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Determination of absolute gas adsorption isotherms: simple method based on the potential theory for buoyancy effect correction of pure gas and gas mixtures adsorption

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Abstract The absolute adsorption isotherms are necessary to correctly evaluate the selectivity of the adsorbent material or to design adsorption processes at high pressure (e.g., H_2 purification from syngas processes, removal of acid gas from natural gas,…). The aim of this work is thus to propose an easy method to correct the buoyancy effect of the bulk phase on the adsorbed phase volume during both pure gas and gas mixtures adsorption for pressures up to 10 MPa. The potential theory of adsorption and the Dubinin–Radushkevich relation are adapted by introducing mixing parameters based on simple Berthelot rules. The concept of internal pressure used to characterize the adsorbed phase is also adapted for mixtures. The method is then improved on a commercial activated carbon (AC), when adsorbing pure H_2S and CH_4, and their mixtures up to 5 MPa. The study points out the importance to carefully consider the buoyancy effect of the bulk phase on the adsorbed phase volume. Its impact on the adsorbent material selectivity at high pressures could affect the design and the performances of PSA or TSA processes. For example, only considering the excess adsorption data leads to an apparent selectivity 13 % greater than the absolute one for a concentration of 6 ppm of H_2S in a CH_4 matrix at 5 MPa (298 K) on the AC.

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1 Introduction

The treatment of large volumes of natural gas, syngas or biogas can be achieved by the use of pressure swing adsorption (PSA) processes. These processes allow the removal of pollutants and impurities to increase the heat value of such gases or to remove corrosive species such as sulphur compounds (Ruthven et al. 1994; Sircar and Golden 2010). Such processes are generally designed following simulations based on thermodynamic and kinetic data obtained from measurements at the laboratory scale. But increasing the pressure, the adsorbed amounts raise inducing a significant variation of the apparent volume of the adsorbent: the volume of the adsorbed phase hides the accessible volume of the adsorbent solid bringing about a variation of the adsorbent material porosity. These effects induce under estimations of the adsorbent working capacities and, in the case of impurities removal, an over estimation of the selectivity of the adsorbent.

Experimental techniques as manometric, volumetric or gravimetric techniques allow to acquire thermodynamic data in the range of pressures corresponding to the production conditions of PSA processes. But the excess isotherms have to be corrected from the buoyancy effect of the gas phase on the adsorbed phase volume: Gibbsian excess and not absolute adsorbed amounts are measured using these techniques (Sircar 1999). For manometric or volumetric techniques, the variation of the adsorbed phase volume leads to a decrease of the volume available to the bulk phase whereas the volume has to be kept constant to

apply a mass balance: this causes an underestimation of the adsorbed amounts. For gravimetric techniques, the increase of the adsorbed phase volume occasions a decrease of the measured mass, the gas phase density bearing the adsorbed phase (Billemont et al. 2011).

A correction due to the presence of the adsorbed phase, in other word the Archimedes' principle of the fluid phase on the adsorbed phase volume, has to be given to acquire absolute adsorption data, i.e. data which can be used in the design of separation processes by adsorption. Several theories have already been developed to evaluate the correction due to adsorbate phase. For example, the density functional theory can be used to determine the adsorbed volume (Murata et al. 2001, 2002) or the correlation between the energetic distribution function and the pore size distribution function (Frère et al. 1996; Jagiello et al. 1994; Jagiello and Schwarz 1993). In this paper, we propose to focus on the potential theory developed by Polányi (1914, 1916, 1932) and the pore filling theory by Dubinin (1960, 1967). While the mechanisms of adsorption are the same for manometric, volumetric, and gravimetric techniques, we here develop an adaptation of the potential theory applying it, as for instance, to the gravimetric measurements. The same methodology could be used for the other techniques.

The absolute adsorbed amount (n_{abs}) of gases can be expressed as a function of the excess amount (n_{exc}) as:

$$n_{abs} = n_{exc} + \rho_{bulk} \cdot V_{\varphi\, ads} \quad (1)$$

where ρ_{bulk} is the bulk fluid density and $V_{\varphi\, ads}$ is the adsorbed phase volume. The excess amount, or "surface excess amount", comes from the concept of Gibbs Dividing Surface (Rouquerol et al. 1999): this concept is very useful because the density profile of the fluid phase near the adsorbent surface is not linear and the boundary between the adsorbed phase and the bulk fluid is blurred (see Fig. 1). The terminology of such a concept is identical to chemical thermodynamics, the reference state here corresponding to density of the bulk fluid (at the thermodynamic equilibrium, for given temperature and pressure). From the point of view of experimental measurement, the excess amount corresponds to the measured adsorbed amount. Thus, to determine the absolute amount, the adsorbed phase volume has to be established. But there is no an a priori experimental method to determine this adsorbed phase volume: it has to be estimated using theoretical way.

The paper thus presents the theory developed to carry out the buoyancy effect correction for both pure gas and gas mixture adsorption in order to show that this conversion from excess to absolute adsorbed amounts is essential for the selectivity determination (Myers and Monson 2002; Krishna 2012). In the context of the PSA process design for natural gas compounds separation, this theory is then applied to the measurement of pure CH_4 and H_2S adsorption isotherms on a commercial activated carbon (AC) and to the CH_4–H_2S mixtures. The impact of the variation of the accessible volume is finally discussed by analysing the variation of the adsorbent selectivity and its adsorption capacities.

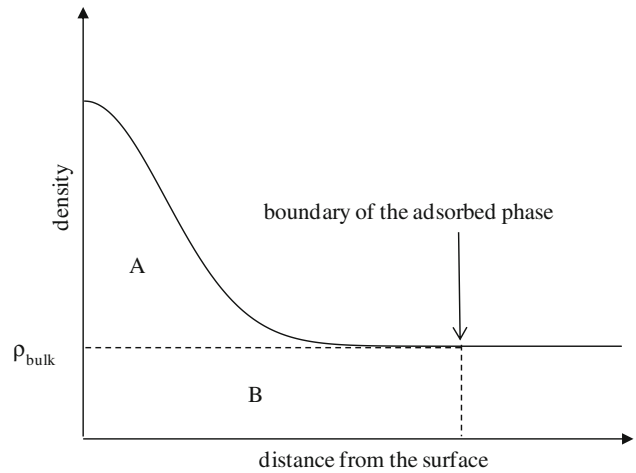

Fig. 1 Schematic view of the density profile of fluid phases as a function of the distance from the solid surface of the adsorbent. *A* excess amount; *A*+*B* absolute adsorbed amount. Adapted from Rouquerol et al. (1999)

An other approach proposed by Gumma and Talu (Gumma and Talu 2010; Talu 2013) recently introduced an original concept: the net adsorption isotherm. This concept only requires the determination of the volume of the system tank (i.e. in gravimetric measurement: the crucible containing the adsorbent material without the adsorbent material). Indeed, this concept presents some majors benefits: (i) it is not necessary to make some assumptions on pore volume of adsorbent by helium measurement to determine the excess isotherm, (ii) the comparison between different materials is easy, and (iii) the formulation is well adapted for the determination of gas storage in defined volume (H_2 or CH_4 storage).

