

**DERIVATIVE ENTHALPIES OF ADSORPTION OF  
*p*-XYLENE AND *m*-XYLENE ONTO NaY AND BaY  
ZEOLITES AT 150°C  
Contribution to the prediction of adsorption selectivity**

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**Abstract**

The derivative enthalpies of adsorption of *m*-xylene and *p*-xylene onto the NaY and BaY zeolites were measured at 150°C, then compared with those obtained at 25°C, and finally used to predict the selectivity of adsorption of xylene mixtures. Significant differences were observed as the temperature was elevated: for the NaY zeolite, the adsorbate-adsorbate interactions became prevalent, in contrast with the BaY zeolite, between zeolite and derivative interactions were stronger. The difference between the adsorption derivative enthalpies of the two xylenes displayed an abrupt variation from 2 molec. $\alpha^{-1}$  for both zeolites, the filling from which selectivity towards *m*-xylene for the NaY zeolite and towards *p*-xylene for the BaY zeolite appeared. The preferentially adsorbed xylene was closely connected with the sense of this difference, which changed with the zeolite.

**Keywords:** adsorption, calorimetry, derivative enthalpy, prediction, selectivity, single xylene, xylene mixture, zeolite

**Introduction**

*m*-Xylene and *p*-xylene are separated by selective adsorption onto microporous adsorbents; the adsorbent currently used in industrial processes is a faujasite exchanged with potassium or barium. The separation is performed in the liquid phase at 150°C. The selective adsorption process is relatively complex and, for a better understanding, the thermodynamic data must be analysed according to the characteristic properties of the adsorbent.

In previous publications [1, 2], the derivative enthalpies of adsorption of the single xylenes onto the Y faujasites were determined at 25°C in order to estimate the contributions of the different interactions during adsorption, but such a study should

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also be performed at 150°C. Accordingly, the adsorption derivative enthalpies of *p*-xylene and *m*-xylene onto the NaY and BaY zeolites were measured at 150°C by using the same calorimetric device. The thermal effects observed were then compared with those obtained at 25°C and analysed with the aim of predicting the selectivities of the zeolites in the adsorption of *p*-xylene/*m*-xylene mixtures. Finally, these predictions were compared with the experimental selectivities previously determined at the same temperature [3, 4].

Literature data on the isotherms and the heats of adsorption of *p*-xylene and *m*-xylene onto the NaY and BaY faujasites were previously discussed in detail [1, 2]. Results relating to the adsorption heats at 25°C will be reported during the comparative discussion.

## Experimental

The NaY parent zeolite was a pure crystalline powder produced by Linde-Union Carbide and having a Si/Al ratio of 2.43. The BaY zeolite was prepared by cation-exchange of the NaY zeolite. The degree of exchange was 99.5%. The chemical formulas of the dehydrated zeolites are  $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$  and  $\text{Ba}_{28}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$  [5, 6]. Y faujasite, a well-known zeolite, has 8  $\alpha$ -cages and 8  $\beta$ -cages per unit cell. Only the  $\alpha$ -cages are accessible to xylene molecules.

The adsorption heats of the single xylenes were determined with the same experimental device as used in our previous study at 25°C, i.e. a differential heat flow calorimeter coupled with a manometer. This device, described earlier [1, 2], allows simultaneous measurement of the adsorbed amount and the adsorption heat of xylene.

The adsorption temperature was 150°C and before each experiment the zeolite was activated in situ at 400°C and  $10^{-3}$  hPa during 12 h. The calorimetric heats of the single xylenes were measured in the pressure range  $10^{-3}$ –10 hPa, with 1 g of non-activated absorbent. The relative error was about 5%, and the experiments were reproducible with a relative error estimated as 2%.

Adsorbed amounts and calorimetric heats were obtained by the successive adsorption of small amounts of xylene. Under these conditions, the measured heats were similar to the derivative enthalpies of adsorption (designated later as adsorption enthalpies) [1, 7–8]. The adsorbed amounts were expressed in molecules of xylene per  $\alpha$ -cage of activated zeolite,  $\text{N}^{\alpha}$ .

## Results and discussion

### *Adsorption enthalpies of single xylenes*

#### Adsorption at 150°C

The maximum adsorption capacity of the NaY zeolite was higher for *m*-xylene than for *p*-xylene: 3.4 and 3 molec. $\alpha^{-1}$ , respectively. The BaY zeolite adsorbed less xylene than the NaY zeolite and, whatever the xylene, the maximum amount adsorbed onto the BaY zeolite was of the same order of magnitude, i.e.

