead volume (i.e. free space) of a volumetric apparatus. As a result, they chose to vary the temperature instead of the pressure, because gas adsorption onto a porous medium usually does not increase linearly with decreasing temperature. They hereby show that the apparent dead volume of the volumetric apparatus seems to increase with decreasing temperature, if it is assumed that helium does not adsorb to the porous medium. The higher the beginning temperature is, the less pronounced is the effect of temperature increments.

Moreover, Suzuki et al. (1987) published a series of dead volume measurements applying a temperature range from 77 to 673 K. Like Maggs et al, they assumed that the helium adsorption at the highest measured temperature is negligible. From the adsorption data measured at several discrete temperatures, a first-order correction was calculated for the adsorption constant of helium on different porous material. From an experimental point of view, this method is highly complex, since it involves ten different real or apparent volumes.

More recently Staudt et al. (1997) performed gravimetric measurements of helium adsorption on activated carbon. Over a period of several weeks, no state of equilibrium of adsorption could be observed. Furthermore these researchers found, volume deviations about 2 % at room temperature using a helium pycnometer and pressures of up to 120 kPa (Keller et al. 1999). For more precise volume determination, other authors recommend using either high temperatures and low pressures or using other gases/methods (e.g. mercury porosimetry) (Keller and Staudt 2005; Robens et al. 1999).

Sircar used both volumetry and gravimetry to determine the volume of porous samples with helium as test gas (Sircar 2001). Moreover Talu and Myers (2001) compared simulation and empirical results to obtain better insight into evaluating Gibbs' dividing surface. This work, based on the aforementioned experimental work of Sircar, concerns the determination of helium isotherms to correct sample volume measurements with helium.

As a follow up on his previous work on helium void measurements, Sircar published another study in (2002). In this work he develops a method to calculate the true Henry's Law constant from helium sorption measurements performed over a large temperature range. In contrast to several authors mentioned before, he raises the awareness, that helium sorption at high temperatures is not necessarily negligible, even though the measured helium void volume reaches a constant value for high temperatures. Based on adsorption thermodynamics it is carefully argumented, that the linear extrapolation proposed by Suzuki et al can lead to large deviations from the real Henry's Law constant. For the application of Sircar's method the isosteric heat of adsorption of helium ($q^0_{He}$) is needed. Experimentally $q^0_{He}$ can be determined by plotting the apparent Henry's Law constant over the temperature in the low temperature regime—meaning at temperatures around 77 K. As all previous methods, this method only leads to reasonable corrections, if measurements over a temperature range of several hundred Kelvin are performed.

Gumma and Talu (2003) developed the aforementioned methods even further by using a MSB and measuring the sample weight at different temperatures and pressures. Here they define a so-called β-value: $\beta = (\alpha + V_{SC})/m_s$; where $\alpha$ is the slope at the origin of the raw weight data plotted as a function of gas density of helium and $V_{SC}$ denotes the volume of the sample container and $m_S$ the vacuum mass of the sample. All of these parameters can be directly measured. For their correction for helium sorption, a huge amount of data measured at different temperatures, was necessary, because a minimum of β has to be found for the evaluation of helium sorption. This method is both experimentally and computationally tedious.

All the previously cited studies infer that the determination of helium adsorption on porous media is a dilemma. On one hand, the sample volume has to be known in order to evaluate the helium sorption. On the other hand, however, knowledge about the helium sorption is necessary in order to ascertain the sample volume. Altogether these studies on porous media point to the fact that helium adsorption to the adsorbent may significantly influence the measurement of sample volumes.

With respect to the selection of the temperature range, a high temperature range is only feasible provided that the experimental set-up and the adsorbent tolerate it. Many experimental devices for analyzing organic material simply do not tolerate high temperatures over 200 °C. Moreover, polymers show very different properties below and above their particular glass transition temperature or they might melt and decompose at high temperatures. Consequently, the methods for correcting helium adsorption onto porous media are not applicable for polymers.

The current study with the block copolymer Pebax® MH 1657 has discovered that this polymer considerably absorbs helium. This absorption will be elucidated in the following Experimental section.

## 2 Experimental

### 2.1 Materials

Pebax® MH 1657 was supplied in small pellets by the company Arkema. Pebax® MH 1657 is a block copolymer composed of a polyethylenoxide as one block and a Nylon 6 as the other.