2 Theory

2.1 Potential theories developed for buoyancy effect correction of pure gas adsorption isotherms

The potential theory exposed by Polányi (1916) is based on the classic expression of the potential equilibrium between liquid and vapour phases: the adsorption potential is defined as the difference between chemical potential in the standard state of an adsorbed liquid phase μ_0 and the chemical potential of the adsorbed phase μ. Thus, the adsorption potential ε can be expressed as:

$$\varepsilon = \mu_0 - \mu = R \cdot T \cdot \ln \frac{f_0(T)}{f} \quad (2)$$

f is the fugacity of the bulk phase, $f_0(T)$ is the saturation fugacity for the given temperature T (we chose, in the paper, to not use the pressure but directly the fugacity which is a corrected pressure depending of the pressure and the temperature). The adsorption potential is not temperature dependent as experimentally observed by Polányi (1932). Thus, this potential is unique for a given adsorbate–adsorbent couple.

2.1.1 Pore filling theory

Considering an unique relationship between the adsorption potential and the adsorbed phase volume, Dubinin and Radushkevich (1947) proposed to express the adsorbed phase volume as a function of the adsorption potential:

$$V_{\varphi\, ads} = V_{DR} \cdot \exp\left(-\left(\frac{\varepsilon}{E}\right)^2\right) \quad (3)$$

V_{DR} is the theoretical maximum volume which can be filled by the adsorbate. This volume characterizing the adsorbent is a hypothetical volume. E is the characteristic potential of adsorption of the considered couple adsorbate-adsorbent. Compared to other model such as Langmuir or Toth, the Dubinin model only considers two fitted parameters (V_{DR} and E) whereas, for example, for the Langmuir model, the adsorption equilibrium constant, the adsorbed quantity at saturation, and the enthalpy of adsorption (because the proposed procedure is here temperature dependent) have to be taken into account in this model. Moreover, the Dubinin model is intrinsically a consequence of the definition of the adsorption potential defined by Polányi. The combination of Eqs. 2 and 3 gives the Dubinin–Radushkevich relationship which expresses the adsorbed phase volume as a function of fugacity (Dubinin et al. 1947):

$$V_{\varphi\, ads} = V_{DR} \cdot \exp\left(-\left(\frac{R \cdot T}{E}\right)^2 \cdot \left(\ln \frac{f_0(T)}{f}\right)^2\right) \quad (4)$$

Equation 4 describes a Gaussian curve for which the standard deviation is the characteristic adsorption potential and the maximum is the theoretical maximum volume which can be filled. For low pressures, i.e. in the range of pressures for which the buoyancy effect of the gas phase on the adsorbed phase is negligible, E and V_{DR} are determined by plotting $\ln V_{ads}$ as a function of ε^2:

$$\ln V_{ads} = \ln V_{DR} - \frac{\varepsilon^2}{E^2} \quad (5)$$

The Y-intercept corresponds to $\ln V_{DR}$ and the slope to $-(1/E)^2$.

2.1.2 Affinity coefficient

For a specific adsorbed phase volume, the adsorption potential of different adsorbates ε_i on the same adsorbent can be linked by an affinity coefficient β_i as (Polányi, 1932, 1920; Stoeckli and Morel 1980):

$$\frac{\varepsilon_1}{\beta_1} = \frac{\varepsilon_2}{\beta_2} = \frac{\varepsilon_{ref}}{\beta_{ref}} \quad (6)$$

The affinity coefficient allows to plot a unique characteristic curve for all the adsorbates on an adsorbent linking a reference adsorbate (historically the benzene) with other adsorbates in the representation of the adsorbed volume as a function of the adsorption potential. The function of the characteristic curve is the original Dubinin–Radushkevich equation:

$$V_{\varphi\, ads} = V_{DR} \cdot \exp\left(-\left(\frac{R \cdot T}{\beta \cdot E_{ref}}\right)^2 \cdot \left(\ln \frac{f_0(T)}{f}\right)^2\right) \quad (7)$$

E_{ref} is the characteristic adsorption energy for the reference compound. The β coefficient can be predicted by different ways (Wood 2001). It could be the ratio of molar volume in the liquid state (Dubinin and Tomofeyev 1946), the ratio of parachor factors (Dubinin and Zaverina 1950) or the ratio of coalescing factors (Mehta and Danner 1985). But, assuming that the adsorption forces are due to dispersion from the London theory, the affinity coefficient can be defined as the ratio of the molecular polarizability (Dubinin and Tomofeyev 1946; London 1930):

$$\beta = \frac{P}{P_{ref}} \quad (8)$$

The molecular polarizability is temperature invariant and depends on the constant dipole moment.

To determine V_{DR} and E_{ref}, the characteristic curve (see Eq. 7) is plotted as shown in Fig. 2. Excess data points for which the buoyancy effect is negligible are selected. Two main parameters are thus needed: the adsorbed phase volume (or molar adsorbed phase volume) and the saturation fugacity $f_0(T)$.

