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## Naphthalene Adsorption on 13X Molecular Sieve

R. Joulie<sup>1</sup>, G. M. Rios<sup>1\*</sup> and H. Gibert<sup>2</sup>

<sup>1</sup>*Centre de Génie et Technologie Alimentaires, U.S.T.L. — CC 23 — Place E. Bataillon,  
34095 Montpellier Cédex 5 — France*

and

<sup>2</sup>*Chaire de Génie des Procédés Agro-Alimentaires, I.N.A.P.G. — 16, Rue Claude Bernard,  
75231 Paris Cédex 05*

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In this paper, naphthalene adsorption on 13X molecular sieve has been investigated. The isotherms and the net heat of adsorption have been determined in the range between 40 °C and 380 °C. Analysis of the results clearly indicates that the Dubinin-Radushkevitch model provides the best fitting equation for data points, with a specific limitation due to some steric hindrance effect.

### INTRODUCTION

In a previous work, simultaneous heat and mass transfer between a freely moving object and a gas fluidized bed of adsorbent particles were investigated. Sublimation of naphthalene spheres into a 13X molecular sieve bed was used as a model system.<sup>1,2</sup> In an attempt to give an interpretation of these experimental data, the isotherms and the adsorption heat of this adsorbent/adsorbate pair have been determined and are reported in the present paper.

Two well-known gas-solid chromatography techniques, thoroughly described elsewhere,<sup>3-8</sup> were used in a slightly modified form: the so-called "continuous injection" and "pulse injection" methods. With the first, a high concentration of adsorbate could be reached between 40 °C and 200 °C. The second method, used at higher temperatures (up to 400 °C), gave access to the region of isotherms corresponding to low adsorbed quantity.

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\* Corresponding author

## EXPERIMENTAL

*Adsorbate: Naphthalene (C<sub>10</sub>H<sub>8</sub>)*

- Plane molecule, 0.7 nm long and 0.5 nm wide.
- Pressure vapour (Pa) versus temperature (K):

$$\log_{10} p_s = 13.575 - 3728.75/T$$

0–80 °C range<sup>9</sup>

$$\log_{10} p_s = 10.538 - 2690.08/T$$

80 – 218 °C range<sup>9</sup>

$$\log_{10} p_s = 9.561 - 2210.38/T$$

218 – 477 °C range  
[best fitting equation of data  
points in the literature]*Adsorbent: molecular Sieve – 13X type*

The cavity area is in the order of 760 m<sup>2</sup>/g and the corresponding volume of the pores is 0.32 cm<sup>3</sup>/g.<sup>10,11</sup> The product was pulverized and sieved to get a 200–400 μm particle size.

*Apparatus*

To determine the naphthalene adsorption isotherms on the 13X molecular sieve, a GIRDEL chromatograph (Model 30) equipped with a flame ionisation detector was used.

The adsorbent is placed in a pyrex tube having an internal diameter of 3 mm so as to form a 10 cm long short packed bed. Such a column reduces the influence diffusion of, and operates near the equilibrium conditions.<sup>12</sup>

Before each run, the adsorbent was activated in a nitrogen flow by heating to 390 °C for about 14 hours. Then, the column was isolated from the outside medium and weighed to determine the mass of pure adsorbent.

*Continuous Injection Method*

The experimental apparatus is shown in Figure 1. The columns – C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> – are swept with a constant flow rate of nitrogen.

C<sub>1</sub> is a thermostatically controlled column, 30 cm long, filled with naphthalene crystals, 0.5 to 1 mm in size. This bed thickness offers a large enough exchange area with a negligible pressure drop. The naphthalene vapour resulting from the sublimation of crystals is carried away by nitrogen at a 2 mm/s mean velocity. The partial pressure of the vapour, *p*, is a function of temperature *T*<sub>1</sub>. To keep it at a constant value, column C<sub>1</sub> is jacketed and thermostatically controlled water is circulated around it.

A temperature *T*<sub>2</sub>, 10 °C lower than *T*<sub>1</sub>, brings about a partial condensation of the naphthalene and fixes the saturated vapour pressure at the end of column C<sub>2</sub>.

The gaseous mixture then enters the third column, C<sub>3</sub>, containing the adsorbent. The temperature of this column is maintained at a constant value *T* (*T* > *T*<sub>2</sub>) in the chromatograph furnace. The gaseous flow rate is measured under outside conditions (pressure and temperature) with a soap film burette. Due to the low pressure drop, the total pressure in C<sub>3</sub> only slightly differs from the atmospheric pressure.

The response of the flame ionisation detector was found to be linear up to a partial pressure of 400 Pa naphthalene vapour.

