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## Single and Multicomponent Sorption of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in a Microporous Metal-Organic Framework

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**Abstract:** Single and multicomponent fixed-bed adsorption of CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> on crystals of MOF-508b has been studied in this work. Adsorption equilibrium was measured at temperatures ranging from 303 to 343 K and partial pressures up to 4.5 bar. MOF-508b is very selective for CO<sub>2</sub> and the loadings of CH<sub>4</sub> and N<sub>2</sub> are practically temperature independent. The Langmuir isotherm model provides a good representation of the equilibrium data. A dynamic model based on the LDF approximation for the mass transfer has been used to describe with good accuracy the adsorption kinetics of single, binary and ternary breakthrough curves. It was found that the intra-crystalline diffusivity for CO<sub>2</sub> is one order of magnitude faster than for CH<sub>4</sub> and N<sub>2</sub>.

**Keywords:** CO<sub>2</sub> separation, dynamic simulation, fixed bed, dynamic, metal-organic framework, multi-component adsorption, natural gas

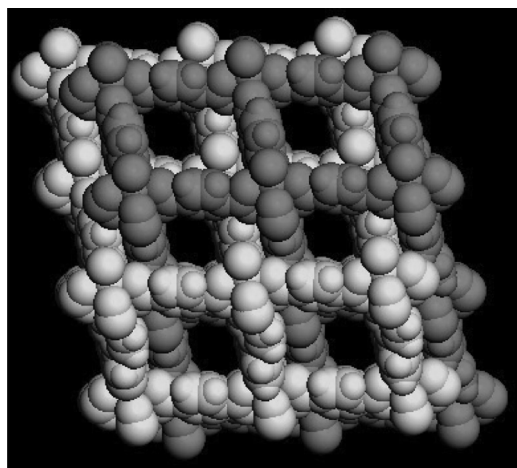
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## INTRODUCTION

The quality of natural gas can vary widely according to the location of the plant; nevertheless its composition can include up to 10% and 5% of carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>), respectively. Natural gas containing high levels of CO<sub>2</sub> and N<sub>2</sub> represent approximately one-third of the U.S. natural gas resource (1). In many cases, this *low quality gas* cannot be treated from the economic point of view with existing processing technology, which means that huge amounts of fuel remain underground (2). The continuous exhaustion of the producing wells, added to the fact that unexploited reserves contain higher fractions of low quality gas will stress the need for more efficient purifying processes able to meet the quality standards specified by the major pipeline transmission and distribution companies.

At the same time, a novel class of crystalline microporous adsorbents has found great interest; the metal-organic frameworks (MOFs) have the potential for making a significant impact in separation processes since they offer the possibility to be tuned varying their pore size and functionality for specific applications. In a recent article (3), we have presented a sorption equilibrium study for the adsorption of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in a microporous MOF Zn(BDC)(4,4'-Bipy)<sub>0.5</sub> (MOF-508b) (4,4'-Bipy = 4,4'-bipyridine) (4) with one-dimensional pores of about  $4.0 \times 4.0 \text{ \AA}$  (See Fig. 1). It was referred to by Bastin et al. (3) that the significant difference in the quadrupole moment of these molecules plays an important role resulting in the preferential adsorption of CO<sub>2</sub>, relatively to CH<sub>4</sub> and N<sub>2</sub>.



**Figure 1.** One-dimensional micropores of about  $4.0 \times 4.0 \text{ \AA}$  in 4 MOF-508b.

In this work, we will present the first example of mathematical modeling for fixed-bed adsorption of gas mixtures in microporous MOFs. Sorption equilibrium data of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in MOF-508b at 303, 323, and 343 K and partial pressures up to 4.5 bar are reported for the three gases. These data are fitted with a simple Langmuir isotherm model, the results being presented in several figures along the article. Single, binary, and ternary breakthrough curves were measured to provide required data to develop and validate a model based on the LDF approximation for the mass transfer, which could be used in the implementation of an adsorption processes for the purification of the natural gas.

## EXPERIMENTAL SECTION

### Adsorbates and Adsorbent

The adsorbates under investigation were CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>. All the gases containing purity higher than 99.5% were supplied by Air Liquide. Physical properties of these gases are summarized in Table 1.

The microporous MOF-508b Zn(BDC)(4,4'-Bipy)<sub>0.5</sub> (**1**) (4,4'-Bipy = 4,4'-bipyridine) was synthesized according to the procedure in ref. (4).

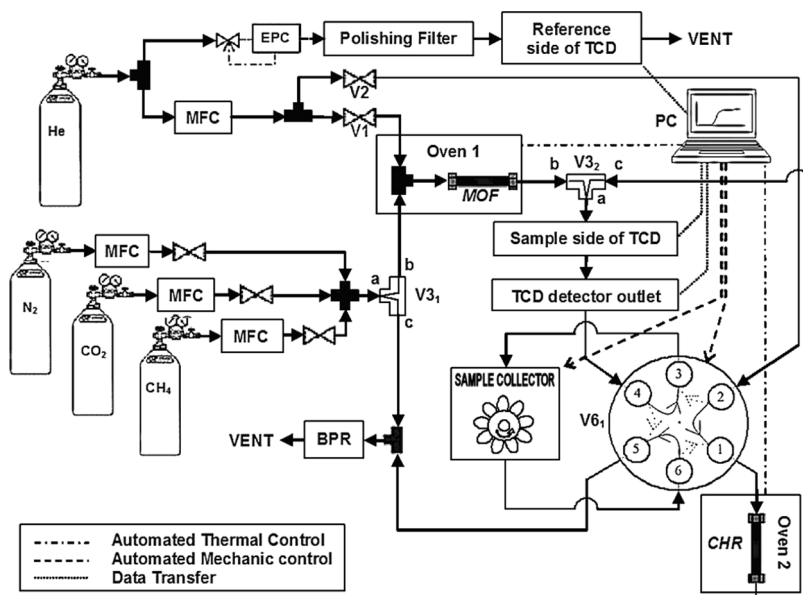
### Equipment and Procedure

Adsorption equilibrium data were obtained from breakthrough experiments in a laboratorial unit existing at LSRE. Figure 2 shows a schematic representation of the apparatus used to measure single and multicomponent breakthrough curves. A detailed description of the apparatus set-up is given in a previous work (3).

The experimental procedure follows: An adsorption column packed with crystals of MOF-508b dispersed in glass wool was operated by introducing a constant flowrate of the adsorbate gas mixture with known

**Table 1.** Adsorbate properties (21,22)

Physical property	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>
Kinetic diameter (Å)	3.30	3.64	3.80
Dipole moment $\times 10^{18}$ (esu cm)	0	0	0
Quadrupole moment $\times 10^{26}$ (esu cm <sup>2</sup> )	4.30	1.52	0
Polarizability $\times 10^{25}$ (cm <sup>3</sup> )	31.0	17.6	26.0



**Figure 2.** Schematic diagram of the apparatus used to measure adsorption equilibrium for mono- and multi-component systems: (BPR) back pressure regulator; (Sample collector) 10 sample-loops; (CHR) chromatographic silica gel column; (MOF) packed column containing MOF; (EPC) electronic pressure controller; (MFC) mass flow controller; (PC) Computer; (TCD) thermal conductivity detector; (V<sub>1</sub>, V<sub>2</sub>) valves; (V<sub>3,1</sub>, V<sub>3,2</sub>) 3-ways valves; (V<sub>6</sub>) 6-ways crossover valve; (①, ②, ③, ④, ⑤, ⑥) streams.

composition in a helium stream at a fixed total pressure. The analysis of the system consists in measuring continuously the mass flow at the outlet of the packed bed with a thermal conductivity detector (TCD). In multi-component experiments, samples are collected from the column output during the breakthrough curve for further analysis in a silica-gel chromatographic column.

