Adsorption (2010) 16: 525–530
DOI 10.1007/s10450-010-9254-x

Studies of C_8 aromatics adsorption in BaY and mordenite molecular sieves using the headspace technique

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Published online: 11 August 2010

Abstract A headspace technique, that consists in analyzing the composition of the vapor phase in equilibrium with the condensed phase of a mixture in a sealed vial containing the adsorbent sample, has been recently applied to acquire equilibrium data for adsorption of xylenes in liquid phase. In this study, we used this technique to measure experimental binary equilibrium data for C_8 aromatics in Y and mordenite zeolitic molecular sieves. For the Y zeolite, we also measured C_8 aromatics quaternary equilibrium data. Measurements were made at temperatures between C 40–80 °C. A more tedious, but traditional, chromatographic pulses method was also used to validate some of the results.

Keywords Xylenes · Adsorption · Headspace · Selectivity · Y zeolite · Mordenite

Symbols

C	Liquid phase concentration (mmol·mL^{-1})
L	Column length (cm)
p_i	Saturation vapor pressure (atm)
q	Adsorbed phase concentration (mmol/g)
Q	Flowrate (mL·min^{-1})
t_{Ri}	Response time of each component i in the chromatographic method (min)
t_o	Response time of non-adsorbed component in the chromatographic method (min)
T	Temperature (°C)
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in vapor phase
z_i	Mole fraction of component i in adsorbed phase

Greek symbols

ε	Bed porosity
ρ_B	Bed density (g·cm^{-3})
ϕ	Column internal diameter (cm)
α	Selectivity
υ	Superficial velocity (cm·min^{-1})

Chemical compounds

EB	Ethylbenzene
MX	*m*-xylene
OX	*o*-xylene
PX	*p*-xylene

1 Introduction

Separation of C_8 aromatics mixtures is an important issue in the petrochemical industry. The C_8 aromatics fraction in a refinery consists of four isomers: *o*-xylene (OX), *m*-xylene (MX), *p*-xylene (PX) and ethylbenzene (EB). *P*-xylene and *o*-xylene have major industrial importance since they are widely used in the manufacture of synthetic fibers. Because of the close boiling points of these compounds, their separation has become one of the most important applications of liquid phase adsorption separation processes (Minceva et al. 2008). In order to achieve that objective, it is important to find a selective adsorbent able to perform the separation based either on selective equilibrium or on kinetics differences. However, experimental data on multi-component C_8 aromatics adsorption equilibria in liquid phase are relatively scarce and only very limited data are available in the open literature.

The faujasite structure, specially Y zeolite, has been intensively studied for the separation of xylenes, mainly for

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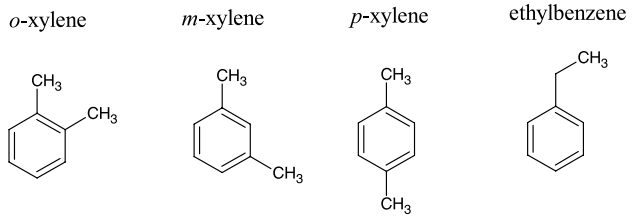

Fig. 1 C_8 aromatic isomers

p-xylene separation (Broughton et al. 1970; Li et al. 1991; Hulme et al. 1991; Buarque et al. 2005; Minceva et al. 2008). Its selectivity can depend on the cationic form of the zeolite, with K and BaY zeolites being mostly applied for this separation.

In order to investigate the influence of the sorbate-adsorbent interaction on the selectivities, the aluminophosphate molecular sieves ($AlPO_4$-*n*) have also been studied for the separation of C_8 aromatics mixtures. This material is free of silica and is a good example of materials showing no significant interaction between sorbates. Barthomeuf and Mallmann (1990) studied the adsorption of benzene and *o*-xylene on $AlPO_4$-5. They suggested that the selectivity in the separation of C_8 aromatics by adsorption on $AlPO_4$-5 (preference for *o*-xylene) is related its high cohesive energy. Chiang et al. (1991) and Cavalcante et al. (2000) studied the sorption and diffusion of *p*-xylene and *o*-xylene in crystals of $AlPO_4$-5 and $AlPO_4$-11, respectively. Their data indicated that, at saturation capacities, equilibrium favored *o*-xylene, probably due to face-to-face packing orientation of the molecules within the micropores. Recent studies have reported adsorption equilibrium of xylenes in $AlPO_4$-*n* framework using molecular simulation (Lucena et al. 2006, 2008). The simulated isotherms reproduced well the ortho-selectivity previously observed in $AlPO_4$-5 and in $AlPO_4$-11. Other porous materials that may improve the operating results in *p*-xylene production plants are mordenite and pentasil zeolites (John et al. 1999).

