

STUDIES ON THE ADSORPTION BEHAVIOR OF CO₂-CH₄ MIXTURES USING ACTIVATED CARBON

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Abstract - Separation of CO₂ from CO₂-CH₄ mixtures is an important issue in natural gas and biogas purification. The design of such separation processes depends on the knowledge of the behavior of multicomponent adsorption, particularly that of CO₂-CH₄ mixtures. In this study, we present a series of experimental binary equilibrium isotherms for CO₂-CH₄ mixtures on an activated carbon at 293 K and compare them with predicted values using the Ideal Adsorption Solution Theory (IAST) and the Extended Langmuir (EL) model. Even at concentrations of ca. 20% for all binary isotherms, CO₂ already presents higher adsorbed amounts with respect to CH₄. A maximum selectivity of around 8.7 was observed for a nearly equimolar mixture at 0.1 MPa. The IAST in conjunction with the Toth equation showed slightly better results than IAST using the Langmuir equation and both showed better results than the EL model.

Keywords: Adsorption; Selectivity; Carbon dioxide; Methane; Activated carbon.

INTRODUCTION

Natural Gas (NG) is a very attractive energy source from an environmental perspective because it presents significantly lower emissions of carbon dioxide, nitrogen oxides, and particulates in comparison with other fuels such as oil and coal (Beronich *et al.*, 2009). Moreover, NG has been widely studied as an important alternative for the expansion of the world's energy supply (Walton *et al.*, 2006; Rios *et al.*, 2011).

However, much of the NG produced worldwide needs significant treatment since the content of CO₂, the major impurity of natural gas, can vary according to the source (Iarikov *et al.*, 2011; Finsy *et al.*, 2009; Bae *et al.*, 2008). The presence of CO₂ in raw natural gas streams considerably decreases the energy density (calorific value) of natural gas and also contributes to pipeline and equipment corrosion due to the corro-

sive properties of carbon dioxide in the presence of water (Ghoufi *et al.*, 2009; Cavenati *et al.*, 2006; Iarikov *et al.*, 2011).

Carbon dioxide is found in NG with an average composition in the range of 0.5-10 vol.% (with peaks reaching 70 vol.%). Unconventional hydrocarbon sources containing CO₂ concentrations of 40-50 vol.% such as landfill gas and coalbed methane have recently drawn energy companies' attention (Tagliabue *et al.*, 2009; Cavenati, 2005). Regulations for natural gas transport through pipelines may vary for different countries. For example, the current US pipeline specifications require CO₂ content to be below 2-3 vol.% (Cavenati *et al.*, 2006; Iarikov *et al.*, 2011; Li *et al.*, 2005). Thus, the separation of carbon dioxide from biogas and natural gas (binary system CO₂-CH₄) is of critical economic importance and is still the subject of intensive fundamental and industrial research (Iarikov *et al.*, 2011; Ghoufi *et al.*, 2009).

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The removal of carbon dioxide from those gases has been carried out by means of several technologies, such as absorption, cryogenic distillation, membrane separation, and adsorption (Bae *et al.*, 2008). The amine based absorption/stripping process has been much used for the separation of CO₂ from natural gas and flue gas streams for many years (Yang *et al.*, 2008; Finsy *et al.*, 2009), but despite its wide commercial use, this process has several drawbacks, including high energy costs during solvent regeneration, low carbon dioxide loading capacity, high equipment corrosion, amine degradation by SO₂, NO₂, HCl, HF and O₂ in flue gas and also the requirement of much attention from the operators (Cavenati *et al.*, 2006; Finsy *et al.*, 2009).

Adsorption-based methods using microporous materials are a very promising cost-efficient technology, particularly in separation systems such as Pressure Swing Adsorption (PSA), which is commonly accepted to be the most attractive, efficient and affordable due to its simple control, low operating and capital investment costs, and higher energy efficiency (Bastin *et al.*, 2008; Bae *et al.*, 2008; Finsy *et al.*, 2009). Thus, PSA technology has begun to supplant some of the absorption technology in natural gas treatment, especially in the so-called shut-in natural gas wells that previously contained considerable amounts of N₂ too high to justify processing (Ebner and Ritter, 2009).

A variety of microporous materials such as activated carbon (AC), zeolites, and metal-organic frameworks (MOFs) have been studied and developed for physical adsorption of gas mixtures containing CO₂ (Dantas *et al.* 2011a; Belmabkhout and Sayari, 2009; Bae *et al.*, 2008). Activated carbons have been tested for applications in CO₂ separation from binary mixtures CO₂-CH₄ (Buss, 1995; Ahmadpour *et al.*, 1998; Dreisbach *et al.*, 1999; Qiao *et al.*, 2000; van der Vaart *et al.*, 2000; Goetz *et al.*, 2006; Bazan *et al.*, 2008) due to their high surface area, micropore volume and suitable pore size distribution (Dantas *et al.*, 2011b). The wide availability of carbon sources makes industrial-scale production relatively affordable (Sircar *et al.*, 1996).

The knowledge of the adsorption equilibrium is of essential importance for the design and optimization of industrial units like PSA and very important for the evaluation of the selectivity and adsorption capacity of adsorbents. On the other hand, multicomponent adsorption experiments are extensive and time-consuming so that it would be desirable that such experimental results could be predicted using classical adsorption models. The extended Langmuir

(EL) model, for its simplicity, as well as the Ideal Adsorbed Solution Theory (IAST), for its relatively good accuracy and applicability, are commonly used to predict binary gas adsorption equilibria from pure component data (Clarkson and Bustin, 2000; Yu *et al.*, 2008).

In this study, we present a series of binary equilibrium data for CO₂-CH₄ mixtures on an activated carbon sample at 293 K and a comparison between experimental data and predicted values (obtained with the two classical adsorption models) for this system.