Prior to each run, the packed bed is regenerated for at least 2 hr at 423 K under helium flow up to 50 ml/min. The next experiment can start as soon as the TCD signal is stable again. In our experimental procedure first experiments were not taking into account. The reversibility is evaluated by repeating some experiments occasionally and verifying the amount adsorbed which generally agree well. In this work, two columns with different internal diameters were used for single and multicomponent experiments. The characteristics of these adsorption units are reported in Table 2.

**Table 2.** Fixed-bed parameters and adsorbent properties used in the modelling of the sorption experiments of N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> in MOF-508b

Fixed bed parameters	Single experiments	Multicomponent experiments
Bed diameter, $d$ [m]	0.0046	0.0077
Bed length, $L$ [m]	0.10	0.10
Bed porosity, $\varepsilon_b$ [–]	0.74	0.68
Bulk density, $\rho_b$ [kg/m <sup>3</sup> ]	390.5	470.7
Mass of adsorbent, $W$ [g]	0.649	2.192
Particle diameter, $d_p$ [μm]		25–100
Particle density, $\rho_a$ [kg/m <sup>3</sup> ]		1492

## MODELING ADSORPTION EQUILIBRIUM

### Pure Component Isotherms

From the engineering point of view, it is important to have a good analytical description of the equilibrium data in order to reduce experimentation. The simplest theoretical model for monolayer adsorption was proposed by Langmuir (5) and it can be represented by the following equation:

$$q(p, T) = q_m \cdot \frac{b(T) \cdot p}{1 + b(T) \cdot p} \quad (1)$$

where  $q$  is the amount adsorbed,  $p$  is the partial pressure of the adsorbate,  $b$  and  $q_m$  are the adsorption affinity constant and the saturation loading, respectively. This model is based on the assumptions that the surface of the adsorbent is energetically homogeneous and the adsorbate occupies one active site when it adsorbs which is reasonable when the adsorbate molecule is small. Adsorption affinity constant,  $b$ , is assumed to vary with temperature according to the following equation:

$$b = b_0 \cdot e^{\left(\frac{-\Delta H}{RT}\right)} \quad (2)$$

where  $b_0$  is the frequency factor of the affinity constant,  $\Delta H$  is the heat of sorption,  $R$  is the universal gas constant and  $T$  is the temperature.

The parameters of the Langmuir isotherm for the three gases on MOF-508b are determined by numerical procedure. The mean absolute deviations,  $\bar{\Delta}q$ , between the predicted,  $q$ , and the experimental,  $q_{\text{exp}}$ ,

values are calculated with:

$$\bar{\Delta}q = \frac{1}{N} \sum_{i=1}^N \sqrt{(q_{\text{exp},i} - q_i)^2} \quad (3)$$

being  $N$  the total number of measurements.

### Multicomponent Adsorption Isotherms

Using the parameters given by the single component adsorption equilibrium fitting, the mixture sorption data can be predicted by an extended Langmuir isotherm model. Accordingly, the amount adsorbed of component  $i$ ,  $q_i$ , in a mixture is given by:

$$q_i(p, T) = q_{m,i} \cdot \frac{b_i(T) \cdot p_i}{1 + \sum_{k=1}^n b_k(T) \cdot p_k} \quad (4)$$

where  $n$  is the number of components present in the mixture.

### Modeling

The adsorption system is a column packed with crystals of MOF-508b through which an inert gas flows in steady-state. At time zero an adsorbate flow of known composition and an inert are introduced at the bottom of column. Several simplifications were introduced to reduce the computational time, thus the following assumptions are made:

1. The gas phase behaves as an ideal gas mixture;
2. The pressure drop through the bed is negligible;
3. The flow pattern is described by the axially dispersed plug flow model;
4. The main resistances to mass transfer for adsorbable species can be combined in a lumped mass transfer coefficient;
5. The column is isothermal.

According to these assumptions, the equations used to simulate single and multicomponent breakthrough curves are summarized in Table 3.

The Linear Driving Force (LDF) model used in this work has been tested successfully in previous studies (6,7) to simulate breakthrough curves of alkanes in zeolitic materials. The set of equations was solved numerically using the orthogonal collocation method (8). The resulting system was solved using a fifth-order Runge-Kutta code in conjunction with a Gauss elimination (algebraic equations). Twelve collocation points

**Table 3.** Dynamic mathematical model equations for fixed bed adsorption

	Equations
Mass balance to sorbate species	$\varepsilon_b D_L \frac{\partial}{\partial z} \left( C \frac{\partial y_a}{\partial z} \right) = \frac{\partial (F y_a)}{\partial z} + \varepsilon_b \frac{\partial (C y_a)}{\partial t} + (1 - \varepsilon_b) \rho_a \frac{\partial \bar{q}_i}{\partial t} \quad (5)$
Boundary conditions:	$z = 0, t > 0 \quad \varepsilon_b D_L C \frac{\partial y_a}{\partial z} = F y_a - F_f y_{af} \quad (5a)$
	$z = L, t > 0 \quad \frac{\partial y_a}{\partial z} = 0 \quad (5b)$
Overall mass balance	$\frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + \sum_{i=1}^N (1 - \varepsilon_b) \rho_a \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (6)$
Boundary condition	$z = 0, t > 0 \quad F = F_f \quad (6a)$
Mass transfer rate	$\frac{\partial \bar{q}_i}{\partial t} = k(q_i - \bar{q}_i) \quad (7)$
Axial dispersion (Wakao and Funazkri, 1978) (9)	$D_L = \frac{20}{\varepsilon_b} D_m + \frac{u d_c}{2} \quad (8)$

gave a good accuracy for all experiments. The parameters used to predict the experimental data are summarized in Table 1.

### Estimation of Model Parameters for Experimental Breakthrough Curves

In order to fit the experimental breakthrough curves, numerical values for both axial dispersion and lumped mass transfer coefficients are required. The axial dispersion coefficients for each of the runs were estimated from the correlation given by Wakao and Funazkri (9) (see Table 3). This correlation follows from experiments in the low Reynolds number regime ( $Re < 2$ ) with sufficiently rapid adsorption within the particle. In the present study, small crystals ( $25 \mu\text{m} < d_p < 100 \mu\text{m}$ ) in a non-pelletized form were used resulting in a fast kinetic, moreover, the Reynolds number from the different runs was in the range  $0.1 < Re < 0.6$ . Therefore, the Wakao correlation was used to predict the axial dispersion. This correlation has been already used in the modeling of pressure swing adsorption separation of mixtures  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$  (10).