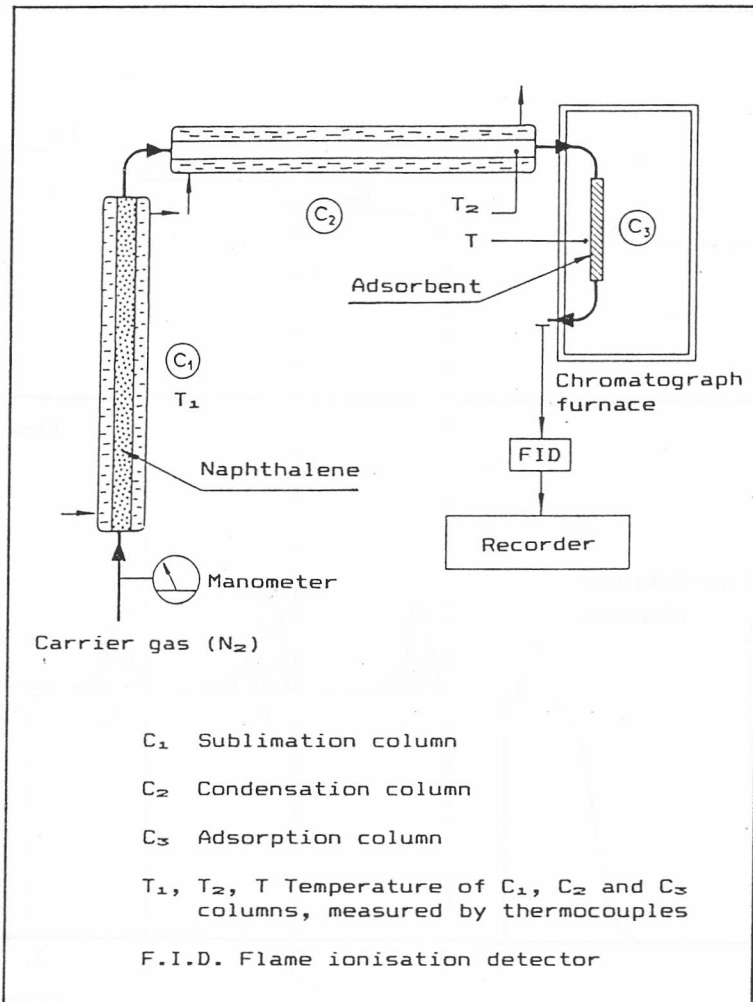


Figure 1. Diagram of the continuous injection system

Experiments proceed as follows: when the condensation and sublimation columns ( $C_1$  and  $C_2$ ) are at their respective equilibrium temperatures,  $C_3$  is placed into the chromatograph. Let  $T_A$  be the initial value of  $T$ . Adsorption takes place until saturation of the adsorbent is reached. This state corresponds to the plateau region of the curve in Figure 2. Then  $C_3$  is weighed again and replaced into the system. Return to the equilibrium level occurs a few minutes. The value of  $m_1$ , the mass of naphthalene that has been adsorbed, is a specific characteristic of the temperature and vapour pressure,  $T_A$  and  $p$ . At times  $t_1, t_2, t_3$  the adsorbent temperature is raised to present values  $T_B, T_C, T_D$  which correspond to the desired isotherms. The areas under the peaks  $A_1, A_2, A_3$  are proportional to the desorbed quantities. When the final temperature  $T_D$  is reached and the last equilibrium established,  $C_3$  is weighed again; thus, the residual mass adsorbed at temperature  $T_D$  and pressure  $p$  is obtained ( $m_4$ ).

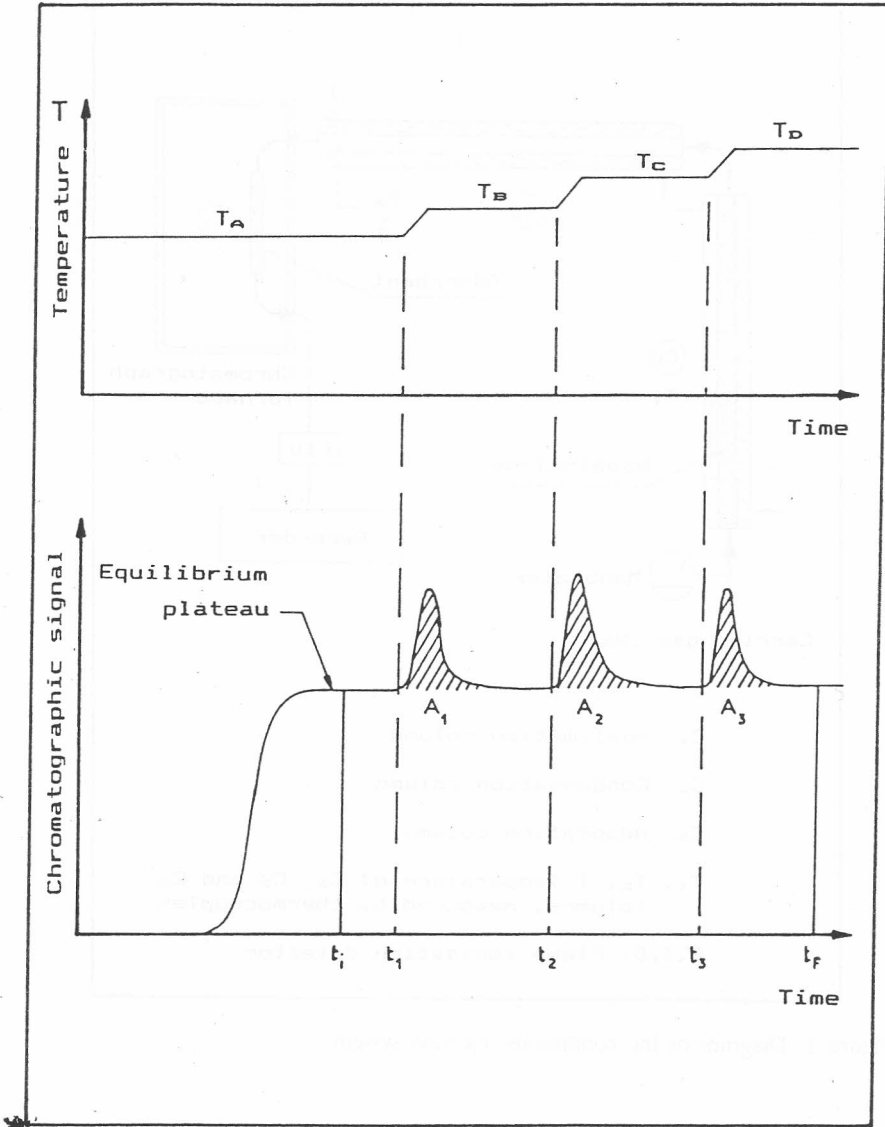


Figure 2. Chromatogram aspect in the modified continuous injection technique

Assuming that the sum of the areas  $A_1 + A_2 + A_3$ , is proportional to the difference  $m_1 - m_4$ , the intermediate adsorbed masses  $m_2$  and  $m_3$  may be easily calculated by the following equations:

$$\frac{m_1 - m_4}{A_1 + A_2 + A_3} = \frac{m_1 - m_2}{A_1} = \frac{m_2 - m_3}{A_2} = \frac{m_3 - m_4}{A_3} \quad (1)$$

Several runs have thus been carried out at different vapour pressures.

### *Pulse Injection Method:*

The basic principles of the method are straightforward. Practically, the procedure is quite difficult to perform because it requires injection of a very small quantity of solid compound into the column.

The injection of given amount of a gaseous mixture with a syringe was not very reproducible. The injection of a solution of naphthalene in a solvent was not satisfactory either because the peak associated with the naphthalene was masked by the peak corresponding to the solvent. For this reason, an injection method of solid naphthalene was chosen.

The classical chromatograph injector is replaced by a "ROSS" injector. This device (Figure 3) consists of a pyrex tube passing through a heating element and connected with the adsorbent column inside the chromatograph furnace. Outside the furnace, a part of the tube not swept by the carrier gas contains a sliding pyrex rod, one end of which is shaped like a small spatula and may be loaded with naphthalene. The other end of the rod is fixed to a piece of ferromagnetic material so that, by means of a magnet, the spatula may be quickly introduced into the heating element.

