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DIFFERENTIAL CALORIMETRIC ENTHALPIES OF ADSORPTION OF *p*-XYLENE AND *m*-XYLENE ON Y FAUJASITES AT 25°C

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Abstract

The differential enthalpies of adsorption of *p*-xylene and *m*-xylene on NaY, KY and BaY zeolites were measured by isothermal calorimetry coupled with isothermal volumetry at 25°C. Whatever the zeolite, the enthalpies of adsorption of *p*-xylene and *m*-xylene at low filling were of the same order of magnitude. They did not show significantly the effect of the dipolar moment of *m*-xylene. Their absolute values varied in the sequence

$Q_0(p\text{X/NaY})<Q_0(p\text{X/KY})=Q_0(m\text{X/KY})<Q_0(p\text{X/BaY})<Q_0(m\text{X/NaY})=Q_0(m\text{X/BaY})$

During the adsorption of the third molecule of xylene per α-cage, BaY zeolite exhibited specific behaviour: the differential enthalpies of adsorption decreased with the filling of the α-cages in such a way that they became lower than those of the other two zeolites. Some arguments concerning the structures of the zeolite and xylene molecules can explain such behaviour. Whatever the zeolite, the adsorption capacity of the α-cages was 3.5 molec.α^{-1}. For relative pressures ranging from 0.2 to 0.5, an additional adsorption of about 0.1 molec.α^{-1} occurred on the external surface.

Keywords: adsorption, calorimetry, differential heat, micropore, xylenes, Y faujasites

Introduction

An understanding of the process of adsorption of gases on zeolite requires a knowledge of both the adsorbed amounts and the adsorption heats. The heats of adsorption allow an assessment of the adsorbate-adsorbent and adsorbate-adsorbate interactions, and also a distinction between the amounts adsorbed into the micropores and on the external surface of the crystallites.

This work forms part of a study of the adsorption of *p*-xylene and *m*-xylene on NaY, KY and BaY zeolites [1–4]. It deals with the experimental measurement by isothermal calorimetry of the differential enthalpies of adsorption.

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Literature survey

The literature data on the heats of adsorption of *p*-xylene and *m*-xylene on faujasites are concerned only with NaY and KY zeolites. They were determined either from calorimetric experiments (integral heats) [5–7] or from adsorption isotherms by using thermodynamic models [8] (Table 1). These experiments were performed on wholly evacuated zeolites, except those of Guth *et al.* [5], which were carried out on partially hydrated zeolites. They show that the heat of adsorption of *p*-xylene is lower than that of *m*-xylene on NaY zeolite [6–8]. Conversely, it is greater than [6, 7] or equal to [8] that of *m*-xylene on KY zeolite. As regards BaY zeolite, no data have been found in the literature.

In previous papers [1–4], we have shown that the adsorption isotherms of *p*-xylene and *m*-xylene on NaY and KY zeolites are described by the Henry, Langmuir and Fowler models. The adsorption of xylenes on BaY zeolite follows only the Polanyi-Dubinin theory. Whatever the zeolite, the standard enthalpies of adsorption deduced from these models are greater for *m*-xylene than for *p*-xylene. Unlike the results in the literature [6–8], the heats of adsorption of *m*-xylene are greater for KY zeolite than for NaY zeolite (Table 1).For each zeolite, the isosteric heats of adsorption of *p*-xylene and *m*-xylene are of the same order of magnitude (Table 1). The dipolar moment of the *m*-xylene molecule seems to undergo no specific interaction with the adsorbent. The isosteric heats of adsorption (extrapolated to filling coefficient $\theta=0$) are much higher for BaY zeolite than for the other two zeolites, and those of NaY and KY zeolites are of the same order of magnitude (considering the large experimental error in this filling range). Nevertheless, as the filling increases, the adsorbate – adsorbate interactions come into effect, and the isosteric heats of adsorption increase in such a way that they become greater for *m*-xylene than for *p*-xylene, in accordance with the previous results. At high filling coefficient ($\theta=0.9$), the isosteric heats of adsorption of a given xylene on each zeolite are of the same order of magnitude.

Considering such a disparity in these various heats of adsorption and as no values of the differential enthalpies of adsorption of xylenes on NaY, KY and BaY zeolites are given in the literature, the experimental measurement of the differential enthalpies of adsorption by isothermal calorimetry is of great interest.

