Adsorption 11: 179–182, 2005

A Complete Set of Experimental Devices for the Determination of the Gas Separation Capacity of Adsorbents

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Abstract. In this work, we present a complete experimental procedure which aims at measuring adsorption isotherms, selectivity curves and kinetics of air compounds on porous media in broad ranges of pressure and temperature. The experimental set-up and the experimental procedures are presented as well as a complete report on treatments of the rough experimental results to obtain the adsorption isotherms, selectivity and kinetics curves. Results are provided for nitrogen/LiLSX and oxygen/LiLSX systems (adsorption isotherms curves at 278 and 303 K in the pressure range 0–400 kPa), for a binary mixture nitrogen/oxygen/LiLSX system at 303 K and 400 kPa (selectivity curves). Kinetics curves are presented for nitrogen/LiLSX and oxygen/LiLSX systems at 303 K and 400 kPa.

Keywords: adsorption, zeolite, isotherm, selectivity, kinetics

1. Introduction

The design of gas separation processes based on adsorption requires the knowledge of basic adsorption data (equilibrium and kinetic data). Generally, these processes are working in wide ranges of operating conditions (temperature, pressure, gas composition). As a consequence it is difficult to obtain a complete set of reliable and consistent experimental data which may be used to develop accurate process simulation models.

In this paper we present an integrated experimental procedure based on three different devices and working in wide ranges of conditions. This procedure was used to study a nitrogen/oxygen/LiLSX system (ZeoMax–Tricat).

2. Experimental Section

2.1. Adsorption Isotherms

The adsorption isotherms measurements are achieved using a volumetric method (Berlier et al., 1995). The principle of this method is based on successive expansions of the gas from a pressure cell to an adsorption cell. Knowing the volumes of the cells, the adsorbed mass can be calculated using an equation of state which provides the molar volume of the adsorbate as a function of temperature and pressure in the system before and after adsorption (Frère et al., 1994). The wholly automated apparatus enables the measurement of pure gas isotherms from 278 to 333 K at pressures up to 4000 kPa. Prior to all measurements, the adsorbent is put under vacuum during one hour at ambient temperature, then it is outgassed under vacuum during ten hours at a constant temperature of 673 K.

The intrinsic sensitivity of the balance (0.01 g) which is used for the determination of the sample mass leads to a very weak relative error (0.03%) on the sample mass measurement (35 g). The estimated relative error on the pressure cell volume is 1.7% (818.7 ± 13.5 cm^3). The maximum relative error on the adsorption cell volume is 3.6% (343.9 ± 12.4 cm^3). The accuracy on the pressure is about 0.2 % of the programmed scale that is to say to 0.8 kPa. These errors on volumes and pressures lead to measurements errors on the adsorbed quantities. It has been estimated that the relative error on

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the adsorbed mass of nitrogen at 303 K ranges from 12.9% for the first point to 2.5% for the last point (Belmabkhout et al., 2004). Such errors result from the indirect procedures which are used both for the volume calibration and for the adsorption measurements. They may me considerably reduced by:

- adapting the pressure transducer working range during an adsorption run,
- determining the adsorbent density from gravimetric measurements.

Experimental data of adsorption isotherms for nitrogen and oxygen on zeolite ZeoMax at 278 and 303 K were obtained at pressures up to 360 kPa and compared with the Langmuir theory (Eq. (1)) (Jayaraman et al., 2002).

$$\frac{N}{N_s} = \frac{b \times p}{1 + b \times p} \tag{1}$$

N – adsorbed mole number per unit of mass of adsorbent (mol/kg);
N_s – adsorbed mole number per unit of mass of adsorbent (mol/kg) at adsorbent saturation;
p – pressure (kPa);
b – energetic Langmuir parameter (kPa^{-1}).

The results are presented in Fig. 1. This model generally fits very well experimental adsorption data for zeolites. Table 1 gives the Langmuir parameters of nitrogen and oxygen on zeolite ZeoMax. They were obtained by minimising the average discrepancies between the calculated and experimental data.