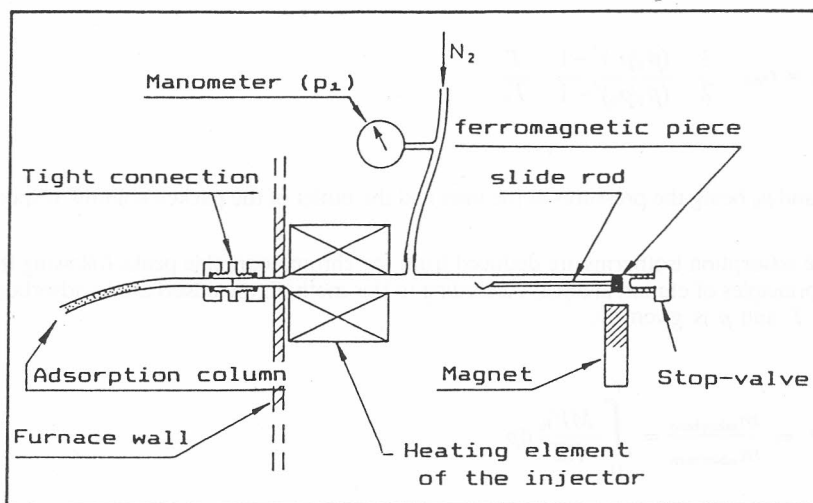


Figure 3. Diagram of the injector in the pulse injection method

At the start of the experiments, a given volume of a titrated solution of naphthalene in hexane is evaporated and naphthalene crystals appear. The slide rod is set into the injector tube. When the pressure of the carrier gas returns to its initial value, naphthalene is quickly introduced into the heating part of the injector. A few seconds later, a very small peak appears due to the trace of hexane injected with the naphthalene. This time is chosen as the origin. The naphthalene peak appears a short time later.

In order to get consistently reproducible results, the mass of the injected naphthalene was kept constant for all experiments. This mass equals  $0.477 \mu\text{g}$ , corresponding to a  $10 \mu\text{l}$  sample of a  $47.7 \text{ mg/l}$  standard naphthalene/hexane solution. Injections were repeated at various decreased temperatures. As a general rule, an increase in both the retention time and the width of the peaks was observed.

A preliminary standardisation of the detection system is needed for a correct use of chromatographic recordings. The sensitivity of the detector was determined by successively injecting increased amounts of naphthalene and plotting the area of the peak,  $A_p$ , versus the injected mass  $m_i$ . In the working range, the curve is linear and fits the classical relationship:

$$m_i = \int_{V_1}^{V_2} \frac{M_p}{RT} dV = K_1 A_p \quad (2)$$

where  $V_1$  and  $V_2$  are, respectively, gas volumes passed through the column at the beginning and the end of elution. Constant  $K_1$  depends both on the recorder velocity and nitrogen flow rate. The variation of the retention time,  $t_{CR}$ , as a function of the injected mass of naphthalene,  $m_i$ , was thus determined (Figure 4). (It is worth noting that, in order to relate the measured retention times,  $t_{MR}$ , to the ambient temperature  $T_0$  and to the mean atmospheric pressure  $p_0$ , the following correction is carried out:

$$t_{CR} = t_{MR} \cdot \frac{3}{2} \cdot \frac{(p_1/p_0)^2 - 1}{(p_1/p_0)^3 - 1} \cdot \frac{T}{T_0} \quad (3)$$

with  $p_1$  and  $p_0$  being the pressures at the inlet and the outlet of the packed column, respectively).

The adsorption isotherms are deduced from the chromatographic peaks following the well-known principles of elution analysis. According to this method, the adsorbate to adsorbent mass ratio at  $T$  and  $p$  is given by:

$$m^* = \frac{m_{\text{adsorbate}}}{m_{\text{adsorbent}}} = \int_0^p \frac{MV_R}{RT} dp \quad (4)$$

In this equation,  $V_R$  represents the specific retention volume, i.e. the volume corresponding to the unit of mass of adsorbent when the temperature is  $T$  and the mean pressure in the column  $p_m$  (calculated from the James and Martin formula.<sup>13</sup>

The correct interpretation of experimental recordings involves classical correction steps to account for both the temperature/pressure of gas flow rate and diffusion phenomena.<sup>14</sup>

## RESULTS

### *Isotherms Obtained by Continuous Injection:*

In a first series of experiments the isotherms between 40 and 80 °C were obtained. The results clearly show that at any temperature the adsorbed quantities of naphthalene are relatively important and largely independent of the partial pressure.

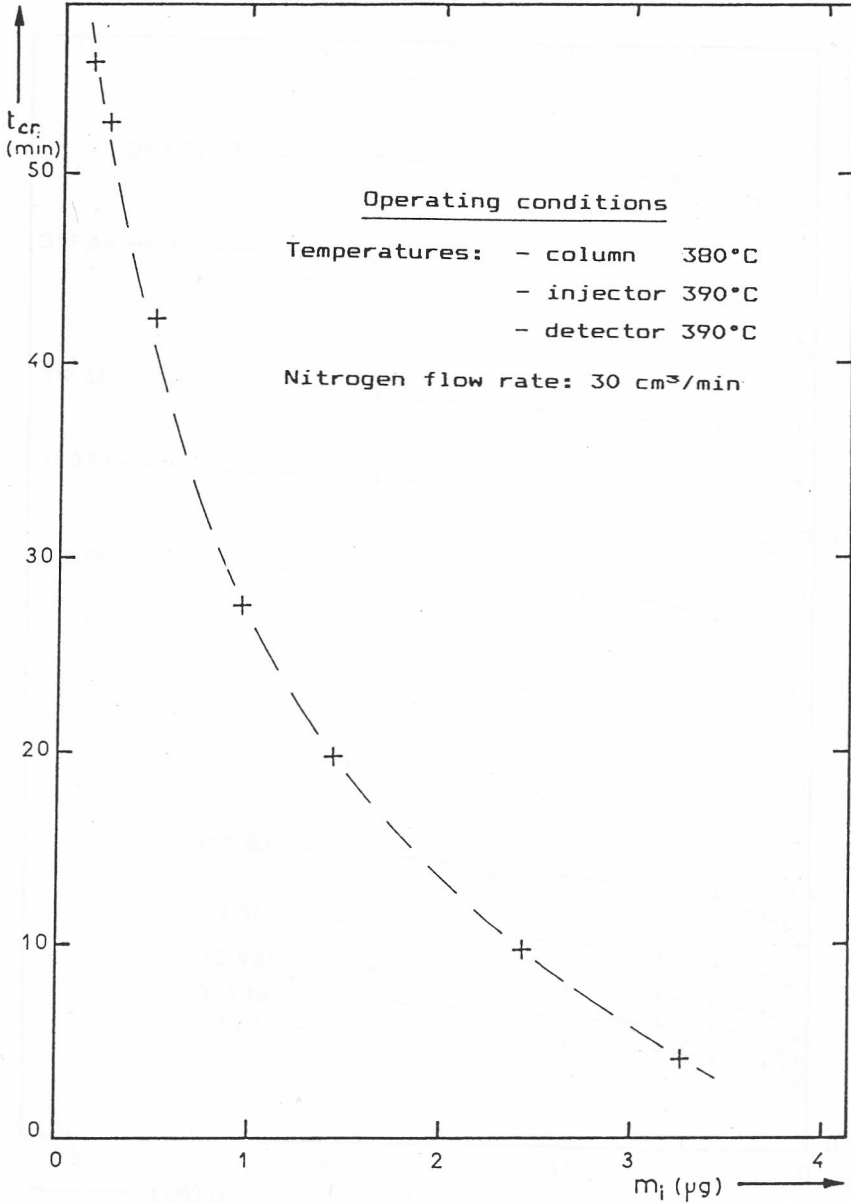


Figure 4. Corrected retention time versus the injected mass

Then, other measurements were carried out to get isotherms in the 120 °C–200 °C. Adsorption was less than expected, but the shape of the curves remained the same leading to the same conclusion: almost independent of the partial pressure (Figure 5). Thus, it is worth noting that little information is available concerning the low pressure zone on the curves  $m^*(p)$ , which is detrimental to modelling.