Experimental

The heats of adsorption were determined with a specific experimental device comprising a differential heat flow calorimeter coupled with a volumeter. This apparatus allows measurement of the adsorbed amount and the adsorption heat of xylenes simultaneously.

The isothermal differential calorimeter was a Setaram C80 model (sensitivity$=10^{-3}$ J, operating temperature 25–300°C). One chamber of volume V_2, including the two calorimetric cells ($V=17$ cm^3 per cell), was connected with another one of volume V_1 (Fig. 1). This latter chamber was fitted with pressure gauges, a vac-

Table 1 Heats of adsorption of *p*-xylene and *m*-xylene on NaY, KY and BaY zeolites from literature

	$\lvert Q\rvert$ kJ mol^{-1}					
Zeolite	*p*-xylene	*m*-xylene	Method	Heat type	T/°C	Reference
NaY	113	125	calorimetry	$\Delta H_{\theta\to 0}$	130–200	[6, 7]
with binder	76	86	calorimetry	$\Delta H_{\theta-1}$	130–200	[6, 7]
	76	84	Henry	ΔH^{∞}	170	[8]
NaY pure	50	58	Henry	ΔH^{∞}	150–400	[1, 2]
	64	89	Fowler	$\Delta H^{o}_{\theta=0.5}$	150–400	[1, 2]
	64	67	Langmuir	$\Delta H^{o}_{\theta=0.5}$	150–400	[1, 2]
	70	75	isosteric	$\Delta_{iso}H_{\theta\to 0}$	25–400	[4]
	80	100	isosteric	$\Delta_{iso}H_{\theta-0.9}$	25–400	[4]
KY	104	71	calorimetry	$\Delta H_{\theta\to 0}$	150	[6, 7]
with binder	65	51	calorimetry	$\Delta H_{\theta-1}$	150	[6, 7]
	76	78	Henry	ΔH^{∞}	170	[8]
KY pure	52	69	Henry	ΔH^{∞}	150–400	[1, 2, 4]
	58	98	Fowler	$\Delta H^{o}_{\theta=0.5}$	150–400	[1, 2, 4]
	58	69	Langmuir	$\Delta H^{o}_{\theta=0.5}$	150–400	[1, 2, 4]
	65	60	isosteric	$\Delta_{iso}H_{\theta\to 0}$	25–400	[4]
	90	95	isosteric	$\Delta_{iso}H_{\theta-0.9}$	25–400	[4]
BaY pure	150	150	isosteric	$\Delta_{iso}H_{\theta\to 0}$	25–400	[4]
	80	95	isosteric	$\Delta_{iso}H_{\theta-0.9}$	25–400	[4]

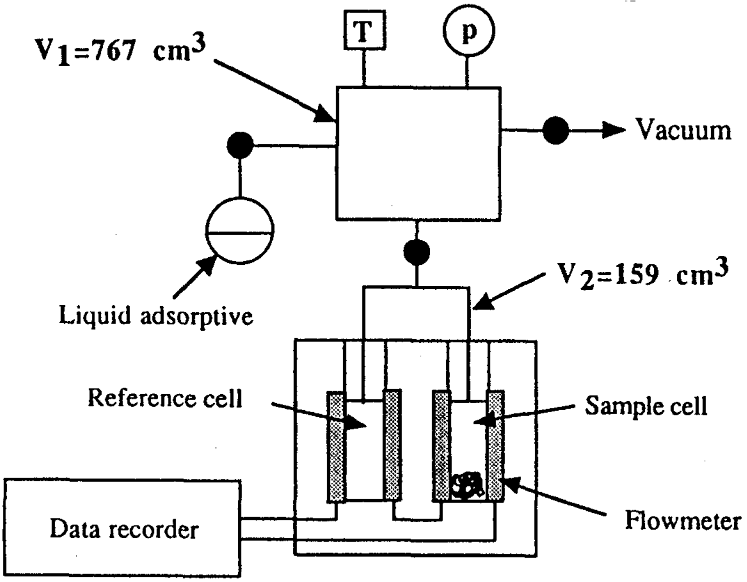

Fig. 1 Experimental setup

uum line (vacuum pump and cryogenic adsorption pump) and a gas inlet. The adsorptive was stocked in the liquid state in an evacuated bulb. It was previously outgassed and dehydrated *in situ* by means of hydrophilic zeolite [3]. Both chambers could be removed from the calorimeter to regenerate the sample *in situ* with an external furnace at a temperature higher than 300°C. The experimental set-up was located in an air-conditioned room at 20°C.

