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Adsorption of toluene, methylcyclohexane and neopentane on silica MCM-41

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Abstract Adsorption-desorption isotherms of toluene, methylcyclohexane and neopentane were determined on a silica MCM-41 material of pore diameter ∼3.4 nm over the temperature range 258 K to 308 K (278 K for neopentane). The isosteric enthalpies of adsorption were determined from the isotherms at the various temperatures. It was found that the isotherms of toluene and methylcyclohexane have a similar variation with the temperature, exhibiting hysteresis at 268 K and at lower temperature, while the adsorption of neopentane is reversible at all temperatures. The three organic adsorptives interact differently with the silica surface and the isosteric enthalpies of adsorption indicated that methylcyclohexane has the weakest interaction and toluene the strongest. A slight increase in the adsorption enthalpy at the beginning of the capillary condensation step is observed with methylcyclohexane and neopentane but not with toluene.

Keywords Hydrocarbon vapour adsorption · Model adsorbents · Hysteresis · Criticality · Isosteric enthalpies of adsorption

Abbreviations

a_m	Molecular cross sectional area
A_s	Total surface area
A_{ext}	External surface area
D_{ch}	Hysteresis critical diameter
$D_p(g)$	Geometric pore diameter
$D_p(H)$	Hydraulic pore diameter
L	Avogadro's constant
M	Molar mass
n_{ads}	Adsorbed amount
p/p^o	Relative pressure
q_{st}	Isosteric heat of adsorption
R	Gas constant
T	Temperature
T_{ch}	Hysteresis critical temperature
V_{ads}	Adsorbed volume
V_p	Pore volume
ρ_l	Density of the liquid
ρ_{sil}	Silica density

1 Introduction

The textural characterisation of porous materials is an important stage for their practical application and is normally accomplished by adsorption techniques. The distinct feature of the adsorption isotherms of gases and vapours on mesoporous materials is the sharp increase in the amount adsorbed at pressures below the saturation pressure that is frequently associated with a hysteresis loop (desorption occurs at lower pressures than adsorption). The hysteretic behaviour of the isotherms and the nature of the two branches of the hysteresis loop are aspects not fully understood.

The well defined pore structure of ordered mesoporous materials such as MCM-41, whose extraordinary features were disclosed in 1992 (Beck et al. 1992; Kresge et al. 1992), makes them ideal adsorbents for testing adsorption models and theories. Adsorption of gases such as nitrogen, argon or oxygen, has been widely used for characterising the materials and also to perform fundamental studies (Branton et al. 1994; Ravikovitch et al. 1995, 1997, 1998; Kruk et

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al. 1997a, 1997b; Morishige and Shikimi 1998; Inoue et al. 1998; Sonwane and Bhatia 1999; Kowalczyk et al. 2005; He and Seaton 2006; Zukal 2006). Adsorption of gases on samples with different pore size and/or at several temperatures has been used to analyse the nature of the branches of the hysteresis cycle, to test theoretical predictions of phase transitions in confined geometries and improve pore size distribution methods (Morishige et al. 1997; Neimark et al. 2003; Morishige and Nakamura 2004; Morishige and Tateishi 2006) and progress has been made on the knowledge of the capillary condensation process. Until recently, it was accepted that hysteresis on the adsorption isotherm was not observed below the pore critical temperature corresponding to the critical temperature of capillary condensation inside the pores, which is lower than the bulk critical temperature. Studies of adsorption of gases on MCM-41 demonstrated that the capillary condensation can occur without hysteresis in open-ended non-intersecting cylindrical pores depending on temperature and pore size (Ravikovitch et al. 1995). Consequently, in addition to the pore critical temperature, T_{cc}, and critical pore diameter, D_{cc}, the concepts of hysteresis critical temperature, T_{ch}, and hysteresis critical diameter, D_{ch}, were introduced (Morishige and Shikimi 1998). T_{ch} is the temperature above which hysteresis is not observed and D_{ch} is the pore size below which adsorption is reversible at a given temperature.

On the other hand, a relatively low number of studies on the adsorption of organic vapours on ordered mesoporous materials are available (Franke et al. 1993; Branton et al. 1995; Rathouský et al. 1995; Branton et al. 1997; Bambrough et al. 1998; Ribeiro Carrott et al. 2001; Schreiber et al. 2002; Choma et al. 2004; Qiao et al. 2004; Tanchoux et al. 2004; Trens et al. 2004; Ravikovitch et al. 2006).