The lumped mass transfer coefficients for the experimental runs were estimated from the following correlation (11):

$$k = \left( \frac{d_p q_0}{6k_f c_0} + \frac{d_p^2}{60D_c} \right)^{-1} \quad (9)$$

which consider micropore and film resistances to mass transfer. The macropore diffusion mechanisms were neglected since we are dealing



with non-binded microporous crystals dispersed on an inert glass wool. The contribution of the external film for the mass transport resistance was taken into account despite the fact that its importance is two orders of magnitude lower than the micropore mass transport resistance. An average crystal radius of  $31\text{ }\mu\text{m}$  was considered. The values for the ratio  $q_0/c_0$  were obtained from the equilibrium model. The external mass transfer coefficient,  $k_f$ , was given by (12):

$$k_f = \frac{u}{Sc^{2/3}} \left( \frac{0.765}{(Re\ \varepsilon_b)^{0.82}} + \frac{0.365}{(Re\ \varepsilon_b)^{0.386}} \right) \quad (10)$$

where  $u$  is the interstitial velocity,  $Re$  the particle Reynolds number, both calculated with the feed flow rate and  $Sc$  is the Schmidt number. Molecular diffusivity was estimated from the Chapman-Enskog equation.

The micropore diffusivity,  $D_c$  in Equation (9) was used as a temperature dependent fitting parameter for the simulated pure component breakthrough curves, since is the only unknown term of the mathematical model. The value of  $D_c$  follows the expression:

$$D_c = D_0 \exp(-E_a/RT) \quad (11)$$

where,  $D_0$  is the pre-exponential factor and  $E_a$  is the diffusional activation energy. The micropore diffusivity fitted for single component breakthrough curves was also used to predict the binary and ternary experiments.

## RESULTS AND DISCUSSION

### Pure Component Isotherms

The first step in the characterization of an adsorbent for a specific separation process is the measurement of the adsorption equilibrium of pure components. Pure component isotherms were determined from breakthrough experiments performed with single components diluted in helium used as the inert carrier gas. The loading was determined by numerical integration of the breakthrough data following the procedure describe in previous works (6). The experiments were performed at temperatures of 303 K, 323 K, and 343 K and partial pressures between 0.1 and 4.5 bar. Complete information of the experimental fixed-bed runs performed, including partial pressure, temperature, flow-rate, mass of adsorbent used in the column, and the amount adsorbed for each run by the integration of the molar flowrate histories, is shown in Table 4.

**Table 4.** Experimental conditions and dynamic model parameters for single component breakthrough curves of N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>

Run	<i>T</i> (K)	<i>p</i> (bar)	<i>P</i> (bar)	<i>V</i> <sub>Helium</sub> (ml/min)	<i>q</i> (mmol/g <sub>ads</sub> )	<i>k</i> (s <sup>-1</sup> )	<i>D</i> <sub>L</sub> (10 <sup>-4</sup> m <sup>2</sup> /s)	<i>D</i> <sub>c</sub> (10 <sup>-11</sup> m <sup>2</sup> /s)	<i>E</i> <sub>a</sub> (kJ/mol)
<i>N</i> <sub>2</sub>									
1	303	0.10	2	43.1	0.08	0.46	7.4	3.0	6.2
2		0.53	5	30.3	0.41	0.46	3.0		
3		1.00	5	26.9	0.65	0.46	3.0		
4		2.01	5	19.2	1.00	0.46	3.0		
5		3.04	5	13.2	1.42	0.46	3.0		
6	323	4.52	5	3.0	1.95	0.46	3.0	3.5	
7		0.10	2	48.2	0.08	0.54	8.2		
8		0.50	5	35.7	0.37	0.54	3.3		
9		0.94	5	26.2	0.60	0.54	3.3		
10		2.01	5	19.5	0.97	0.54	3.3		
11	343	3.03	5	13.7	1.39	0.54	3.3	4.0	
12		4.61	5	2.8	1.96	0.54	3.3		
13		0.13	2	49.4	0.09	0.61	9.1		
14		0.56	5	34.9	0.37	0.61	3.6		
15		1.02	5	27.7	0.57	0.61	3.6		
18		2.05	5	21.8	0.95	0.61	3.6		
17		3.03	5	13.7	1.35	0.61	3.6		
18		4.51	5	3.2	1.90	0.61	3.6		
<i>CH</i> <sub>4</sub>									
19	303	0.15	2	40.2	0.17	0.46	7.4	3.0	6.2

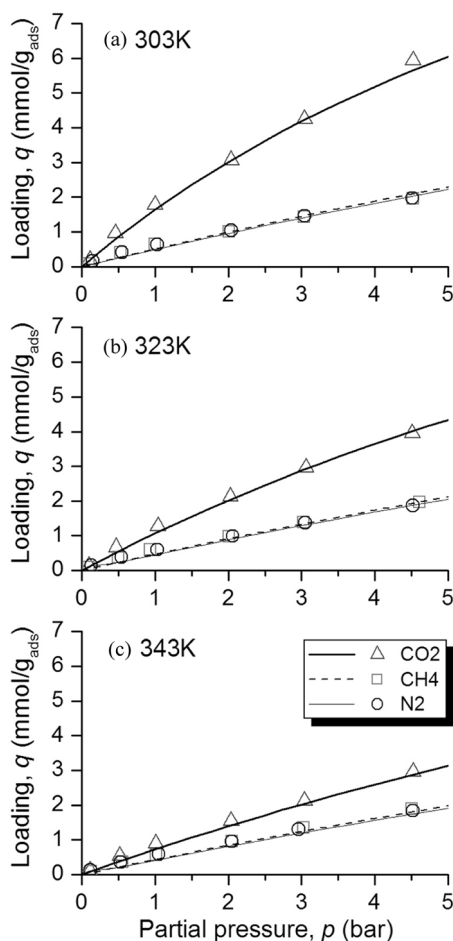
20		0.55	5	29.7	0.42	0.46	3.0	
21		1.03	5	26.4	0.64	0.46	3.0	
22		2.04	5	19.6	1.05	0.46	3.0	
23		3.04	5	13.4	1.47	0.46	3.0	
24		4.51	5	3.3	1.98	0.46	3.0	
25	323	0.13	2	38.9	0.15	0.54	8.2	3.5
26		0.54	5	29.2	0.38	0.54	3.3	
27		1.03	5	25.9	0.60	0.54	3.3	
28		2.06	5	19.6	0.99	0.54	3.3	
29		3.05	5	13.0	1.38	0.54	3.3	
30		4.52	5	2.9	1.87	0.54	3.3	
31	343	0.12	2	38.5	0.13	0.61	9.1	4.0
32		0.53	5	31.4	0.36	0.61	3.7	
33		1.05	5	26.4	0.59	0.61	3.7	
34		2.05	5	19.7	0.95	0.61	3.7	
35		2.96	5	12.9	1.31	0.61	3.7	
36		4.52	5	3.0	1.84	0.61	3.7	
CO <sub>2</sub>								
37	303	0.11	2	45.4	0.20	7.58	6.1	50
38		0.46	5	31.9	0.96	7.47	2.5	3.9

(Continued)