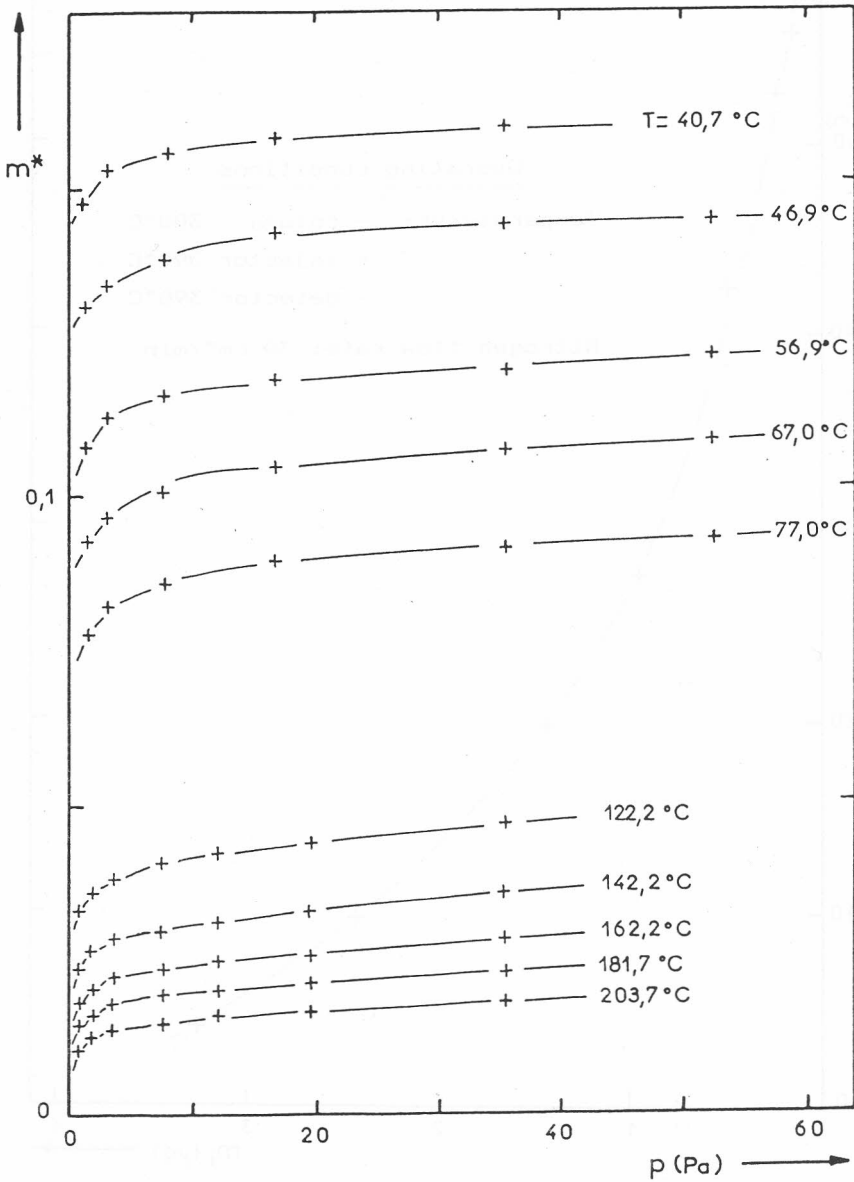


Figure 5. Adsorption isotherms in  $m^*$  vs  $p$  coordinates (40 °C/200 °C)

To interpret the adsorption isotherms, we compared the experimental results to the following classical models<sup>5</sup>:

- Langmuir (localised monolayer adsorption);
- B.E.T. (localised adsorption with multimolecular layers);



- Harkins and Jura (non-localised monolayer adsorption);
- Dubinin, first and second structural types (adsorption involving the volume filling of micropores).

The examination of these models led us to the conclusion that the Dubinin models were those giving the best-fitting curves. Assuming that the ratio  $W/W_0$  between the volume  $W$  filled under the relative pressure  $p/p_s$  and the total volume  $W_0$  of the micropore is a function of the adsorption free energy:  $\varepsilon_{ad} = RT \ln(p/p_s)$  as defined by Polanyi<sup>15</sup> (the standard state corresponds to the equilibrium between the condensed phase and its saturation vapour), and also assuming that  $W$  is proportional to the mass adsorbed per unit-mass of adsorbent, the Dubinin–Radushkevitch model leads to the equation:

$$\ln(m^*) = \ln(m_0^*) - K_2 \varepsilon_{ad}^2 \quad (5)$$

As Shown in Figures 6 –A and 6–B, experimental  $\ln(m^*)$  versus  $\varepsilon_{ad}^2$  curves are linear.

From a phenomenological point of view, the steep increase of  $m^*$  at low partial pressures might be explained by the Polanyi–Dubinin hypothesis, namely the instantaneous filling of micropores by the adsorbate.

#### *Isotherms Obtained by Pulse Injection:*

To get valuable information on the low adsorbed quantities, the isotherms were determined in a range of high temperatures between 330 °C and 380 °C (at lower temperatures, the retention time quickly increases and the concentration too slowly falls to zero).

A reversible adsorption of naphthalene may be observed again. The curves  $m^*(p)$  thus obtained are presented in Figure 7. As before, the Dubinin model appears to be the one that best agrees with data points (Figure 8).

#### *Isosteric Heat of Adsorption:*

According to the Clausius Clapeyron equation, the net isosteric heat of adsorption,  $Q_{st}^*$ , may be calculated from the slope of  $\ln(p/p_s)$  versus  $1/T$  curves according to:

$$Q_{st}^* = Q_{st} - Q_L = R \cdot \left[ \frac{\partial \ln(p/p_s)}{\partial (1/T)} \right]_{m^*} \quad (6)$$

with  $Q_{st}$ , the absolute isosteric heat of adsorption and  $Q_L$ , the latent heat of naphthalene condensation.