The study of the adsorption of organic vapours on ordered mesoporous materials is interesting for several reasons. Ordered mesoporous materials have potential for practical applications as adsorbents and so adsorption of all kinds of adsorptives should be investigated. Organic adsorptives can be more sensitive to the surface heterogeneity and chemical composition than other vapours like nitrogen or argon at lower temperatures and therefore can be more adequate for characterising the surface of some modified ordered mesoporous materials. In addition, data for the adsorption of a wide range of adsorptives, namely different organic vapours, over a wide range of high temperatures on ordered mesoporous materials, may contribute to the clarification of the capillary condensation and evaporation processes.

In this work, we compare the adsorption of toluene, methylcyclohexane and neopentane on MCM-41 and analyse the effect of the temperature on the capillary condensation and evaporation processes of the different hydrocarbons inside the MCM-41 mesopores. In addition the isosteric enthalpies of adsorption, calculated from the adsorption isotherms at the various temperatures, are also compared.

2 Experimental

2.1 Synthesis and characterisation

The MCM-41 sample was synthesised at room temperature, using tetradecyltrimethylammonium bromide as surfactant, TEOS and ammonia, followed by aging in hydrothermal conditions, according to a procedure previously described (Grün et al. 1997). After stirring for 1 h at room temperature the synthesis gel was heated in a Teflon lined autoclave at 378 K for 3 days. The solid was recovered by filtration, dried and calcined at 823 K for 8 h using a heating rate of 3 $\mathrm{K\,min^{-1}}$ to achieve the final temperature.

The X-ray diffraction (XRD) measurements were carried out on a Bruker AXS-D8 Advance powder diffractometer, using CuKα radiation (40 kV, 30 mA), with a step size of 0.01° (2θ) and 5 s per step. Nitrogen adsorption at 77 K was determined on a CE Instruments Sorptomatic 1990, using helium (for dead space calibration) and nitrogen of 99.999% purity supplied, respectively, by Linde and Air Liquide. Prior to the adsorption measurements, the sample was outgassed for 8 h at 453 K, achieved using a heating rate of 1 $\mathrm{K\,min^{-1}}$.

2.2 Hydrocarbon adsorption

Neopentane (>99%, Linde), toluene (>99%, Riedel-de-Haën) and methylcyclohexane (>99 %, Aldrich) were the adsorptives used. The liquid adsorptives were first double distilled and then outgassed in the vacuum rig by repeated freeze-thaw cycles prior to the determination of the isotherms. The saturation pressure and density of the hydrocarbons at temperatures between 258 and 298 K were calculated using data and equations recommended in the literature (Reid et al. 1986).

The adsorption of toluene, methylcyclohexane and neopentane was determined gravimetrically using a CI Electronics vacuum microbalance with a DISBAL control unit. Pressure measurements were performed using Edwards Barocel capacitance manometers. The temperature of the circulating liquid jacket around the balance tubes was controlled within ±0.1 K using a Grant LTD thermostat and a Masterflex peristaltic pump. Prior to the adsorption experiments the sample was always outgassed at 473 K for 8 hours.

3 Results and discussion

3.1 Sample characterisation

The X-ray diffraction patterns and the nitrogen adsorption isotherm determined on the MCM-41 sample are shown in Fig. 1(a) and (b), respectively. The diffraction pattern is typical of a good quality MCM-41 material with long range structural ordering, exhibiting four diffraction peaks. The adsorption isotherm is of type IV of the IUPAC classification and completely reversible. The highly vertical capillary condensation step indicates that the sample has a very narrow pore size distribution.