Table 4. Continued

Run	$T$ (K)	$p$ (bar)	$P$ (bar)	$V_{\text{Helium}}$ (ml/min)	$q$ (mmol/g <sub>ads</sub> )	$k$ (s <sup>-1</sup> )	$D_L$ (10 <sup>-4</sup> m <sup>2</sup> /s)	$D_c$ (10 <sup>-11</sup> m <sup>2</sup> /s)	$E_a$ (kJ/mol)
39		1.00	5	25.6	1.78	7.47	2.5		
40		2.04	5	19.1	3.07	7.48	2.5		
41		3.04	5	13.8	4.25	7.50	2.5		
42		4.52	5	3.1	5.93	7.51	2.5		
43	323	0.10	2	47.5	0.14	8.37	6.7	55	
44		0.47	5	33.5	0.67	8.29	2.7		
45		1.04	5	25.6	1.28	8.29	2.7		
46		2.03	5	20.3	2.13	8.30	2.7		
47		3.06	5	13.4	2.96	8.30	2.7		
48		4.51	5	3.0	3.95	8.31	2.7		
49	343	0.11	2	47.8	0.11	9.16	7.5	60	
50		0.52	5	32.5	0.54	9.09	3.0		
51		1.01	5	27.1	0.90	9.09	3.0		
52		2.04	5	21.9	1.55	9.10	3.0		
53		3.04	5	13.8	2.12	9.10	3.0		
54		4.52	5	3.3	2.96	9.10	3.0		

Figure 3 shows the adsorption equilibrium isotherms plotted in terms of the loading in mmol/g<sub>ads</sub> as a function of the partial pressure. It can be seen from the figure that the isotherms are Type I in IUPAC classification. The saturation was not reached because of operating pressure limitations in our setup. The equilibrium data shows that CO<sub>2</sub> is much more adsorbed than CH<sub>4</sub> and N<sub>2</sub>. This difference is considerably higher at 303 K but it decrease significantly when the temperature is increased. The one-dimensional  $4.0 \times 4.0 \text{ \AA}$  channels in MOF-508b seems large



**Figure 3.** Pure component adsorption equilibrium isotherm of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> at (a) 303 K, (b) 323 K and (c) 343 K on 4 MOF-508b. The continuous lines represent the fitting with the Langmuir model. Isotherm model parameters in Table 5.

enough to neglect shape selectivity effects when compared with the kinetics diameters of the gas molecules. Moreover, the van der Waals interaction surfaces of the three gases are too much close to being the reason for such difference. However, the large quadrupolar moment and polarizability of  $\text{CO}_2$  are predominantly the cause of the difference in adsorption behavior (Table 1). The quadrupole moment produces a strong attraction to the adsorbent surface resulting in a higher uptake (13). The high level of polarizability of  $\text{CO}_2$  and  $\text{CH}_4$  can create a momentary shift in its neutral electrostatic field when the molecule is close to the metallic sites of the structure. Nevertheless, this attraction force is much weaker than the quadrupole moment. The nitrogen molecule also exhibits a quadrupolar moment but its magnitude is much lower than the one for  $\text{CO}_2$ .

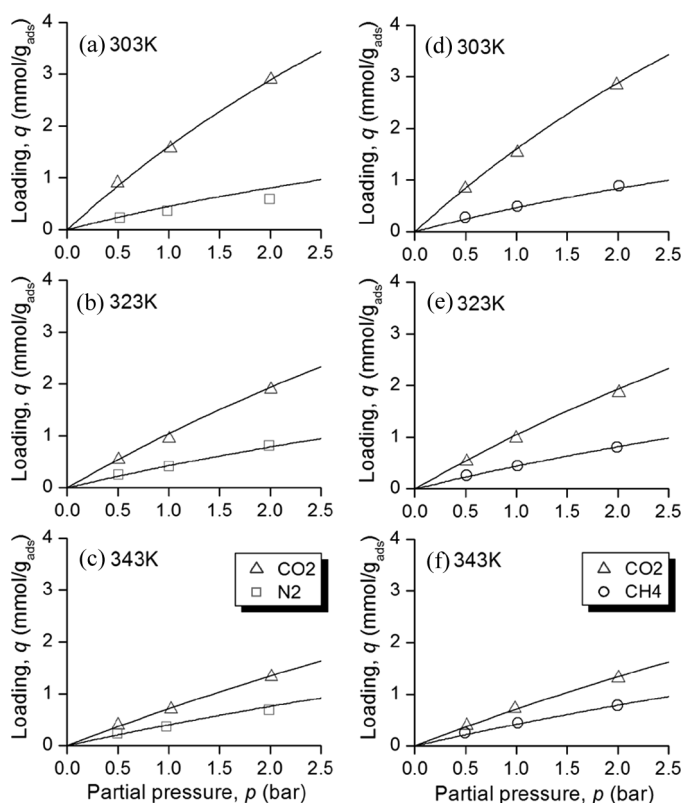
Another interesting feature that can be seen in Fig. 3 is the absence of steps in all the adsorption isotherms and for the entire range of partial pressure and temperature studied in this work. Such effect is often due to structural transformations which can include for example “breathing” and scissoring mechanisms (14–16). These transformations can make impracticable the utilization of MOFs in industrial processes because the pellets can crumble if the framework undergoes a cell volume change. A consequence of such phenomena could be a sharp increasing of the pressure drop in the column, which can result in serious damages in the equipment.

The fitted pure component isotherms with the Langmuir model are the lines in Fig. 3. Langmuir parameters obtained from numerical optimization, as well as the mean absolute deviations between experimental data and predicted values are shown in Table 5. The saturation loading for the three components were kept constant during the optimization procedure; such restriction allows giving thermodynamic consistency to the isotherm model (17). The fitted value for the saturation capacity,  $q = 18.34 \text{ mmol/g}$ , is similar to the ones found in MOF materials with larger pores (18). The heat of adsorption fitted by numerical procedure for  $\text{CO}_2$  ( $18.8 \text{ kJ/mol}$ ) is 5 times higher than the ones for  $\text{CH}_4$  and  $\text{N}_2$  ( $\sim 3.7 \text{ kJ/mol}$ ). However, these values are lower than those found in porous MOFs (15). This enthalpy difference can be related to endothermic processes which involve structural transformations caused by the flexibility of MOF-508b. Such endothermic framework transformation, to some extent, compensates the exothermic adsorption behaviour as rationalized in MIL-53 (15), leading to the low heats of sorption in MOF-508b. It is clear from Fig. 3 that the Langmuir model is reasonable in predicting isotherm sorption behavior of pure  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  in the range of temperatures and partial pressures studied.

## Binary Adsorption Isotherms

Figures 4(a–c) and 4(d–f) show the binary adsorption isotherms for an equimolar mixtures of  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$ , respectively. The experiments were performed at 303 K, 323 K, and 343 K and partial pressure up to 2 bar. The experimental conditions for binary experiments as well as the amount adsorbed are given in Table 6.