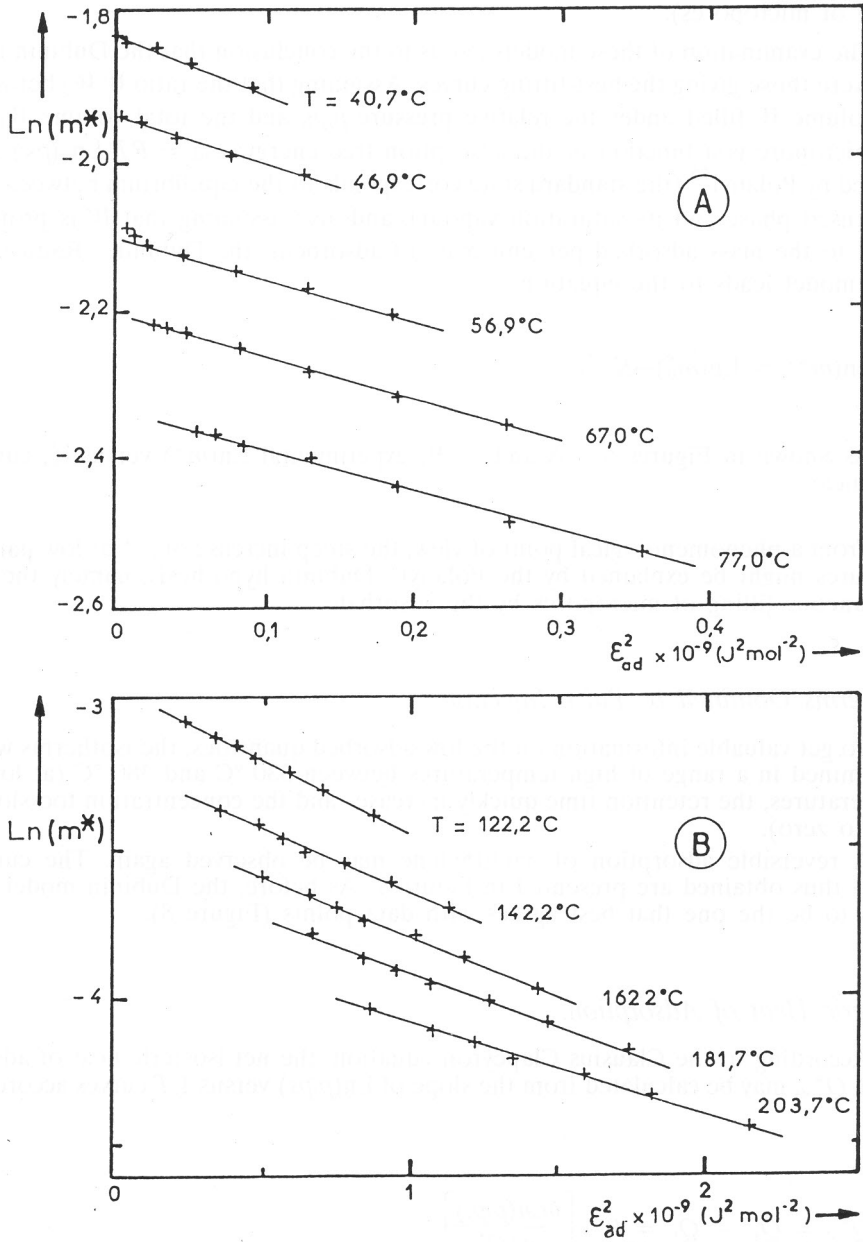


Figure 6. Adsorption isotherms in Dubinin coordinates (40 °C/200 °C)

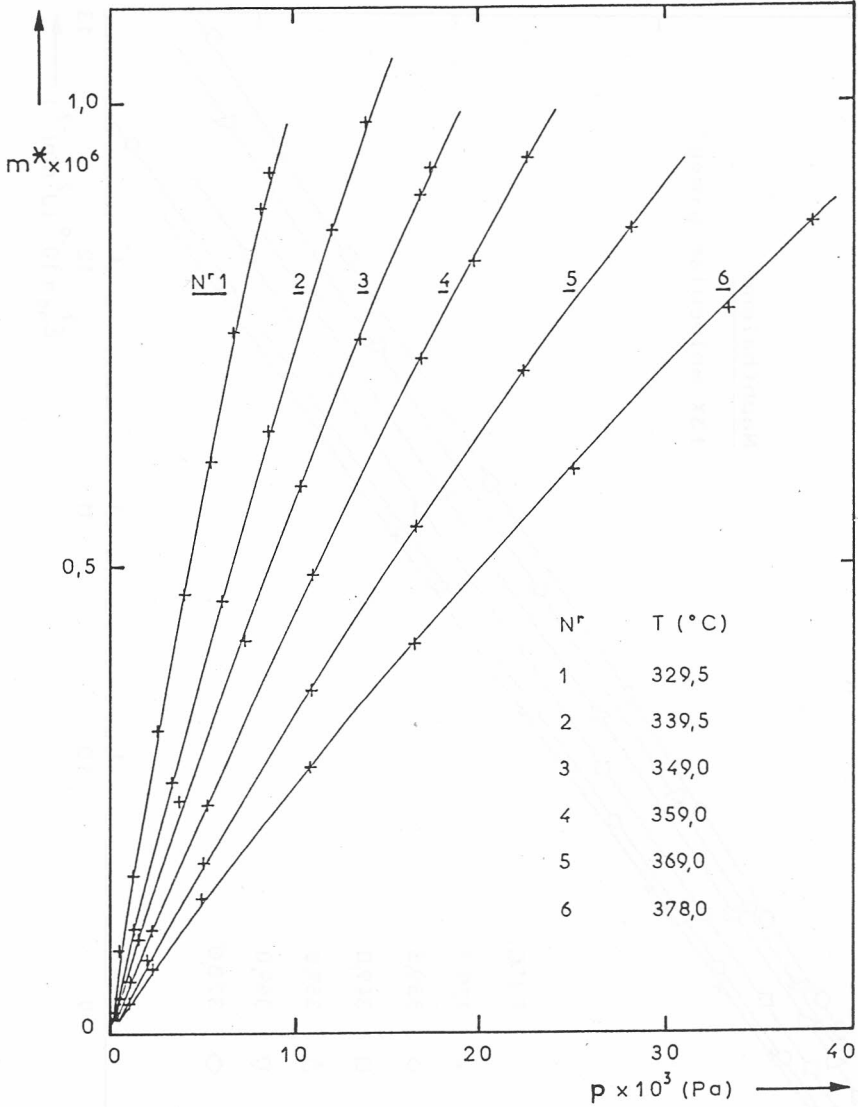


Figure 7. Adsorption isotherms in  $m^*$  vs  $p$  coordinates (300 °C/400 °C)