2.1.3 Molar adsorbed phase volume determination for subcritical conditions

For subcritical compounds, the molar volume can be approximated by the molar volume of the saturated liquid at the experimental temperature if temperature is lower than the boiling point temperature; if experimental temperature is between boiling point temperature and critical temperature, it can be estimated as (De Weireld 2000):

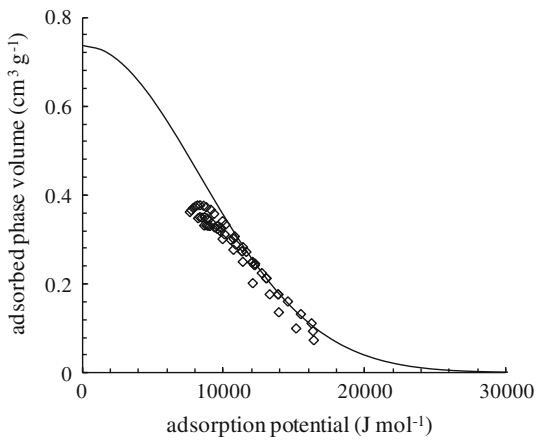

Fig. 2 Example of a characteristic curve obtained on an AC for methane adsorption at 275, 298 and 323 K for pressure from 0.1 up to 10.0 MPa

$$v_{\varphi\,ads} = \frac{b_{vw} - v_b}{T_c - T_b} \cdot (T - T_b) + v_b \tag{9}$$

where b_{vw} is the van der Waals covolume, v_b is the molar volume at the boiling point temperature, T_b is the boiling point temperature and T_c is the critical temperature. Agarwal and Schwartz (1988) suggested another definition which considers the adsorbed phase as a sort of superheated liquid:

$$v_{\varphi\,ads} = v_b \cdot \exp\left(\Omega_T \cdot (T - T_b)\right) \tag{10}$$

where Ω_T is the thermal expansion coefficient. It can be a constant equal to 0.0025 such as suggested by Ozawa et al. who considered that the pressure variations are negligible and the constant is independent of the adsorbent (Ozawa et al. 1976) or a function of the van der Waals covolume as proposed by Dubinin (1960):

$$\Omega_T = \frac{\ln \frac{b_{vw}}{v_b}}{T_c - T_b} \tag{11}$$

Many other empirical correlations can be used to determine the molar volume for subcritical conditions (Cook and Basmadjian 1964; Lewis et al. 1950).

2.1.4 *Molar adsorbed phase volume determination for supercritical conditions*

For supercritical conditions, some authors proposed to describe a specific equation of state (EoS) for the adsorbed phase based on a separation between the fluid-fluid and fluid-solid interactions (using the perturbed-chain statistical associating fluid theory, PC-SAFT) (Monsalvo and Shapiro 2007, 2009). A simpler approach is here developed following the concept of internal fugacity (of the adsorbed phase) which has initially been proposed by Dubinin et al. (1993) and Neimark (1994): the adsorbed phase is considered as gaseous but with a fugacity describing a dense phase. By using an appropriate EoS, knowing the temperature and this internal fugacity, molar volume can be estimated. The concept of internal fugacity, also described by Berezin (1979), suggests to link the differential adsorption energy with critical parameters. Observing that the internal energy of an isolated gas molecule adsorbed at zero coverage is linearly proportional to $T_c/\sqrt{p_c}$ (p_c is the critical pressure), Berezin expressed the internal energy variation as a function of the van der Waals parameters. Its approach consists in the expression of the differential heat of adsorption q_{diff} (between the adsorbate and the adsorbent surface) as a function of the critical parameters:

$$-q_{diff} = D_b \cdot \frac{T_c}{p_c} \tag{12}$$

where D_b is a constant function of the adsorbent. For microporous sorbent, he proposed an empirical relationship (Berezin 1983):

$$D_b = 1.3 \cdot R \cdot \sqrt{p_a} \tag{13}$$

Thus, writing the isosteric heat as a function of the differential heat, the internal pressure becomes:

$$p_a = \left(\frac{q_{isost} + R \cdot T}{1.3 \cdot R \cdot T_c}\right) \cdot p_c \tag{14}$$

However we have decided to work with the fugacity rather than the pressure. Thus, the internal fugacity f_a depends on the critical temperature T_c, the critical fugacity f_c and the adsorption isosteric heat q_{isost}:

$$f_a = \left(\frac{q_{isost} + R \cdot T}{1.3 \cdot R \cdot T_c}\right) \cdot f_c \tag{15}$$

For supercritical conditions, $f_0(T)$ from Eqs. 2, 4, and 7 could be replace by f_a. For temperatures slightly greater than critical temperature, $f_0(T)$ can be expressed with the following empirical expression (Dubinin 1975):

$$f_0(T) = \left(\frac{T}{T_c}\right)^2 \cdot f_c \tag{16}$$

To sum up, by selecting excess data for which the buoyancy effect is negligible, the characteristic curve allows to determine the Dubinin–Radushkevich volume V_{DR} and the characteristic adsorption energy E_{ref}. Calculating V_{DR} and E_{ref}, and determining the internal fugacity f_a and the affinity coefficient β, the adsorbed phase volume is estimated. Then, after determining the bulk density using an appropriate EoS, the absolute amounts are estimated according to Eq. 1.

2.2 Potential theory for buoyancy effect correction on gas mixture adsorption isotherms

For gas mixture adsorption, the adsorbed volume described by Eq. 7 could be adapted as:

$$V_{\varphi\,ads} = V_{DR} \cdot \exp\left(-\left(\frac{R \cdot T}{\beta^{mix} \cdot E_{ref}^{mix}}\right)^2\right) \cdot \exp\left(\left(\ln \frac{f_0^{mix}(T)}{f^{mix}}\right)^2\right) \quad (17)$$

where β^{mix} is the affinity coefficient of the mixture, E_{ref}^{mix} is the characteristic adsorption energy of the mixture, f_0^{mix} and f^{mix} are the internal fugacity of the mixture and the fugacity of the gas mixture respectively. At this stage, pure adsorption data are needed to estimate V_{DR}, E_{ref}^{mix}, β^{mix}. The pure adsorption isosteric heats are also needed to be able to determine an isosteric heat of the gas mixture adsorption in the aim to determine the internal fugacity.

2.2.1 *Iterative procedure*

An iterative procedure (see Fig. 3) is proposed to determine absolute adsorbed amounts from pure and mixture excess adsorption data. The initialization of this method consists in the excess amount determination from which a first estimation of $V_{\varphi\,ads}$ (using Eq. 7) is made: the characteristic adsorption energy for the reference compound is quantified via pure adsorption excess data at moderate pressures, i.e. for pressure so low that the adsorbed phase volume is so small to not be affected by the buoyancy effect. The adsorbed mole fractions are also carried out during the initialization. From the knowledge of $V_{\varphi\,ads}$, the absolute adsorbed amounts are determined according to Eq. 1; from the adsorbed mole fractions, the isosteric heat of the mixture and the parameters E_{ref}^{mix} and β^{mix} are calculated. The procedure is then iterated to adjust $V_{\varphi\,ads}$ until convergence using Eq. 17. Mixing rules have now to be applied to determine the parameters E_{ref}^{mix}, β^{mix}, and q_{isost}^{mix}.