2.2. Selectivity Curves of Binary Gaseous Mixtures

The device is based on the volumetric method. The principle of this method is based on the expansion of the gaseous mixture from a circulation circuit to the adsorption cell. Knowing the volumes of the adsorption cell and of the circulation circuit, the calculation of the adsorbed mass of each compound of the gaseous mixture can be determined using an equation of state providing the molar volume of the gas phase as a function of temperature, pressure and mole fraction of each compound in the system before and after adsorption (Olivier et al., 1996).

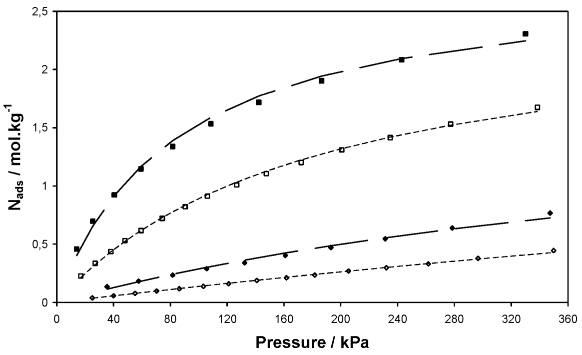

Figure 1. Experimental adsorption isotherms of nitrogen (■), oxygen (◆) at 287 K and nitrogen (□), oxygen (◇) at 303 K on zeolite ZeoMax, the dashed lines are the Langmuir predictions.

Table 1. Langmuir parameters of nitrogen and oxygen on zeolite ZeoMax at 278 K and 303 K.

Parameters	278 K	303 K
N_{SO_2} (mol/kg)	2.8185	2.5291
N_{SO_2} (mol/kg)	1.8772	2.8050
b_{N_2} (kPa^{-1})	0.0119	0.0054
b_{O_2} (kPa^{-1})	0.0018	0.0005

The interest of the apparatus lies in its capacity to determine isothermal and isobaric selectivity curves for pressure ranging from 150 to 1000 kPa and temperature ranging from 298 to 333 K.

The gas expansion from the circulation circuit to the adsorption cell and the adsorption process tend to reduce the pressure in the installation. This pressure is kept constant by reducing the volume of the device during the expansion—adsorption step. This is achieved thanks to a piston the position of which sets the volume of the gas phase. Homogenisation of the gaseous mixture is ensured by a circulation pump. The temperature is kept constant thanks to a thermostated room. The mole fractions of each compound are measured by a gas chromatograph.

The outgassing conditions are the same as for pure gas adsorption isotherms measurements.

An experimental run provides the temperature, the pressure, the gas phase composition (mole fractions y_{O_2} and y_{N2}) and the adsorbed mole numbers of each compound ($N_{\text{ads } O_2}$ and $N_{\text{ads } N_2}$) per kg of adsorbent. The mole fraction of each compound in the adsorbed phase (x_{O_2} and x_{N_2}), may be calculated by:

$$x_{O_2} = \frac{N_{\text{ads } O_2}}{N_{\text{ads } O_2} + N_{\text{ads } N_2}} \quad \text{and} \quad x_{N_2} = \frac{N_{\text{ads } N_2}}{N_{\text{ads } O_2} + N_{\text{ads } N_2}}$$

The intrinsic sensitivity of the balance used for the sample mass determination (0.01 g) leads to a very weak relative error (0.03%) on the sample mass measurement (35 g). The estimated relative error on the circulation circuit volume is 0.7% (605 ± 4.2 cm^3). The relative error on the adsorption cell volume is 2.6% (382.6 ± 9.9 cm^3). The error on the pressure is about 0.2% of the programmed scale that is to say 0.8 kPa. The error on the gas phase composition is about 0.3%. These errors on volumes, pressures and gas phase compositions lead to measurements errors on the adsorbed quantities. The relative error on the adsorbed mass of nitrogen is ranging from 3% to 4% and the relative error on the adsorbed mass of oxygen is ranging from 6% to 8%.