METHODS AND MATERIALS

Experimental Devices

Single and binary gas adsorption equilibria were measured using a volumetric-chromatographic apparatus. Specific volume of the solid phase was measured gravimetrically with the aid of a magnetic suspension balance (Rubotherm, Germany). Carbon textural properties were obtained by measuring adsorption isotherms of nitrogen at 77 K using an Autosorb-1 MP (Quantachrome, USA).

The volumetric-chromatographic apparatus was developed in our labs and is illustrated in Fig. 1. It basically consists of a closed loop containing a dosing system and an adsorption chamber, where the adsorbent sample is tested. The experimental setup was equipped with four P-10 pressure sensors (WIKA, Germany) with an accuracy of 0.1% and two PT-100 temperature sensors (Garlock, Brazil). This apparatus also includes a GK-M 24/02 gas circulation pump (Rietschle Thomas, Germany) between the dosing and the adsorption chambers in order to ensure a homogeneous gas phase composition in the system and to reduce the time needed to reach the equilibrium.

The experimental temperature was room temperature (293 K), which was controlled by air-conditioning with maximal oscillations of ± 1 K along the day. The gas phase composition at equilibrium was analyzed by a CP4900 gas chromatograph (GC) (Varian, USA). Heating of the adsorbent (bed regeneration and pre-treatment) was accomplished using a heating tape surrounding the whole cylinder filled with the AC. A 34401A digital multimeter (Agilent, USA) and a signal selector were employed to read the signal output from the sensors. An AC31 programmable logic controller (PLC) (ABB, Germany) was used to control the system instruments of the experimental setup.

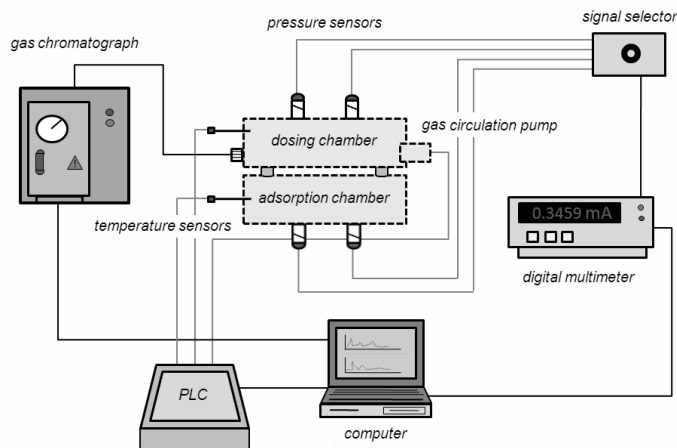


Figure 1: Experimental device for volumetric-chromatographic measurements.

Pure Component Adsorption Isotherms

Adsorption isotherms of CO₂ and CH₄ were measured for WV1050 activated carbon (MeadWestvaco, USA) in the pressure range of 0-1.5 MPa at 293 K. For gravimetric measurements, the AC was regenerated *in situ* at 373 K under vacuum (1.3×10^{-8} MPa) until no mass variation in the system was observed. Experiments with helium (non-adsorbed gas) were carried out in order to determine the specific volume of the solid phase, enabling the evaluation of the buoyancy effects on measurements with adsorbing gases. Further details of the determination of these adsorption isotherms may be found elsewhere (Dreisbach *et al.*, 2002; Bastos-Neto *et al.*, 2005).

In volumetric experiments, the sample was degassed under the same conditions previously described for 5 hours. The volume of the sample, as well as all internal volumes of the system, were precisely determined by gas expansion experiments using He as described by Rouquerol *et al.* (1999). The mass of regenerated activated carbon (m_{AC}) was calculated by Eq. (1).

$$m_{AC} = (V_{int} - V_{void}) / V_s \quad (1)$$

Changes in pressure and temperature were continuously monitored until thermodynamic equilibrium was reached. The amount adsorbed was determined by mass balances applied to the gaseous phase using pressure-volume-temperature (PVT) measurements and the ideal gas equation, as reported by Talu (1998) and Llewellyn and Maurin (2007). For pressures above 1 bar, the compressibility factor was incorporated into the mass balance equations and

estimated by Bender's equation of state for pure fluids (Ghazouani *et al.*, 2005). For these calculations, the density was deduced from the Ideal Gas equation and determined using the temperature and pressure of the experiments, R and the molar mass of the gas.

Binary Adsorption Isotherms

Binary adsorption equilibria of CO₂ and CH₄ were measured on the WV1050 AC at 293 K, at total pressures of 0.1, 0.25, 0.5 and 1.0 MPa for different gas phase compositions using the volumetric-chromatographic method.

Initially, the sample was pre-treated in the same way as for single gas adsorption. Then, the gas mixture was prepared in the dosing chamber and its composition was analyzed with a GC. The PVT data were registered and the gas mixture was expanded into the adsorption chamber containing the AC. After the temperature and pressure reached constant values the gas composition could still vary due to the displacement mechanism of multicomponent adsorption. Therefore, to confirm equilibrium, the gas concentration was constantly monitored by GC until no significant variation was detected. For all experimental points, less than 3 hours were required for the adsorption equilibrium to be achieved with the aid of the gas circulation pump. Then, the bulk gas phase composition at equilibrium was measured using the GC and afterwards new PVT data were registered.