2.2.2 *Simple mixing rules*

The affinity coefficient can be evaluated as an adsorbed mole fractions weighted sum of the pure affinity coefficients. From the same way, isosteric heat of the mixture is the adsorbed mole fractions weighted sum of the pure isosteric heat:

$$\beta_{mix} = x_1 \cdot \beta_1 + x_2 \cdot \beta_2 \quad (18)$$

$$q_{isost}^{mix} = x_1 \cdot q_{isost1} + x_2 \cdot q_{isost2} \quad (19)$$

Mixture critical parameters are deduced from the corresponding states mixing rules with three parameters. The Lorentz-Berthelot rules applying the London theory suggest that the interaction potential between two molecules having nearly the same size and the same ionization potential can be expressed as (Prausnitz et al. 1986):

$$\varepsilon_{ij} = \sqrt{\varepsilon_i} \cdot \sqrt{\varepsilon_j} \quad (20)$$

Considering hard sphere model for molecular interactions, the intermolecular distance is:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (21)$$

Mixture critical parameters are determined from these semi-empirical rules as:

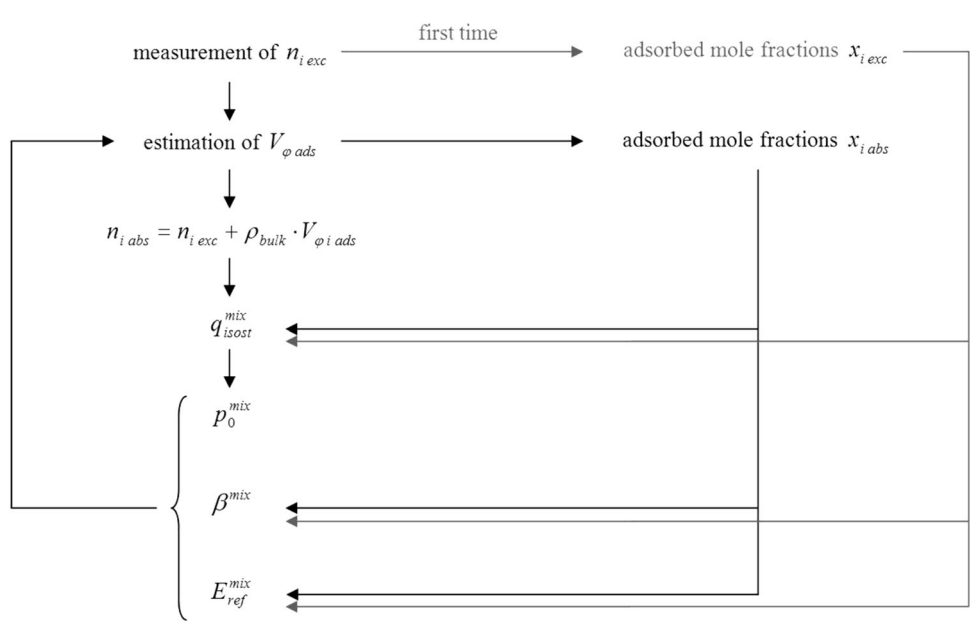

Fig. 3 Iterative procedure for absolute adsorbed quantities determination of multicomponent system

$$v_c^{mix} = \frac{1}{8}\left((v_{c1})^{\frac{1}{3}} + (v_{c2})^{\frac{1}{3}}\right)^3 \quad (22)$$

$$T_c^{mix} = \sqrt{T_{c1}} \cdot \sqrt{T_{c2}} \quad (23)$$

$$p_c^{mix} = 0.291 \cdot \frac{R \cdot T_c^{mix}}{v_c^{mix}} \quad (24)$$

In the expression of the mixture critical pressure, the compressibility factor is approximated to 0.291 according to the Lennard-Jones potential expression.

To summarize, the buoyancy effect of the gas phase applied on the adsorbed phase volume can be corrected by evaluating the adsorbed phase volume applying the pore filling theory which is an extension of the potential theory. This method is based on the hypothesis that only one characteristic curve linking the adsorbed phase volume to the adsorption potential exists for a specific adsorbent-adsorbate couple. The curve is determined only using excess adsorbed amount for which the buoyancy effect of the bulk phase on the adsorbed phase is moderate, i.e. for low pressures.

The plot of the characteristic curve requires the determination of the adsorbed phase molar volume which is estimated via the concept of internal pressure deduced from the isosteric heat and the use of an appropriate EoS. This method is used for the correction of buoyancy effect for pure gas adsorption measurement and is extended for gas mixture adsorption measurement by simple mixing rules based on the corresponding states with two parameters. The method proposed above is adapted for both subcritical and supercritical conditions and for adsorbents presenting both homogeneous or heterogeneous energetic surfaces.

3 Experimental results

3.1 Adsorbent and gases properties

A commercial AC has been used to improve the proposed buoyancy effect correction method. This AC is provided by PICA (France); its precursor is coconut calcinated at 1,123 K and activated under water atmosphere at the same temperature. It presents a microporous volume of 0.585 $cm^3\ g^{-1}$ and a mesoporous volume of 0.082 $cm^3\ g^{-1}$. Its BET surface area (determined by nitrogen adsorption experiment at 77 K) is of 1,493 $m^2\ g^{-1}$. The AC is denoted as NC100. CH_4 (purity of 99.995 %) and H_2S (purity of 99.5 %) gases provide by Praxair. EoS used for pure gas phase density calculation, by Lemmon and Span (2006) for H_2S and by Setzmann and Wagner (1991) for CH_4, are of Helmholtz type. For gas mixture density determination, the Gerg-2004 EoS are used (Kunz et al. 2007).