DISCUSSION

It is interesting to find that the maximum adsorbed volume at the lower temperature (40.7 °C) is only half of the pore volume of the 13X molecular sieve: 320  $\text{cm}^3/\text{kg}$  offered and 153  $\text{cm}^3/\text{kg}$  filled under these conditions. This behaviour can be ascribed to steric hindrance within the pores, due to the form and size of the naphthalene molecule. This hypothesis is in agreement with the results obtained by

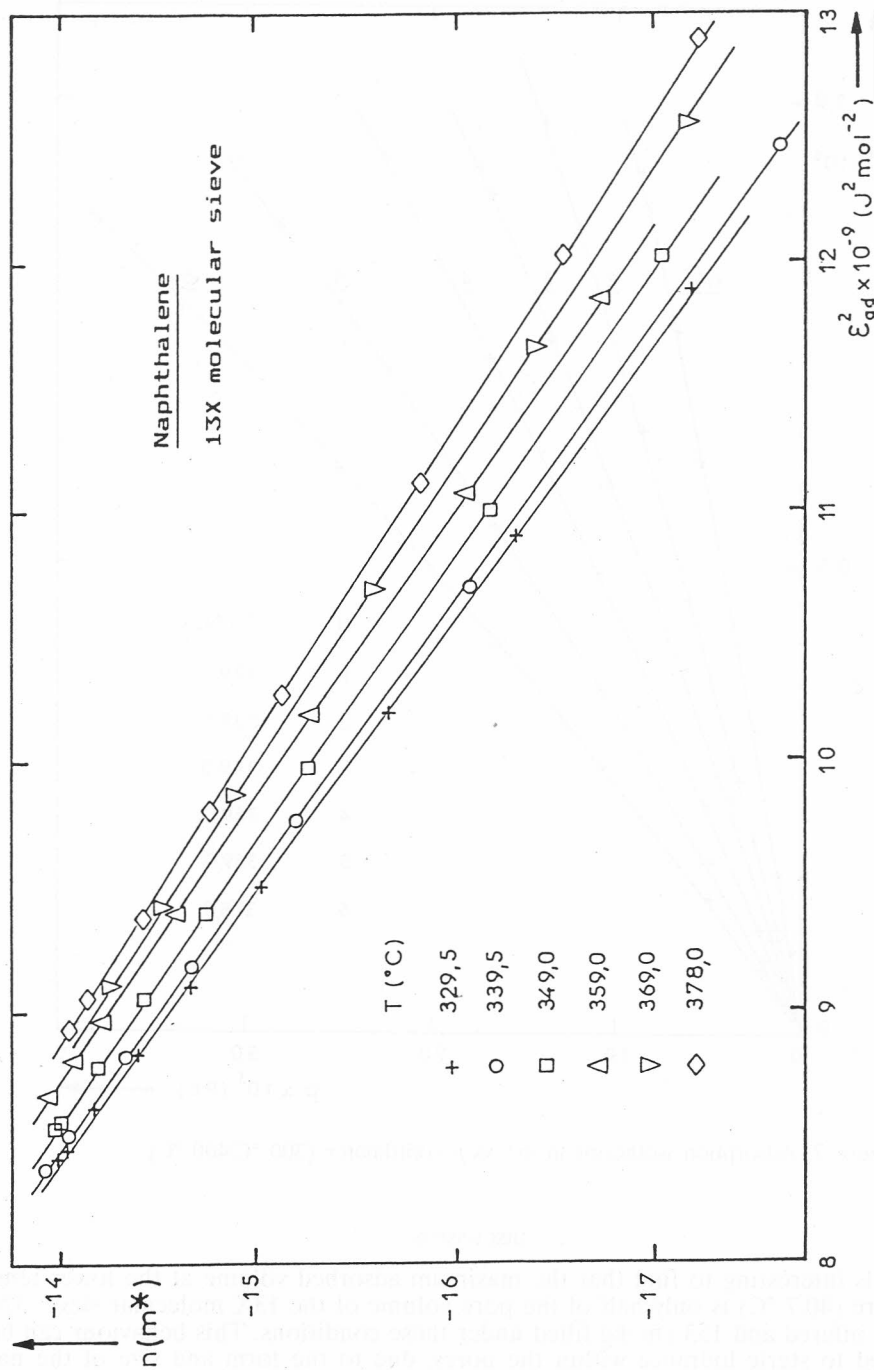


Figure 8. Adsorption isotherms in Dubinin coordinates (300 °C/400 °C)

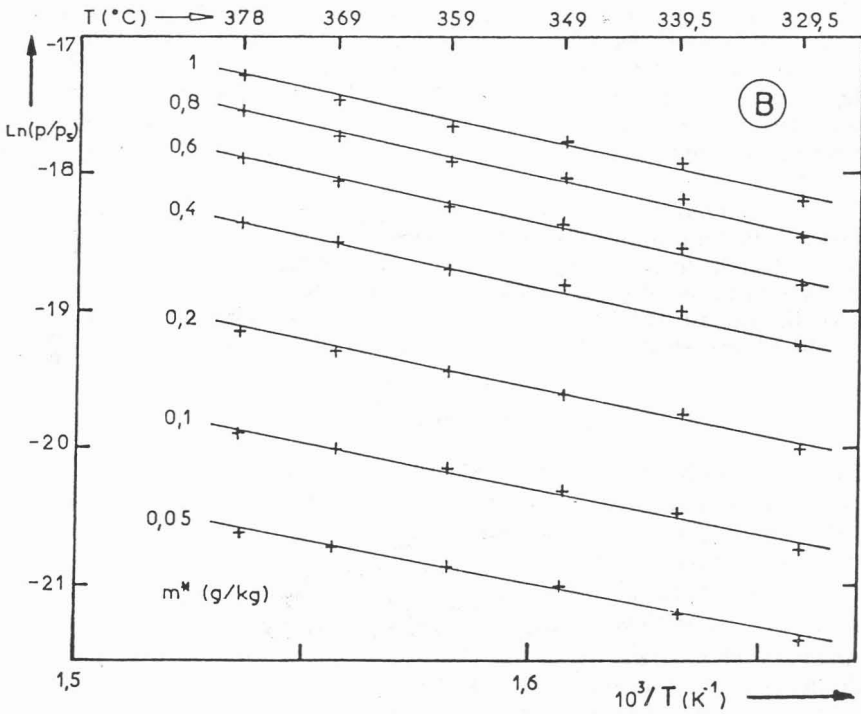
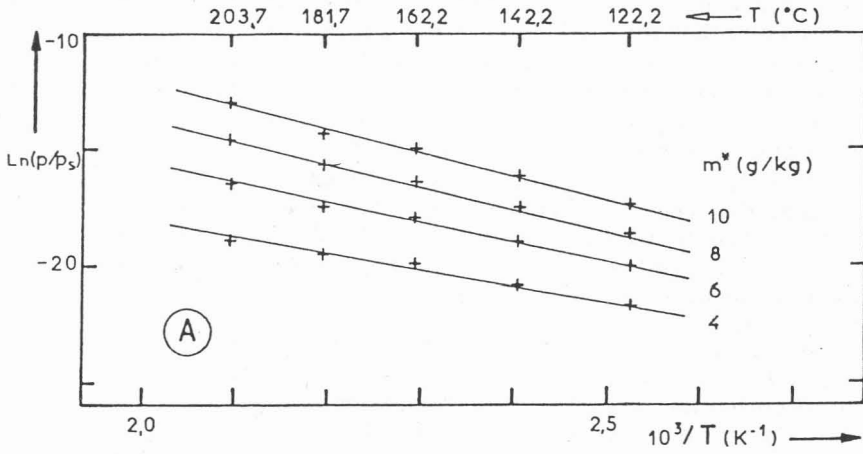