The initial number of moles of the component i (n_i^o) and the final number of moles of component i (n_i^f) were calculated according to Eqs. (2) and (3), respectively.

$$n_i^o = y_i^o \cdot \frac{P_{mixt}^o \cdot V_{dos_chb}}{R \cdot T_{mixt}^o \cdot Z_{mixt}^o} \quad (2)$$

$$n_i^f = y_i^f \cdot \frac{P_{mixt}^f \cdot (V_{dos_chb} + V_{ads_chb} - V_{ac})}{R \cdot T_{mixt}^f \cdot Z_{mixt}^f} \quad (3)$$

The compressibility factor of the gas mixture (Z_{mixt}) was estimated according to Amagat's law, as described by Zhu and Xu (1991). In Eq. (4), Z_i was calculated using Bender's equation, expressed in terms of the compressibility factor (Ghazouani *et al.*, 2005).

$$Z_{mixt} = \sum_{i=1}^n y_i \cdot Z_i \quad (4)$$

Thus, the amount adsorbed of component i (q_i) was determined using Eq. (5). The total amount adsorbed was calculated by the sum of the amount adsorbed of each component in the mixture.

$$q_i = \frac{n_i^o - n_i^f}{m_{AC}} \quad (5)$$

The efficiency of carbon dioxide separation was evaluated by the selectivity of CO₂ over CH₄, which was calculated from the ratios of mole fractions in the gas phase and in the adsorbed phase, as shown in Eq. (6).

$$S_{i/j} = \frac{x_i \cdot y_j^f}{x_j \cdot y_i^f} \quad (6)$$

Predictions of Binary Adsorption Equilibrium

The extended Langmuir (EL) model (Markham and Benton, 1931) and the Ideal Adsorbed Solution Theory (IAST) (Myers and Prausnitz, 1965) were used to predict the amounts adsorbed of each gas in the CO₂-CH₄ binary mixtures. Both EL (Eq. (7)) and IAST make use of the adsorption data of pure components obtained by volumetry to calculate the multicomponent adsorption equilibria.

$$q_i = \frac{q_{max,i} \cdot b_i \cdot P_i}{1 + \sum_{j=1}^n b_j \cdot P_j} \quad (7)$$

The IAST was applied in conjunction with the Langmuir equation (Ruthven, 1984) (IAST-L) and with the Toth equation (Toth, 2002) (IAST-T). The

integration of the Gibbs' adsorption isotherm was used to calculate the reduced spreading pressure of component i in the standard state (Π_i^*), which is defined as:

$$\Pi_i^* = \frac{\pi_i A}{RT} = \int_0^{P_i^0(\pi)} \frac{n_i(P_i)}{P_i} dP_i \quad (8)$$

$n_i(P_i)$ can be expressed according to a local adsorption isotherm (e.g. Henry, Langmuir, Toth adsorption isotherm equation). As this standard state may be defined in a way that the surface potential of the mixture is the same as the surface potentials of all pure components (Do, 1998), Π_i^* is equal to the reduced spreading pressure (Π^*) of the adsorbed mixture (Yu *et al.*, 2008). Therefore, for the IAST-L and IAST-T models, Π^* was obtained from the substitution of the Langmuir and Toth pure component equilibrium equations (Eqs. (9a) and (9b), respectively) and integration of this term. The reduced spreading pressures resulting from this integration (Π_L^* and Π_T^*) are shown respectively in Eqs. (10a) and (10b).

$$q_i = \frac{q_{max,i} \cdot b_i \cdot P_i}{1 + b_i \cdot P_i} \quad (9a)$$

$$q_i = \frac{q_{max,i} \cdot b_i \cdot P_i}{(1 + (b_i \cdot P_i)^{t_i})^{1/t_i}} \quad (9b)$$

$$\begin{aligned} \Pi_L^* &= \frac{\pi A}{RT} = q_{max,i} \ln(1 + b_i P_i) \\ &= q_{max,j} \ln(1 + b_j P_j) \end{aligned} \quad (10a)$$

$$\begin{aligned} \Pi_T^* &= \frac{\pi A}{RT} = q_{max,i} \int_0^{P_i} \frac{b_i}{(1 + (b_i P_i)^{t_i})^{1/t_i}} dP_i \\ &= q_{max,j} \int_0^{P_j} \frac{b_j}{(1 + (b_j P_j)^{t_j})^{1/t_j}} dP_j \end{aligned} \quad (10b)$$

The Langmuir and Toth model parameters needed for the solution of the IAST-L and IAST-T were obtained from the fit of the corresponding models to each isotherm of the pure gas. Likewise, for the EL model, the parameters for pure components were obtained from the Langmuir fit to the adsorption isotherm data. These pure component isotherm data were fitted with the aid of the least-squares method

with the Levenberg-Marquardt algorithm, as shown in Bardsley *et al.* (1995).

A more detailed description of the procedure to predict the adsorption of binary mixtures using IAST in conjunction with a single adsorption isotherm equation can be found elsewhere (Clarkson and Bustin, 2000; Goetz *et al.*, 2006; Yu *et al.*, 2008; Do, 1998).

IAST predictions are strongly dependent upon the choice of the model used and the fit quality that it provides to describe pure gas adsorption (Yu *et al.*, 2008). To evaluate the influence of the model and the accuracy of the predictions in relation to experimental results of binary adsorption, the average relative error (δq), as expressed in Eq. (11), was calculated and used as a parameter of analysis.

$$\delta q = \frac{100}{N} \sum_{i=1}^N \left(\left(\frac{q_i - q_{pred,i}}{q_i} \right)^2 \right)^{1/2} \quad (11)$$

RESULTS AND DISCUSSION

Adsorbent Particle

The main textural characteristics of the activated carbon sample used in the experiments (surface area = 1615 m² g⁻¹ and micropore volume = 0.76 cm³ g⁻¹) are summarized in Rios *et al.* (2011). Using helium expansion experiments, the estimated volume of the solid phase of the AC was 1.451 cm³. The specific volume of the solid phase of WV1050 AC measured in the magnetic suspension balance was 0.586 cm³ g⁻¹. The mass of regenerated adsorbent used in the experiments was 2.476 g.

Adsorption Isotherms of CO₂, CH₄ and of their Binary Mixtures

Adsorption isotherms of the pure gases CO₂ and CH₄ on WV1050 AC at 293 K in the pressure range from 0 to 1.5 MPa measured with the volumetric apparatus, as well as their respective fits using the Langmuir and the Toth equations, are shown in Fig. 2.