Ethanol was purchased with 96 % purity (Ph. Eur., pure grade) from Carl Roth GmbH & Co. KG. Room-temperature vulcanizing polydimethylsiloxane (PDMS, RTV 615 Part A and B) was purchased from Momentive™.

To prepare thick Pebax® MH 1657 films, 12 wt% of the polymer was mixed with ethanol and water (70:30 wt%) and refluxed at 80 °C for 24 h. The resulting polymer solution was filtered through a metal filter (pore size 50 µm) and poured into a Petri dish to a height of 5 mm. To slowly evaporate the solvent, the dish was kept at room temperature in a fume hood for several days. After that, the sample was dried and degassed at 60 °C under vacuum until no further weight loss could be detected.

A 2mm-thick PDMS film was prepared as follows: The two silicone components RTV615 Part A and B were mixed in the recommended ratio of 10:1 by weight, poured in a Petri dish to a height of 2 mm and degassed at a pressure of 10 mbar until no bubbles could be seen. After this degassing, the film was cured at 80 °C and ambient pressure for 2 h. Before use, the film was degassed analogously to the Pebax® MH 1657-film.

### 2.2 Methods

#### 2.2.1 *Working principle of a magnetic suspension balance*

For all experiments a MSB was used. A MSB measures the weight of a sample enclosed in a pressure vessel made of non-magnetizable stainless steel. The sample holder is coupled electromagnetically with the microbalance. Because the balance is physically separated from the sample chamber, the MSB can be operated at a broad pressure and temperature range. The equipment used for this study is operable at pressures ranging from zero to 30 bar and at temperatures from −10 to 180 °C.

As Fig. 1 illustrates, the sample holder may have two different positions (see arrows): one used to measure the sample weight and the other used to calibrate and tare the balance.

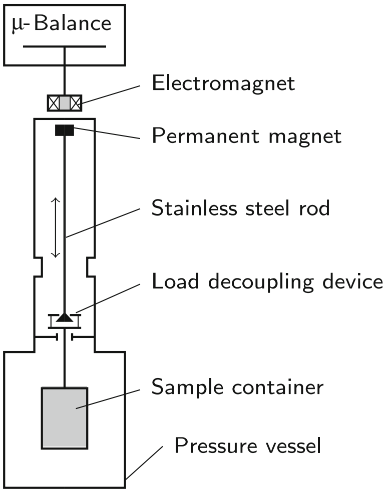

**Fig. 1** Scheme of a magnetic suspension balance (MSB)

All laboratory balances show a weight drift if ambient conditions vary. Thus, they need to be occasionally tared and calibrated. During a sorption measurement, this drift of weight can considerably influence the results if nothing is done to compensate for it. A MSB has a so-called zero position where the sample container is decoupled from the balance, and only the weights of the permanent magnet and the stainless steel rod are measured. The balance software applies an algorithm that uses the recorded zero point data to compensate for the balance drift.

As the pressure in the pressure vessel changes drastically during a sorption measurement, another correction is needed to eliminate the buoyancy effect. Archimedes' Principle shows that the measured weight of a given sample depends on the sample volume. Thus, the volume of each sample has to be determined.

Such a determination is considered to be daily routine. However, the precise determination of the sample volume is very important and cannot be neglected. Similarly, as helium is assumed not to react with the sample, this oversight may lead to a systemic error in the actual sorption measurement.

### 2.2.2 *Conventional measurement routine using a magnetic suspension balance*

In gravimetry, volumes and vacuum masses of the sample holder and sample must be precisely measured. These four parameters are determined by performing two measurements. Afterwards, the sorption of a particular gas can be measured.

### 2.2.3 *Mass and volume determinations*

The respective volume and vacuum masses of the sample holder and sample are measured with the same routine: First only the sample holder volume and mass are measured, followed by that of the sample. The whole measurement with the MSB can be summarized as follows:

- Degassing and tempering of the pressure vessel.
- Incremental pressurization of the pressure vessel with helium at constant temperature.
- Evaluation of the measured data to determine volume and mass of the sample holder/ sample.

