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Development of a new apparatus for gas mixture adsorption measurements coupling gravimetric and chromatographic techniques

Lomig Hamon · Marc Frère · Guy De Weireld

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Abstract An experimental apparatus which allows to measure adsorption isotherms for binary, ternary or quaternary mixtures for pressures between vacuum and 5.0 MPa and temperatures between 263 K and 373 K is presented. This system couples gravimetric and chromatographic techniques. The use of a mass spectrometer as gas analyzer allows to investigate a large variety of gases (such as carbon dioxide, hydrogen sulfide, mercaptans). In this paper, we measure the binary adsorption of hydrogen sulfide in a methane matrix on a commercial activated carbon at 1.0 MPa and at 298 K. Molar ratio in hydrogen sulfide is between 10 mol. ppm and 3 mol.%. Experimental results are then compared to simulated ones. The model which is tested is the classical Ideal Adsorbed Solution theory. This simulation step requires the pure gas equilibrium data obtained and fitted with the Langmuir's law, which are also presented here.

Keywords Fundamentals of adsorption · Gas phase adsorption · Bio, energy and environmental applications

1 Introduction

A lot of methods have been developed during the last twenty years to measure adsorption isotherms for gas mixtures in different concentrations domains. Talu (1998) proposed to classify these techniques into two categories: the open systems on the one hand and the closed systems on the other hand. In open systems, the gas mixture passes through a column containing the adsorbent and the gas mixture composition is analyzed at the column outlet. The breakthrough curve analysis is used to determine kinetic and thermodynamic parameters. For closed systems, the gases are introduced into vessels where volumes are accurately determined; the gases are then circulated through a vessel containing the adsorbent. Thermodynamics adsorption data can be measured by volumetric-chromatographic (Olivier et al. 1996) or gravimetric-chromatographic methods (Keller et al. 1999).

Gas separation techniques using adsorption are commonly used in industrial processes. Therefore, gas mixture adsorption measurements are of main interest for their correct design and operation. Nevertheless, as far as ultrapurification of adsorbable gases is concerned, it appears necessary to obtain experimental adsorption data at low concentrations for one of several components of the mixture (acid gases or impurities in hydrogen for fuel cells, sulfur and nitrogenous compounds in natural gas, carbon dioxide in air or impurities in gases for semi-conductor applications). The classical techniques for the determination of thermodynamic adsorption data have then to be adapted to such particular systems. Our work is devoted to the study of the desulfuration of natural gas, focusing on the methane-hydrogen sulfide binary system. For such a purpose, we developed an apparatus coupling gravimetric and chromatographic techniques with volumetric part for gas mixture preparation. Here, we present the apparatus and the method used to determine the adsorbed quantities. Experimental adsorbed values are also presented. Finally a comparison between our adsorption results and simulated ones obtained by using the Ideal Adsorbed Solution Theory (IAST) is made.

L. Hamon · M. Frère · G. De Weireld (✉)
Thermodynamics Department, Faculté Polytechnique de Mons,
31 bd Dolez, 7000 Mons, Belgium
e-mail: guy.deweireld@fpms.ac.be

2 Experimental section

2.1 General description of the apparatus

The apparatus is based on a Rubotherm (Bochum, Germany) magnetic suspension balance (Dreisbach et al. 1996; De Weireld et al. 1999). The principle of such a balance is that a crucible containing the adsorbent is magnetically connected to an analytical balance. This technique allows to separate physically the balance from the adsorption cell containing the gas. So that corrosive gases can be manipulated and wide temperature and pressure ranges may be investigated without damaging the balance and avoiding any condensation point.

The whole apparatus is shown in Fig. 1.