The shapes of the isotherms are of Type I, according to the International Union of Pure Applied Chemistry (IUPAC) classification (Sing, 1982), typical for microporous solids. One can also observe that, as expected, the adsorbent exhibits preferential adsorption for carbon dioxide in relation to methane over the whole pressure range.

The parameter b_i in Eqs. (9) and (10) indicates how strongly an adsorbate molecule is attracted onto

an adsorbent surface (Do, 1998). As expected, higher b_i values were obtained for CO₂ in comparison with CH₄ (see Table 1). It can also be observed in Table 1 that higher values for q_{max} are obtained for CO₂ in both the Langmuir and Toth fits. The average relative errors presented in Table 1 suggest that the Toth equation showed the best fit quality for the isotherm of pure CO₂, whereas the Langmuir equation presented a slightly better fit for the adsorption data of pure CH₄, although the average errors obtained with both equations are quite similar to each other.

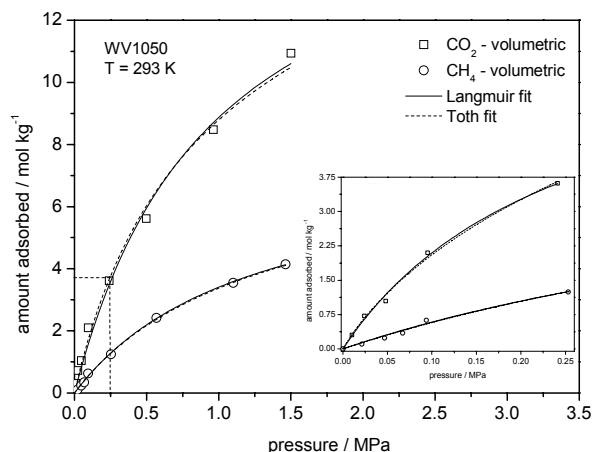


Figure 2: Adsorption isotherms of the pure gases CO₂ (squares) and CH₄ (circles) on the AC WV1050 at 293 K measured with the volumetric apparatus. Solid lines are the Langmuir fits and dashed lines are the Toth fits.

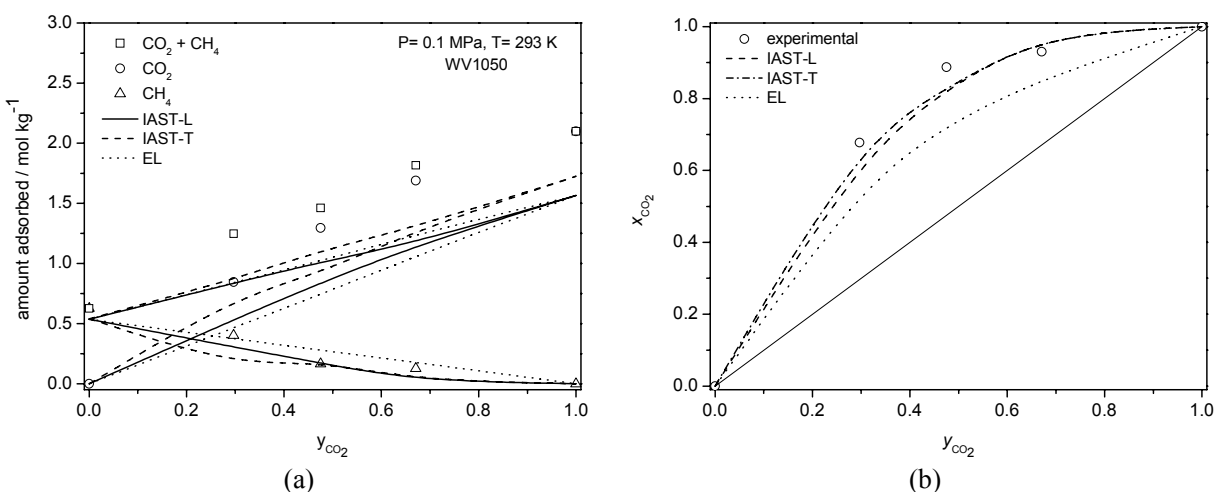
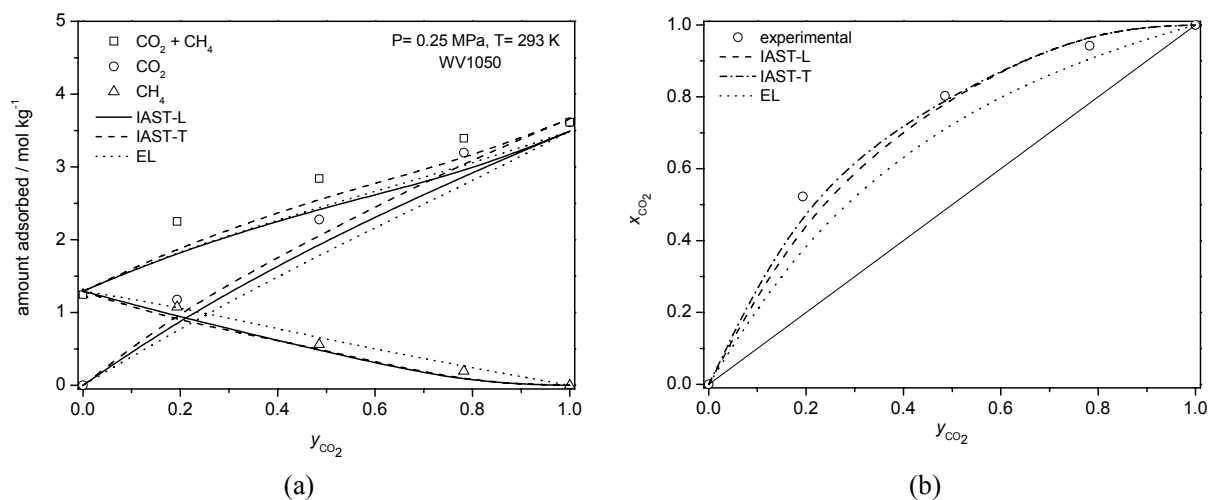
Table 1: Parameters and average relative errors of Langmuir and Toth fits of CO₂ and CH₄ isotherms at 293 K on AC WV1050.