2.7–2.8 molec. $\alpha^{-1}$  (Table 1). The maximum adsorption capacities previously obtained from TG [5, 6] and manometry were the same.

**Table 1** Derivative enthalpies of adsorption (in kJ mol $^{-1}$ ) of xylenes onto NaY and BaY at 25 and 150°C as a function of filling (in molec. $\alpha^{-1}$ )

	NaY		BaY		NaY		BaY	
	<i>p</i> -xylene at 25°C				<i>m</i> -xylene at 25°C			
	$N^a$	$ \Delta_{\text{ads}} \dot{H}_m $	$N^a$	$ \Delta_{\text{ads}} \dot{H}_m $	$N^a$	$ \Delta_{\text{ads}} \dot{H}_m $	$N^a$	$ \Delta_{\text{ads}} \dot{H}_m $
beginning	0	86	0	95	0	100	0	103
filling	3.2	95	2	95	3.3	100	2	103
			3	87			3	95
saturation	3.6	$Q_{\text{vap}}$	3.6	$Q_{\text{vap}}$	3.7	$Q_{\text{vap}}$	3.6	$Q_{\text{vap}}$
	<i>p</i> -xylene at 150°C				<i>m</i> -xylene at 150°C			
beginning	0	76	0	107	0	78	0	115
filling	2.5	88	2	100	3.1	107	2	107
saturation	3	$Q_{\text{vap}}$	2.8	$Q_{\text{vap}}$	3.4	$Q_{\text{vap}}$	2.7	$Q_{\text{vap}}$

$|\Delta_{\text{ads}} \dot{H}_m|$ : absolute value of molar derivative enthalpy of adsorption

$Q_{\text{vap}}=42.5$  kJ mol $^{-1}$ : order of magnitude of vaporization enthalpy of xylenes at 25°C

$N^a$ : adsorbed amount of single xylene in molecules per  $\alpha$ -cage

$N_{\text{total}}^a$ : total adsorbed amount of xylene mixture in molecules per  $\alpha$ -cage

$\alpha_{\text{pX/mX}} = \frac{x_{\text{pX}} y_{\text{mX}}}{y_{\text{pX}} x_{\text{mX}}}$ : adsorption selectivity of zeolite towards xylene mixture

(if  $\alpha_{\text{pX/mX}} > 1$ , zeolite selective towards *p*-xylene, and conversely;  $x_{\text{pX}}$ ,  $x_{\text{mX}}$ ,  $y_{\text{pX}}$ ,  $y_{\text{mX}}$ : mole fractions of *p*-xylene and *m*-xylene at equilibrium in adsorbate and gas, respectively)

For both zeolites, the adsorption enthalpies (expressed in absolute values:  $|\Delta_{\text{ads}} \dot{H}_m|$ ) of the single xylenes depended on the  $\alpha$ -cage filling [2]. Two ranges of filling were discerned.

Low filling,  $N^a < 2$  molec. $\alpha^{-1}$

At zero filling, where only the adsorbate-adsorbent interactions occurred, the adsorption enthalpies were higher for the BaY zeolite than for the NaY zeolite (Table 1, Fig. 1) and, if they were of the same order of magnitude for the two xylenes for the NaY zeolite, for the BaY zeolite the adsorption enthalpies of *m*-xylene were higher than those of *p*-xylene. Thus, the prevalent interactions, which are those between the aromatic ring of the xylene molecule and the exchanged cation, are stronger for Ba $^{2+}$  than for Na $^{+}$ . Indeed, these cations, which are located on the sites II inside the  $\alpha$ -cages [9, 10] and have different charges and sizes, do not occupy the same positions: in contrast with the monovalent Na $^{+}$ , the large bivalent Ba $^{2+}$  is more accessible to the xylene molecule, because it lies out of the plane of the hexagonal window of the  $\alpha$ -cage [1].

When filling occurred, the adsorbent-adsorbate interactions decreased, while the adsorbate-adsorbate interactions increased. It appears then that the adsorption en-

