PREDICTION OF THREE COMPONENT GAS ADSORPTION WITH IAST AND LANGMUIR

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ABSTRACT – Purification of natural gas is important to avoid pipe corrosion and improve its specific heat. This operation is mainly focused on hydrogen sulfide and carbon dioxide removal from methane, and adsorption is one of the proposed techniques. In this work, experimental adsorption isotherms for CH_4, CO_2 or H_2S, in NaY zeolite, at 30°C were determined and the Ideal adsorption solution theory (IAST) and Langmuir adsorption isotherm were used to predict the adsorption behavior of the gas mixture composed by $CH_4 + CO_2 + H_2S$, at 1, 20 or 50 bar. According to Langmuir equation, the maximum adsorbed capacity was approximately 3.77, 7.06, and 7.02 mol/kg, for CH_4, CO_2, and H_2S, respectively. The calculated values of distribution coefficient (K) and selectivity (S) indicate zeolite adsorbs more H_2S than CO_2. Also, K values are increased with CH_4 content, although S values are greater for high H_2S concentration.

1. INTRODUCTION

In the production of natural gas, purification is necessary to meet pipeline specifications or for commercial use as fuel, and this involves the removal of H_2S and CO_2, among other components (Koyun *et al.*, 2012; Kunz and Wagner, 2012).

The current technologies for CO_2 separation from gas streams in mainly composed by solvents, membranes and sorbents (Li *et al.*, 2013). The sorbent technology includes materials such as zeolite (Maurin *et al.*, 2007), activated carbon (Schell *et al.*, 2012), silica (Watabe and Yogo, 2013), and metal organic frameworks (Chaemchuen *et al.*, 2013).

Removal of H_2S from gas mixtures, such as natural gas, belongs to a broader and important area, namely, the desulfurization of hydrocarbons. Remove sulfur from hydrocarbon streams can be carried out by: a) extraction with amine solution, b) catalytic hydrodesulfurization at elevated temperatures and pressures, c) catalytic oxidation/adsorption with metal oxides, and d) adsorption on solid adsorbents at mild conditions of temperature and pressure (Kumar *et al.*, 2011; Ratsanamy *et al.*, 2012). Considering adsorption, the majority of the studies are about H_2S adsorbed on activated carbon, as an example, the work of Bandosz (1999), but also there are some works using zeolites,

such as those reported by Cruz *et al.* (2005), Melo *et al.* (2006), Crespo *et al.* (2008), Alonso-Vicario et al. (2010), and Kumar *et al.* (2011)

The sorbent technology is used in different ways, depending on the degree of purification desired. In this way, swing adsorption processes can be used with operation variables such as pressure (PSA), temperature (TSA), pressure and temperature (PTSA), concentration (CSA) and electric systems (ESA) can take place.

Design and optimization of industrial operations like PSA can be realized after the knowledge of equilibrium in adsorption process. It is also necessary for the evaluation of adsorption capacity and adsorbents selectivity. Besides, multicomponent adsorption experiments are too laborious, and it is desirable to employ approaches that allow the prediction of such systems from experimental data (Rios *et al.*, 2013)

In this work, isotherms for CH_4, CO_2 or H_2S adsorbed in NaY zeolite were measured experimentally. One-component data were modelled with conventional equations that provided a prediction for adsorption behavior of the ternary mixture.

2. EXPERIMENTAL

Pure component isotherms were measured in a Rubotherm Magnetic Suspension Balance (Bochum, Germany) without an in-situ density measurement. The gas density was estimated with Peng-Robinson equation of state (Peng and Robinson, 1976). The measurements were made as pointed out by Dreisbach *et al.* (2002) and Keller and Staudt (2005). The pressure range used was: 0.4 to 45 bar, for CH_4; 0.4 to 40 bar, for CO_2; 0.02 to 1.8 bar, for H_2S. Temperature was kept constant at 30°C with a water circulating bath.

3. MODELLING

Modelling used in this work is similar to that reported by Schell *et al.* (2012), but here the ternary behavior was predicted instead of the binary.

The one-component data was correlated with Langmuir isotherm, shown by Equation 1:

$$q = q_{max} \frac{bP}{1 + bP} \tag{1}$$

In Equation 1, P is the pressure (bar), q is the adsorbed amount (mol/kg), q_{max} is the maximum adsorbed amount (mol/kg), and b is the energetic parameter (1/bar).

With the Langmuir isotherm parameters fitted to the experimental results of the pure components, ternary equilibria were predicted using ideal adsorbed solution theory, or IAST (Myers and Prausnitz, 1965).

3.1. Calculation procedure

Initially, the pressure (P) and mole fraction (y) of the gas phase in equilibrium with an adsorbed phase is chosen. Considering that gas phase can be described by Raoult's law, the partial pressure of each i component is calculated as $P \cdot y_i$.