Isotherm	Langmuir			Toth			
	q_{max}	b	δq	q_{max}	b	t	δq
CO ₂	17.396	1.041	17.9	19.107	1.134	0.827	13.4
CH ₄	7.616	0.809	9.1	8.193	0.769	0.927	9.5

Experimental and predicted (using the EL, IAST-L and IAST-T models) adsorption data of CO₂-CH₄ mixtures at pressures of 0.1, 0.25, 0.5 and 1.0 MPa for different molar compositions at 293 K are shown in Figs. 3(a), 4(a), 5(a), and 6(a), respectively. The predicted co-adsorption isotherms were extrapolated to $y_{CO_2} = 0$ and $y_{CO_2} = 1$ with the fits of Langmuir and Toth equations for the single component data. All measured binary data and the corresponding CO₂ mole fractions in the feed mixture ($y_{CO_2}^{feed}$) are summarized in Table 2.

Table 2: Binary adsorption data on AC WV1050 at 293 K.

P [MPa]	$y_{CO_2}^{feed}$	y_{CO_2}	q_{CO_2} [mol.kg ⁻¹]	q_{CH_4} [mol.kg ⁻¹]	x_{CO_2}	S_{CO_2/CH_4}
0.094	0.485	0.297	0.845	0.403	0.677	4.968
0.094	0.695	0.475	1.296	0.165	0.887	8.686
0.095	0.822	0.671	1.689	0.127	0.930	6.521
0.267	0.319	0.194	1.176	1.074	0.522	4.558
0.253	0.628	0.485	2.278	0.560	0.803	4.318
0.240	0.863	0.782	3.197	0.197	0.942	4.522
0.543	0.276	0.181	1.652	1.746	0.486	4.282
0.504	0.475	0.352	2.743	1.230	0.690	4.100
0.499	0.848	0.777	4.884	0.286	0.945	4.915
1.068	0.223	0.153	2.173	2.838	0.434	4.249
1.010	0.473	0.355	4.604	1.603	0.742	5.226
0.965	0.830	0.768	7.240	0.457	0.941	4.771

**Figure 3:** Binary adsorption isotherm for CO₂-CH₄ mixtures at 293 K on AC WV1050 at 0.1 MPa (a) and the respective x-y diagram (b). Symbols represent experimental data and lines represent prediction models.**Figure 4:** Binary adsorption isotherm for CO₂-CH₄ mixtures at 293 K on AC WV1050 at 0.25 MPa (a) and the respective x-y diagram (b). Symbols represent experimental data and lines represent prediction models.

For all pressures studied in this work, the total adsorbed amount increased along with CO₂ composition, while the amount of methane adsorbed decreased, indicating competition for adsorption sites and, again, preferential adsorption of carbon dioxide over methane. This result agrees with the higher value of the parameter b for CO₂ in relation to CH₄. The main reason for this behavior is the significantly higher critical temperature of CO₂ in comparison with CH₄

(see Table 3). Carbon dioxide is more likely to behave as a condensable steam than as a supercritical gas, becoming less volatile and increasing its adsorption. Moreover, CO₂ presents a higher polarizability (α) which may enhance attractive forces with the surface and a permanent quadrupole (Θ), leading to stronger interactions with the solid surface. Even at concentrations of ca. 20% for all binary isotherms, CO₂ already presented higher adsorbed amounts with respect to CH₄.

Table 3: Physical-chemical properties of CO₂ and CH₄ [modified from Tagliabue *et al.* (2009)].

Molecule	σ [Å]	α [Å ³]	μ [D]	Θ [D. Å]	T_c [K]
CO ₂	3.30	2.51	0.00	4.30	304
CH ₄	3.80	2.45	0.00	0.02	190

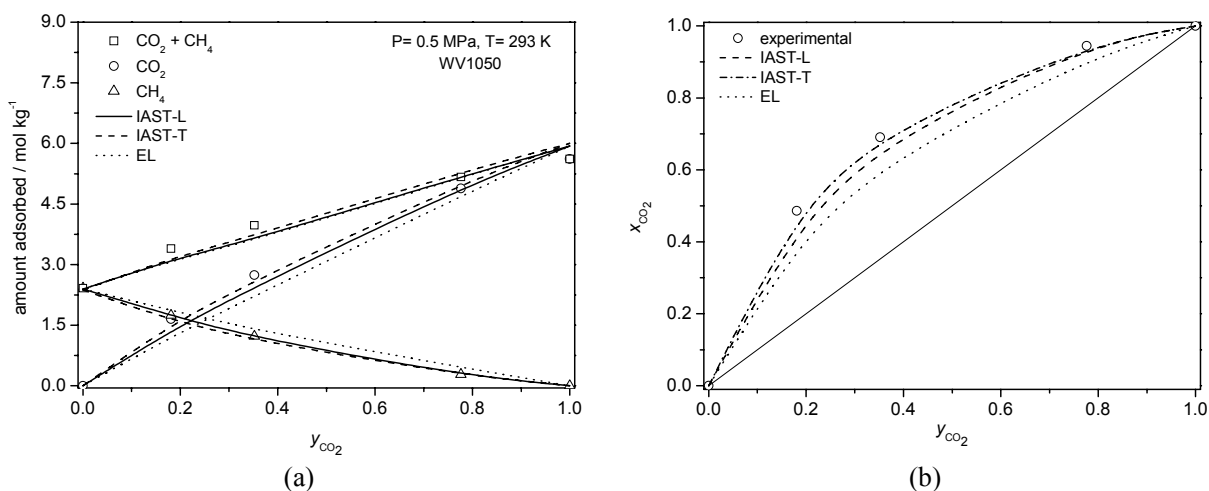


Figure 5: Binary adsorption isotherm for CO₂-CH₄ mixtures at 293 K on AC WV1050 at 0.5 MPa (a) and the respective x - y diagram (b). Symbols represent experimental data and lines represent prediction models.