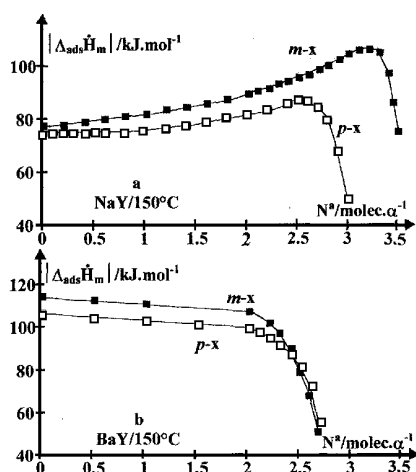


Fig. 1 Derivative enthalpies of adsorption of xylenes onto NaY and BaY at 150°C

thalpies increase for the NaY zeolite, while they decrease for the BaY zeolite (Table 1, Fig. 1). Hence, the interactions between the aromatic ring and the exchanged cation remain prevalent for the BaY zeolite, while they become less than the molecule-molecule interactions for the NaY zeolite. Whatever the zeolite may be, the adsorption enthalpy of *m*-xylene is always higher than that of *p*-xylene. The methyl-oxygen interactions for *m*-xylene are stronger than those for *p*-xylene, because the methyl groups are in a better orientation to give optimal interactions with the oxygen atoms of the D6R units, which are also in the meta position to the hexagonal window [9–10].

High filling,  $N^3 > 2 \text{ molec.}\alpha^{-1}$

In this domain, where the adsorbate-adsorbate interactions were prevalent (molecular clusters are probably formed), the adsorption enthalpies of the NaY zeolite increased, those of *m*-xylene becoming larger than those of *p*-xylene. For the BaY zeolite, however, they decreased strongly and became slightly higher for *p*-xylene than for *m*-xylene (Table 1, Fig. 1).

At saturation, the adsorption enthalpies decreased to the vaporization enthalpies of the xylenes as total filling of the  $\alpha$ -cages was reached, and the adsorption occurred on the external surface of the adsorbent.

Comparison between adsorptions at 150°C and at 25°C

For both zeolites, the maximum adsorption capacities of the xylenes were lower at 150°C than at 25°C (Table 1). If the  $\text{Na}^+/\text{Ba}^{2+}$  cation-exchange does not change the maximum adsorbed amounts of both isomers at 25°C (Figs 2c,d), at 150°C the behaviour of the NaY zeolite is different, since this zeolite adsorbs more *m*-xylene than *p*-xylene and more xylenes than the BaY zeolite (Figs 2a,b).

For the NaY zeolite, the adsorption enthalpies at zero filling are higher at 25°C than at 150°C (Table 1, Fig. 2), this phenomenon being much more important for *m*-

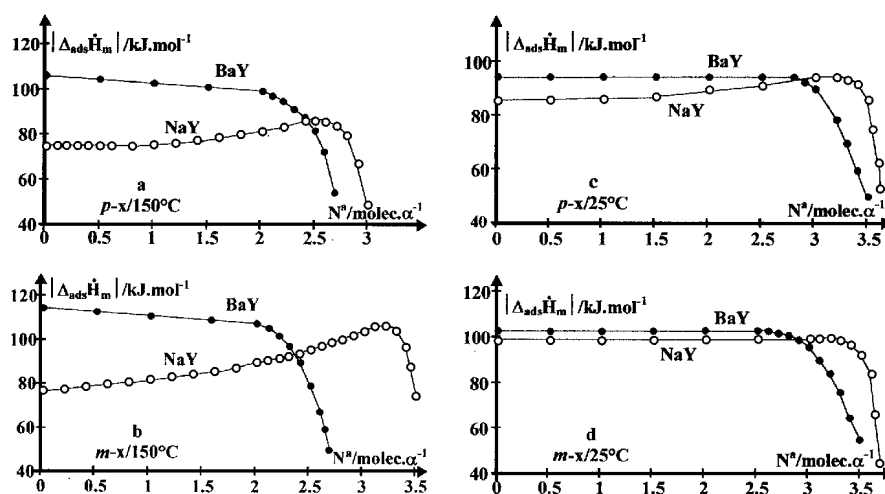


Fig. 2 Comparison between adsorption derivative enthalpies at 25 and 150°C

xylene than for *p*-xylene. Neutron diffraction revealed an increase in the distance between the aromatic ring of the xylene molecule and the exchanged cation, and a rotation of the xylene molecules parallel to the cavities walls when the adsorption temperature was increased [11]. Both these phenomena reduce the interactions between the aromatic ring and the  $\text{Na}^+$ , and the interactions between the methyl groups and the framework oxygen atoms, so that at zero filling the adsorption enthalpies decrease as the temperature is raised. At the maximum of the calorimetric curve, where the adsorbate-adsorbate interactions are the most dominant, the adsorption enthalpies of *m*-xylene are a little higher at 150°C than at 25°C, in contrast with *p*-xylene, and the amounts of adsorbed *m*-xylene and *p*-xylene are different at 150°C, in contrast with the situation at 25°C (Table 1).