3.2 Pure gas adsorption measurements

3.2.1 Apparatus

Pure gas adsorption data have been measured using a gravimetric method. The measurement system is based on a magnetic suspension system allowing to separate the analytical balance at ambient conditions from the adsorption cell containing the adsorbent which is exposed to pressure, temperature and potentially corrosive operating conditions. This system is a home-made apparatus for which the magnetic coupling balance was provided by Rubotherm Präzisionsmesstechnik GmbH (Dreisbach et al. 1996). Measurements can be performed for pressures from secondary vacuum up to 10 MPa and for temperatures from 263 to 373 K. More details on material and experimental procedure are provided in a previous paper (De Weireld et al. 1999).

3.2.2 Excess results

The excess isotherms are obtained by taking into account the buoyancy effect of the gas phase on the adsorbent solid. The volume of adsorbent is evaluated by direct helium isotherm measurement at 303 K assuming that helium does not adsorb (Rouquerol et al. 1999). Helium density is determined using a modified Benedict–Webb–Rubin EoS (McCarty and Arp 1990). Pure gas excess adsorption isotherms obtained for H_2S (276, 298 and 323 K) up to the saturation pressure and CH_4 (273, 298 and 323 K) up to 10 MPa are produced by Figs. 4 and 5.

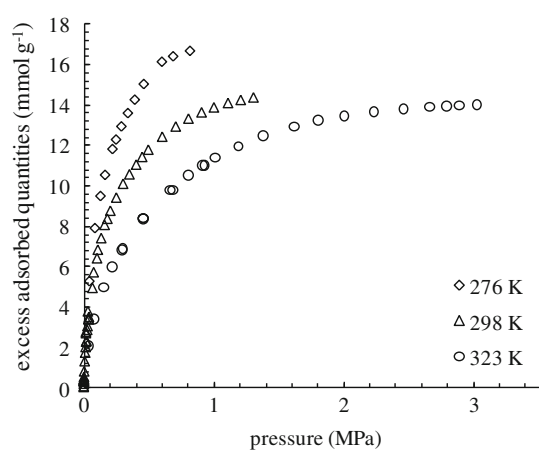

Fig. 4 Adsorption isotherms of H_2S on NC100 at 276, 298 and 323 K

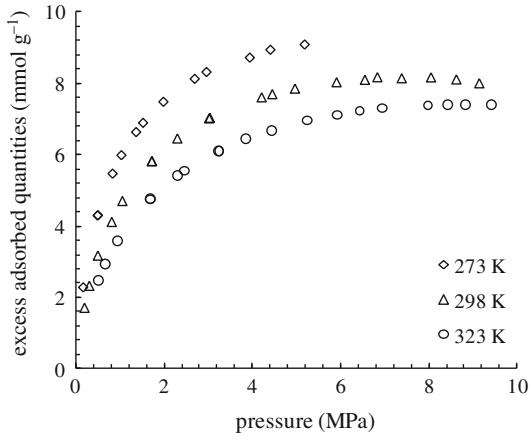

Fig. 5 Adsorption isotherms of CH_4 on NC100 at 273, 298 and 323 K

CH_4 and H_2S adsorption isotherms present a type I shape (according to IUPAC classification) with maximum H_2S adsorbed quantity of 16.7, 14.4 and 14.0 mmol g^{-1} at 276, 298 and 323 K respectively, and maximum CH_4 adsorbed quantities of 9.2, 8.18 and 7.40 mmol g^{-1} at 273, 298 and 323 K respectively. Adsorbed quantities uncertainties are determined following the Guide to the expression of Uncertainty in Measurement (Joint Committee for Guides in Metrology 2008). They are estimated to 3.5 % of the adsorbed quantity for lower pressures for H_2S adsorption and average up to 0.2 % for pressure >0.4 MPa. Uncertainties are <1 % for CH_4.

CH_4 adsorption isotherms decrease at high pressures: this effect is attributed to the non taking into account of the buoyancy effect of the gas phase on the adsorbed volume. Indeed, for high pressures, the variation of the product of the gas phase density by the adsorbed phase volume is higher than the variation of mass uptake due to the adsorption inducing a decrease of the recorded excess mass. This effect should be the same by using manometric techniques: at high pressures, the adsorbed amounts which are determined by mass balances between two vessels (one containing the adsorbent, the other being the gas storage vessel) are decreasing when increasing pressure because the volume of the cell containing the adsorbent material is apparently decreasing because of the increase of the adsorbed phase volume.

3.2.3 Data fitting

To evaluate the isosteric heat of adsorption and then to determine the internal fugacity for the adsorbed phase, excess data at low pressures (<1.0 MPa) for pure gases are fitted using the Toth model (Toth 1971):

Table 1 Parameters of the Toth model

Compounds	Temperatures (K)	q_{sat} (mmol g^{-1})	b (MPa^{-1})	t
H_2S	276	24.8	13.61	0.58
	298	23.8	12.51	0.49
	323	22.3	4.39	0.54
CH_4	273	13.4	1.95	0.62
	298	12.6	1.22	0.63
	323	11.3	0.84	0.67

$$q = q_{sat} \cdot \frac{b \cdot p}{\left(1 + (b \cdot p)^t\right)^{\frac{1}{t}}} \tag{25}$$

The model parameters obtained by fitting (using the least squares method) are produced by Table 1.

The heats of adsorption for these two gases are then determined from the measured adsorption isotherms at three different temperatures (276, 298 and 323 K for H_2S and 273, 298 and 323 K for CH_4) using the isosteric method. In this method, the isosteric heat of adsorption $Q_{isost} = -\Delta H$ is estimated at a given adsorbed amount n_{ads} using the Clausius–Clapeyron equation (Eq. 26): for low pressures assuming the ideal gas conditions, the representation of the logarithm of the pressure as a function of the inverse of the temperature for different isotherms with the same adsorbed quantity allows to determine the slope which is the isosteric heat for a given adsorbed quantity. At zero coverage, the isosteric heat is of −23.3 kJ mol^{-1} for H_2S and of −13.9 kJ mol^{-1} for CH_4.

$$q_{isost}(n_{ads}) = -\Delta H = R \cdot T^2 \cdot \left(\frac{\partial \ln p}{\partial T}\right)_{n_{ads}} \tag{26}$$

3.2.4 Buoyancy effect correction

Using adsorbed volume determined with the concept of internal fugacity presented in the Sect. 2.1.4, adsorption potential and adsorbed volume are calculated from excess adsorption data. Then a characteristic curve is plotted for each adsorbate (see Fig. 6). Experimental data for which buoyancy effect is negligible are fitted to deduce V_{DR} and E parameters (see Table 2). Excess data points for which the buoyancy effect is negligible are selected: arbitrary criteria are fixed at 4 % of deviation between molar volumes for supercritical conditions and fixed at 2 % for subcritical conditions (De Weireld 2000).