In both equimolar mixtures, Fig. 4 shows a large difference relatively to the loading of  $\text{CO}_2$  which significantly decreases as the temperature increases. Also, at the same time that the loading of  $\text{CO}_2$  decreases, the amounts adsorbed of  $\text{CH}_4$  and  $\text{N}_2$  remain practically unchanged



**Figure 4.** Binary adsorption equilibrium isotherms for equimolar mixtures of (a–c)  $\text{N}_2$ – $\text{CO}_2$  and (d–f)  $\text{CH}_4$ – $\text{CO}_2$  on 4 MOF-508b at 303 K, 323 K and 343 K. The continuous lines represent the prediction of the Langmuir model. Isotherm model parameters in Table 5.

**Table 5.** Langmuir model parameters and deviations between model and experiments

Parameter	Unit	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
$q_m$	(mmol/g <sub>ads</sub> )	18.34	18.34	18.34
$b_0$	(bar <sup>-1</sup> )	$6.37 \times 10^{-3}$	$6.73 \times 10^{-3}$	$5.64 \times 10^{-5}$
$b$ (303 K)	(bar <sup>-1</sup> )	0.027	0.029	0.098
$b$ (323 K)	(bar <sup>-1</sup> )	0.025	0.026	0.062
$b$ (343 K)	(bar <sup>-1</sup> )	0.023	0.024	0.041
$-\Delta H$	(kJ/mol)	3.70	3.65	18.80
$\Delta q$	(mmol/g <sub>ads</sub> )	0.098	0.084	0.098

strengthening the idea that quadrupole moment of CO<sub>2</sub> plays an important role in this separation.

We also note that the extended Langmuir model prediction represented by the lines in Fig. 4 gives a proper description of the binary adsorption data.

**Ternary Adsorption Isotherms**

Figure 5(a–c) shows the ternary adsorption isotherms for an equimolar mixture CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>. The experiments were performed at 303 K, 323 K, and 343 K and partial pressure up to 1.4 bar.

As shown in Fig. 5, the adsorption behavior does not seem to be affected by the simultaneous presence of the tree gases in the adsorbent structure when compared with the binary experiments. The adsorption capacities of MOF-508b decrease in the following order CO<sub>2</sub> ≫ CH<sub>4</sub> > N<sub>2</sub>. The CO<sub>2</sub> uptake is significantly dependent on the temperature decreasing as the temperature increases. Conversely, adsorption capacities for CH<sub>4</sub> and N<sub>2</sub> in MOF-508b are almost independent of the temperature. Such difference in temperature dependence of the adsorption behaviors might be specifically useful to optimize the operating conditions for the CO<sub>2</sub> removal from natural gas.

Once more, the experimental sorption isotherms are predicted by the Langmuir model.

**Modeling of the Single Breakthrough Experiments**

The comparison between experimental and theoretical pure component breakthrough curves is shown in Fig. 6 for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in terms of the adsorbate mol fraction in the gas phase at the outlet of the column



**Table 6.** Experimental conditions and dynamic model parameters for breakthrough curves of binary mixtures CH<sub>4</sub>/CO<sub>2</sub> and N<sub>2</sub>/CO<sub>2</sub> and ternary mixtures N<sub>2</sub>/CH<sub>4</sub>/CO<sub>2</sub>; mean absolute deviations between predicted (extended Langmuir) and measured adsorption equilibria on MOF-508b

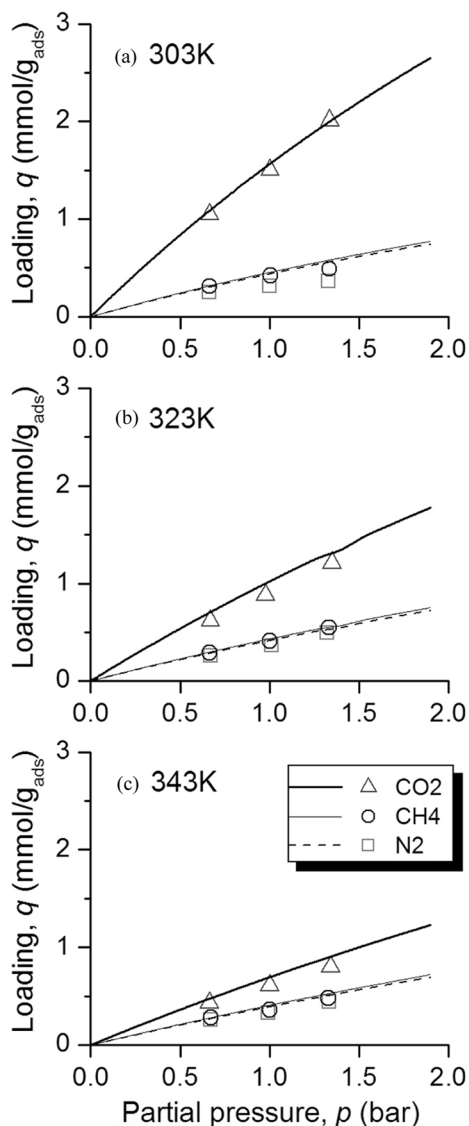
Run	T (K)	P (bar)	$V_{\text{Helium}}$ (ml/min)	$V$ (ml/min)			$q$ (mmol/g <sub>ads</sub> )			$k$ (s <sup>-1</sup> )			$D_L$ (10 <sup>-4</sup> m <sup>2</sup> /s)	
				N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>		
b1_1 b1_2 b1_3	303	5	27.8	–	3.4	3.4	1	–	0.28	0.84	–	0.46	7.45	2.8
		5	19.5	–	6.6	6.6	2	–	0.49	1.53	–	0.46	7.45	2.7
		5	6.0	–	11.9	11.8	4	–	0.89	2.84	–	0.46	7.45	2.5
b1_4 b1_5 b1_6	323	5	28.5	–	3.6	3.6	2	–	0.26	0.53	–	0.54	8.28	3.1
		5	20.0	–	6.8	6.7	2	–	0.45	0.98	–	0.54	8.27	2.9
		5	6.2	–	12.4	12.5	4	–	0.81	1.86	–	0.54	8.26	2.7
b1_7 b1_8 b1_9	343	5	28.7	–	3.5	3.7	1	–	0.25	0.39	–	0.61	9.08	3.4
		5	19.7	–	6.7	6.5	2	–	0.44	0.72	–	0.61	9.08	3.2
		5	6.2	–	12.4	12.5	4	–	0.78	1.31	–	0.61	9.07	3.0
b2_1 b2_2 b2_3	303	5	28.6	3.7	–	3.6	1	0.23	–	0.90	0.46	–	7.45	2.6
		5	19.9	6.6	–	6.8	2	0.36	–	1.57	0.46	–	7.44	2.4
		5	6.5	13	–	13	4	0.59	–	2.89	0.46	–	7.44	2.1
b2_4 b2_5 b2_6	323	5	28.7	3.7	–	3.6	1	0.25	–	0.54	0.54	–	8.27	2.9
		5	19.4	6.5	–	6.5	2	0.41	–	0.95	0.54	–	8.26	2.7
		5	6.4	12.8	–	12.8	4	0.81	–	1.89	0.54	–	8.25	2.3
b2_7 b2_8 b2_9	343	5	28.7	3.6	–	3.6	1	0.23	–	0.39	0.61	–	9.08	3.2
		5	19.0	6.2	–	6.5	2	0.36	–	0.70	0.61	–	9.07	3.0
		5	6.5	13.0	–	13.2	4	0.68	–	1.32	0.61	–	9.05	2.6