NaY zeolite [$Na_{56}(AlO_2)_{56}(SiO_2)_{136}$] was produced in pure crystalline powder form by Linde Union Carbide. KY and BaY zeolites were obtained by cation exchange [3]. The cation exchange ratio was 86% for KY zeolite, and 99.5% for BaY zeolite. The Y faujasite has 8 α-cages (aperture diameter=0.74 nm) and 8 β-cages (aperture diameter=0.22 nm) per unit cell.

Table 2 Physical characteristics of xylenes

Adsorbate	Length L/nm	Width l/nm	Thickness e/nm	Kinetic diameter σ/nm	Dipolar moment μ/D
p-xylene	0.98	0.67	0.4	0.67	0
m-xylene	0.86	0.79	0.4	0.74	0.32

The xylenes (trademark Prolabo) had a purity of 99%. Their physical characteristics are listed in Table 2. Only the α-cages are accessible to xylene isomers. With aromatic compounds, adsorbate-adsorbent interactions occur mainly between the aromatic ring and the compensation cation located at site II in the α-cages

[9–12]. With NaY and KY zeolites, the four sites II per α-cage are occupied by Na^+ and K^+, while with BaY zeolite, only two of them are occupied by Ba^{2+} [13].

The mass of the sample was 1 g. Before each experiment, the zeolite was evacuated at 400°C under 10^{-2} Pa during 12 h. The mass loss on activation was determined at the same time on another sample by thermogravimetry under the same experimental conditions.

The experiments were performed by the successive adsorption of small amounts of xylene. The gas introduced into volume V_1 under pressure p_i ($p_i = 1$ to 2 hPa) was released into volume $V_1 + V_2$. The heat emitted by the adsorption was converted by the calorimeter into a voltage, which was recorded as a function of time on a computer. As the adsorption equilibrium was reached, the pressure of gas, p_f, became constant. The graphic recorder then gave a peak shape whose area was proportional to the heat of adsorption.

The amount of adsorbed gas for a mass of outgassed sample, m, in experiment k is given by the relation

$$\Delta n_{a,k} = \frac{1}{RT}\left[V_1\left(p_{i,k} - p_{f,k}\right) - V_2\left(p_{f,k} - p_{f,k-1}\right)\right] = n_{a,k} - n_{a,k-1}$$

where $p_{f,k-1}$ is the final pressure at the adsorption equilibrium of the previous experiment k-1.

The total amount of adsorbed gas under the final pressure $p_{f,k}$ is

$$n_{a,k} = \sum_{1}^{k} \Delta n_{a,k}$$

Afterwards, this amount is expressed in molecules per α-cage (molec.α^{-1}), N^a, calculated as follows:

$$N^a = \frac{n_{a,k} M_z}{8m}$$

where M_z=molar mass of anhydrous zeolite.

The amount of heat emitted in each experiment varied from 7 to 12 J, with a relative error of about 5%. The experiments were reproducible with a relative error estimated as 2%.

Theoretical

In the calorimetric cell, the adsorption occurred in an open system at constant volume and temperature. According to Letoquart *et al.* [14], under such conditions the molar heat $Q_m(T)$ measured in the filling range $\Delta n_{a,k}$ is related to the internal energy by the expression

$$Q_m(T) = \tilde{U}_{m,a}(T) - U_{m,g}(T) - RT + (p_{f,k} - p_{f,k-1}) \frac{v_{adsorbent}}{\Delta n_{a,k}}$$

with

$$\tilde{U}_{m,a}(T) = \frac{1}{\Delta n_{a,k}} \left[n_{a,k} U_{m,a,k}(T) - n_{a,k-1} U_{m,a,k-1}(T) \right]$$

where $U_{m,a,k}(T)$ is the molar internal energy of the adsorbate at the final equilibrium, i.e. under the conditions $p_{f,k}$, T and $n_{a,k}$; $U_{m,a,k-1}(T)$ is the molar internal energy of the adsorbate at the initial equilibrium, i.e. under the condi- tions $p_{f,k-1}$, T and $n_{a,k-1}$; and $U_{m,g}(T)$ is the molar internal energy of the ideal gas at temperature T.