An incubator (Binder, KB400) maintains the whole device at the desired temperature. The analytical balance (Mettler Toledo, AT261; resolution: 10 µg; thermal deviation: 1.5 ppm K^{-1} for temperatures between 283 K and 303 K) is outside the incubator. The magnetic coupling system passes through the upper wall of the incubator. A temperature probe (Pt100 A class; accuracy: 0.15 K) is located nearby the crucible for its temperature measurement. Two different piezoresistive pressure transmitters are used: the first one (pressure transmitter 1, MKS Baratron 627 B) is adapted for

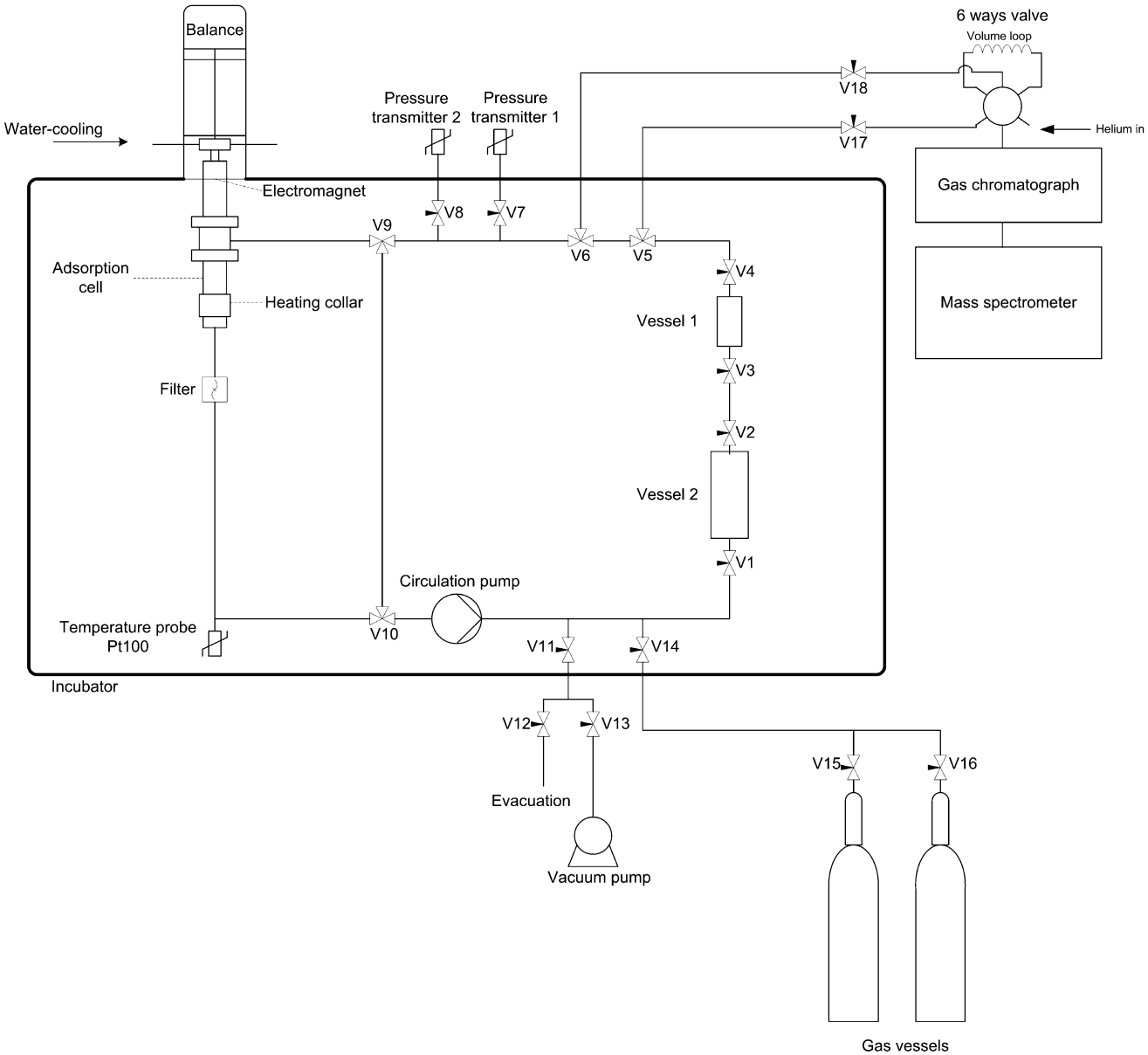

Fig. 1 Gravimetric-chromatographic apparatus

pressure under 1,000 Torr and is thermoregulated at 318 K; its accuracy is 0.02 Torr. The second pressure transmitter (pressure transmitter 2, Endress-Hauser, Cerabar S PMP 635) presents a maximum range of 10.0 MPa; its operating range can be selected from 0–0.5 to 0–10.0 MPa; its accuracy is 0.1% of the full scale selected. Two storage vessels made of stainless steel and designed to withstand the experimental pressure are used to prepare the mixture; the smallest one (Vessel 1, 42.63 ± 0.16 cm^3) is used to store the trace gas; the second one (Vessel 2, 512.56 ± 0.35 cm^3) is used to store the matrix gas. The total volume of the installation is estimated to be approximately 775 cm^3. More than two vessels can be used for ternary or quaternary gas mixture preparation. The gas analyzer is a gas chromatograph (Thermo, Focus), using a sulfur compounds specific silica plot column, coupled to a mass spectrometer (Thermo, DSQ). This system allows to separate hydrocarbon compounds from sulfur compounds and to detect low sulfur compound contents (up to 1.0 mol. ppm) in a methane matrix. The gas mixture injection is made through a 6-way valve (Valco) using an injection loop of 1 µL. A rotary magnetically coupled circulation pump (ASF Thomas, GK-M-02) is used to circulate the mixture on the adsorbent.

The adsorbent sample is placed in a crucible: its 12 cm^3 volume can contain 0.1 g to 1.5 g of adsorbent depending of the adsorbent volume. It is outgassed *in situ* during period depending of the adsorbent nature (with a maximum temperature of 673 K) before the adsorbent mass is measured. At the beginning of one experiment, the whole installation is under vacuum. The first gas, i.e., the trace gas, is injected in vessel 1; temperature and pressure (using the pressure transmitter 1) are measured. Knowing the vessel volume and using an appropriate $(p - v - T)$ equation of state (EOS), the mass of gas is determined. Vessel 1 in