(Continued)

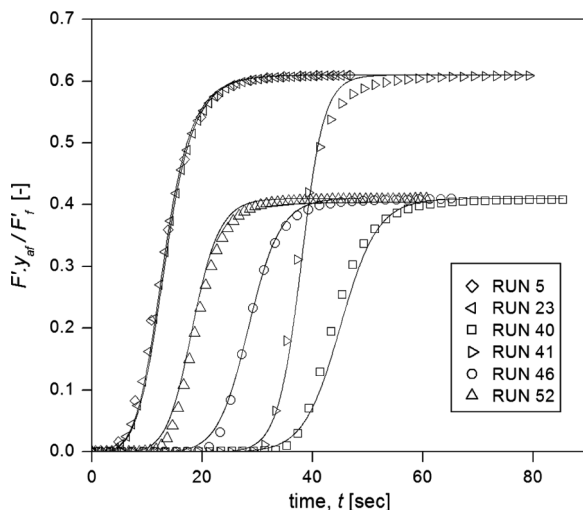
Table 6. Continued

Run	T (K)	P	$V_{\text{Helium}}$ (ml/min)	$V$ (ml/min)			$q$ (mmol/g <sub>ads</sub> )			$k$ (s <sup>-1</sup> )			$D_L$ (10 <sup>-4</sup> m <sup>2</sup> /s)	
				N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	$p_{\text{mix}}$ (bar)	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>		CO <sub>2</sub>
t.1	303	5	19.6	4.3	4.3	4.3	2	0.25	0.31	1.05	0.46	0.46	7.42	2.2
t.2		5	12.6	6.3	6.4	6.4	3	0.31	0.42	1.50	0.46	0.46	7.40	2.0
t.3		5	6.4	8.5	8.6	8.6	4	0.36	0.49	2.01	0.46	0.46	7.39	1.8
t.4	323	5	19.8	4.5	4.4	4.4	2	0.26	0.29	0.62	0.54	0.54	8.25	2.5
t.5		5	12.5	6.3	6.2	6.1	3	0.36	0.41	0.88	0.54	0.54	8.23	2.2
t.6		5	6.2	8.3	8.3	8.4	4	0.49	0.55	1.21	0.54	0.54	8.22	2.0
t.7	343	5	19.3	4.3	4.3	4.3	2	0.26	0.28	0.43	0.61	0.61	9.06	2.7
t.8		5	12.6	6.3	6.3	6.3	3	0.33	0.36	0.61	0.61	0.61	9.05	2.4
t.9		5	6.3	8.4	8.3	8.4	4	0.44	0.48	0.80	0.61	0.61	9.03	2.2
<i>Binary mixtures</i>														
			CO <sub>2</sub> + N <sub>2</sub> 0.049			CO <sub>2</sub> + CH <sub>4</sub> 0.028			<i>Ternary mixture</i> CO <sub>2</sub> + CH <sub>4</sub> + N <sub>2</sub> 0.059					
$\overline{\Delta q}$ (mmol/g <sub>ads</sub> )														

*b*, Binary experiment; *t*, Ternary experiment.



**Figure 5.** Ternary adsorption equilibrium isotherms for an equimolar mixture of CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> on 4 MOF-508b at a) 303 K, b) 323 K and c) 343 K. The lines represent the prediction of the Langmuir model. *Isotherm model parameters in Table 5.*



**Figure 6.** Pure component breakthrough curves of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in 4 MOF-508b. Experimental conditions are in Table 4. Continuous lines are obtained with the mathematical model. N<sub>2</sub>, run 5; CH<sub>4</sub>, run 23; CO<sub>2</sub>, runs 40, 41, 46 and 52.

as a function of the time. The experimental conditions are detailed in Table 4. The sharpness of the breakthrough curves indicates a fast kinetics which is good for the development of separation processes based on equilibrium properties.

The experimental breakthrough curve was matched by fitting the micropore diffusion parameter,  $D_c$ . The estimated diffusional parameters, listed in Table 4, were considered to be independent of the loading since the experimental conditions still far from the saturation region. The micropore diffusion within the channels of MOF-508b for CO<sub>2</sub> ( $D_c$  (303 K) =  $5 \times 10^{-10}$  m<sup>2</sup>/s) is one order of magnitude faster than for CH<sub>4</sub> and N<sub>2</sub>. Such results can be explained by the fact that the kinetic diameter of CH<sub>4</sub> and N<sub>2</sub> is greater than the one of CO<sub>2</sub> (see Table 1). In a general way, the diffusivity of the molecules studied in this work is lower than the ones reported in the literature for MFI (19,20); for instance, Krishna and Baten (20) have determined by molecular dynamic simulation diffusivity values ranging from  $10^{-9}$  to  $10^{-8}$  m<sup>2</sup>/s for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in MFI at  $T = 300$  K. This difference can also be explained by the relation between the molecular diameter and the pore dimension since the channels of MFI ( $5.1 \times 5.6$  Å) are larger than the ones of MOF-508b ( $4.0 \times 4.0$  Å), consequently the diffusion can be faster in the first case. The temperature dependence of the intra-crystalline diffusion

in MOF-508b was found to be very low for the three molecules as it can be seen from the diffusional activation energy,  $E_a$ , listed in Table 4. Data reported in the literature for micropore diffusion of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$  in zeolite 4A at 303 K show values in the order  $10^{-12} \text{ m}^2/\text{s}$  with activation energies for diffusion around 20 kJ/mol for the three molecules (23). Taking into account the similarity of the pore dimension of both adsorbents, and the high diffusivity found in MOF-508b, the diffusion mechanism in this metal-organic framework can be characterized as “fast diffusion” and this can explain the low activation energy found.

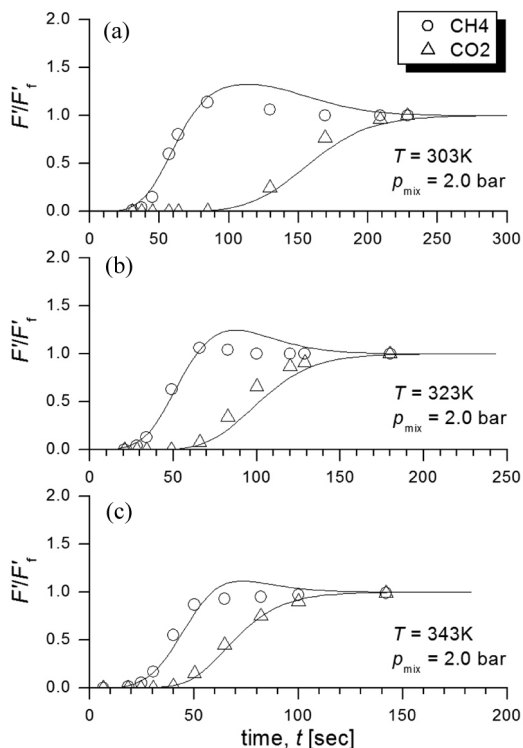
From the practical point of view, this approach for the estimation of the diffusional parameters seems fair considering the explanation given in a previous section; nevertheless, results should be read with caution since they were obtained from the match of breakthrough curves.