A unit cell parameter, a_o, of 4.25 nm was calculated from the XRD data. The surface areas and pore volume were assessed by analysis of the adsorption isotherms by the α_s method (Gregg and Sing 1982; Rouquérol et al. 1999). The α_s plot was constructed using standard data for the adsorption of nitrogen on non porous partially hydroxylated silica, and, as usual, presented two regions of linearity. A linear region prior to capillary condensation associated with the adsorption on the entire surface of the material, which could be back-extrapolated through the origin confirming the absence of primary micropore filling and therefore of ultramicropores on the material. From the slope of this first linear region the total surface area, A_s, was calculated. At high relative pressures after the filling of the mesopores a second linear region is associated with adsorption on the external surface of the sample. From the slope of this linear region the external surface area, A_{ext}, was calculated and from the intercept the value of mesopore volume Vp. The total surface area, external surface area and mesopore volume of the sample are 882 $m^2\,g^{-1}$, 20 $m^2\,g^{-1}$ and 0.63 $cm^3\,g^{-1}$, respectively. The high surface area and pore volume together with the very low external surface area confirm that the material is well structured.

The sample pore size was calculated by two different methods. The mean pore size was calculated from the results of the analysis of the nitrogen adsorption isotherm by the α_s method, making use of the concept of hydraulic pore width, with the equation: $D_p(H) = 4V_p/(A_s - A_{ext})$. It is well known that hydraulic pore widths underestimate the pore size. Therefore to get more realistic values of the pore dimensions the hydraulic pore widths were corrected ($D_p(H)_{cor} = (0.162/0.137)D_p(H)$) by using 0.137 nm^2 as the nitrogen cross sectional area, in accordance with previous findings (Ribeiro Carrott et al. 2001) that allowed us to obtain good agreement with the pore sizes calculated by the NLDFT method. Considering the high regularity of the sample the pore size can also be estimated assuming the ideal model of a hexagonal array of cylindrical pores from the X-ray diffraction and nitrogen adsorption data, with the equation:

$$D_p(g) = 2 \cdot \left(a_0 \sqrt{\frac{\sqrt{3}}{2\pi} \left(\frac{\rho_{sil} V_p}{1 + \rho_{sil} V_p} \right)} \right),$$

where ρ_{sil} is the density of the silica walls (assumed as 2.2 $g\,cm^{-3}$). The values of pore size calculated in these ways were $D_p(H)_{cor} = 3.46$ nm and $D_p(g) = 3.40$ nm.

3.2 Hydrocarbon adsorption isotherms

The adsorption-desorption isotherms of toluene, methylcyclohexane and neopentane at 273 K determined on the MCM-41 sample is shown in Fig. 2. The amounts adsorbed are expressed as equivalent liquid volumes by assuming the adsorbates to have the normal bulk liquid density.

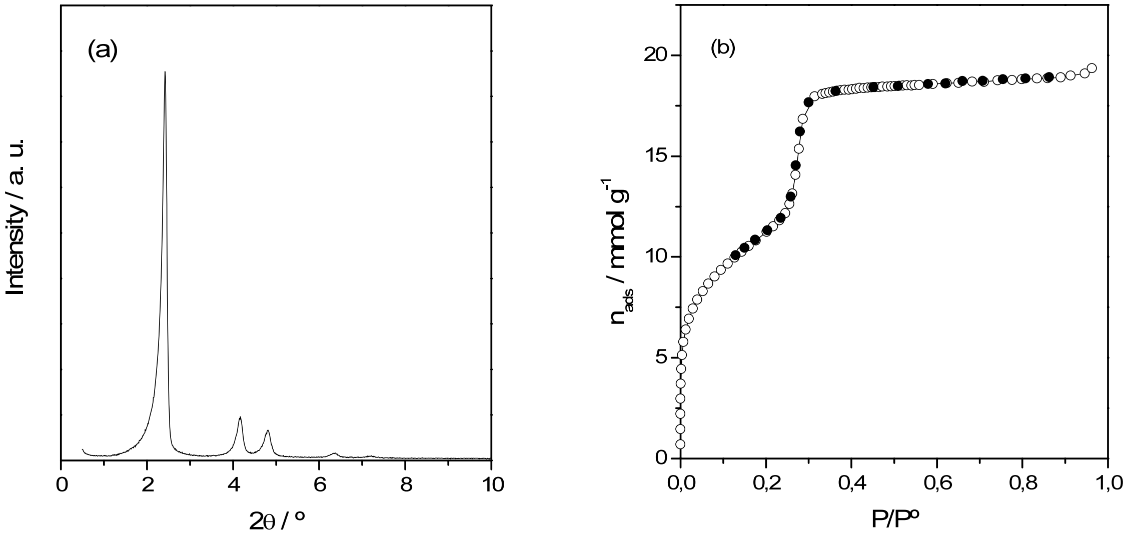

Fig. 1 (**a**) X-ray diffraction pattern and (**b**) nitrogen adsorption isotherm at 77 K of the MCM-41 material