then isolated closing valves V3 and V4; the rest of the installation is placed under vacuum and the same operation is repeated for the second gas in vessel 2 using the pressure transmitter 2. After filling the vessel 2, the whole installation except the vessels is under vacuum. The two gases are then injected in the adsorption cell by opening valves V1, V2, V3 and V4. The three-way valves V5, V6, V9 and V10 are in horizontal position, i.e., flow goes from V4 to the adsorption cell, and from the adsorption cell to the circulation pump (the tube between V9 and V10 is under vacuum, the gas mixture circulates through the adsorption cell and does not circulate in the volume loop). The circulation pump is switched on. Because of dead volume issue, the pressure transmitters remain under vacuum (valves V7 and V8 closed). Once the adsorption equilibrium is supposed to be reached, the circulation pump is switched off and the mass is monitored with the magnetic balance, the mass being recorded every 3 minutes for 15 minutes. If the standard deviation is under 80 µg, the value is recorded; otherwise, the circulation pump is switched on for 2 hours and the control of equilibrium state is repeated. When the mass is stable, valve V8 is opened: when new thermodynamic equilibrium is reached, i.e., temperature and pressure are constant and the mass criterion for five consecutive measurements presents a maximum deviation under 80 µg (3 minutes between each measurement), mass, temperature and pressure (using pressure transmitter 2) are recorded. This method is used to avoid the dead volume issue, i.e., partial or non-homogenization of the gas mixture in this volume. Valves V5 and V6 are then moved in vertical position and valves V17 and V18 are opened. A gas composition analysis is then performed by the gas chromatograph and the mass spectrometer. By using an appropriate $(p - v - T)$ EOS, the pressure, the temperature and the gas mixture composition known, the gas density can be determined.

2.2 Determination of the adsorbed quantities

The molar composition of compound 1 in gas phase can be expressed as a function of final gas quantities ($n_{1\,\mathrm{final}}$ and $n_{2\,\mathrm{final}}$) or expressed as a function of initial ($n_{1\,\mathrm{initial}}$ and $n_{2\,\mathrm{initial}}$) and adsorbed ($n_{1\,\mathrm{ads}}$ and $n_{2\,\mathrm{ads}}$) quantities as:

$$y_1 = \frac{n_{1\,\mathrm{final}}}{n_{1\,\mathrm{final}} + n_{2\,\mathrm{final}}} = \frac{n_{1\,\mathrm{init}} - n_{1\,\mathrm{ads}}}{n_{1\,\mathrm{init}} - n_{1\,\mathrm{ads}} + n_{2\,\mathrm{init}} - n_{2\,\mathrm{ads}}} \quad (1)$$