The required parameters are calculated as follows:

- The measured balance read $m_{\mathrm{Bal}}$ is plotted as function of the density $\rho_{\mathrm{gas}}$ of the surrounding gas atmosphere.
- A line of best fit is numerically determined.
- The volume V of the sample/ sample holder corresponds to the absolute value of the slope, whereas the vacuum mass $m_0$ is determined from the y-intercept:

$$m_{\mathrm{Bal}} = m_0 - V\rho_{\mathrm{gas}} \tag{2}$$

This evaluation method is first applied to the data of the empty sample holder, so that the volume and weight are known. In a second iteration—the so-called buoyancy measurement—the same procedure is conducted for the filled sample container. In this case, the combined volume and mass of sample holder and sample are measured. This last step is crucial in order to find out if the typically assumption of helium as a non-interacting gas holds. The Results section gives a detailed analysis of possible helium sorption and the proposed HSC Algorithm to compensate for it.

### 2.2.4 *The sorption measurement*

After the respective volumes and masses of the sample holder/sample have been measured, the actual sorption of the given gas is measured. The relevant question for any given sorption study is: How much gas is ad- or absorbed by a sample material at a certain pressure and at constant temperature. To gain this knowledge, the sample has to be measured till equilibrium, i.e. no weight change, is reached. This can take several days or even weeks, depending on factors such as the diffusion coefficient or the sample thickness. If one is only interested in a rough estimation, the measurement can be stopped automatically after a user-defined termination condition has been reached.

To precisely analyze sorption data, the respective volumes and vacuum masses are used to compensate for the effect of buoyancy. These parameters are usually plotted as a sorption/desorption isotherm, i.e. the amount of gas sorbed per amount of sample as a function of the surrounding pressure. The units used to describe the different values vary considerably. For example, it is common to characterize the sorbate gas in terms of volume at standard pressure, by mol or by weight. The sample, however, is either characterized by its weight or its volume. For pressure, atmospheres, psi, bar, gas density or normalized pressures are used. Consequently, the comparison of sorption data published by different authors is tedious.

In order to validate the measuring routine and the computations for evaluating the sorption of a given gas, PDMS was used as a model sample of a rubbery polymer. By contrast, Pebax® MH 1657 was used to represent a semi-crystalline polymer.

## 3 Results and discussion

The aforementioned routine to determine all necessary volumes and masses works well for a completely rubbery polymer sample such as PDMS. As expected, the measured sample weight drops due to the effect of buoyancy; after the maximum pressure has been reached, the sample weight stays stable (Fig. 2). All figures in this section only show a selection of the many data points for the sake of simplicity.

If after several pressure increments the sample weight is plotted as function of the gas density, the diagram ideally shows a straight line (Fig. 3). The determined sample density (1.08 g $\text{cm}^{-3}$) agrees with the specifications in the material data sheet. The measured sorption coefficient for $CO_2$ of 1.55 $\text{cm}^3$(STP) $\text{cm}^{-3}$(polym.) $\text{atm}^{-1}$ at 23 °C is in good agreement with the literature value of 1.39 $\text{cm}^3$(STP) $\text{cm}^{-3}$(polym.)$\text{atm}^{-1}$ at 35 °C (Fleming and Koros 1986), since gas sorption usually decreases with increasing temperature.

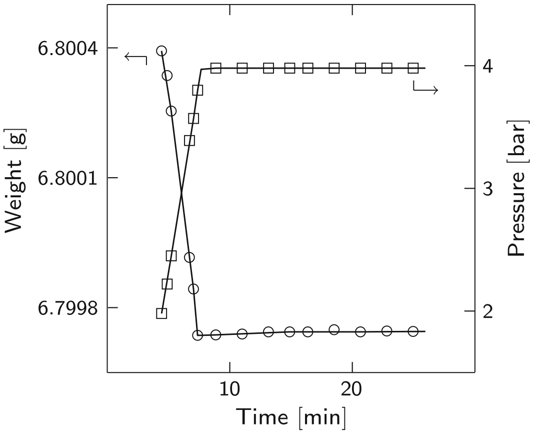

**Fig. 2** The influence of buoyancy: The weight of PDMS (*white circle*) as a function of time as well as the pressure (*white square*) of helium as a function of time. As the pressure of helium increases, the weight of PDMS decreases and remains stable after the maximum He-pressure has been reached

When using semi-crystalline Pebax® MH 1657 the same way as the PDMS sample, surprisingly a negative sample volume resulted. This results in a negative sorption coefficient, if calculated in terms of the mass of $CO_2$ in g with respect to the sample weight. A closer look at the kinetic weight data of the buoyancy measurement with helium indicated helium sorption, because at constant helium pressure the weight of the sample increased (see Fig. 4). This is impossible under the common assumption that helium does not sorb. Consequently, a more precise method to compensate for this proven helium sorption had to be found.