The affinity coefficient β is estimated from molecular polarizabilities (see Table 2) (Olney et al. 1997), taking CH_4 as reference, allowing to plot a unique characteristic curve (Fig. 7). The value of β is 1.176. The parameters V_{DR}

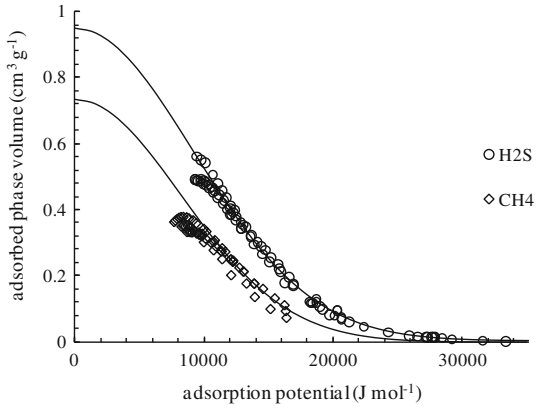

Fig. 6 Adsorbed phase volume as a function of adsorption potential and characteristic curve for CH_4 and H_2S

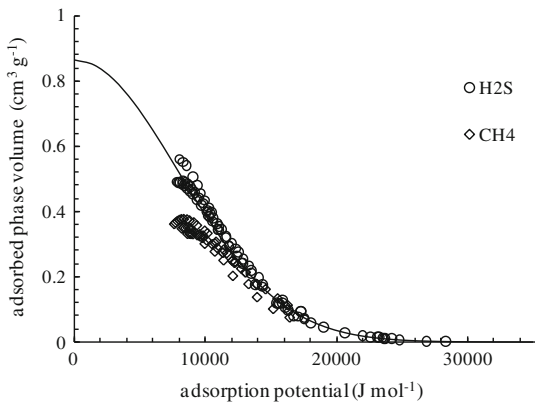

Fig. 7 Unique characteristic curve (CH_4 is the adsorbate reference)

Table 2 Parameters of characteristic curves

	E_{ref} (kJ mol^{-1})	V_{DR} (cm^3 g^{-1})	Polarizability (Å^3)
H_2S	13.02	0.951	1.865
CH_4	11.67	0.736	2.194

and E are deduced from this curve: V_{DR} = 0.867 cm^{-3} g^{-1}; $E = 11.18$ kJ mol^{-1}. Since adsorbed phase volume is determined using Eq. 7, experimental data are corrected for the buoyancy effect. CH_4 and H_2S corrected and experimental data are shown by Fig. 8 and 9.

The difference between excess and absolute data increases when pressure increases, and presents a maximum of 24 % for CH_4 adsorption; it shows a large difference between excess and absolute data when the adsorbed phase volume is taken into account for pressures above 10 MPa. Absolute data calculated considering the affinity coefficient are slightly higher than those calculated without adsorbate reference. These effects are directly linked to the value of the adsorbed phase volume which is considered to perform the buoyancy effect correction: for

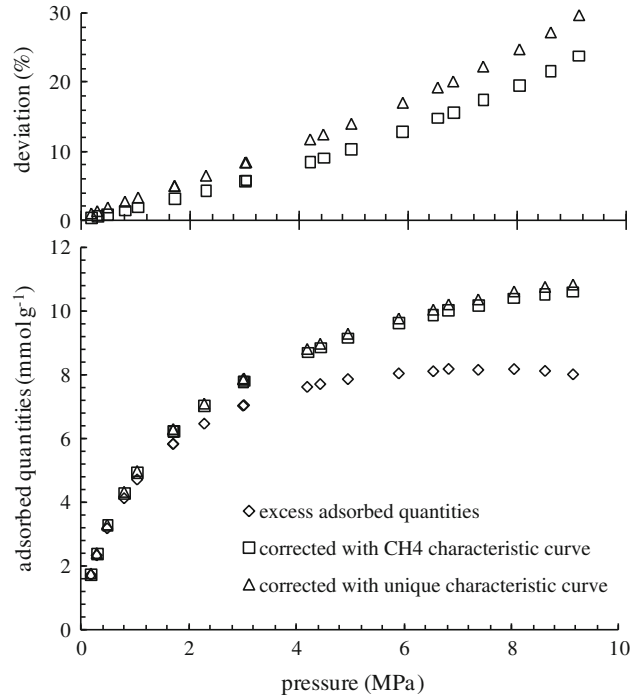

Fig. 8 Excess and absolute adsorbed amounts of CH_4 at 298 K with deviation (%) from the excess amounts

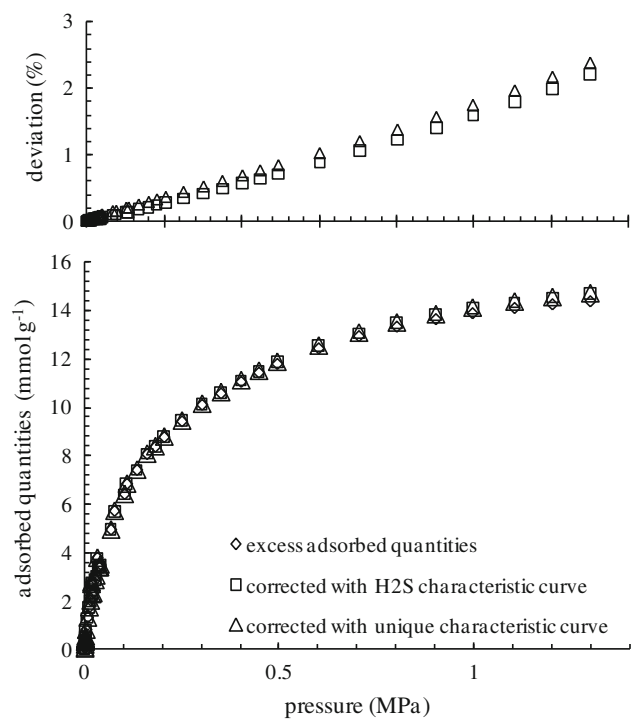

Fig. 9 Excess and absolute adsorbed amounts of H_2S at 298 K with deviation (%) from the excess amounts

both corrections with the unique characteristic curve and the CH_4 characteristic curve, the adsorbed phase volume depends on the adsorption potential, and the CH_4

characteristic curve is lower than the unique one for all the range of adsorption potential which induces that absolute adsorbed amounts of CH_4 are lower when considering the correction using the CH_4 characteristic curve.