Figure 6 shows clearly that the dynamic mathematical model reproduces very well the experimental data for the temperature and feed concentration range studied in this work.

### Modeling of the Binary Breakthrough Experiments for Equimolar Mixtures $\text{CO}_2/\text{CH}_4$ and $\text{CO}_2/\text{N}_2$

In practice we wish to separate the  $\text{CO}_2$  molecules from  $\text{CH}_4$  and  $\text{N}_2$  in a fixed bed. In this section we give an overview of the typical multicomponent breakthrough curves obtained. In Fig. 7, the breakthrough curves of a binary equimolar mixture of  $\text{CO}_2/\text{CH}_4$  are shown for the temperatures 303 K, 323 K, and 343 K and total adsorbate pressure around 2 bar. We plot the breakthrough curves in terms of the normalized mass flow of the adsorptive species  $F'/F'_f$ , as a function of time. Interesting to note that for  $T=303 \text{ K}$ , methane appears at the outlet of the column at a time of approximately 40 sec compared to a time value of 100 sec for  $\text{CO}_2$ . This time difference is suitable for a separation in a fixed bed. For the mixture  $\text{CO}_2/\text{N}_2$  the separation degree is quite similar as can be seen in Fig. 8. This result allows us to conclude that the separation degree observed between these isomers can lead to the development of a separation process by adsorption.

Figures 7 and 8 also shows some dispersion in the shape of breakthrough curves and this is due to a combined effect of mass transfer resistance, and axial dispersion. The dynamic model parameters of the LDF-based mathematical model can be seen in Table 6. The value  $k$  can be considered as lumped parameters. It can be concluded from the multicomponent breakthrough experiments that this simple model does a good job for the prediction of both dispersion and overshoot phenomena.

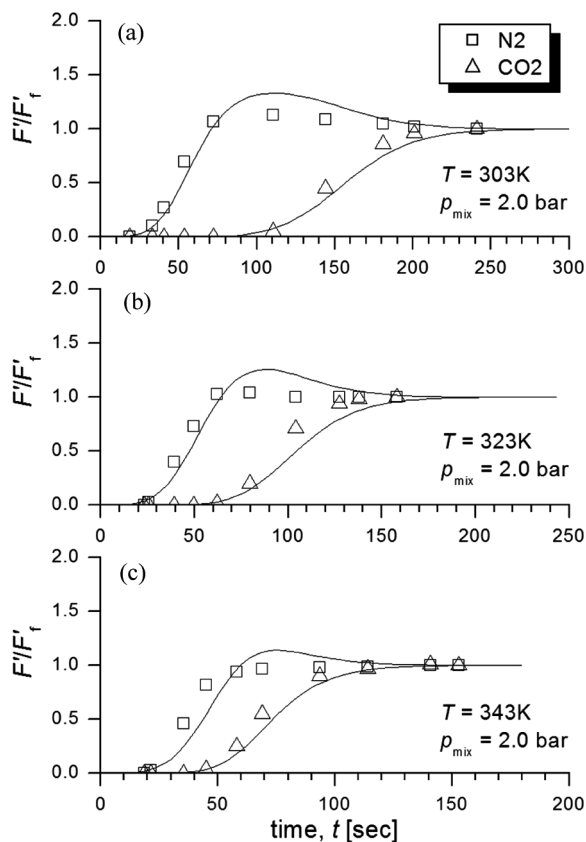


**Figure 7.** Effect of temperature on binary breakthrough curves for equimolar mixtures of CH<sub>4</sub>–CO<sub>2</sub> at a) T = 303 K, b) T = 323 K and c) T = 343 K at a total mixture pressure around 2 bar. Total system pressure was fixed at 5 bar. *Experimental conditions and model parameters in Table 6. Lines represent the dynamic mathematical model simulation and points are experimental data.*

### Modeling of the Ternary Breakthrough Experiments for Equimolar Mixtures CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>

The breakthrough curves in Fig. 9 show that N<sub>2</sub> leaves the bed slightly before CH<sub>4</sub>. The last component to go out, CO<sub>2</sub>, is clearly the most strongly adsorbed component which explains the difference in the amount adsorbed of CO<sub>2</sub> relatively to the other components, already observed in the ternary adsorption equilibrium isotherms shown in Fig. 5.

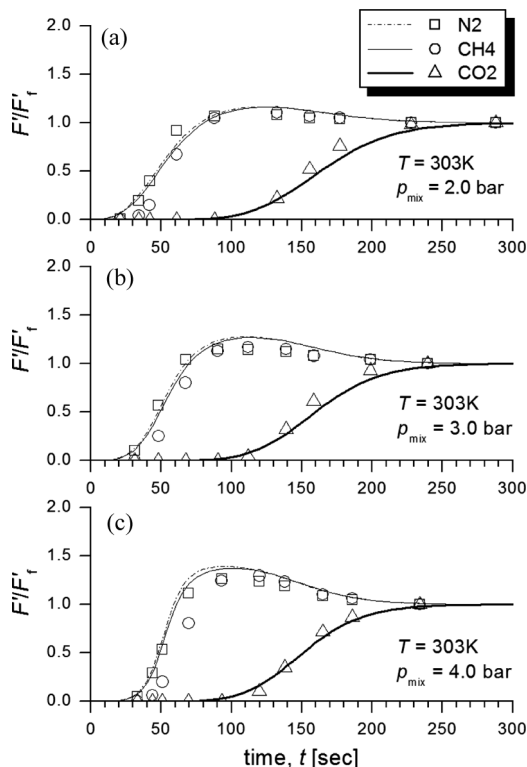
The agreement between experimental data and the mathematical model is reasonably good, and this is remarkably taken into consideration that we are using a simple LDF model in a simulation of a



**Figure 8.** Effect of temperature on binary breakthrough curves for equimolar mixtures of  $\text{N}_2$ – $\text{CO}_2$  at a)  $T = 303\text{ K}$ , b)  $T = 323\text{ K}$  and c)  $T = 343\text{ K}$  at a total mixture pressure around 2 bar. Total system pressure was fixed at 5 bar. Experimental conditions and model parameters in Table 6. Lines represent the dynamic mathematical model simulation and points are experimental data.

nonlinear multicomponent system of three adsorbable species in a complex metal-organic structure.