Under the experimental conditions, the final term of this expression is lower than 0.5% and can be disregarded. It follows that the molar heat $Q_m(T)$ becomes an average integral molar enthalpy:

$$Q_m(T) = H_{m,a}(T) - H_{m,g}(T)$$

As the filling increments $\Delta n_{a,k}$ are sufficiently small, this enthalpy is equivalent to a differential enthalpy:

$$Q_m(T) = \Delta_{ads}\dot{H}_m(T)$$

Results and discussion

In the adsorption experiments at low filling, because of the strong adsorption affinity of faujasites for xylenes, the final pressure $p_{f,k}$ (<0.05 hPa) was so low that it could not be measured with the experimental set-up. The initial amount of xylene introduced into volume V_1 was then assumed to be wholly adsorbed after its release into volume V_1+V_2. The non-measurable pressure range corresponds to the ascending portion of the adsorption isothermal below point B (Fig. 2).

The volumetric adsorption isotherms (Figs 2 and 3) and the calorimetric curves (Figs 4 and 5) were reproducible. The adsorption isotherms determined by volumetry were in good agreement with those obtained by thermogravimetry [1–3].

Description of curves

Whatever the zeolite or the isomer, the plots representing the differential molar enthalpies of adsorption as a function of N^a were similar in shape (Figs 4 and 5). The adsorption heats of *p*-xylene and *m*-xylene differed slightly and did not change much with the filling. Therefore, the nature of the exchanged cation and the adsorbate (especially the dipolar moment of the *m*-xylene molecule) seemed to have no effect. Small differences were observed only at low and high fillings.

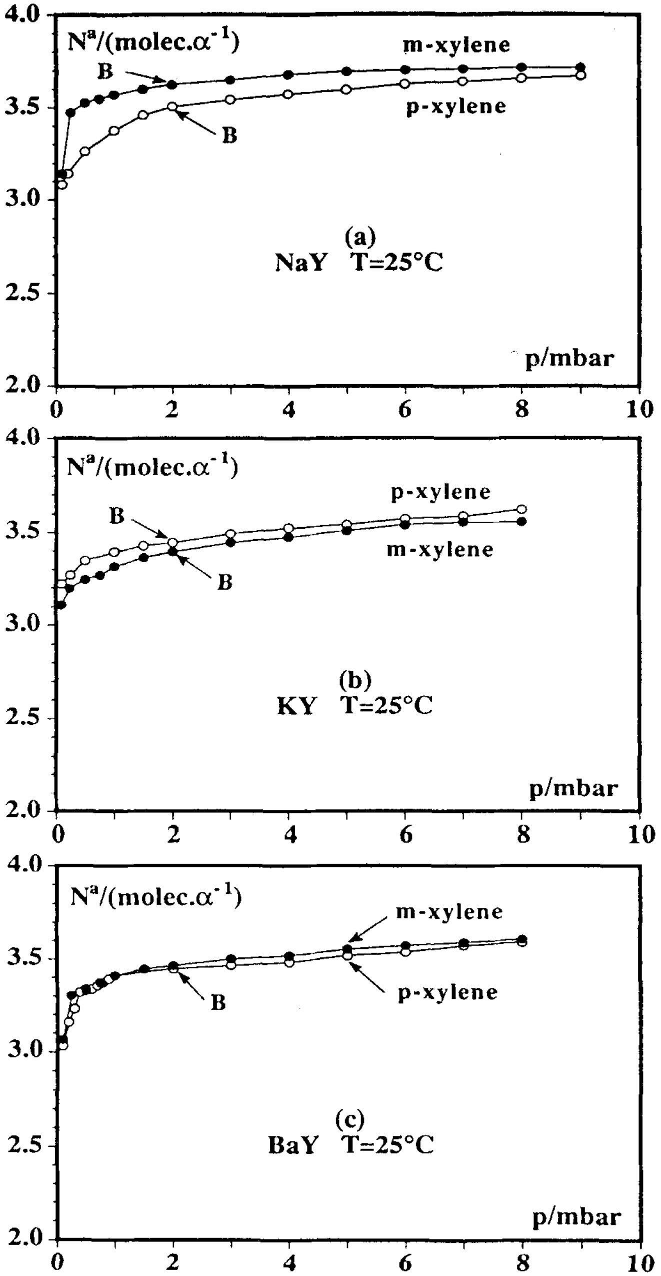

Fig. 2 Adsorption isotherms of xylenes on the same zeolite at 25°C [a) NaY; b) KY; c) BaY]