As explained earlier, methods developed for inorganic porous material are not applicable to polymers, because changes in temperature always alter the properties of polymers. Another method to determine the density of polymers is immersion in liquids of different density until the polymer sample floats. Since Pebax® MH 1657 is hydrophilic, immersing the polymer in hydrophilic liquids will corrupt the density measurements; the results will be wrong. Therefore, this is not applicable.

A better approach to determine the sample density is to use the kinetic data. The kinetics data revealed that the helium sorption is relatively slow and that a distinct minimum in the kinetic curve can be seen, as the pressure reaches its maximum value (see Fig. 4). If one assumes that the amount of helium sorbed during the rise in pressure is negligible, one can calculate the mass of helium sorbed during each pressure increment. As Fig. 5 illustrates, the variable, $\Delta m_i$, denotes the difference between the minimal and maximal weight of the sample during one pressure step. This variable can be calculated for subsequent pressure increments.

Having calculated $\Delta m_i$ for all pressure steps, one begins correcting the sample weight at the start of the second pressure step by subtracting the calculated sample mass

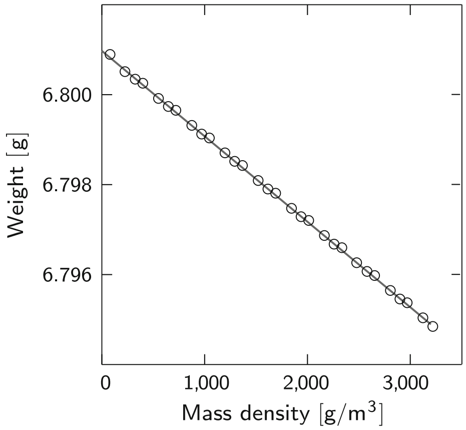

**Fig. 3** The weight of PDMS (*white circle*) as a function of mass density of helium

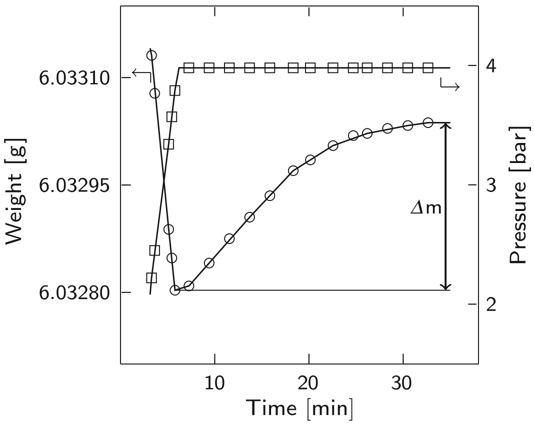

**Fig. 4** The weight of Pebax® MH 1657 (*white circle*) as a function of time as well as the pressure (*white square*) of helium as a function of time. As the pressure of helium increases, the weight of Pebax® MH 1657 decreases till it reaches a minimum. After that the pressure is kept stable, but the sample mass increases again. This indicates helium sorption

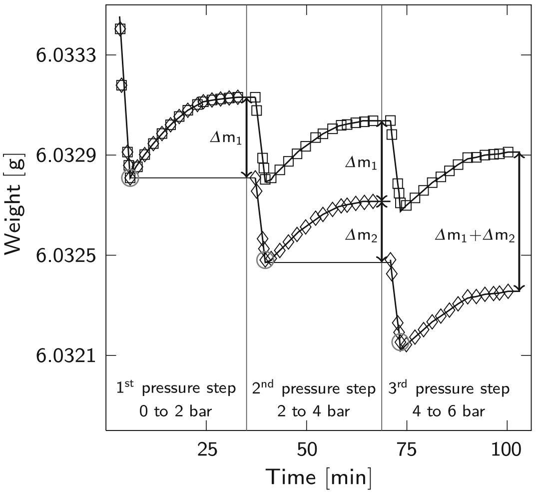

**Fig. 5** The sample weight during pressure increments as a function of time, whereby *white square* indicates the measured sample weight, *white diamond* denotes the helium sorption-corrected weight and *open circle* delineates the minimal sample weight at each pressure step

difference for the first pressure step ($\Delta m_1$), as depicted in Fig. 5.