The separation potential of an equimolar mixture can be described in terms of the sorption selectivity,  $S$ , defined on a molar basis by  $S = q_1/q_2$ , where compound 1 is more adsorbed. Figure 10 shows the effect of temperature and mixture pressure on the sorption selectivity a)  $S_{\text{CO}_2/\text{CH}_4}$  and b)  $S_{\text{CO}_2/\text{N}_2}$  for a ternary equimolar mixture  $\text{CO}_2/\text{CH}_4/\text{N}_2$  on MOF-508b. In both cases, the drop in temperature favor the selectivity. For the three temperatures, we can see that the selectivity is higher for the mixture

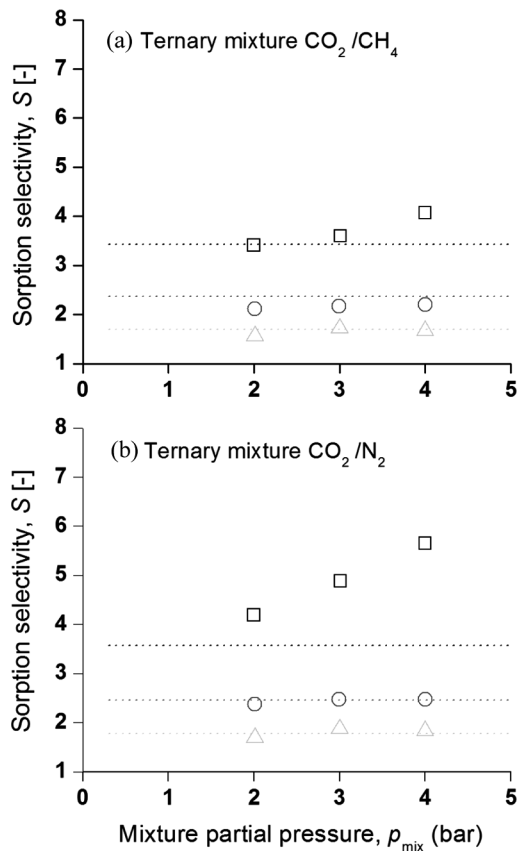


**Figure 9.** Effect of partial pressure on ternary breakthrough curves for equimolar mixtures of  $\text{N}_2$ – $\text{CH}_4$ – $\text{CO}_2$  at  $T = 303\text{ K}$  and a)  $p_{\text{mix}} = 2.0\text{ bar}$ , b)  $p_{\text{mix}} = 3.0\text{ bar}$  and c)  $p_{\text{mix}} = 4.0\text{ bar}$ . Total system pressure was fixed at 5 bar. *Experimental conditions and model parameters in Table 6. Lines represent the dynamic mathematical model simulation and points are experimental data.*

$\text{CO}_2/\text{N}_2$ ; also the mixture pressure does not seem to have significant influence on the sorption selectivity, except at 303 K where a slight increase is observed.

Note that the predictions of the extended Langmuir model (lines in Fig. 10) give pressure-independent values for the selectivities  $S_{\text{CO}_2/\text{CH}_4}$  and  $S_{\text{CO}_2/\text{N}_2}$ , indicating the absence of competition for the active sites between the three types of gas molecules studied. However, the slight increase previously mentioned for the experimental data at 303 K requires some experiments at mixture pressure higher than 4 bar in order to check if the cause of this phenomenon is or not related to an experimental problem.





**Figure 10.** Temperature-dependent sorption selectivity for (a)  $\text{CO}_2/\text{CH}_4$  and (b)  $\text{CO}_2/\text{N}_2$  in equimolar ternary  $\text{CO}_2/\text{CH}_4/\text{N}_2$  mixtures, as function of the mixture partial pressure ( $\square$ ,  $T = 303$  K;  $\circ$ ,  $T = 323$  K;  $\triangle$ ,  $T = 343$  K). Points are experimental data and lines represent the sorption selectivity predicted by the Langmuir model.

## CONCLUSIONS

The adsorption and separation of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  on MOF-508b by fixed bed process have been studied. Single and multicomponent equilibrium data have been obtained through experimental breakthrough curves in a temperature range comprised between 303 K and 343 K. The gas partial pressure has been increased up to 4.5 bar without reaching the saturation stage.

The single isotherm data was fitted with good accuracy by a simple Langmuir model. The Langmuir model parameters were used to predict the multicomponent equilibrium giving a well description of the adsorption behavior of the gas mixture on MOF-508b. A model based on the LDF approximation which has taken into account the isotherm model predictions was able to described both mono- and multicomponent experimental breakthrough curves. The micropore diffusivity estimated by the dynamic mathematical model gives values of the order of  $10^{-10} \text{ m}^2/\text{s}$  for  $\text{CO}_2$  and  $10^{-11} \text{ m}^2/\text{s}$  for  $\text{CH}_4$  and  $\text{N}_2$ .

The experiments performed allow concluding that MOF-508b is a highly selective material for  $\text{CO}_2$  separation at room temperature. If the rise in temperature causes a sharp decrease in  $\text{CO}_2$  affinity, on the other hand the change in partial pressure seems to not have a strong influence. The low amount adsorbed of  $\text{CH}_4$  and  $\text{N}_2$  are practically temperature independent offering a large range of operating conditions favorable to the  $\text{CO}_2$  removal from natural gas. The sharpness in breakthrough curves indicates a fast kinetic which contribute to the short regeneration time of MOF-508b.

These results show that MOF-508b can be a suitable adsorbent for the development of processes for  $\text{CO}_2$  separation from natural gas.

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## NOTATION

$b$	affinity constant ( $\text{bar}^{-1}$ )
$b_0$	frequency factor of the affinity constant ( $\text{bar}^{-1}$ )
$c_0$	molar gas concentration at the inlet of the fixed bed ( $\text{mol}/\text{m}^3$ )
$c_i$	molar concentration of sorbate species $i$ in the bulk gas phase ( $\text{mol}/\text{m}^3$ )
$C$	total molar gas concentration in bulk gas phase ( $\text{mol}/\text{m}^3$ )

$d$	column diameter (m)
$d_p$	particle diameter (m)
$D_c$	micropore diffusivity ( $\text{m}^2/\text{s}$ )
$D_L$	axial dispersion coefficient in fixed bed ( $\text{m}^2/\text{s}$ )
$D_m$	molecular diffusivity ( $\text{m}^2/\text{s}$ )
$D_0$	pre-exponential factor ( $\text{m}^2/\text{s}$ )
$E_a$	diffusional activation energy (kJ/mol)
$F'$	molar rate of adsorptive species at the column outlet (mol/s)
$F_f'$	molar rate of the adsorptive species in the feed (mol/s)
$F$	total molar flux ( $\text{mol}/(\text{m}^2.\text{s})$ )
$F_f$	total molar flux of feed ( $\text{mol}/(\text{m}^2.\text{s})$ )
$\Delta H$	adsorption enthalpy (J/mol)
$k$	mass transfer coefficient ( $\text{s}^{-1}$ )
$k_f$	external film mass transfer coefficient (m/s)
$L$	column length (m)
$p$	partial pressure (bar)
$P$	total system pressure (bar)
$q$	adsorbed concentration of sorbate in the adsorbent particle (mmol/g)
$\bar{q}$	average adsorbed concentration of sorbate in adsorbent particle (mmol/g)
$q_m$	saturation loading capacity of sorbate in the adsorbent (mmol/g)
$R$	gas constant (kJ/mol/K)
$Re$	Reynolds number (—)
$Sc$	Schmidt number (—)
$t$	time (s)
$T$	temperature (K)
$u$	interstitial velocity in packed bed (m/s)
$W$	mass of adsorbent in the column (kg)
$y_a$	mole fraction of the sorbate in the bulk phase (—)
$y_{af}$	mole fraction of the sorbate at the inlet of the column (—)
$z$	distance coordinate along fixed bed (m)

### Greek Letters

$\rho_a$	apparent density ( $\text{kg}/\text{m}^3$ )
$\rho_b$	bulk density ( $\text{kg}/\text{m}^3$ )
$\varepsilon_b$	bulk porosity (—)

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