Various traditional techniques, such as batch, thermogravimetry, chromatographic breakthrough and pulse experiments, can be used to measure adsorption equilibrium of xylenes in zeolites (Santacesaria et al. 1982; Li et al. 1991; Cottier et al. 1997; Cavalcante et al. 2000; Tournier et al. 2001; Minceva and Rodrigues 2004). Another method that has been more recently applied is the headspace chromatography (Torres et al. 2001; Buarque et al. 2005; Oliveira et al. 2009), which allows the use of a much smaller quantity of liquid and higher solid to liquid ratio, thus increasing the magnitude of the change in concentration and the accuracy of the experimental results (Torres et al. 2001). This technique consists in analyzing the composition of the vapor phase in equilibrium with the condensed phase of a mixture in a sealed vial containing the adsorbent sample.

Table 1 Properties of commercial adsorbents

Adsorbents	BaY zeolite	Mordenite
BET surface area (m^2/g)	313	410
Pore diameter, DR (Å)	7.0	6.2
Total pore volume (cm^3/g)	0.408	0.395
Micropore volume, DR (cm^3/g)	0.315	0.280

In this study, we used the headspace technique to measure experimental equilibrium data for C_8 aromatics in two commercial molecular sieves (BaY zeolite and mordenite). Chromatographic pulses were also used to validate the results. Measurements were made for binary and multicomponent C_8 aromatics systems, at temperatures between 40–80 °C.

2 Experimental section

2.1 Materials

Xylene isomers (Fig. 1) and *n*-octane (as inert) with purity higher than 99% wt were used in the experiments. The adsorbents were commercial samples of BaY zeolite and mordenite. Prior to use in the experiments, the adsorbent was thermally treated using an electrical oven, initially at 80 °C for 1 h, and then heated slowly at approximately 40 °C/h up to 320 °C. The sample was then left at this temperature for at least 4 hours, after which, it was allowed to cool down to room temperature, under vacuum, and immediately used in the equilibrium cells.

2.2 Adsorbents properties

The adsorbents used in this work were characterized for their textural properties using Autosorb-1 MP (Quantachrome, USA) to measure N_2 isotherms at 77 K for the determination of textural properties such as surface area, total pore volume, micropore volume and mean pore diameter. The specific surface area was calculated using the BET methodology. The mean pore diameter and micropore volume were determined using the Dubinin–Radushkevich (DR) equation, according to the procedure described by Rouquerol et al. (1999). The textural properties calculated for the adsorbents used in this study are listed in Table 1.

2.3 Headspace technique

The headspace technique consists of contacting a given liquid volume with a given adsorbent mass in equilibrium cells (vials). After a sufficient amount of time is allowed, there are three equilibrated phases: vapor, liquid and adsorbed.

The vapor phase is sampled and, from its composition, we may use a proper Vapor-Liquid Equilibrium relationship to calculate the composition of the liquid phase. The adsorbed-phase concentration may then be determined by a simple mass balance (Torres et al. 2001).

The experimental setup had a Headspace Sampler (HP-7694) connected to a Varian Gas Chromatograph-CP-3380 (their operational parameters are shown in Supporting Information). A thermostatic bath was also used to preheat the equilibrium cells to attain approximate equilibrium conditions, reducing the equilibrium time into the heater of the headspace sampler.

A series of headspace vials was prepared, each containing the same weight of regenerated adsorbent with successively increasing quantities of liquid sorbate. These are allowed to equilibrate at a given temperature inside the headspace oven (minimum 4 hours), then the composition of the vapor phase is analyzed and plotted against the amount of liquid sorbate added, as shown in Fig. 2.

To calculate the ratio of liquid phase mole fractions from the ratio of vapor phase mole fractions obtained experimentally we require vapor liquid equilibrium data. Since xylene isomers form essentially an ideal system (Raoult's Law), the ratio can be calculated by (1):

$$\frac{x_A}{x_B} = \frac{p_B}{p_A}.\frac{y_A}{y_B} \tag{1}$$

and the adsorbed phase/liquid phase selectivity is therefore given by (2):

$$\alpha_{AB} = \frac{z_A/z_B}{x_A/x_B} \tag{2}$$

This approach can be easily extended to a multi-component mixture using a similar approach.