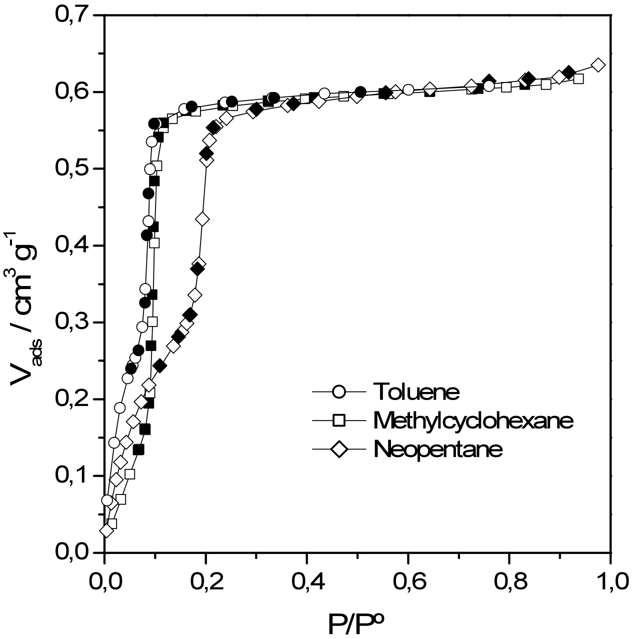

Fig. 2 Adsorption-desorption isotherms of toluene, methylcyclohexane and neopentane determined at 273 K on a MCM-41 sample with pore size ~3.4 nm (*closed symbols*—desorption)

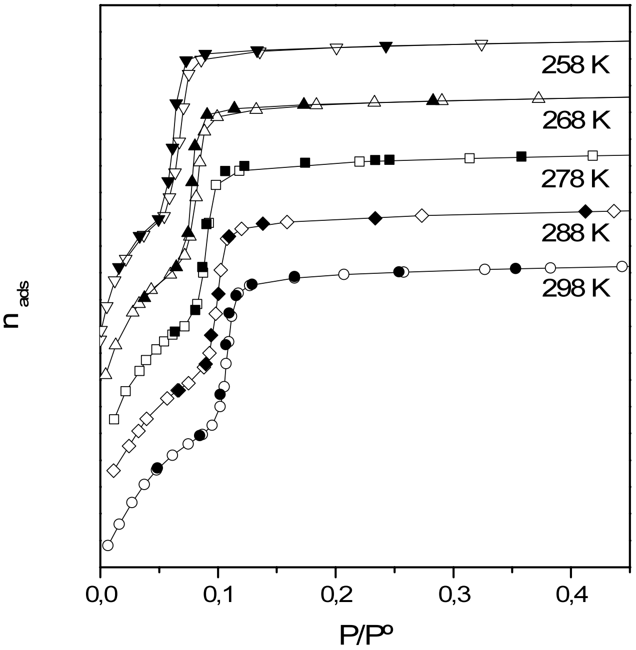

Fig. 3 Adsorption-desorption isotherms of toluene determined at temperatures between 258 K and 298 K on MCM-41 with pores of size ~3.4 nm (*closed symbols*—desorption). The vertical scale is shifted by 1 mmol g^{-1} for each temperature