Figure 9. Isothermic curves

Laurent and Bonnetain<sup>17</sup> for the adsorption of organic molecules of various size by 5 Å molecular sieve. These authors clearly demonstrate that the adsorbed volume becomes smaller than the total offered volume if cavities cannot contain more than 4 or 5 molecules. In our case, the mean maximum number of naphthalene molecules which can pack into a single cavity is approximately 5 to 8. Consequently, at 40.7 °C, the number of naphthalene molecules adsorbed does not exceed 3 to 4. Thus, the steric hindrance hypothesis seems to be realistic.

The hypothesis of the heterogeneous distribution of pores was shown not to hold because the crystalline greating of zeolithes 13X is a regular arrangement of truncated octahedrals, constituting a stable, rigid and regular structural framework.<sup>18</sup>

Similarly, it is worth recalling that adsorbed quantities of benzene 25 times higher than the ones obtained in this work have been reported in literature for similar working conditions (at 427 °C with 13X molecular sieve<sup>10</sup>). This result corroborates the assumption of a steric hindrance in the pores. Indeed, the two molecules ( $C_6H_6$  and  $C_{10}H_8$ ) do exhibit similar planar structures; their properties are very similar in many respects but they notably differ in dimensions, the first with one aromatic nucleus and the second with two of them joined together.

As previously mentioned, with the continuous injection method the mass of naphthalene adsorbed cannot be directly obtained from experiments in the range of very low  $p$ -values. To circumvent this problem, the isotherms have been calculated from the Dubinin model in that range and then the isosteric curves drawn from the extrapolated curves. The straight-lines thus obtained are shown in Figure 9–A: we only draw them in a narrow range of the adsorbed amount between 0.4 and 1%. From them,  $Q_{st}^*$  values have been estimated by the exposed method and reported in Figure 10–A as a function of the adsorption rate. The heat of adsorption, which could be expected to be independent of the mass adsorbed, there appears to slightly increase with it. This is probably due to some inaccuracy inherent in the method. A mean value around 540 kJ/kg (70 kJ/mol) may be roughly proposed for  $Q_{st}^*$  within 20%.

The isotherms obtained by the elution method give much more reliable values for isosteric diagram drawing (Figure 9–B). The correlation coefficients of linear regression straight-lines are all in the 0.990–0.996 range. As it appears from Figure 10–B, the variation of  $Q_{st}^*$  as a function of  $m^*$  is negligible and a value of 450 kJ/kg for the net isosteric heat of adsorption is found. It agrees with the previous value (540 kJ/kg) within the confidence interval already indicated (20%).

#### CONCLUSIONS

From this study, three main points become clear:

- the heat of adsorption of naphthalene on 13X molecular sieve, around 450 kJ/kg (60 kJ/mol), is of about the same magnitude as those traditionally associated with reversible physical adsorption;
- reversible adsorption occurs even at temperatures as high as 400 °C;
- the best fitting curve for data points is obtained with the Dubinin model.

However, when compared to the adsorption of benzene under the same working conditions (temperature, pressure, adsorbent), the adsorption of naphthalene appears to involve much lower quantities of product. In an attempt to explain this gap, the idea of steric hindrance in the pores has been hinted at. This assumption agrees well with the existence of an unoccupied pore volume even at fairly low temperatures (in Figure 11, where the reduced mass,  $m^*$ , at saturation conditions,  $p$