2.4 Chromatographic pulses method

The adsorption behavior of xylene isomers in a fixed bed system was also investigated by pulse chromatography. An adsorption column ($L = 25.0$ cm, $\phi = 0.46$ cm) containing the adsorbent was connected to a HPLC pumping system from Varian ProStar 210. The column was manually packed under continuous and gentle vibration with a mechanical agitator. Initially, the pumping system delivered pure *n*-octane as solvent to establish the flow rates through the column. After that, the pulse was injected through the column at the same flow rate, and samples were taken periodically at the outlet and analyzed for aromatics content.

The experiments for C_8 aromatics were performed using short concentration pulses (20 μL) following a time interval necessary for initial stabilization of the system, for a flow rate of 0.1 mL/min. The chromatographic experiments were performed at 80 °C. The aromatics concentrations were obtained using gas chromatography as done previously with the headspace experiments.

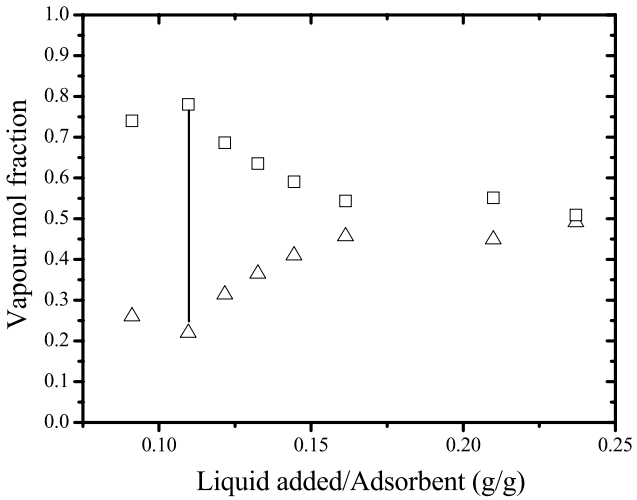

Fig. 2 Binary experimental run: (△) *p*-xylene and (□) *o*-xylene equimolar mixture on BaY zeolite at 80 °C

Selectivity was calculated through the relationship between the initial concentrations and the adsorption capacity for the related components, using (3) (Ruthven 1984)

$$\alpha_{AB} = \frac{q_A/c_A}{q_B/c_B} \tag{3}$$

The response time of each component, for experiments in fixed bed with a pulse of concentration (at the low concentrations equilibrium region), can be calculated by (4)

$$t_{Ri} = \frac{L}{\upsilon}\left(1 + \frac{1-\varepsilon}{\varepsilon}.\frac{q_i}{C_i}\right) \tag{4}$$

Considering t_0 as being the response time of a component that is not adsorbed, (5) can be obtained

$$t_{Ri} = t_0\left(1 + \frac{1-\varepsilon}{\varepsilon}.\frac{q_i}{c_i}\right) \tag{5}$$

We may then rewrite (3) as:

$$\alpha_{AB} = \frac{t_{R_A} - t_0}{t_{R_B} - t_0} \tag{6}$$

The non-linear fitting of the Origin 7.0 software package (Microcal Software) was employed to obtain an estimate of the response times for each component in our pulse experiments.

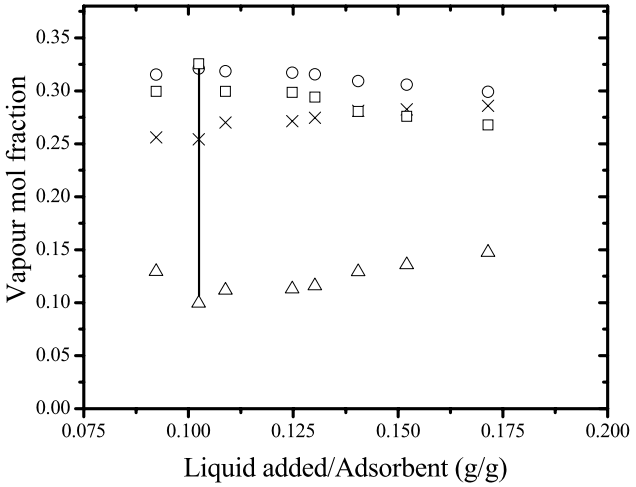

Fig. 3 Quaternary experimental run: (△) *p*-xylene, (○) *m*-xylene, (□) *o*-xylene and (×) ethylbenzene equimolar mixture on BaY zeolite at 80 °C