After the sample weight data has been corrected for the second pressure step, one corrects the sample weight for the third pressure step as follows: The sum of the masses of the sorbed helium during the first and second pressure step ($\Delta m_1 + \Delta m_2$) are subtracted. This subtraction is iterated until the last pressure increment has been corrected for. The following equation gives this corrected sample mass

$$m_{j,\mathrm{cor}} = m_j - \sum_{i=1}^{j} \Delta m_i, \tag{3}$$

where the index $j$ denotes the current pressure step and $i$ indicates all previous pressure steps.

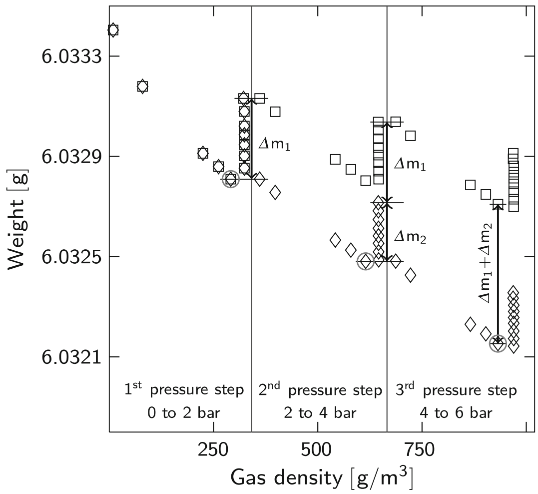

**Fig. 6** The corrected and uncorrected weight data from Fig. 5 now plotted as a function of the helium density

The sorption occurring during each particular step cannot be corrected with Eq. (3) alone. Thus a curve of the corrected data as a function of helium density, will not yield a straight line, but rather a line with some “knobs” at the maximal pressure of each increment (see Fig. 6). If the data is linearly fitted (Eq. 2), the slope has the same value but the y-intercept varies. This means that a final correction is needed. As Eq. (4) shows, instead of using all data points of a pressure-step, only the minimal value is used for calculating the sample mass at vacuum and the sample volume:

$$m_{j,\mathrm{cor}} = m_{j,\mathrm{min}} - \sum_{i=1}^{j} \Delta m_i, \tag{4}$$

The above formula represents the proposed HSC algorithm. This algorithm can be included in automated evaluation routines for gas sorption data.

### 3.1 Application to experimental data

Figure 7 shows the discrepancy between the uncorrected data points and the helium-sorption corrected data points obtained with the proposed HSC algorithm. If the uncorrected conventional data are used, the absolute value of the slope maybe smaller than that obtained for the empty sample holder alone. This would result in a negative volume being measured. Consequently, the proposed HSC algorithm was applied to several complete datasets for evaluating $CO_2$-sorption on Pebax® MH 1657.

For a thick Pebax® MH 1657 film (200 µm), a negative sample density of $-2.19\ \mathrm{g\ cm^{-3}}$ was calculated with the conventional approach. Compared to the dataset corrected

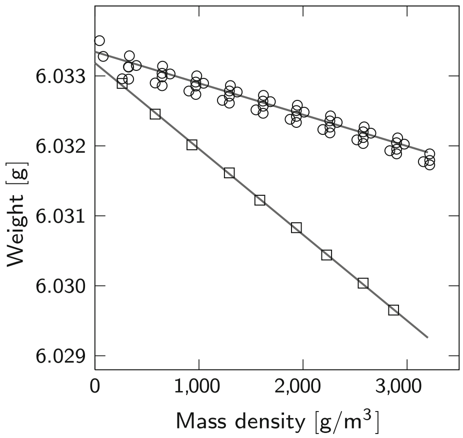

**Fig. 7** Weight of Pebax® MH 1657 as a function of mass density of helium, whereby *open circle* indicates the raw and *white square* the helium sorption-corrected weight data

with the HSC Algorithm, a sample density of 1.01 g cm$^{-3}$ was determined. Though this is smaller, than the one reported in the material data sheet (1.14 g cm$^{-3}$), it is much closer to it than the former value obtained conventionally.