Figure 2 presents a selectivity curve for a $N_2 - O_2$ – ZeoMax zeolite system at 400 kPa and 303 K. Figure 3 presents the adsorbed mole numbers ($N_{\text{ads } O_2}$ and $N_{\text{ads } N_2}$) as a function of the oxygen molar fraction in the adsorbed phase (x_{O2}) (Talu et al., 1996).

The Langmuir model extended to mixtures was used to simulate these experimental results (Eqs. (2) and (3)):

$$\frac{N_{\text{ads N}_2}}{N_{\text{SN}_2}} = \frac{b_{N_2} \times y_{N_2} \times p}{\left(1 + b_{N_2} \times y_{N_2} \times p + b_{O_2} \times \left(1 - y_{N_2}\right) \times p\right)} \tag{2}$$

$$\frac{N_{\text{ads O}_2}}{N_{\text{SO}_2}} = \frac{b_{O_2} \times y_{O_2} \times p}{\left(1 + b_{N_2} \times y_{N_2} \times p + b_{O_2} \times \left(1 - y_{N_2}\right) \times p\right)} \tag{3}$$

The parameters N_{SN_2}, N_{SO_2}, b_{N_2} and b_{O_2} are those obtained from the isotherms of pure substances (Table 1).

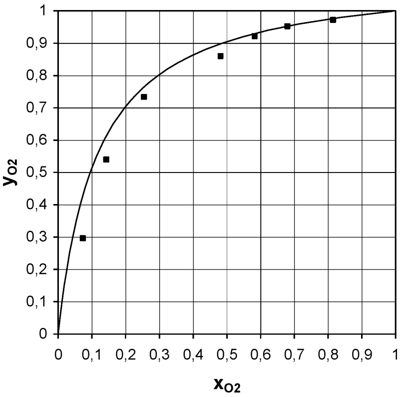

Figure 2. Oxygen mole fraction in the gas phase versus oxygen mole fraction in the adsorbed phase at 400 kPa and 303 K on zeolite ZeoMax. Experimental data (■), the dashed lines are the Langmuir prediction.

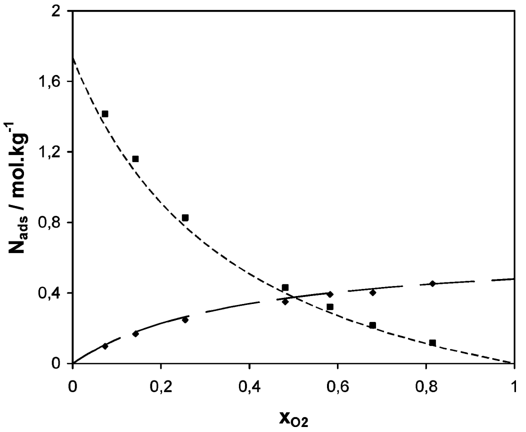

Figure 3. Adsorbed mole numbers of nitrogen (■) and oxygen (♦) versus oxygen mole fraction in the adsorbed phase at 400 kPa and 303 K on zeolite ZeoMax, the dashed lines are the Langmuir predictions.

The average deviation between the experimental adsorbed mole numbers and the Langmuir predictions is 6%.

2.3. Kinetics Curves

The determination of the kinetics curves is based on a gravimetric method. The gravimetric method consists of exposing a clean adsorbent sample to a pure gas pressure step at a constant temperature. Measurements of the mass uptake of the adsorbent sample are achieved by a magnetic balance. This method allows for the direct measurement of the amount adsorbed versus time (De Weireld et al., 1999).

The outgassing conditions are the same as in the previous experimental procedures. An automatically-controlled system allows setting a constant pressure in the device. Pressure and temperature are also measured as a function of time.

The experimental device may work with increasing gas pressure from 0 to 10 000 kPa and for a temperature ranging from 223 to 383 K.

The mass is measured by the balance with an absolute error equal to 0.1 mg. The relative error on the sample mass taking into account 2 g of sample is thus 0.005%. The relative error on the pressure is 0.1% of the full scale. The main source of error comes from the determination of the system volume (V_{syst}) on which the buoyancy effect occurs; the relative error on the system volume is estimated to 0.3%. The relative error on the adsorbed quantities is 0.3%.