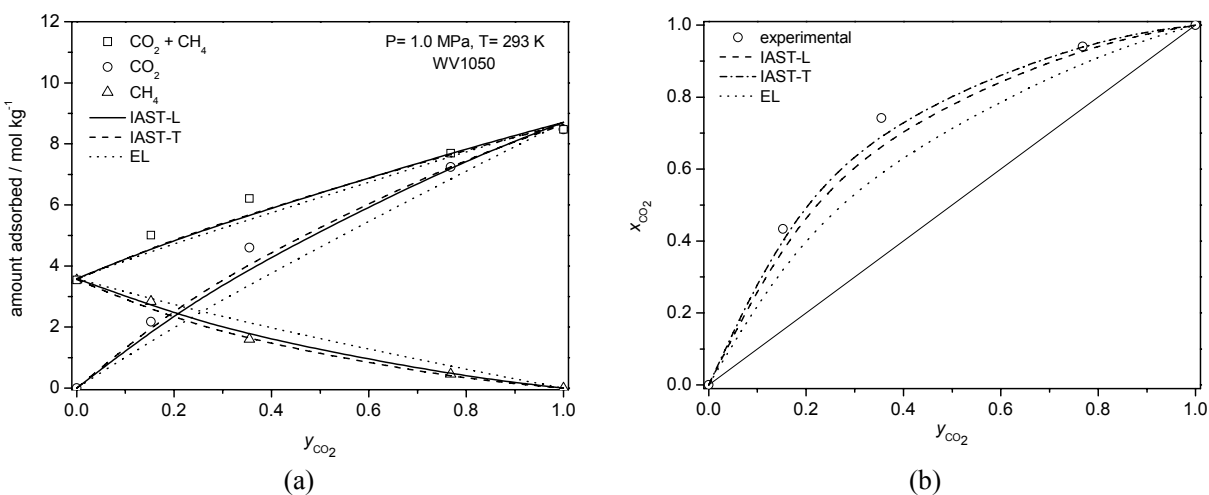


Figure 6: Binary adsorption isotherm for CO₂-CH₄ mixtures at 293 K on AC WV1050 at 1.0 MPa (a) and the respective x - y diagram (b). Symbols represent experimental data and lines represent prediction models.

The x - y diagrams at 0.1, 0.25, 0.5 and 1.0 MPa are shown in Figs. 3(b), 4(b), 5(b), and 6(b), respectively. An increase in the CO₂ composition of the adsorbed phase in relation to that in the gas phase was observed in the equilibrium, which represents positive deviations from Raoult's law for all measured pressures. Comparing these graphs one can observe that the highest deviation is found for the experimental curve at 0.1 MPa (see Fig. 3(b)), which confirms a stronger selective behavior for CO₂ over CH₄ at this pressure.

From an analysis of Figs. 3(a)-6(a) and Table 4, one may observe that the IAST models showed better results than the EL model for almost all predictions, as expected. The IAST-T model showed slightly better results for the prediction of CO₂ and total (CO₂ + CH₄) adsorbed amounts in comparison with the IAST-L model. However, the IAST-L model presented the best predictions for CH₄ in general. This might be explained by the better fit quality to the CO₂ adsorption data when using the Toth equation and to the CH₄ adsorption data when using the Langmuir equation (see Table 1).

Buss (1995) reported that at higher surface coverage in a CO₂-CH₄ system, if the interactions in the adsorbed phase become dominant, the applicability of the IAST model can decrease. Since at higher pressures the surface is more filled with adsorbate, this loss of accuracy would not be observed and the IAST model presented the best fits for the highest pressures (0.5 and 1.0 MPa) in this study. Once again, it may be explained by the difference between the pure component isotherm curve-fits.

From all the mixture data, the highest deviations, considering both IAST models, were observed for 0.1 MPa with δq around 30.3% (average between δq_{total} for IAST-L and IAST-T) and at 0.25 MPa with δq around 13.4% (average between δq_{total} for IAST-L and IAST-T). For 0.5 MPa and 1.0 MPa, the δq were around 5.4 and 5.6% (average between δq_{total} for IAST-L and IAST-T), respectively (see Table 4). This discrepancy is explained by the fit quality of the pure component isotherms, since in the pressure range of 0 to 0.25 MPa the errors between the experimental points and the fit were much larger than the corresponding error in the pressures at 0.5 and 1.0 MPa for both gases and for the pure gas models (see Table 5). In other words, when individually comparing points from fit isotherms to the experimental points used to generate these fits, the highest deviations of these pure component fits were observed for the pressure range of 0 to 0.25 MPa, which is the same pressure region where the highest IAST errors were observed (binary isotherms at 0.1 MPa and 0.25 MPa).

Table 4: Average relative errors for the predicted binary adsorption data on AC WV1050 at 293 K.

P [MPa]	Prediction Model	δq_{CO_2} [%]	δq_{CH_4} [%]	δq_{total} [%]
0.1	IAST-L	34.8	36.6	33.0
	IAST-T	23.0	51.8	27.6
	EL	41.6	38.6	31.5
0.25	IAST-L	16.2	36.1	15.6
	IAST-T	9.2	36.0	11.3
	EL	23.4	16.3	14.4
0.5	IAST-L	9.4	2.8	5.7
	IAST-T	5.1	6.2	5.2
	EL	16.4	27.1	6.1
1.0	IAST-L	9.2	5.7	5.7
	IAST-T	5.7	13.7	5.5
	EL	19.8	29.8	7.6

Table 5: Average relative errors of Langmuir and Toth fits of CO₂ and CH₄ isotherms at 293 K on AC WV1050 for two different pressure ranges.