For the ideal adsorption solution, at constant temperature, Equation 2 gives the equilibrium criterion:

$$P y_i = P_i^o x_i \tag{2}$$

where P_i^o is the pure adsorbate vapor pressure for component i at the temperature and spreading pressure (π) of the solution, and x_i is the mole fraction of component i in adsorbed phase. P_i^o is obtained by Equation 3:

$$Z = \int_{P=0}^{P=P_i^O} q \, d \ln P \tag{3}$$

where Z is the compressibility factor. For adsorbed phase, Z is determined according to Equation 4:

$$Z = \frac{PV}{RT} = \frac{\pi A}{RT} \tag{4}$$

where R is the ideal gas constant (J/mol.K), T is the absolute temperature (K), A is the area occupied by adsorbed phase (m²), and π is the spreading pressure (bar·m). Inserting Equation 1 into 3 and solving the integral, Equation 5 is obtained:

$$P_i^o = \frac{exp\left(\dfrac{Z}{q_{m,i}}\right) - 1}{b_i} \tag{5}$$

where $q_{m,i}$ and b_i are the Langmuir parameters for component i.

With Equations 2 and 5, the values of x_i can be estimated guessing values for Z and minimizing the objective function (F) shown by Equation 6:

$$F = \sum_i (x_i) - 1 \tag{6}$$

As a result, partition coefficients for each component (K) and the selectivity (S), given by Equations 7 and 8, can be calculated:

$$K_i = \frac{x_i}{y_i} \tag{7}$$

$$S_i = \frac{K_i}{K_j} \tag{8}$$

In Equation 8, $i = CO_2$ or H_2S, and $j = CH_4$.

The conditions used for modelling were: pressure equal to 1, 20, and 50 bar; and temperature equal to 30°C. The calculation procedure was performed with Microsoft Excel® Solver; and Evolutionary method was employed without change the initial set of variables.

4. RESULTS AND DISCUSSION

4.1. Adsorption isotherms

The adsorption isotherms obtained for CH_4, CO_2 or H_2S are shown in Figure 1. It can be verified that H_2S presents a greater affinity for NaY zeolite than CO_2 or CH_4. This is due to its strong interaction with zeolite behavior, characterized by three different adsorption behavior (Maugé et al., 2002).

Langmuir curves fitted to each experimental adsorption isotherm are also shown in Figure 1, and the estimated parameters are in Table 1. The b values shown indicate quantitatively that adsorption interaction with NaY zeolite presents the order $H_2S > CO_2 > CH_4$.

4.2. Partition coefficients and selectivities

The modelling results are grouped in Figure 2. They covered all range of compositions for the ternary mixture, and so equilateral triangles were employed. The pressures chosen to input the modelling were 1, 20 and 50 bar, but only the results at 1 bar are shown, since the results for the other two pressures were very similar.

From calculated data depicted in Figures 2a and 2b, it is verified that Langmuir joined with IAST indicate higher partition coefficients for both low H_2S and CO_2 concentration. The partition coefficient for H_2S is higher than for CO_2, and it is related with the b value for each gas shown in
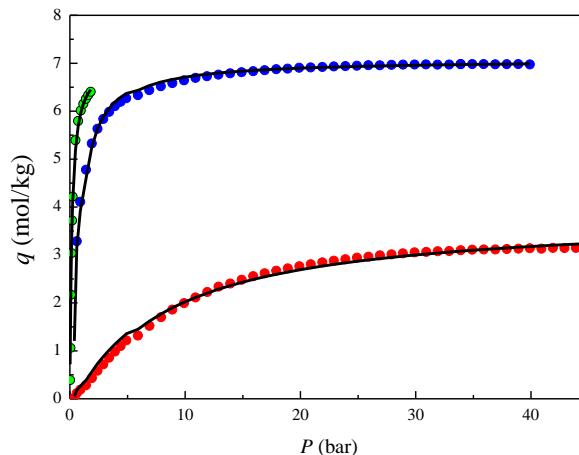
Table 1.

Figure 1 – Adsorption isotherms obtained for CH_4 (red), CO_2 (blue) and H_2S (green), in NaY zeolite, at 30°C.

Table 1 – Langmuir estimated parameters

Gas	q_{max} (mol/kg)	b (bar^{-1})
CH_4	3.7762	0.0032
CO_2	7.0553	2.0586
H_2S	7.0183	5.6354

Selectivities values shown in Figures 2c and 2d, indicate that zeolite have great affinity for H_2S and CO_2, and that S_{H2S} is greater than two times S_{CO2}. Also, a different trend is presented for selectivity. As the concentration of CH_4 is increased, the S values for both gases decrease.

These results are interesting, since they provide that the possible use for zeolites on the natural gas purification should be downstream a bulk purification, generally carried out with with amines, membranes or oxides, as stated in Introduction section.