The adsorption isotherms of toluene and neopentane are of type IV, as those of nitrogen, while that of methylcyclohexane is almost linear in the low pressure region prior to capillary condensation, not exhibiting a defined knee. The linear character of the methylcyclohexane isotherms at low relative pressure suggests that the interactions between this hydrocarbon and the silica surface are weaker when compared with the other two. The stronger interactions between toluene and the silica surface can be related with the aromatic nature and small dipole moment of this molecule, leading to a certain degree of specificity associated with the adsorbate-adsorbent interactions, namely with surface hydroxyl groups, as also indicated in other studies on ordered mesoporous materials (Ravikovitch et al. 2006; Russo et al. 2007) and on nonporous silicas (Schlangen et al. 1995). Both neopentane and methylcyclohexane are non polar and the latter has a higher polarisability. Therefore, adsorbate-adsorbate interactions are stronger for the methylcyclohexane system and probably predominate over adsorbate-silica surface interactions, which can explain the difference in the isotherms at low relative pressures and also the lower p/p^o at which methylcyclohexane condenses inside the mesopores in comparison with neopentane. Despite the difference in the low pressure region, it was found that toluene and methylcyclohexane exhibit similar features in the pore filling region. All isotherms exhibit a very well defined capillary condensation step in a limited range of relative pressure, with the exact p/p^o of condensation depending on the adsorptive: toluene condenses at the lowest p/p^o and neopentane at the highest. For methylcyclohexane pore filling starts at a p/p^o relatively close to that of toluene. By comparing the isotherms of the three organics and that of nitrogen it can be seen that the uptakes of the three organic adsorptives at the plateau of the isotherms are identical and lower than the corresponding nitrogen uptake, in agreement with previous studies involving the adsorption of these and other hydrocarbons on other grades of pure silica MCM-41 materials (Ribeiro Carrott et al. 2001; Ravikovitch et al. 2006).

It can be seen that all the isotherms are reversible, meaning that at this adsorption temperature the diameter of the mesopores is below the hysteresis critical diameter of all the adsorptives.

Figures 3, 4 and 5 show the adsorption-desorption isotherms of, respectively, toluene and methylcyclohexane determined at temperatures between 298 and 258 K and of neopentane at temperatures between 273 and 258 K, of the MCM-41 sample. A common feature to the three organics isotherms is that the capillary condensation step is displaced to higher p/p^o as the adsorption temperature increases, as previously reported by other authors for different organic adsorbate-adsorbent systems (Qiao et al. 2004; Tanchoux et al. 2004). As expected, the total amount adsorbed and the adsorbed amount at low p/p^o prior to the inset of pore filling gradually increases with the decrease of the temperature. Moreover, it can be seen that in addition to the changes in the position of the condensation step the

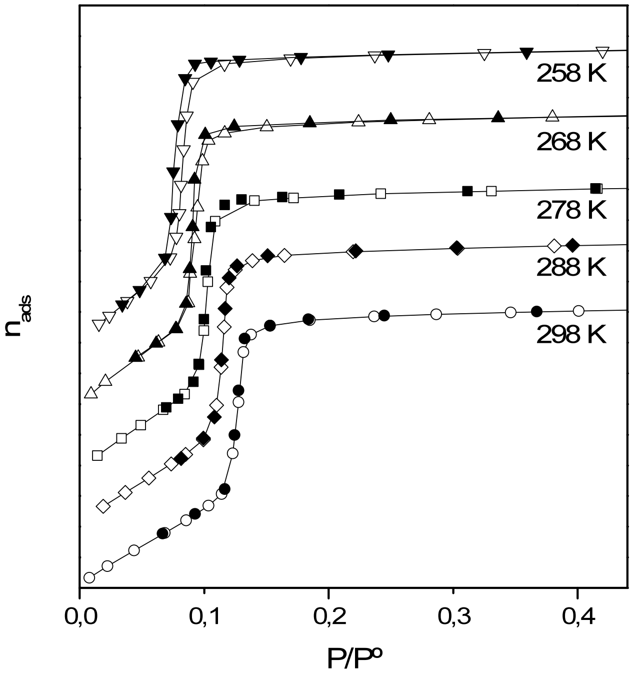

Fig. 4 Adsorption-desorption isotherms of methylcyclohexane determined at temperatures between 258 K and 298 K on MCM-41 with pores of size ~3.4 nm (*closed symbols*—desorption). The vertical scale is shifted by 1 mmol g^{-1} for each temperature