Moreover, total adsorbed mass can be expressed as:

$$m_{\mathrm{tot\,ads}} = m_{1\,\mathrm{ads}} + m_{2\,\mathrm{ads}} = n_{1\,\mathrm{ads}} \cdot M_1 + n_{2\,\mathrm{ads}} \cdot M_2 \quad (2)$$

where M_1 and M_2 are the molar mass of compounds 1 and 2 respectively, $m_{\mathrm{tot\,ads}}$ is the total adsorbed mass. Combining (1) and (2), adsorbed quantities of compound 1 is expressed by (3):

$$n_{1\,\mathrm{ads}} = \frac{n_{1\,\mathrm{init}} + y_1\left(\frac{m_{\mathrm{tot\,ads}}}{M_2} - n_{1\,\mathrm{init}} - n_{2\,\mathrm{init}}\right)}{1 + y_1\left(\frac{M_1}{M_2} - 1\right)} \quad (3)$$

The same calculation can be performed for compound 2.

2.3 Buoyancy effect treatment

The main error on the measured mass is due to the buoyancy effect of the gas phase on the adsorbent-crucible volume $V_{\mathrm{crucible+adsorbent}}$. This volume is obtained by recording a preliminary helium isotherm: it is generally assumed that helium does not adsorb on any adsorbent, thus the evolution of measured mass for different helium pressures is directly linked to the volume of the adsorbent-crucible system. Helium measurements are performed at 298 K by measuring 5 isotherm points for pressures from 0.2 MPa to 2.0 MPa. For the determination of $V_{\mathrm{crucible+adsorbent}}$, the helium density is calculated using the $(p - v - T)$ modified Benedict-Webb-Rubin EOS proposed by McCarty and Arp (1990). This volume is determined with a maximum accuracy of 0.10 cm^3

(interval of confidence of 95%, Guide to the expression of Uncertainty in Measurement method, International Organization for Standardization 1995). Once $V_{\text{crucible+adsorbent}}$ is determined, the excess adsorbed mass $m_{\text{tot ads}}$ required in (3) may be calculated by (4).

$$m_{\text{tot ads}} = m_{\text{ads mes}} + V_{\text{crucible+adsorbent}} \cdot \rho_{\text{gas}} \quad (4)$$

where ρ_{gas} is density of the gas mixture and $m_{\text{ads mes}}$ the mass recorded during one experiment. It should be noticed that the correction of the buoyancy effect on the volume of the adsorbed phase is not considered, the pressure (1.0 MPa) used is low enough for this effect to remain weak (De Weireld and Frère 2002).

3 Results and discussion

The first results were obtained on a commercial activated carbon (AC NC100) provided by Pica (France). It was produced from coconut calcinated at 1100 K and activated at the same temperature in presence of water. The BET surface area is 1493 $m^2\,g^{-1}$. The microporous volume is 0.585 $cm^3\,g^{-1}$ and the mesoporous volume is 0.082 $cm^3\,g^{-1}$.

Methane ($T_c = 190.6$ K; $p_c = 4.61$ MPa) was provided by L'Air Liquide (purity of 99.995%). Hydrogen sulfide ($T_c = 373.3$ K; $p_c = 8.97$ MPa) was provided by Praxair (purity of 99.95%).

3.1 EOS choices

The use of an EOS is required at three steps of the procedure:

- determination of $V_{\text{crucible+adsorbent}}$, as explained in the previous section. We used the $(p - v - T)$ modified Benedict-Webb-Rubin EOS proposed by McCarty and Arp (1990);
- determination of the initial quantities of the pure gases injected in vessels 1 and 2 required in (1);
- determination of ρ_{gas}, the density of the gas mixture required in (4).