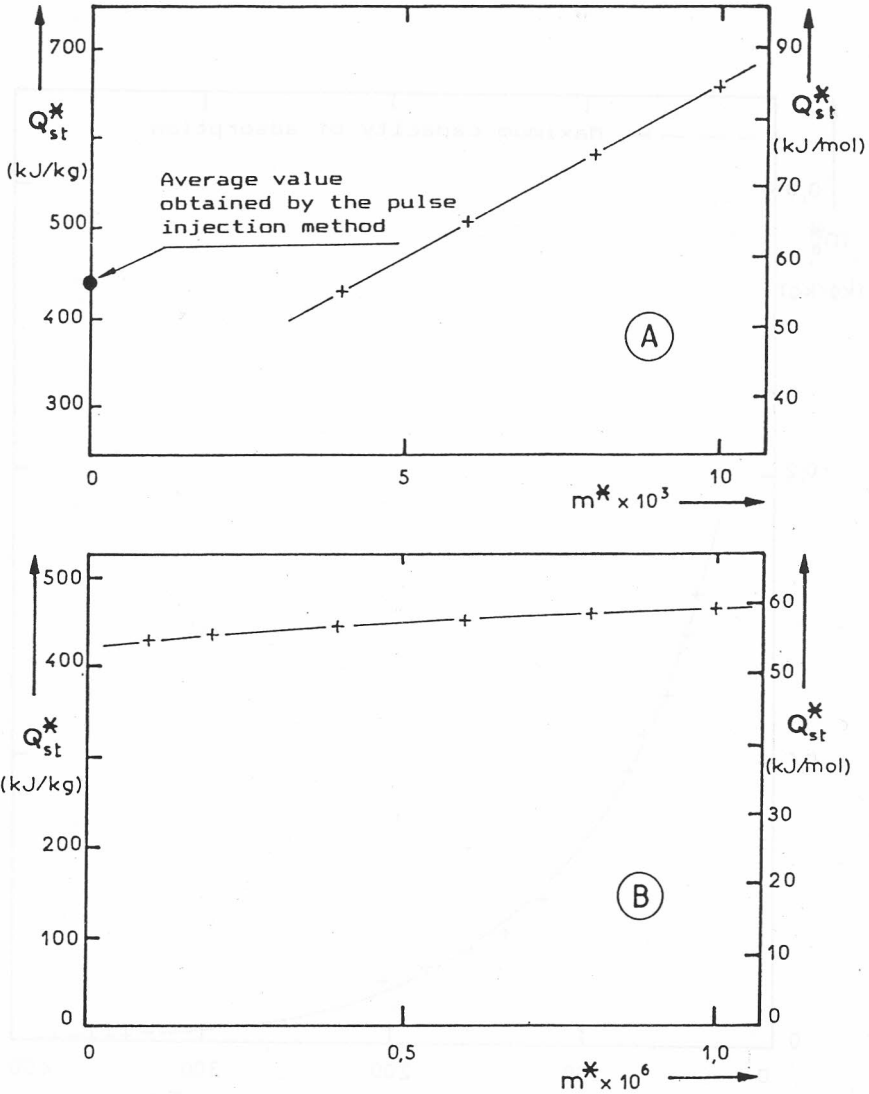


Figure 10. Isosteric heat of adsorption vs recovery rate

$= p_s$ , has been plotted against temperature, the difference from the theoretical mass that could entirely fill the pores, 0.32 kg/kg, is clearly shown). From these remarks it follows that the isotherms may not be entirely adequate to give a complete description of the phenomena occurring when naphthalene vapour and 13X molecular sieve are put into contact, due to distortions induced by the hindrance effect.

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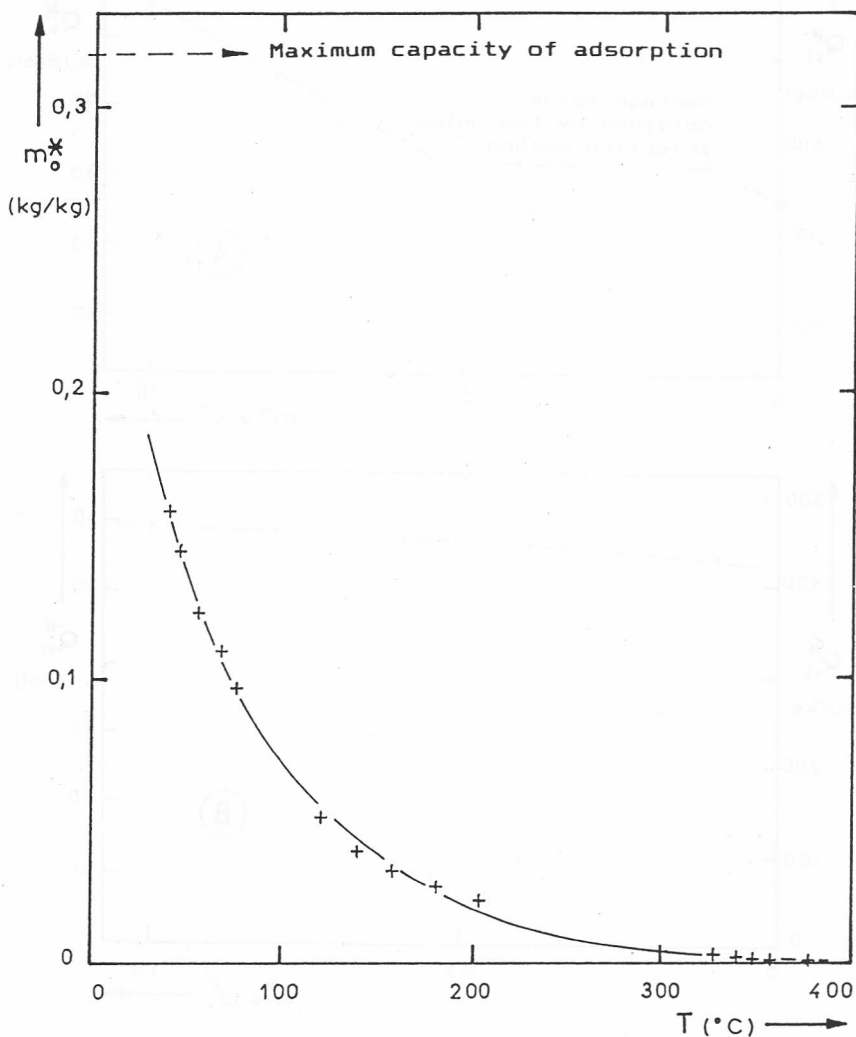


Figure 11. Adsorbed masses under saturated vapour pressure vs. temperature

SYMBOLS

$A_p, A, A_2, A_3$	Areas of chromatographic peaks	$L^2 \cdot T$
$K_1, K_2$	Constants	—
$m_i$	Mass injected into the chromatograph	M
$m_1 \dots m_4$	Adsorbed masses at $T_A \dots T_D$	M
$m^*$	Adsorbed mass per unit mass of adsorbent	—



$m^*_o$	Value of $m^*$ corresponding to filled up micropores	—
$M$	Molecular weight	M
$p$	Partial pressure of the vapour	$M.L^{-1}.T^{-2}$
$p_m$	Mean pressure in the adsorption column	$M.L^{-1}.T^{-2}$
$p_s$	Saturation vapour pressure	$M.L^{-1}.T^{-2}$
$p_o$	Atmospheric pressure	$M.L^{-1}.T^{-2}$
$p_l$	Inlet chromatograph pressure	$M.L^{-1}.T^{-2}$
$Q_L$	Latent heat of condensation	$L^2.T^{-2}$
$Q_{St}$	Absolute isosteric heat of adsorption	$L^2.T^{-2}$
$Q^*_{St}$	Net isosteric heat of adsorption	$L^2.T^{-2}$
$R$	Universal gas constant (per mol)	$M.L^2.T^{-2}.\theta^{-1}$
$t_1...t_3$	Intermediate times	T
$t_{CR}$	Corrected retention time	T
$t_{MR}$	Measured retention time	T
$T$	Adsorption temperature (chromatograph furnace)	$\theta$
$T_A...T_D$	Particular of $T$	$\theta$
$T_o$	Outside temperature	$\theta$
$T_1, T_2$	$C_1$ and $C_2$ column temperatures	$\theta$
$V_R$	Specific retention volume	$L^3$
$V_1, V_2$	Gas volumes passed through the adsorption column	$L^3$
$W$	Volume of adsorbate filling the micropore	$L^3$
$W_0$	Total volume of the micropore	$L^3$
$\epsilon_{ad}$	Adsorption free energy (per mol)	$M.L^2.T^{-2}$

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**SAŽETAK****Adsorpcija naftalena na molekulskim sitima 13X***R. Joulie, G. M. Rios i H. Gibert*

Ispitivana je adsorpcija naftalena na molekulskim sitima 13X. Adsorpcijske izoterme i topline adsorpcije određene su u području između 40 i 380 °C. Rezultati analize jasno pokazuju da Dubinin – Radushkevitsch-ev model daje jednadžbu koja se najbolje slaže s eksperimentalnim rezultatom, uz specifično ograničenje zbog steričkih smetnji.