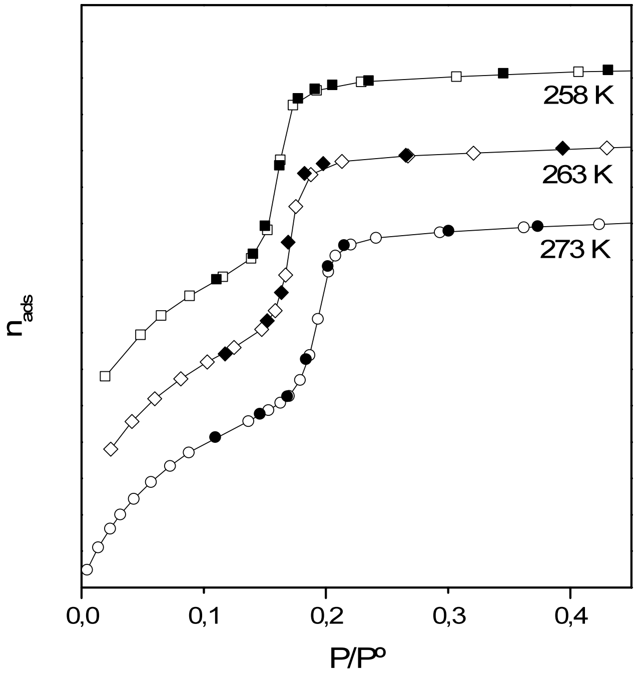

Fig. 5 Adsorption-desorption isotherms of neopentane determined at temperatures between 258 K and 273 K on MCM-41 with pores of size ~3.4 nm (*closed symbols*—desorption). The vertical scale is shifted by 1 mmol g^{-1} for each temperature

reversibility of the condensation and evaporation processes of toluene and methylcyclohexane is also affected by the temperature.

It can be seen from Fig. 3 that the isotherms determined at 298, 288 and 278 K are reversible. However, at 268 K hysteresis on the adsorption-desorption isotherm can be observed. At this temperature the hysteresis loop is very narrow and occurs only at the upper end of the capillary condensation step. This "triangular" hysteresis loop may be a result of the sample's pore size distribution. The larger pores are filled at higher p/p^o and hysteresis is first observed in these pores. This shows that the sample has some pores of diameter below the D_{ch} of toluene for 268 K. At 258 K the toluene isotherm exhibits a clear H1 type hysteresis cycle. On the basis of these and the results previously reported in Fig. 2, it can be established that the critical hysteresis temperature of toluene in pores of dimension ~3.4 nm is above 268 K and below 273 K.

The adsorption behaviour of methylcyclohexane at temperatures between 258 and 298 K on the MCM-41 sample with pore size ~3.4 nm is similar to that of toluene. The isotherms at higher temperatures are reversible and at 268 K a narrow hysteresis cycle is observed, identical to the one exhibited by the toluene isotherm at the same temperature. Therefore, it can be concluded that the hysteresis critical temperature of methylcyclohexane also lies between 268 and 273 K. Interestingly, the toluene and methylcyclohexane hysteresis critical temperatures in pores of dimension ~3.4 nm are very close, despite the fact that the later adsorptive condenses at a slightly higher p/p^o in a given pore and also the differences noted prior to pore filling.

The behaviour of neopentane is different to that of the other two organics and the adsorption isotherms are completely reversible at all temperatures. The lower temperature studied was limited by the solidification temperature which is at ~256.6 K (Reid et al. 1986).

It was found by other authors that a plot of $(T_c - T_{ch})/T_c$ *vs* d/r_p for Ar, N_2, O_2 and C_2H_4 on MCM-41 formed a straight line passing through the origin (Morishige et al. 1997; Morishige and Shikimi 1998). Since the adsorptives studied in this work are similar in size, if we assume that the relative shift of the hysteresis critical temperature with respect to the bulk critical temperature, $(T_c - T_{ch})/T_c$, will be identical for all three organics, an estimation of T_{ch} for neopentane can be obtained. In fact, the relative shift of T_{ch} from T_c is 0.55–0.54 and 0.53–0.52 (considering T_c values from Reid et al. 1986) for toluene and methylcyclohexane, respectively, and from these values T_{ch} for neopentane is estimated in the range 195–208 K. This is well below the temperatures studied in this work and this result is consistent with the absence of hysteresis observed on neopentane adsorption isotherms.