For pure hydrogen sulfide, it appears that the Peng–Robinson EOS (Peng and Robinson 1976), the Coquelet et al. EOS (Coquelet et al. 2004) and the Twu et al. EOS (Twu et al. 1995) lead to the best results when comparing experimental results to calculated ones (maximum deviation equal to 0.2%). The experimental results which were considered are given by Reamer et al. (1950) and Liu et al. (1986) in temperature and pressure ranges similar to our experimental conditions. We chose the Peng–Robinson EOS because of its low number of parameters. For pure methane, the modified Helmholtz EOS presented by Setzmann and Wagner (1991) gives uncertainties on density less than 0.03% for pressures below 12 MPa and temperatures below 350 K when compared to experimental data (Kleinrahm et al. 1988; Pieperbeck et al. 1991) while the Peng–Robinson EOS shows uncertainties greater than 4%. The modified Helmholtz EOS (presented by Setzmann and Wagner) was thus used to calculate the initial amount of methane in vessel 2.

For binary mixtures of hydrogen sulfide in a methane matrix, the preliminary choice of using the Peng–Robinson EOS to describe the hydrogen sulfide properties decided us to use the same kind of EOS with a mixing rule describing the interactions between the two components. We chose the Peng–Robinson EOS described by Nishiumi and Aray (1988) for which interaction parameters have been generalized. This method seems to present low uncertainties in our domain of pressure and hydrogen sulfide content in comparison with experimental values measured by Reamer et al. (1951).

3.2 Results presentation

The first step of the study was the record of pure compounds isotherms data, which were obtained using the magnetic suspension balance. The experimental procedure is described elsewhere (De Weireld et al. 1999). Figures 2 and 3 present the pure gas adsorption isotherm obtained for hydrogen sulfide and methane at 298 K.

The hydrogen sulfide isotherm exhibits a higher initial slope than the methane isotherm which is related to the high interactions between the hydrogen sulfide molecules and the carbonaceous surface. Moreover, saturated adsorbed quantities are more important for hydrogen sulfide: similarly, interactions between hydrogen sulfide and the activated carbon surface are more important than interactions between

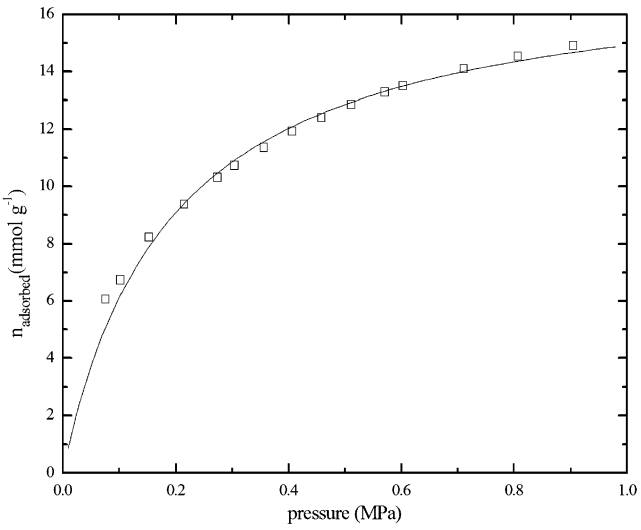

Fig. 2 Hydrogen sulfide isotherm at 298 K on NC100 AC. Experimental data and Langmuir fit

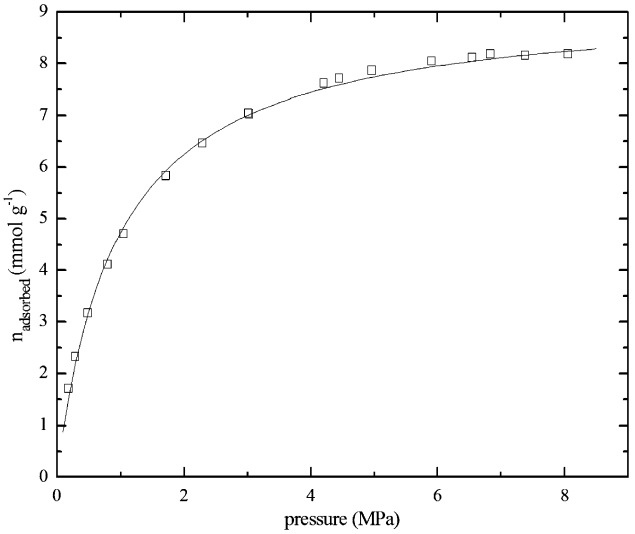

Fig. 3 Methane isotherm at 298 K on the NC100 AC. Experimental data and Langmuir fit