3 Results and discussion

3.1 Selectivity measurements for an equimolar mixture of *p*-xylene and *o*-xylene on BaY zeolite

Binary experiments for equimolar mixtures of *o*-xylene and *p*-xylene at 80 °C are presented in Fig. 2. According to Torres et al. (2001) the maximum and minimum in these plots represent the concentrations at which the intracrystalline pores have just become saturated with the sorbates. At this point, one may calculate the adsorption selectivity at saturation conditions using (2). The selectivity value, calculated for this binary experiment is 3.8, in agreement with previously reported values using other methods (Tournier et al. 2000; Minceva and Rodrigues 2004).

3.2 Selectivity measurements for an equimolar quaternary mixture of C_8 aromatics isomers on BaY zeolite

A multi-component experimental run at 80 °C, using an equimolar mixture of all C_8 aromatics isomers, is shown in Fig. 3. Table 2 presents the selectivities thus calculated. As expected the selectivities of *p*-xylene with respect to *m*-xylene, *o*-xylene and ethylbenzene are always greater than one, and show agreement with previously measured selectivities data for this system (Santacesaria et al. 1982; Cottier et al. 1997; Tournier et al. 2000; Minceva and Rodrigues 2004; Buarque et al. 2005).

3.3 Chromatographic pulses for equimolar C_8 aromatics mixtures on BaY zeolite

Binary and multi-component experiments were performed by the chromatographic pulses method in order to investigate the C_8 aromatics adsorption equilibria, using *n*-octane as inert.

Table 2 Experimental selectivities of C_8 aromatics in BaY zeolite at 80 °C

Methods	$\alpha_{PX/OX}$	$\alpha_{PX/MX}$	$\alpha_{PX/EB}$
Headspace Technique	3.8	3.9	1.5
Pulse Chromatography	4.0	3.9	1.8

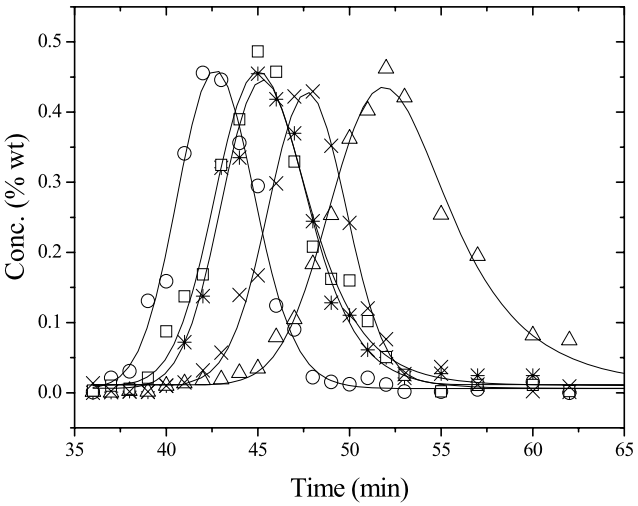

Fig. 4 Concentration profile of (△) *p*-xylene, (*) *m*-xylene, (□) *o*−xylene, (×) ethylbenzene and (○) *n*-octane at 80 °C. $Q = 0.1$ mL/min, $\rho_B = 0.891$ g/cm^3, $\varepsilon = 0.49$

The binary measurements were carried out with *p*-xylene, *o*-xylene and *n*-octane at 80 °C. According to (6), the selectivity value ($\alpha_{PX/OX}$) obtained was 3.6, showing the same *p*-selectivity behavior characteristic of the Y zeolite structure and in good agreement with our headspace measurement.

A multi-component experimental run, using an equimolar mixture of C_8 aromatics and *n*-octane, is shown in Fig. 4. The mixture contained 19.8 wt% EB, 20.1 wt% PX, 19.9 wt% MX, 20.2 wt% OX and 19.9 wt% *n*-octane. From the experimental concentration profiles we estimated the response times of all components (C_8 aromatics and inert). The selectivities were then calculated using (6) (see Table 2). As expected the selectivities of PX with respect to MX, OX and EB are always greater than one, and larger for MX and OX when compared to EB. As seen for the binary data, a relative good agreement is observed between the headspace and chromatographic pulses methods.