However, zeolite NaY seem to be technically promising for CH_4 separation due to high S values achieved. A more robust modelling allied to experiments with binary and ternary mixtures, in equilibrium and dynamic forms, should give a definitive answer for this process.
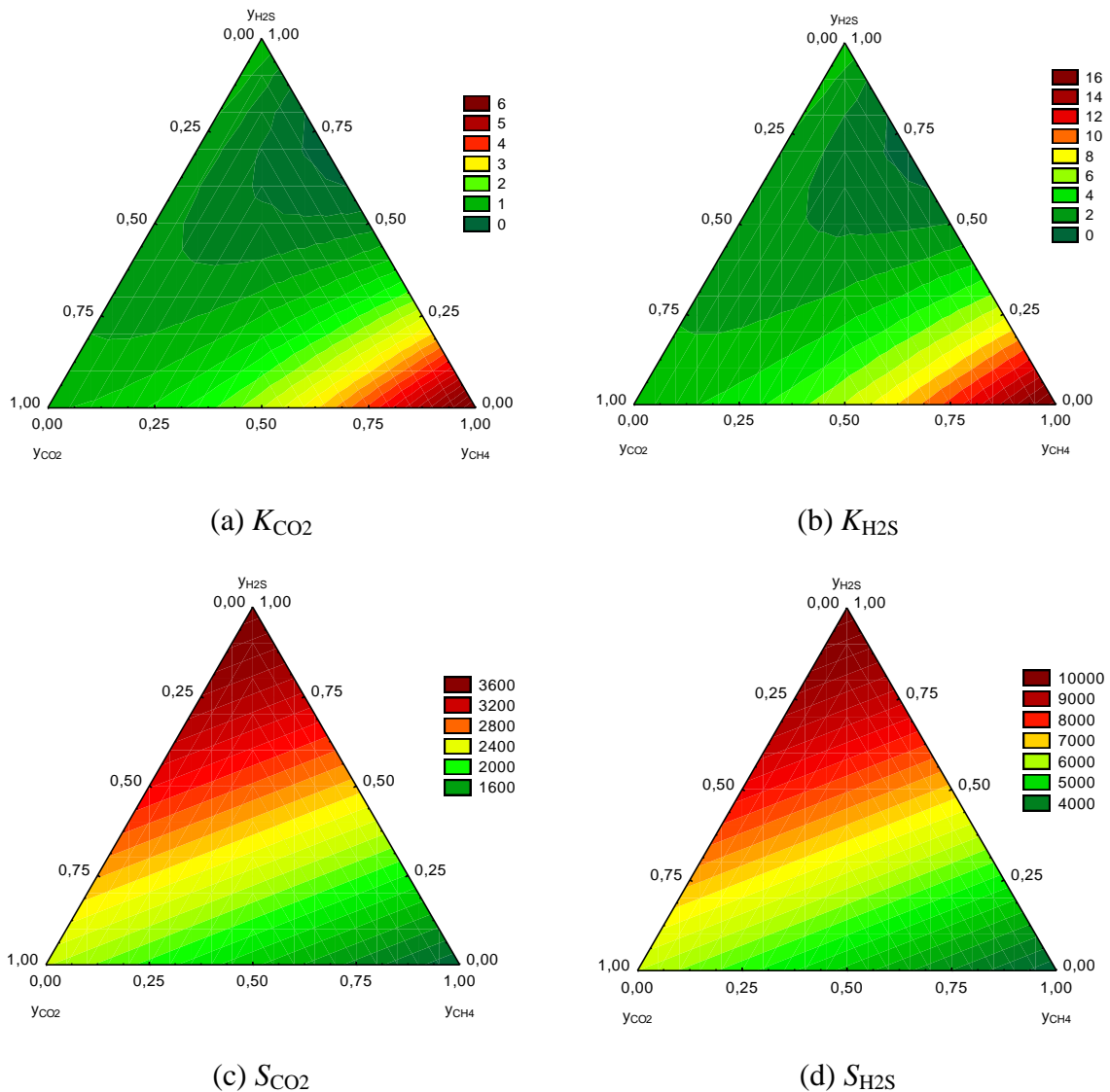
(a) K_{CO2}

(b) K_{H2S}

(c) S_{CO2}

(d) S_{H2S}

Figure 2 – Partition coefficients and selectivities for CO_2 and H_2S at 30°C and 1 bar.

5. CONCLUSIONS

Ideal adsorption solution theory (IAST) and Langmuir adsorption isotherm were used to predict the adsorption behavior of the gas mixture $CH_4 + CO_2 + H_2S$ in NaY zeolite, at 30°C and 1, 20 or 50 bar. Langmuir equation gives a maximum adsorbed capacity of 3.77, 7.06, and 7.02 mol/kg, for CH_4, CO_2, and H_2S, respectively. Distribution coefficient (K) and selectivity (S) indicate zeolite adsorbs more H_2S than the other gases. Also, K values are increased with CH_4 content, although S values are greater for high H_2S concentration. These results accord with the sequence of affinity presented by b parameter of Langmuir equation. Hence, NaY zeolite seem to be technically promising for CH_4 separation due to high S values achieved.

5. ACKNOWLEDGEMENTS

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