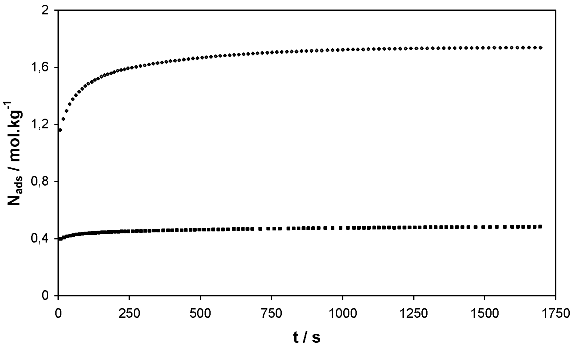

Figure 4. Adsorbed mole numbers of nitrogen (◇) and oxygen (■) on zeolite ZeoMax versus time at 400 kPa and 303 K.

The different errors inherent to the method may be considered as very low and have no significant effect on the measurement accuracy of the adsorbed quantities (Belmabkhout et al., 2004).

Adsorption kinetics for nitrogen and oxygen on zeolite ZeoMax were obtained at 400 kPa and 303 K. The results are presented in Fig. 4.

If the kinetics of adsorption is modelled by a linear driving model (Eqs. (4) and (5)):

$$\frac{\partial N_{\text{ads N}_2}}{\partial t} = k_{\text{N}_2} \times (N^*_{\text{ads N}_2} - N_{\text{ads N}_2}) \tag{4}$$

$$\frac{\partial N_{\text{ads O}_2}}{\partial t} = k_{O_2} \times (N^*_{\text{ads O}_2} - N_{\text{ads O}_2}) \tag{5}$$

In which k_{N_2} and k_{O_2} are the kinetics coefficients of nitrogen and oxygen (s^{-1}) on zeolite ZeoMax;

$N^*_{\text{ads N}_2}$ and $N^*_{\text{ads O}_2}$ are the adsorbed mole numbers of nitrogen and oxygen per unit of adsorbent mass at equilibrium (mol/kg).

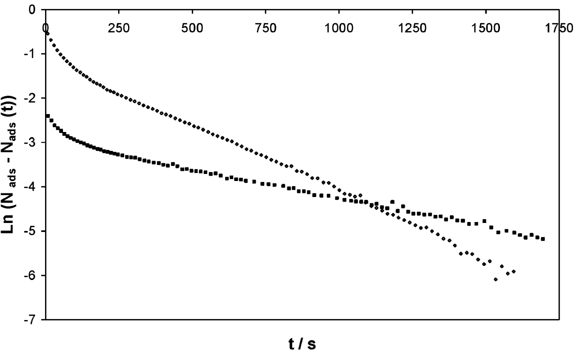

Figure 5. Mathematical treatment of the experimental kinetics data of nitrogen (◇) and oxygen (■) at 400 kPa and 303 K on zeolite ZeoMax.

The plot ln (N^*_{ads}–N_{ads}) versus time is then linear. This mathematical treatment of the experimental data is presented in Fig. 5. This treatment allows the determination of the kinetic constants: $k_{\text{N}_2} = 0.0031\ \text{s}^{-1}$ and $k_{\text{O}_2} = 0.0014\ \text{s}^{-1}$.

3. Conclusions

In this paper with present an integrated experimental procedure based on three different experimental devices and allowing the determination of fundamental data for the design of gas separation processes. The experimental set-up is able to work in wide ranges of temperature, pressure and gas composition so that most of the industrial applications may be studied. The consistency of the techniques may be checked as the three techniques may provide the equilibrium adsorbed mole numbers for pure gases.

Results are presented for a N_2–O_2–ZeoMax (LiLSX) system and classic models are applied to describe both the thermodynamic and the kinetic data.

Acknowledgment

This work was supported by the department for Technology and Research of the Walloon Region (Belgium).

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