Adsorbate-adsorbent interactions

The absolute values of the molar differential enthalpies of adsorption at zero filling Q_0, obtained by extrapolating the calorimetric plots as N^a tended to zero (Figs 4 and 5), lay between 85 and 100 kJ mol^{-1} (Table 3). They varied as follows:

$$Q_0(p\mathrm{X/NaY})<Q_0(p\mathrm{X/KY})=Q_0(m\mathrm{X/KY})<Q_0(p\mathrm{X/BaY})<Q_0(m\mathrm{X/NaY})$$
$$=Q_0(m\mathrm{X/BaY})$$

These values account for only adsorbate-adsorbent interactions. They indicate that:

– Whatever the compensation cation, the adsorbate-adsorbent interactions with *m*-xylene were stronger than or equal to those with *p*-xylene:

$$Q_0(p\mathrm{X})<Q_0(m\mathrm{X}) \text{ for NaY and BaY zeolites}$$
$$Q_0(p\mathrm{X})=Q_0(m\mathrm{X}) \text{ for KY zeolite}$$

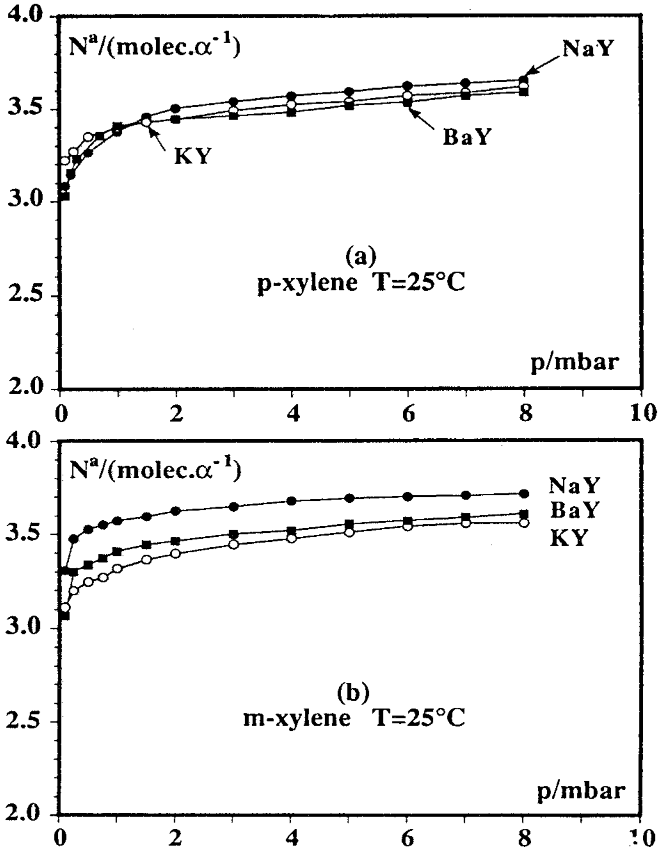

Fig. 3 Adsorption isotherms of a same xylene on NaY, KY and BaY zeolites at 25°C [a) *p*-xylene; b) *m*-xylene]