3.4 Selectivity measurements for *p*-xylene and *o*-xylene mixtures on mordenite

The adsorption selectivities at different temperatures on mordenite were investigated by the Headspace technique. A binary experiment performed with equimolar mixture of *o*-xylene and *p*-xylene at 40 °C is presented in Fig. 5. From

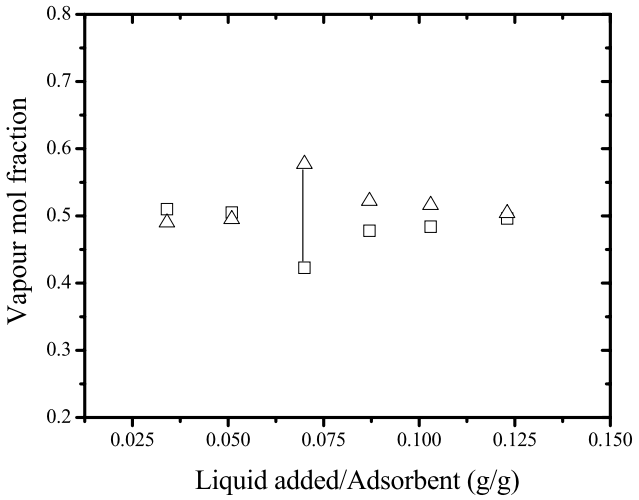

Fig. 5 Binary experimental run: (△) *p*-xylene and (□) *o*-xylene equimolar mixture on mordenite at 40 °C

Table 3 Selectivities of equimolar OX/PX mixture on mordenite using the Headspace technique

Temp. (°C)	$\alpha_{OX/PX}$	Liquid/solid ratio (g/g)
40	1.7	0.07
60	1.8	0.05
80	1.6	0.04

these data, it can be seen that mordenite presents ortho-selectivity at these conditions ($\alpha_{OX/PX} = 1.7$).

Adsorption selectivities obtained at 60 °C and 80 °C were also carried out using the same mordenite sample (Table 3). Again, all experiments indicated ortho-selectivity within the same range (1.6–1.8).

The liquid/solid ratio achieved for the saturation of the mordenite with C_8 aromatics was much smaller than for the BaY zeolite (about 0.07 g/g, compared to ca. 0.12 g/g). It was also observed that the liquid/solid ratio at saturation decreased with temperature (see also Table 3). The same behavior had been previously reported for other systems using different experimental procedures (Cottier et al. 1997; Tournier et al. 2001).

We also evaluated the influence of the xylenes concentration ratio on the selectivity at 40 °C (Table 4). It may be observed that the selectivity values were not significantly affected by the relative concentration of the xylene isomers.

Ortho-selectivity has also been experimentally observed previously for two aluminophosphate molecular sieves, $AlPO_4$-5 and $AlPO_4$-11 (Barthomeuf and Mallmann 1990; Chiang et al. 1991; Cavalcante et al. 2000). This has been further studied by molecular simulation by Lucena et al. (2006, 2008). It may be observed that all these structures (AlPO's and mordenite) have one-dimensional adsorption

Table 4 Influence of xylenes concentration ratio on selectivities using mordenite as adsorbent, from Headspace measurements at 40 °C

OX/PX Concentration ratio (mol/mol)	$\alpha_{OX/PX}$
20	1.6
50	1.7
80	1.7

channels of similar sizes (about 0.6–0.7 nm), which may be related to the face-to-face packing orientation of the *o*-xylene molecules within the micropores in this size range.

4 Conclusions

The headspace technique provides a simple and useful method for measuring single, binary and multi-component equilibrium data at full loading in liquid phase. This approach can be very useful for screening potential adsorbents as well as for investigating the variation in selectivity in relation to composition. Results are comparable to other more costly and time-consuming techniques. As expected, para-xylene selectivity in relation to all the other C_8 aromatics was observed for the BaY zeolite sample. On the other hand, ortho-xylene selectivity in relation to para-xylene was observed for the mordenite sample, which has a similar channel structure with aluminophosphate molecular sieves that had been also previously reported as ortho-selective.

Acknowledgements The authors wish to thank financial support provided by CNPq (Conselho Nacional de Pesquisa e Desenvolvimento Científico), FUNCAP (Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico) and BRASKEM S.A.

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