For the BaY zeolite, different behaviour was observed. The adsorption enthalpies at zero filling increased with temperature (Table 1) (Fig. 2). The adsorbate-adsorbent interactions were then intensified by increase of the temperature. Although the adsorption enthalpies at 25°C remained constant during the filling, the general behaviour of the calorimetric curve did not vary with temperature.

As the adsorption enthalpies at 150°C were different from those at 25°C, it was necessary to measure them with a view to predicting the selectivities of these zeolites in the case of the adsorption of *p*-xylene/*m*-xylene mixtures at this temperature.

### Adsorption selectivities

The previous results [3, 4] concerning the adsorption of *p*-xylene/*m*-xylene mixtures demonstrated that the adsorption selectivities of the two faujasites depend on the  $\alpha$ -cage filling  $N_{\text{total}}^a$ , the initial mixture composition and the nature of the exchanged cation (Fig. 3). Two adsorption processes are to be discerned, depending on the range of filling.

Low filling,  $N_{\text{total}}^a < 2 \text{ molec.}\alpha^{-1}$

Both zeolites were non-selective in the presence of an equimolar mixture (Figs 3b, e), but they preferentially adsorbed the prevalent isomer of an enriched mixture (Fig. 3a,c,d,f). However, if the adsorption selectivity of the BaY zeolite remained constant as the filling occurred, it varied slightly for the NaY zeolite (Figs 3a,b,c).

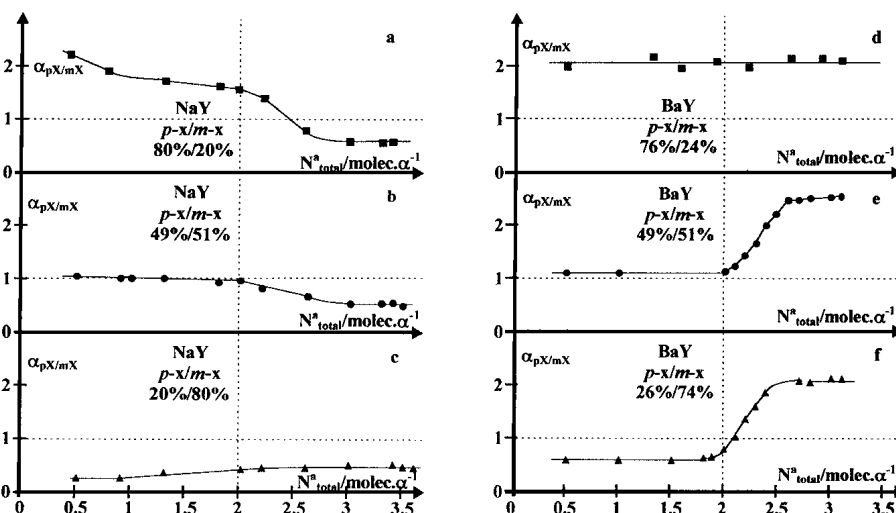


Fig. 3 Selectivities of NaY and BaY towards adsorption of xylenes according to [3]

High filling,  $N_{\text{total}}^a > 2 \text{ molec.}\alpha^{-1}$

The NaY zeolite became or remained selective towards *m*-xylene from the adsorption of  $2 \text{ molec.}\alpha^{-1}$  for the equimolar and *m*-xylene-richer mixtures (Figs 3b,c) and from  $2.5 \text{ molec.}\alpha^{-1}$  (a strong decrease in selectivity between 2 and  $2.5 \text{ molec.}\alpha^{-1}$ ) for the *p*-xylene-richer mixture (Fig. 3). The BaY zeolite became or remained selective for *p*-xylene (Figs 3d,e,f), whatever the composition of the initial mixture might be, a strong increase in selectivity being observed between 2 and  $2.5 \text{ molec.}\alpha^{-1}$  in the presence of the equimolar and *m*-xylene-richer mixtures (Figs 3e,f). Thus, the selective adsorption process occurred only for the high filling of the  $\alpha$ -cages and then depended on the nature of the exchanged cation.

#### Comparison between the calorimetric heats of the single xylenes and the selectivities

The differences between the adsorption enthalpies of single *m*-xylene and *p*-xylene (designated *m*-x/*p*-x enthalpies) were calculated for both zeolites as a function of filling (Fig. 4). The two ranges of filling previously defined were then observed.