Isotherm	Langmuir		Toth	
	δq (0-0.25MPa)	δq (0.5-1.0 MPa)	δq (0-0.25MPa)	δq (0.5-1.0 MPa)
CO ₂	26.17	4.27	30.04	1.99
CH ₄	14.18	1.03	21.20	11.31

These observations indicate that IAST predictions, i.e., the description of multicomponent equilibria based on single component data, are dependent on the fit quality to the pure gas data (Goetz *et al.*, 2006). The fit quality is determined not only factors such as the accuracy of the experimental results, but also by the particular isotherm model adopted for the description of the monocomponent adsorption. Consequently, as reported by Bastos-Neto *et al.* (2011), we may infer that predictions of mixture equilibrium also rely on the isotherm model.

To further investigate this, a new fit was performed considering only the data within the pressure range of 0 to 0.25 MPa (see Fig. 2). The recalculated parameters and average relative errors of these fits are presented in Table 6. With this new data set, the IAST-L and IAST-T were reevaluated for the binary isotherm corresponding to the pressure of 0.1 MPa and the new errors (δq) are presented in Table 7. A comparison between this last fit with the previous one using IAST-T for the binary equilibrium at 0.1 MPa is shown in Fig. 7.

Comparing the average errors, one can observe that a decrease from 17.9 to 8.12% (Langmuir fit) and 13.4 to 5.77% (Toth fit) in the average error of the fit for the isotherm of pure CO₂ resulted in a considerable decrease in the prediction error of CO₂ in the mixture from 34.8 to 9.11% (IAST-L) and

23.0 to 8.26% (IAST-T). Analogously, an increase in the error for the new fit to the isotherm of pure CH₄ led to an increase in prediction error for this gas when using IAST-L. The same behavior was not observed for the predictions of CH₄ in the mixture using IAST-T.

Table 6: New parameters and average relative errors of Langmuir and Toth fits of CO₂ and CH₄ pure component isotherms at 293 K from 0 to 0.25 MPa on AC WV1050.

Isotherm	Langmuir			Toth			
	q_{max}	b	Δq	q_{max}	b	t	δq
CO ₂	7.366	3.980	8.12	17.510	2.126	0.577	5.77
CH ₄	4.831	1.380	16.91	5.577	1.155	0.984	15.19

Table 7: New average relative errors for the predicted binary adsorption data on AC WV1050 at 0.1 MPa and 293 K from the new fit pressure range.

Prediction Model	δq_{CO_2} [%]	δq_{CH_4} [%]	δq_{total} [%]
IAST-L	9.11	55.40	14.50
IAST-T	8.26	50.88	14.29

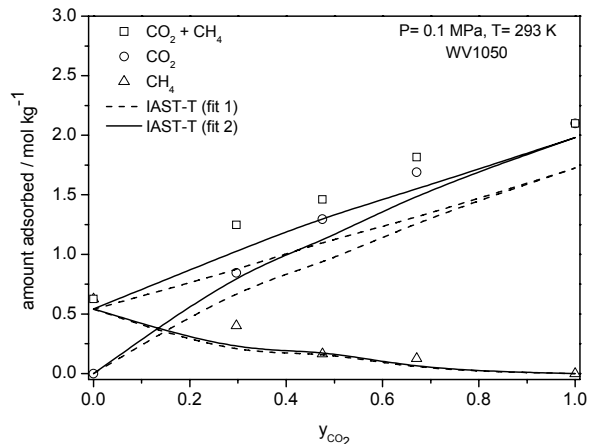


Figure 7: Comparison between IAST-T, IAST-T (new fit) and experimental points for the binary adsorption isotherm of CO₂-CH₄ at 293 K and 0.1 MPa on AC WV1050. Symbols represent experimental data and lines represent prediction models.

However, since CO₂ showed a strong adsorption preference in the mixture at 0.1MPa, the new Toth equation fit for CO₂ may have been sufficient to ensure better results for both gases. This suggests that to assure a satisfactory IAST prediction, an

appropriate choice of the equation adopted and a high fit quality of the single component data are required, especially for the most preferentially adsorbed component in the mixture, confirming previous reports (Goetz *et al.*, 2006; Harlick and Tezel, 2003).

Selectivity of CO₂ Over CH₄

Adsorption selectivity is one of the most important parameters for practical applications and gives an idea of the efficiency of the separation (Ustinov *et al.*, 2004; Belmabkhout and Sayari, 2009). The selectivities of CO₂-CH₄ for the activated carbon WV1050 at 293 K are shown in Table 2 for each experimental point.

The highest values of selectivity were observed at 0.1 MPa with a maximum selectivity of around 8.7 for a nearly equimolar mixture. This higher selectivity observed for lower experimental pressures (0.1 MPa) may be explained by the fact that, for energetically heterogeneous adsorbents, there is an initial and preferential filling of high-energy sites for which the more strongly adsorbed component is even more preferred in the competition for the sites than when competing for energetically weaker adsorption sites. Since a greater amount of CO₂ can be adsorbed at lower pressures on those high-energy sites, this behavior seems more evident in the results. Furthermore, as the pressure increases and the high-energy sites are filled, the more strongly adsorbed component begins to compete for energetically weaker sites for which the local values of selectivity are lower. In general, this may lead to a decrease in the selectivity with increasing pressure at similar compositions, as observed in Table 2.

Buss (1995) observed for their binary adsorption data of CO₂-CH₄ mixtures on AC A 35/4 at 293 K that the selectivity increased with the composition of CO₂ in the mixture. However, this was not observed in our studies for the experimental results presented in Table 2.

A comparison between the selectivity values of CO₂ over CH₄ on AC from this study with other studies is also shown in Fig. 8. It includes mixtures of around 42% CO₂ on AC Norit R1 extra at 298 K (Dreisbach *et al.*, 1999), around 50% CO₂ on AC A 35/4 at 293 K (Buss, 1995), and around 41% CO₂ on AC Norit RB2 at 298 K (Goetz *et al.*, 2006). For this comparison, an average between similar composition values was calculated. The results show that AC WV1050 shows higher selectivity values than Norit R1 extra, A 35/4, and Norit RB2 activated carbons, when compared at similar CO₂ compositions.