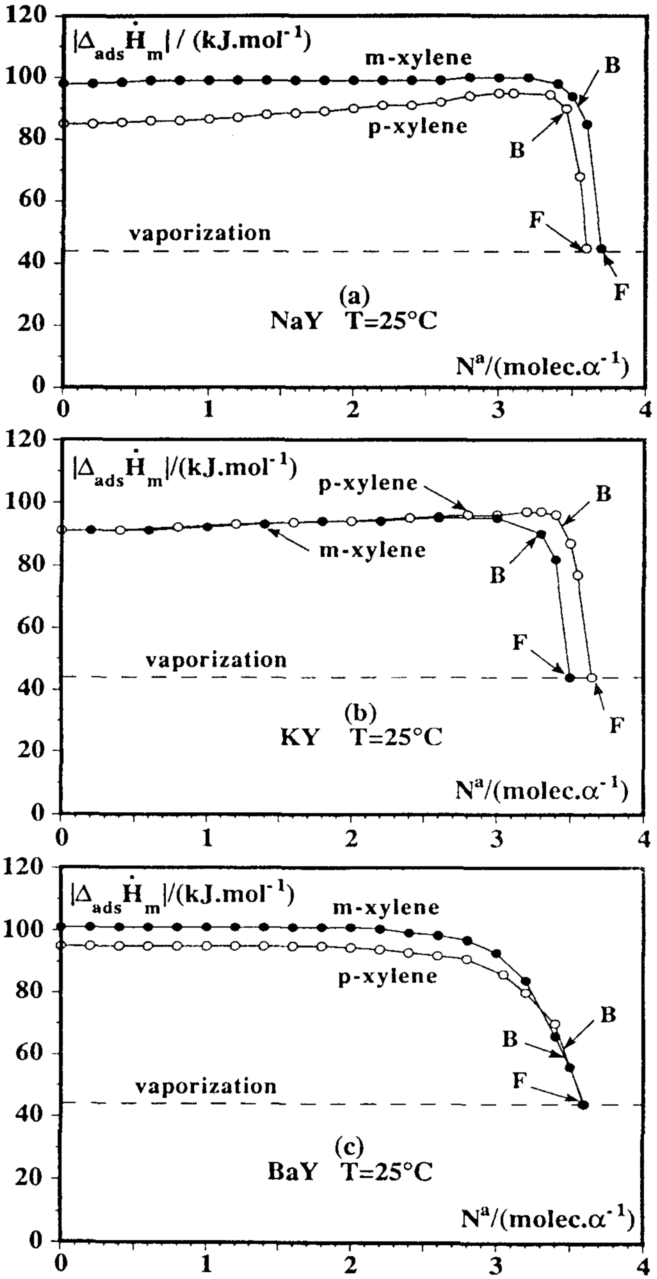

Fig. 4 Adsorption calorimetric curves of xylenes on the same zeolite at 25°C [a) NaY; b) KY; c) BaY]

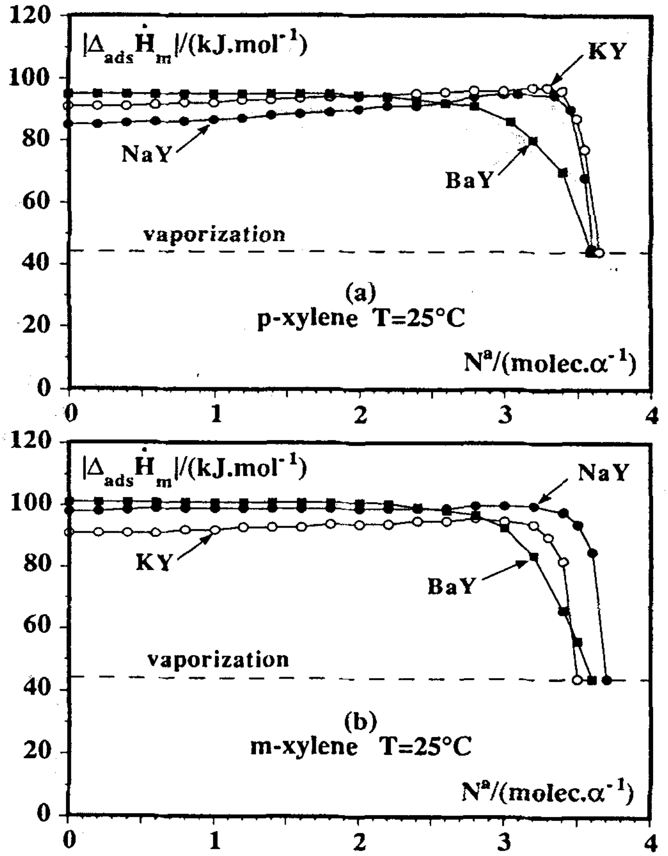

Fig. 5 Adsorption calorimetric curves of a same xylene on NaY, KY and BaY zeolites at 25°C [a) *p*-xylene; b) *m*-xylene]

The difference between the heat of adsorption of *p*-xylene and that of *m*-xylene was maximal for Na^+, two times less for Ba^{2+} than for Na^+, and insignificant for K^+.

– The adsorbate-adsorbent interactions increased according to the sequences

$$Q_0(\text{NaY})<Q_0(\text{KY})<Q_0(\text{BaY}) \text{ for } p\text{-xylene}$$

$$Q_0(\text{KY})<Q_0(\text{NaY})=Q_0(\text{BaY}) \text{ for } m\text{-xylene}$$

This comparison revealed the specific behaviour of NaY zeolite with the two xylenes.