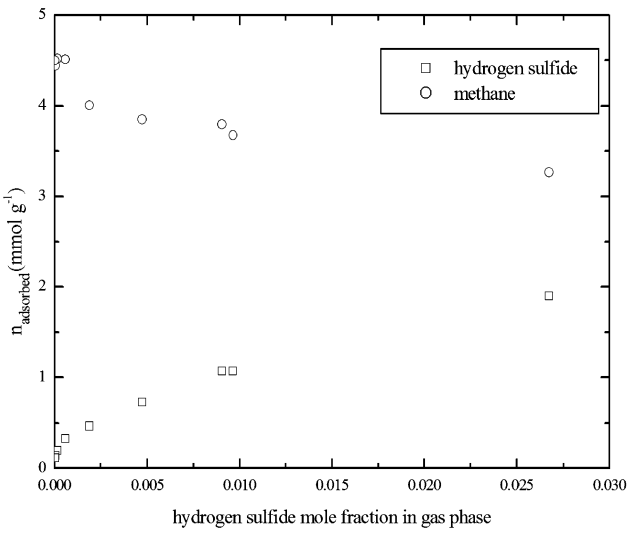

Fig. 4 Hydrogen sulfide and methane adsorbed quantities for methane-hydrogen sulfide binary adsorption on NC100 AC at 298 K and at 1.0 MPa

Table 1 Langmuirian fitted values of adsorption isotherm of methane and hydrogen sulfide on NC100 activated carbon at 298 K

Methane	Saturated adsorbed quantity	9.18 mmol g^{-1}
	Langmuirian constant	1.07 MPa^{-1}
	Correlation coefficient R^2	0.99623
Hydrogen sulfide	Saturated adsorbed quantity	15.55 mmol g^{-1}
	Langmuirian constant	6.93 MPa^{-1}
	Correlation coefficient R^2	0.99602

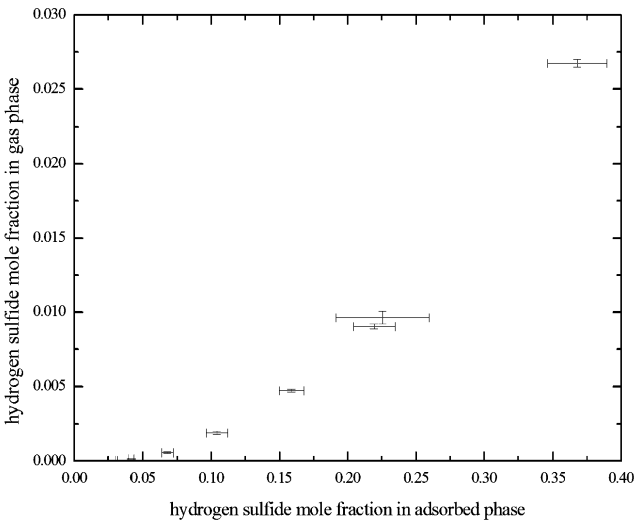

Fig. 5 Selectivity of hydrogen sulfide for methane-hydrogen sulfide binary adsorption on NC100 AC at 298 K and at 1.0 MPa

methane and the same surface. The presence of basic oxides, such as described by Vagner (2003), could explain the preferential interactions between the surface and an acid gas such as hydrogen sulfide. These experimental results were fitted using the Langmuir's law as shown in Table 1.

Figure 4 presents the amount (molar basis) of methane and hydrogen sulfide adsorbed at 298 K and 1.0 MPa for molar ratios of hydrogen sulfide in the gas phase ranging from 34 mol. ppm to 2.7 mol.%. Figure 5 presents the related selectivity curve, i.e. the mole fraction of hydrogen sulfide in the gas phase as a function of the mole fraction of hydrogen sulfide in the adsorbed phase.