Using the pore volume obtained for the organic adsorptives (~0.60 cm^3 g^{-1}) to calculate the geometric pore width, a value of ∼3.37 nm was obtained, in close agreement with that calculated from nitrogen data. The mean molecular cross sectional area, a_m, of the toluene, methylcyclohexane and neopentane adsorbed on the surface of the MCM-41 mesopores was calculated from the corresponding statistical monolayer capacities, n_m, determined by application of the BET equation to the isotherms prior to pore filling: $a_m(\text{MCM-41}) = A_s/(n_m \cdot L)$, where A_s is the surface area of the sample for these adsorptives. This was obtained by adding external surface area of 20 $m^2\,g^{-1}$ to the pore area for the organic adsorptives, calculated as $A_p = 4V_p/d_p(g)$, using the values above referring to the organic adsorption. Not very different values were obtained for each adsorptive at the different temperatures, respectively, 0.37, 0.38 and 0.44 nm^2, for toluene, methylcyclohexane and neopentane. For comparison, the molecular cross sectional areas in the liquid, $a_m(\text{liq})$, were calculated assuming a hexagonal packing of the molecules with the expression:

$$a_m = 1.091\left(\frac{M}{\rho_l \cdot L}\right)^{2/3},$$

where 1.091 is a packing factor, ρ_l is the liquid density and M is the molar mass of the hydrocarbon (Gregg and Sing 1982). The values for toluene, methylcyclohexane and neopentane are respectively, 0.34, 0.38 and 0.36 nm^2. It can be seen that the a_m of toluene and methylcyclohexane adsorbed in the MCM-41 are closer to the corresponding values in the liquid, than that of neopentane for which a higher value is observed. Higher values have also been reported for non porous silica (Carrott et al. 1988), but of 0.60–0.62 nm^2, indicating that confinement caused a decrease of the a_m with respect to that on a non-porous surface silica.

3.3 Isosteric enthalpies of adsorption

The isosteric enthalpy of adsorption at a fixed adsorbed amount was determined from the adsorption isotherms at different temperatures by applying the equation:

$$\left(\frac{\partial \ln p}{\partial T}\right)_n = -\frac{\Delta_{ads}\dot{h}}{RT^2}$$

that, after integration yields (at a fixed adsorbed amount):

$$\ln p = \frac{\Delta_{ads}\dot{h}}{RT} + \text{const}$$

where $\Delta_{ads}\dot{h}$ is the differential enthalpy of adsorption at a fixed adsorbed amount, R is the gas constant and T the adsorption temperature. The differential enthalpy of adsorption corresponds to $-q_{st}$, usually denoted by isosteric heat of adsorption, but now recommended to be designated as isosteric enthalpy of adsorption (Rouquérol et al. 1999). To obtain the adsorption enthalpy values the isotherms were first fitted by a series of polynomials carefully chosen for different pressure regions to reproduce the experimental curves. Then the values of p for different n were calculated and the isosteres plotted to obtain the isosteric enthalpies of adsorption.

The variation of the isosteric enthalpy of adsorption with the adsorbed amount of toluene, methylcyclohexane and neopentane is shown in Fig. 6(a), (b) and (c), respectively. For comparison, the molar enthalpy of condensation of the bulk of the corresponding adsorptive was also calculated from vapour pressure data in the considered temperature range and is also represented on the figures. For all the hydrocarbons the enthalpy of condensation of the adsorbate inside the MCM-41 pores is always above that of the bulk, as previously reported for other adsorptives. The highest difference between the adsorption enthalpy and the enthalpy of condensation at low adsorbed amounts is obtained for toluene and the lowest for methylcyclohexane, which suggests that the adsorbate-adsorbent interactions are strongest for toluene and the weakest for methylcyclohexane. It can be seen from the figures that the variation of the adsorption enthalpy with the adsorbed amount is not exactly the same for the three organics. The isosteric enthalpy of adsorption of toluene decreases gradually with the amount adsorbed in the region prior to capillary condensation and it becomes practically constant during capillary condensation inside the pores of MCM-41. The isosteric enthalpy of adsorption of methylcyclohexane slightly decreases at low adsorbed amounts. At the beginning of the condensation step a slight increase of the adsorption enthalpy is observed, which attains a constant value during capillary condensation. On the other hand, the adsorption enthalpy of neopentane gradually increases at very low amounts of hydrocarbon adsorbed, during monolayer formation until a maximum is achieved and then decreases progressively in the region prior to capillary condensation. Capillary condensation is evidenced by a slight increase in the adsorption enthalpy at the beginning of the step, which is attributed to the enhanced adsorbate-adsorbate interactions during condensation inside the MCM-41 mesopores.