For H_2S, differences between excess surface amounts and calculated absolute adsorbed quantities are negligible in the experimental pressure range (the maximum difference between excess and absolute amounts is only 2.1 %). It could be due to the weak volume of the adsorbed phase compared to this volume for high pressure. With CH_4 as adsorbate reference, it leads to a slightly higher correction.

3.3 Gas mixture adsorption measurements

3.3.1 Apparatus

Gas mixture adsorption measurements have been performed using a home-made apparatus coupling volumetric, gravimetric and chromatographic techniques. With this equipment, measurements are carried out for pressures from vacuum up to 5 MPa and for temperatures from 263 to 373 K. Gas mixture is produced in situ by using two or more vessels (depending if binary mixture or more compound mixture adsorption, respectively) of known volumes. After the gas mixture generation, gases are injected in the adsorption cell which contains the adsorbent. Until thermodynamic equilibrium is reached (constant gas phase mole fraction and constant measured mass at fixed temperature and pressure), gases are homogenized using a circulation pump. At equilibrium, the adsorbed mass is recorded using the magnetic suspension system, temperature and pressure are recorded too, and gas phase composition is determined using a gas chromatograph coupled with a mass spectrometer. Thus, knowing the initial gas quantities, measuring the adsorbent mass variations and determining the final gas phase composition, each adsorbed quantity is established. The excess amounts are directly estimated by the evaluation of the buoyancy effect of the gas mixture phase on the adsorbent volume. Finally, the excess isotherms are obtained by taking into account the buoyancy effect of the gas phase on the adsorbent solid. The detailed description and procedure is described in a previous paper (Hamon et al. 2008).

3.3.2 Excess and corrected results

Measurements for CH_4–H_2S binary mixtures are performed at 1 and 5 MPa, at 298 K. Starting from the unique characteristic curve parameters (Table 2), excess data are corrected following the iterative procedure and using mixing rules presented in Sect. 2.2.1. Figures 10 and 11 show excess and absolute adsorbed amounts at 1 MPa and 5 MPa, respectively. Average uncertainties of adsorbed quantities are of 0.77 % for CH_4 and 3 % for H_2S at 1 MPa. At 5 MPa, they are of 0.53 % for CH_4 adsorbed quantities and from 2.5 to 24 % for H_2S adsorbed quantities. H_2S absolute data are not presented because of the low significance of corrections compared to experimental uncertainties: at 1.0 MPa, the differences between excess and absolute adsorbed amounts vary from 0.003 to 0.09 % of the absolute amounts, and from 0.13 to 0.1 % at 5.0 MPa. Corrections for CH_4 are of 2.8 % of the adsorbed amount at 1 MPa and of 19.7 % at 5 MPa (Fig. 12).

Table 3 "Excess" and "absolute" selectivities of the AC for H_2S as a function of the adsorbed mole fraction of H_2S in the gas phase at 298 K

1.0 MPa			5.0 MPa		
Selectivities			Selectivities		
y_{H_2S} (ppm)	Excess	Absolute	y_{H_2S} (ppm)	Excess	Absolute
25,535	30.1	29.3	1,446	77.9	64.7
9,648	29.9	29.1	722	116.1	97.1
9,050	30.8	29.9	193	244.1	205.5
4,731	39.7	38.7	36	648.4	543.5
1,907	60.9	59.3	6	1,355.3	1,132.3
590	123.7	120.1			
170	256.0	248.8			
65	496.2	482.6			
34	746.3	725.6			

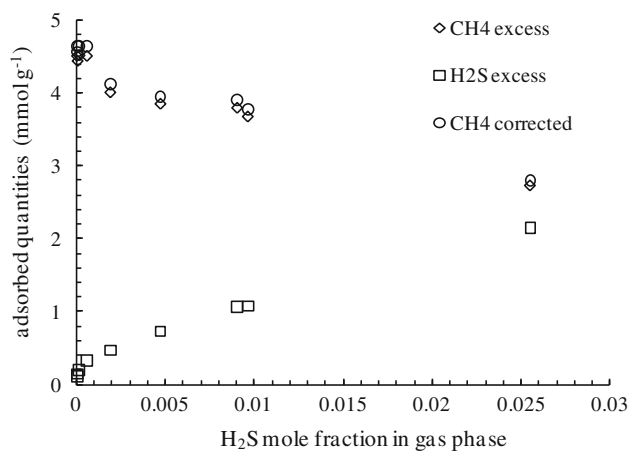

Fig. 10 Excess and absolute adsorbed amount for CH_4 and H_2S at 298 K and 1 MPa

3.4 Discussion

Comparison between excess and absolute amounts shows significant deviation for pressure up to 2.0 MPa: thus, for pure adsorption isotherms, the interest of the correction is more meaningful for CH_4. Whereas excess adsorbed amounts of CH_4 are slightly decreasing for pressure >7 MPa, absolute amounts keep constant increase. In our