The discrepancy between the corrected value and that reported in the material datasheet can be explained as follows: First, different processing of a complex block copolymer can lead to different structures and therefore different sample densities. Second, sample densities measured with different methods tend to vary. As discussed before in this current paper the liquid immersion technique applied for the material data sheet value may also lead to wrong densities for hydrophilic polymers.

Table 1 gives an overview of the various sorption coefficients for $CO_2$ on Pebax® MH 1657 measured with different methods and found in literature.

Depending on the sorption method used and the temperature selected, the $CO_2$ sorption coefficients vary: In a temperature range from 25 to 35 °C, the yielded $CO_2$ sorption coefficients are $7.92 \times 10^{-6}$ to $1.33 \times 10^{-5}$ cm$^3$(STP) cm$^{-3}$Pa$^{-1}$. These deviations imply that all the above methods of measuring $CO_2$-sorption are not comparable and therefore cannot be used for validation of the algorithm.

The highest value was measured by a gravimetric measurement with an IGA 002 from Hiden Analytical. One can see, that our results with $1.48 \times 10^{-5}$cm$^3$(STP) cm$^{-3}$Pa$^{-1}$ compare best to this other gravimetric measurement published by Marcq et al.

Another interesting facet of the use of sorption corrected volumes, is the fact, that without correct volumes unrealistic sorption and desorption isotherms might be calculated. One example for an unrealistic sorption isotherm is given in Fig. 8, if the same experimental data set is evaluated using the HSC-Algorithm, the sorption curve shows realistic behaviour as depicted in Fig. 9.

## 3.2 Application to simulated data

To validate the reliabilty of the porposed sorption correction algorithm, the algorithm has been applied to simulated data for a buoyancy measurement during which helium sorption occures. For the simulation formulas published by Vopicka et al. were used. These formulas were derived for the typical experimental situation in gravimetric sorption, where the pressure increase does not occur instantaneously. Therefore the following formula s used to fit the pressure (Vopicka et al. 2009):

$$\frac{p_{III}}{p_\infty}(\tau) = \begin{cases} 0 & \text{if} \quad \tau \le 0 \\ 1 - \exp(-\xi\tau) - \xi\tau\exp(-\xi\tau) & \text{if} \quad \tau > 0 \end{cases} \tag{5}$$

where the fitting parameter ξ is real and positive.

After fitting the pressure increase, the normalized sorption can be modelled via (Vopicka et al. 2009):

$$\frac{Q_{cII}(\tau)}{Q_\infty} = 1 - \exp(-\xi\tau) - \xi\tau\exp(-\xi\tau) - \frac{8}{\pi}\sum_{i=1}^{N}\frac{A\exp(-d\tau(2i+1)^2) + (C\tau - A)\exp(-\xi\tau)}{(2i+1)^2} \tag{6}$$

where d is the sample thickness and

$$A = \frac{\xi^2}{\xi^2 - 2\xi d(2i+1)^2 + d^2(2i+1)^2}$$

$$C = \frac{\xi^2}{d(2i+1)^2 - \xi}$$

To check if the proposed algorithm is valid, the following path is taken to model a realistic sorption curve:

**Table 1** Sorption coefficients for $CO_2$ on Pebax®MH1657 according to various methods

| | With correction | Bondar et al. (1999) | Car et al. (2008) | Kim and Lee (2001) | Marcq et al. (2005) |
|---|---|---|---|---|---|
| $\frac{cm^3(STP)}{cm^3Pa}$ | $1.48 \times 10^{-5}$ | $8.69 \times 10^{-6}$ | $1.18 \times 10^{-5}$ | $7.92 \times 10^{-6}$ | $1.48 \times 10^{-5}$ |
| Temperature (°C) | 23 | 35 | 30 | 25 | 25 |
| Method | Gravimetric | Volumetric | Time-lag | Flux transients | Gravimetric |