Figure 4 shows that the amount of methane adsorbed is always higher than that of hydrogen sulfide. Nevertheless, the selectivity curve shows that the adsorbent presents a higher affinity for hydrogen sulfide: the gas phase is mainly constituted of methane while the concentration of hydrogen sulfide in the adsorbed phase is particularly important. This difference of hydrogen sulfide concentration in the gas phase and in the adsorbed phase is explained by the preferential selectivity for hydrogen sulfide of the activated carbon. For lower concentrations in hydrogen sulfide in the gas phase, it can be thought that more energetic adsorption sites adsorb preferentially hydrogen sulfide: an elemental analysis shows that this activated carbon is composed of 2.6% of oxygen and contains an important part of basic oxides (Vagner 2003). Combined with a known large pore size distribution, this information can explain that more energetic pore sites can easily adsorb acid molecules such as hydrogen sulfide.

Uncertainties on the results have been determined according to the GUM method (Guide to the expression of Uncertainty in Measurement, International Organization for Standardization, 1995). The interval of confidence is 95%. The maximum uncertainty of the mole fraction of hydrogen sulfide in the adsorbed phase is 9.6%; the minimum uncer-

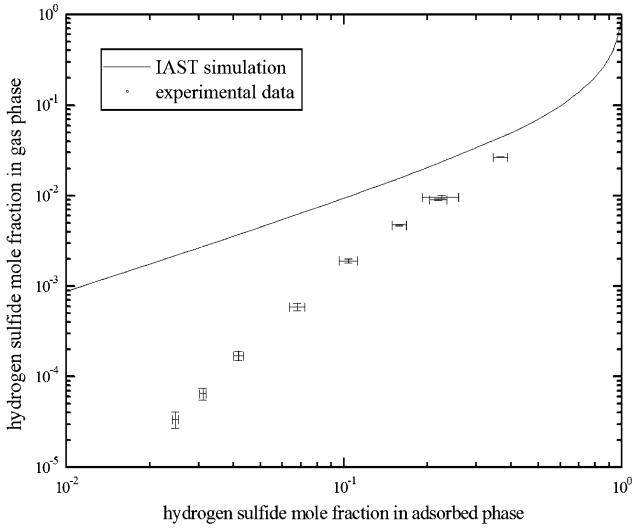

Fig. 6 Selectivity curve: comparison between experimental data and simulation obtained with the IAST model (methane-hydrogen sulfide binary adsorption on NC100 AC at 298 K and at 1.0 MPa)

tainty is 3.1%. In the gas phase, the maximum and minimum uncertainties of the mole fraction of hydrogen sulfide are respectively 12% and 1.7%.

3.3 Simulation results using IAST

We compared our experimental results to simulated ones using the IAST method developed by Myers and Prausnitz (1965) and Do (1998). The pure gas adsorption isotherm model used is the Langmuir's model. Figure 6 presents such a comparison for the selectivity curve; it is represented in a log-log scale.

This comparison between experimental and simulated results suggests that hydrogen sulfide mole fraction in the adsorbed phase for experimental data is more important than for IAST simulated ones. Such a discrepancy can be explained in different ways:

- the thermodynamic model considers the adsorbed phase to be ideal which is maybe not the case;
- the correct use of the IAST model requires low pressure adsorption data for pure hydrogen sulfide.

Further experimental and theoretical developments is necessary to provide a comprehensive comment about the validity of the IAST model for simulating the system studied in our experimental particular conditions.

4 Conclusion and perspectives

We present an experimental device and the related procedure allowing the measurement of binary adsorption isotherms for systems containing a major component (weakly adsorbed) and traces of a second component (strongly adsorbed). The experimental device works in a wide temperature range and up to high pressures (up to 5.0 MPa). The first experimental results are presented for the methane-hydrogen sulfide mixture adsorbed on an activated carbon at 298 K and 1.0 MPa; the investigated range of the hydrogen sulfide mole fraction in the gas phase is 10 mol. ppm to 3 mol.%. A first attempt to simulate these results using the IAST model showed significant discrepancies between experimental and simulated data, especially for low mole fraction in hydrogen sulfide. Further experimental data on this system will be required in order to give a correct explanation of the observed discrepancies. Other sulfur compounds, such as light mercaptans, and carbon dioxide will be studied as well as the effect of increasing pressures, and gas mixture adsorption on novel materials such as metal-organic frameworks will be investigated.

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