The heat of adsorption is a function of the local electric field in the α-cages and the adsorbate-adsorbent electrostatic interactions (mainly aromatic ring – compensation cation and methyl group – framework oxygen interactions). These interactions depend on the nature of the compensation cation and the molecular geometry of the adsorbate.

Table 3 Heats of adsorption and adsorbed amounts of xylene/faujasite systems at 25°C [Heats of adsorption, Q, in absolute value and kJ mol^{-1}; adsorbed amounts, N^a, in molec. α^{-1}; n.m. = no measurable]

		Maximum				Point B			Point F	
		Q_o	Q_M	N^a_M	$(p/p_o)_M$	N^a_B	Q_B	$(p/p_o)_B$	N^a_F	$(p/p_o)_F$
NaY	*p*X	85	95	3.2	0.04	3.45	90	0.2	3.6	0.6
	*m*X	100	100	3.3	0.04	3.60	95	0.2	3.7	0.7
KY	*p*X	90	98	3.3	n.m.	3.44	94	0.2	3.6	0.6
	*m*X	91	96	3.1	n.m.	3.44	91	0.2	3.5	0.7
BaY	*p*X	95	95	0 to 2	n.m.	3.46	65	0.2	3.6	0.6
	*m*X	101	101	0 to 2	n.m.	3.46	63	0.2	3.6	0.7

In NaY zeolite, the Na^+ ($r(Na^+)=0.095$ nm) is located at site II in the plane of the hexagonal window of the sodalite cage (Fig. 6). The xylene molecules are adsorbed on these sites, involving aromatic ring – Na^+ and methyl – oxygen interactions. With *m*-xylene, the methyl-oxygen interactions are stronger than with *p*-xylene because the methyl groups are in a better orientation than those in *p*-xylene to give optimal interactions with the oxygen atoms of the D6R units, which are also in the meta position to the hexagonal window [10–12]. This explains why the heats of adsorption are greater for *m*-xylene than for *p*-xylene. In the other zeolites, the large ion K^+ or Ba^{2+} ($r(K^+)=0.133$ nm and $r(Ba^{2+})=0.143$ nm) lies out of this plane, inside the α-cage (Fig. 6), and consequently is more accessible to xylene molecules. The aromatic ring – cation distance is probably shorter than for NaY zeolite, leading to an increase in the aromatic ring – cation interactions to the det-

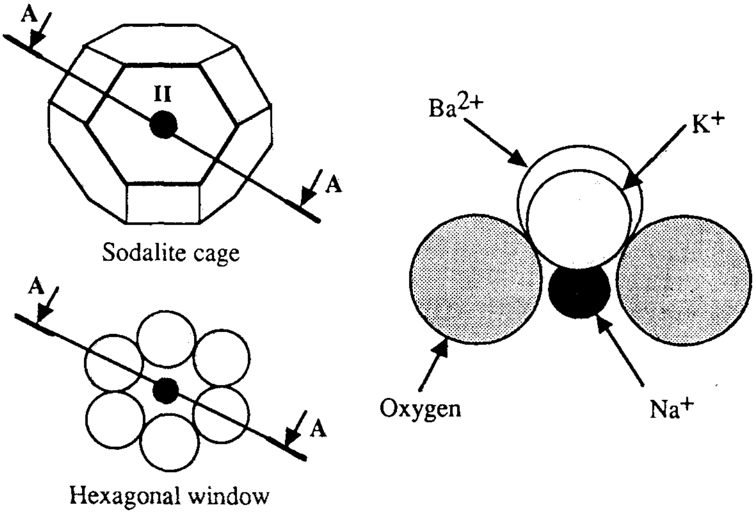

Fig. 6 Compensation cation position inside α-cage of faujasite

riment of the methyl-oxygen interactions, because the methyl groups in this case are farther from the oxygen atoms of the framework. The heats of adsorption at zero filling are then the resultants of two types of interactions, those increasing (aromatic ring – cation interactions) and those decreasing (methyl – oxygen interactions) as the radius of the compensation cation increases. This explains the variations in the heats of adsorption following the previous sequences and the deviations observed between the heats of adsorption of *p*-xylene and *m*-xylene.