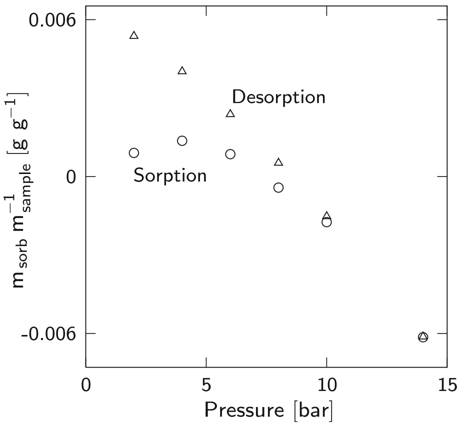

**Fig. 8** Sorption isotherm for Pebax MH 1567, if sample volume is calculated without HSC-algorithm

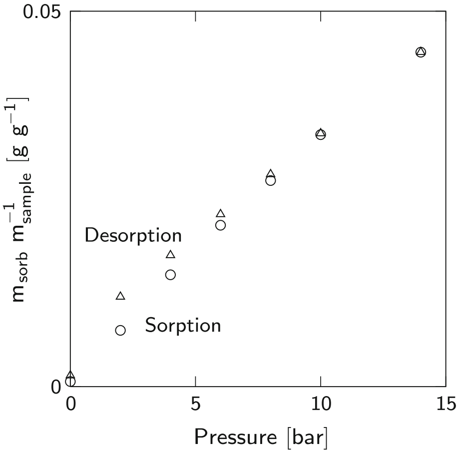

**Fig. 9** Sorption isotherm for Pebax MH 1567, if sample volume is calculated without HSC-algorithm

1. Equation (5) is fitted to the pressure data from the buoyancy measurement used in the previous section.
2. The normalized sorption curve is modelled using the fitting parameter $\xi$ from the previous step, the sample thickness of $d = 300$ μm and a diffusion coefficient of $1 \times 10^{-10}$ m$^2$/s. This is a reasonable value, as the slope of the sorption curve was in good accordance with the slope of the measured curves and diffusion coefficients for $CO_2$ in Pebax MH 1657 are reportet at about $5 \times 10^{-11} \mathrm{m}^2/\mathrm{s}$ (Bondar et al. 1999; Car et al. 2008).
3. To modell the overall mass uptake, a measured value for the sorption coeficient of Helium of $2.6 \times 10^{-4}$g g$^{-1}$ bar$^{-1}$ was used.
4. The buoyancy effect for a sample density of 1.13 g cm$^3$ was applied to the data.

As a last step, the helium sorption correction algorithm was applied to the modelled data, resulting in a sample density of 1.14 g cm$^3$, whereas the uncorrected density was 2.79 g cm$^3$. This result shows, that the proposed approach results in a good approximation, much closer to the real density, than evaluating the data without correction.

## 4 Conclusions

For completely rubbery polymers such as PDMS, helium sorption is negligible. However, using the semi-crystalline polyether block amide Pebax® MH 1657 as the sorbent led to conflicting results concerning $CO_2$ sorption. Upon conventionally evaluating sorption and desorption data for $CO_2$ on Pebax® MH 1657, it was found that the sample volume determined from helium measurements was negative. Thus, this discrepancy was postulated to result from helium-sorption during the gravimetric sample volume determination using the MSB.

Even though several studies have been published regarding helium adsorption on porous media, the knowledge gained from these systematic experimental studies is not applicable to polymer sorbents. Most importantly, the experimental methods to determine and correct helium adsorption on a given sorbent all involve high temperatures that may either destroy or alter the polymer sorbent being investigated.

Consequently, this current study has introduced a simple HSC algorithm to compensate for helium sorption on semi-crystalline, non-rubbery polymer sorbents often used for gas separation membranes. This algorithm is solely based on kinetic data and, since it is based on isotherms, does not involve potentially damaging temperature changes which would compromise the selected polymer material and thus the sample volume data. It is simply derived from the helium isotherms measured after discrete pressure increments. The proposed algorithm has been applied to both experimental and simulated data in order to show prove its validity.

Since sample volume determination is considered to be a trivial step in gas sorption measurements, the hitherto neglect of possible helium sorption to a polymer sorbent has led to false sample volume results. Hence, the proposed HSC algorithm actively addresses this mistake. It is a valuable tool that can be applied in all kinds of future sorption experiments using sophisticated polymers.

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