Low filling,  $N^a < 2 \text{ molec.}\alpha^{-1}$

A slight difference (not exceeding  $5 \text{ kJ mol}^{-1}$ ) was observed between the  $m$ - $x/p$ - $x$  enthalpies of the two zeolites at zero filling. This difference decreased during the adsorption of the first molecule and became equal to zero during the adsorption of the second molecule (Fig. 4). We can therefore assume that both zeolites are non-selective in the presence of an equimolecular mixture of xylenes. This assumption was proved during the study of the adsorption of mixtures (Figs 3b,e).

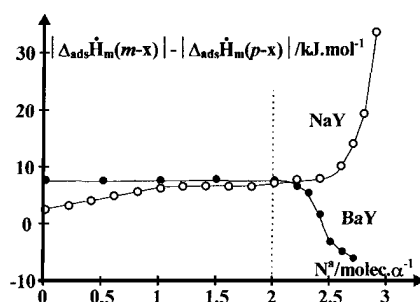


Fig. 4 Difference between adsorption derivative enthalpies of single xylenes at  $150^\circ\text{C}$

For the NaY zeolite, the behaviour was not the same during the adsorption of the first and the second molecules. Indeed, the  $m$ - $x/p$ - $x$  enthalpy increased during the adsorption of the first molecule and remained constant during the adsorption of the second molecule (Fig. 4). This difference in behaviour was also observed (as a trend) in the selectivity curves (Figs 3a,b,c). On the other hand, for the BaY zeolite, the  $m$ - $x/p$ - $x$  enthalpy remained constant in this filling range, and no difference was observed in the selectivity curves.

High filling,  $N^a > 2 \text{ molec.}\alpha^{-1}$

From  $2 \text{ molec.}\alpha^{-1}$ , the  $m$ - $x/p$ - $x$  enthalpies of the two zeolites varied, but in opposite directions.

The  $m$ - $x/p$ - $x$  enthalpy of the NaY zeolite increased slightly up to  $2.5 \text{ molec.}\alpha^{-1}$ , and then strongly beyond this filling (Fig. 4). This result shows that the molecule-molecule interactions, which are maximum at high filling, are much stronger for  $m$ -xylene than for  $p$ -xylene. In the adsorption of xylene mixtures, the NaY zeolite would then preferentially adsorb  $m$ -xylene. Indeed, the experimental study showed that beyond 2 (Figs 3b,c) or  $2.5 \text{ molec.}\alpha^{-1}$  (Fig. 3a) the NaY zeolite was selective towards  $m$ -xylene.

Inversely, the  $m$ - $x/p$ - $x$  enthalpy of the BaY zeolite decreased strongly and its sign changed when the total filling of the  $\alpha$ -cages was reached (Fig. 4). Hence, the  $p$ -xylene/ $p$ -xylene interactions became stronger than the  $m$ -xylene/ $m$ -xylene interactions. It is considered then that, in the coadsorption of the xylenes, the BaY zeolite would preferentially adsorb  $p$ -xylene. This was proved experimentally, since this zeolite is selective towards  $p$ -xylene whatever the composition of the initial mixture (Figs 3d,e,f).

## Conclusions

The derivative enthalpies of adsorption of *m*-xylene and *p*-xylene onto the NaY and BaY zeolites, measured at 150°C and compared with those obtained at 25°C, revealed significant differences as the temperature was increased: for the NaY zeolite, the adsorbate-adsorbate interactions became prevalent, in contrast with the BaY zeolite, for which the adsorbent-adsorbate interactions were stronger.

If there is adsorption selectivity of the NaY and BaY zeolites towards *p*-xylene or *m*-xylene at high filling of the  $\alpha$ -cages, the sense of the selectivity is fixed by the nature of the exchanged cation. The difference between the adsorption derivative enthalpies of *m*-xylene and *p*-xylene exhibited an abrupt variation at 2.5 molec. $\alpha^{-1}$  for the NaY zeolite, and at 2 molec. $\alpha^{-1}$  for the BaY zeolite. This behaviour was closely connected with the selectivity of the two zeolites observed between 2 and 2.5 molec. $\alpha^{-1}$  for the NaY zeolite and from 2 molec. $\alpha^{-1}$  for the BaY zeolite. The preferentially adsorbed xylene was then closely connected with the sense of this difference: for the NaY zeolite, this difference increased and the faujasite was selective towards *m*-xylene; for the BaY zeolite, it decreased and the faujasite was selective towards *p*-xylene.

The analysis of the adsorption enthalpies of the single xylenes therefore yielded information contributing to the prediction of adsorption selectivity in the adsorption of *p*-xylene/*m*-xylene mixtures onto the NaY and BaY faujasites.

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