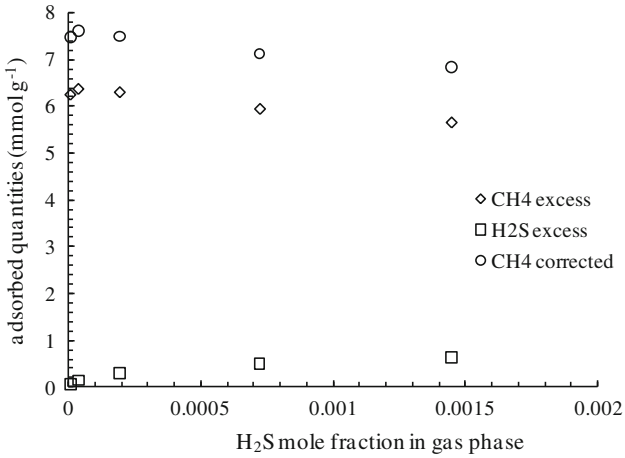

Fig. 11 Excess and absolute adsorbed amount for CH_4 and H_2S at 298 K and 5 MPa

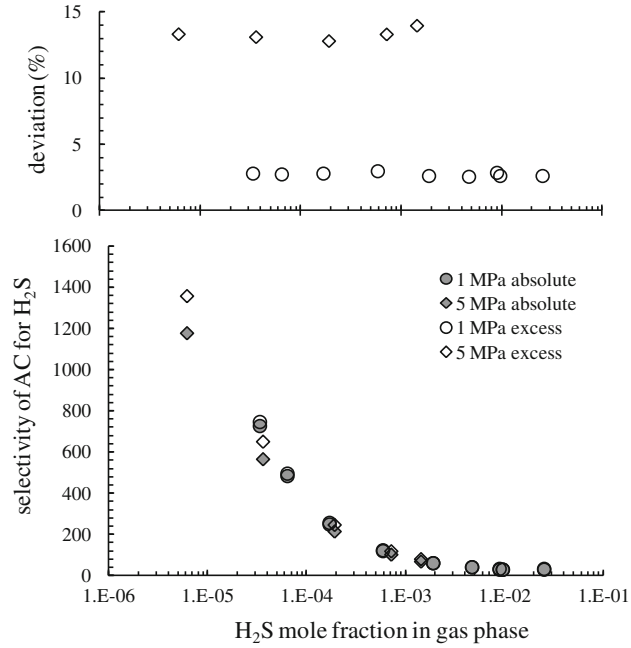

Fig. 12 Selectivity of the AC for H_2S as a function of the H_2S mole fraction in the gas phase at 298 K for the CH_4–H_2S mixture; *circles* 1 MPa; *diamonds* 5 MPa; with deviation (%) between excess and absolute selectivities

mind, the hypothesis of a constant adsorbed phase volume as the total microporous volume overestimates the adsorbed phase volume: this hypothesis appears to be valid for adsorbent material with regular pores able to contain a very limited numbers of molecules such as zeolites or several metal organic frameworks with small cages (non-mesoporous MOFs), but it is not adapted for materials such as ACs presenting large pore size distribution especially if there is a strong variation of the adsorbed volume as a function of the pressure.

The use of a unique characteristic curve intrinsically shifts the adsorption potential to keep a constant adsorbed phase volume for several adsorbed species. According to the results presented by the Fig. 8, the choice of the unique characteristic curve seems to be equivalent to the specific characteristic curve of the CH_4 even with the common CH_4–H_2S characteristic curve the CH_4 absolute adsorbed amounts are slightly higher (maybe because of the most important V_{DR}). For H_2S adsorption isotherm, absolute and excess data are so close that the interpretation could be quite difficult: the main idea could be to explain these so close values by the pressure range, imposed by the H_2S saturation vapour pressure, for which the gas density is too much lower to have a significant buoyancy effect on the adsorbed phase volume.

Concerning the implementation of this buoyancy effect correction to binary gas mixture adsorption, since the H_2S mole fractions are low in the CH_4 matrix, H_2S excess and absolute amounts are not really differentiated (also maybe because of the low mole fractions of H_2S which induces a really thin H_2S adsorbed phase). But CH_4 adsorbed amounts are higher after correction, following the same tendency as for pure CH_4 adsorption isotherms. Thus, the selectivity of the AC for H_2S is strongly affected. The selectivity is defined as:

$$S_{H_2S/CH_4} = \frac{\frac{x_{H_2S}}{y_{H_2S}}}{\frac{x_{CH_4}}{y_{CH_4}}} \tag{27}$$

where x and y are the mole fraction in adsorbed and gas phases, respectively. Thus, increasing the adsorbed amounts of CH_4, i.e. increasing the mole fraction of CH_4 in the adsorbed phase, significantly decreases the selectivity of the adsorbent material for H_2S which amounts are kept quasi constant in the range of low H_2S mole fractions (Table 3). Figure 12 shows the variation of the selectivity for H_2S with and without correction.

The AC is highly selective for H_2S especially for low H_2S mole fractions in the gas phase, but the correction of the buoyancy effect of the gas phase on the adsorbed volume strongly reduces the "excess" selectivity. This correction thus proves the interest to consider absolute data for the design of PSA process in order to not over estimate adsorbent selectivity for pollutants in the state of traces in a less adsorbable matrix.

4 Conclusion

The adaptation of the potential theory and the pore filling theory for the buoyancy effect correction shows that there are significant differences between excess experimental adsorption data and theoretical absolute ones. For gas

mixture adsorption, by using simple mixing rules, the main consequence of this correction is the reduction of the selectivity of compounds presenting the highest affinity for the adsorbent. This study thus shows the importance to take into account the buoyancy effect correction for the design of processes such as PSA processes to evaluate the decrease of the affinity of the most adsorbed species especially at high pressure for low pollutant concentrations.

Nevertheless, in our knowledge, no experimental apparatus has already been developed to measure the volume of the adsorbed phase to confirm our theoretical data. One way which could be explored to check for the validity of our proposed theory is the development of spectroscopy such as infra-red or Raman spectroscopy to estimate the adsorbed phase volume with the difficulty to compensate for gas phase interferences in spectra. Moreover, the question raised by the problem of the boundary between adsorbed phase and bulk phase could not be solved using this method. Another solution could be to compare absolute adsorption amounts with those obtained by breakthrough curve measurements assuming that adsorption data obtained by inverse chromatography are absolute adsorption data which is only true for low pressures, i.e. pressures for which the apparent porosity of the adsorbent material keeps constant.

Finally, this study intrinsically supposes that the adsorbent volume initially determined by a helium adsorption measurement is the true volume for buoyancy effect correction of the gas phase on the adsorbent volume. But, because of its low van der Waals diameter (0.25 nm), helium can access ultramicropores whereas gases such as methane (0.38 nm) or hydrogen sulphide (0.36 nm) can not access all the pores, especially if the pore size distribution is shifted to low pore sizes. It means that it could be interesting to determine an adsorbent volume specific for each adsorbate, and then to their mixtures in the aim to really consider a real accessible surface for adsorption and thus a real volume on which is applied the buoyancy effect. Such question has already been underlined by Ross and Bustin (2007) and could be developed to get a more accurate buoyancy effect correction.

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