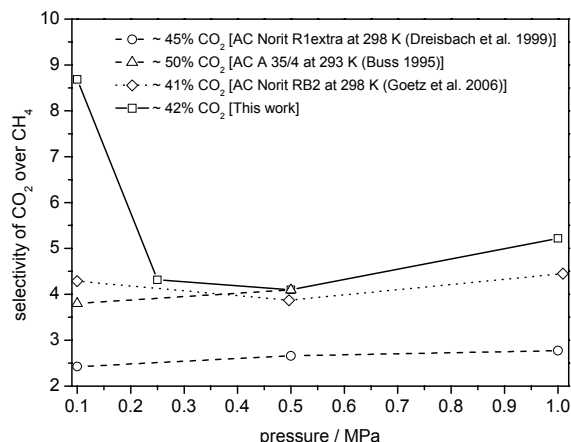


Figure 8: Selectivity of CO₂ over CH₄ at 293 K on AC WV1050 at ca. 42% CO₂ mixture, at 298 K on AC Norit extra at ca. 45% CO₂ mixture, at 293 K on AC A 35/4 at ca. 50% CO₂ mixture, and at 298 K on Norit RB2 at ca. 41% CO₂ mixture. Symbols represent experimental data and lines only indicate trends of the experimental points.

CONCLUSION

Adsorption equilibria of CO₂, CH₄ and their mixtures were experimentally evaluated at 293 K for an activated carbon sample. Single gas isotherms were obtained at pressures between 0.01 and 1.5 MPa and binary adsorption equilibria at pressures of 0.1, 0.25, 0.5 and 1.0 MPa for different gas compositions. The Extended Langmuir model and the IAST model in conjunction with the Toth or Langmuir equations were used to predict the adsorbed amounts of each gas in the CO₂-CH₄ mixtures.

Results showed competition for active adsorption sites and preferential adsorption for carbon dioxide over methane. Even at concentrations of ca. 20% for all binary isotherms, CO₂ presented higher adsorbed amounts with respect to CH₄. The highest selectivity values were observed at 0.1 MPa, showing a maximum selectivity of around 8.7 for a nearly equimolar mixture. In general, the predictions of binary equilibria with IAST models showed relatively good agreement with the experimental data, except for the pressure of 0.1 MPa. On the other hand, EL models did not represent the data well at all the pressures that were evaluated. For 0.1 MPa, recalculation of pure component isotherms using only low pressure data gave better agreement for the estimated binary values.

Positive deviations shown on *x-y* diagrams and the average relative errors between experimental and

predicted adsorption data suggest non-ideality behavior in the adsorbed phase which may be further evaluated in future studies.

NOMENCLATURE

A	specific surface area of adsorbent	$\text{m}^2 \cdot \text{kg}^{-1}$
b_i	Langmuir and Toth parameter of the component i	MPa^{-1}
m_{AC}	mass of regenerated activated carbon	kg
N	number of isotherm points	
n_i^o	initial number of moles of the component i	mol
n_i^f	final number of moles of the component i	mol
$n_i(P_i)$	local adsorption isotherm	$\text{mol} \cdot \text{kg}^{-1}$
P_i	partial pressure of the component i	MPa
P_i^o	pressure of the pure component i at the same π as that of the mixture	MPa
P_{mixt}^o	initial pressure of the gas mixture	MPa
P_{mixt}^f	final pressure of the gas mixture	MPa
q_i	excess amount adsorbed of the component i	$\text{mol} \cdot \text{kg}^{-1}$
$q_{max,i}$	monolayer capacity of component i	$\text{mol} \cdot \text{kg}^{-1}$
$q_{pred,i}$	predicted amount adsorbed of the component i	$\text{mol} \cdot \text{kg}^{-1}$
q_{total}	total excess amount adsorbed	$\text{mol} \cdot \text{kg}^{-1}$
R	ideal gas constant	$8.314 \text{ MPa} \cdot \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
S_{ij}	selectivity of component i in relation to component j	
T	Toth parameter of the component i	
T	temperature	K
T_c	critical temperature	K
T_{mixt}^o	initial temperature of the gas mixture	K
T_{mixt}^f	final temperature of the gas mixture	K
V_{ac}	volume of the solid phase of the AC	cm^3
V_{ads_chb}	volume of the adsorption chamber	cm^3
V_{dos_chb}	volume of the dosing chamber	cm^3

V_{int}	internal volume of the empty system	cm ³
V_s	specific volume of the solid phase of the AC	cm ³ .kg ⁻¹ sample
V_{void}	void volume of the system	cm ³
x_i	composition of the component i in the adsorbed phase	
y_i^o	initial composition (in molar fraction) of the component i in the gas phase	
y_i^f	final composition (in molar fraction) of the component i in the gas phase	
Z_i	compressibility factor of the pure gas	
Z_{mixt}	compressibility factor of the gas mixture	
Z_{mixt}^o	initial compressibility factor of the gas mixture	
Z_{mixt}^f	final compressibility factor of the gas mixture	

Greek Letters

α	polarizability	Å ³
δq_i	average relative error for the component i	%
Θ	quadrupole moment	D. Å
μ	dipole moment	D
π_i	spreading pressure of the component i	J.m ⁻²
Π^*	reduced spreading pressure of the mixture	mol.kg ⁻¹
Π_i^*	reduced spreading pressure of the component i	mol.kg ⁻¹
Π_L^*	reduced spreading pressure of the mixture using Langmuir equation	mol.kg ⁻¹
Π_T^*	reduced spreading pressure of the mixture using Toth equation	mol.kg ⁻¹
σ	kinetic diameter	Å

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