Filling of α-cages

The total filling of the α-cages is assumed to be reached at point B of the isotherm. Whatever the zeolite and the adsorbate, point B lies at a relative pressure of 0.2 (Fig. 2, Table 3). The heats of adsorption vary very slightly with the α-cage filling (Figs 4 and 5). The decrease in adsorbate-adsorbent interactions occurring as the α-cages are filled is compensated by the increase in the adsorbate-adsorbate interactions.

The calorimetric curves (Figs 4 and 5) show that:

– As the filling increases from 0 to 3 molec.α^{-1} for NaY and KY zeolites and to 2 molec.α^{-1} for BaY zeolite, the heats of adsorption remain the same [$Q(pX)=Q(mX)$ for KY and $Q(mX)-Q(pX)=5$ kJ mol^{-1} for BaY], except for the *p*-xylene/NaY system. Indeed, in this last case the heat of adsorption increases slightly with filling [$Q(mX)-Q(pX)=15$ kJ mol^{-1} at zero filling and 5 kJ mol^{-1} at 3 molec.α^{-1}].

– For NaY and KY zeolites, point B of the isotherm lies at the end of the flat portion of the calorimetric curve, i.e. close to the maximum heat of adsorption, whereas for BaY zeolite it lies on the decreasing portion of the curve, close to the minimum heat of adsorption (Fig. 4).

– At point B, the heats of adsorption vary according to a different sequence from that at zero filling:

$$Q(\text{BaY}) < Q(\text{NaY}) < Q(\text{KY}) \text{ for } p\text{-xylene}$$

$$Q(\text{BaY}) < Q(\text{KY}) < Q(\text{NaY}) \text{ for } m\text{-xylene}$$

Conversely to the situation at zero filling, the heats of adsorption on BaY zeolite are lower than on the other two zeolites.

Such results reveal the specific behaviour of BaY zeolite during the adsorption of the third molecule into the α-cage. Indeed, the heats of adsorption on BaY zeolite decrease for filling ranging from 2 molec.α^{-1} to 3 molec.α^{-1}, whereas those on NaY and KY zeolites decrease for filling greater than 3 molec.α^{-1} (Fig. 5). This phenomenon can be explained by structural considerations. In the α-cages of NaY and KY zeolites, compensation cations are located at the four sites II, allowing specific attractions with three xylene molecules. There is not enough free space for the adsorption of a fourth molecule. In the α-cages of BaY zeolite, only two compensation cations are located at sites II. Therefore, only two xylene molecules are adsorbed on these sites by specific attractions. The third xylene molecule is then adsorbed with a lower energy than the first, although it may be attracted by a cation migrating from the framework inside the α-cage [12].

Whatever the zeolite, the amounts of *p*-xylene and *m*-xylene adsorbed at point B are nearly the same (Table 3), about 3.5 molec.α^{-1}. The adsorption capacity of the α-cages then seems to be invariant with the size of the compensation cation.

Adsorption on external surface

Once the α-cages are filled (point B), the heats of adsorption decrease sharply, at a relative pressure of about 0.5 (point F), to reach the enthalpy of vaporization of the pure xylene (Table 3). The portion of the calorimetric curve between points B and F then corresponds to the adsorption of xylene on the external surface of the zeolite (Fig. 4). The amount adsorbed on this surface is about 0.1 molec.α^{-1} and represents 3% of the total amount of xylene adsorbed on the zeolite.

Beyond point F, i.e. for a relative pressure higher than 0.5, the measured heats of adsorption are of the same order of magnitude as the enthalpies of vaporization of the xylenes. Above this relative pressure, a multilayer adsorption process occurs.

Conclusions

The differential heats of adsorption of *p*-xylene and *m*-xylene on NaY, KY and BaY zeolites were determined at 25°C by using a flow calorimeter coupled with a volumeter.

Whatever the zeolite, the enthalpies of adsorption of the two xylenes at zero filling were nearly the same. The effect of the dipolar moment of the *m*-xylene molecule was insignificant.

As the third molecule of xylene is adsorbed in the α-cage, BaY zeolite exhibited behaviour different from that of the two other zeolites. This phenomenon is explained by the fact that the four sites II of the α-cage are occupied by cations in NaY and KY zeolites, whereas only two sites II are occupied in BaY zeolite.

The adsorption capacity of the α-cages was nearly the same for the three zeolites, at about 3.5 molec.α^{-1}. For relative pressures ranging from 0.2 to 0.5, an additional adsorption of 0.1 molec.α^{-1} occurred on the external surface.

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