It is noted that prior to pore filling these results qualitatively agree with what was anticipated by the comparison of the isotherms of the three adsorptives. Nevertheless, it should be mentioned that the linearity of the isosteres was worse then at higher pressures, and in particular for neopentane for which only three temperatures were used, there is a greater degree of uncertainty in the results. However, at higher pressures, namely in the pore filling region the linearity was very good for the three adsorptives, and similar behaviour was observed, in spite of the differences pointed out in previous sections.

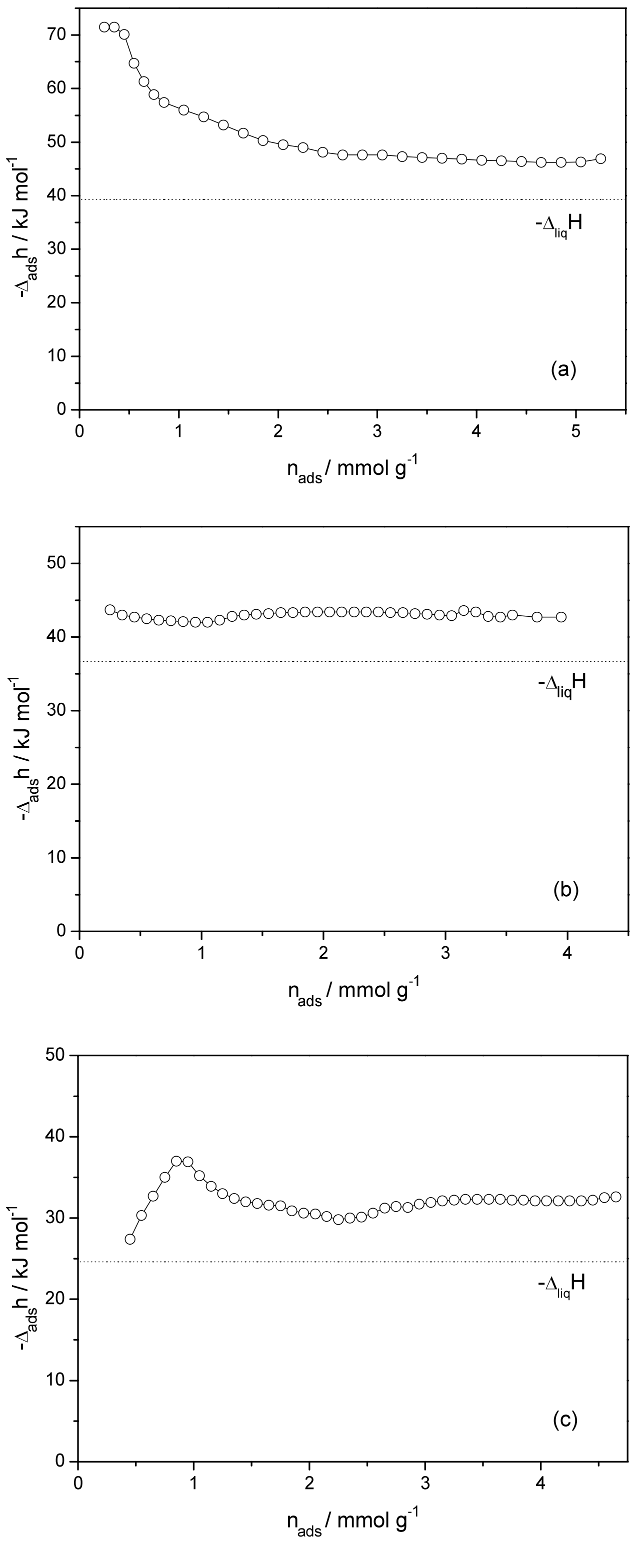

Fig. 6 Isosteric enthalpy of adsorption of (**a**) toluene, (**b**) methylcyclohexane and (**c**) neopentane as a function of the adsorbed amount for MCM-41 with pores of size ~3.4 nm (The *horizontal line* corresponds to the molar enthalpy of condensation of the bulk in the same temperature range)

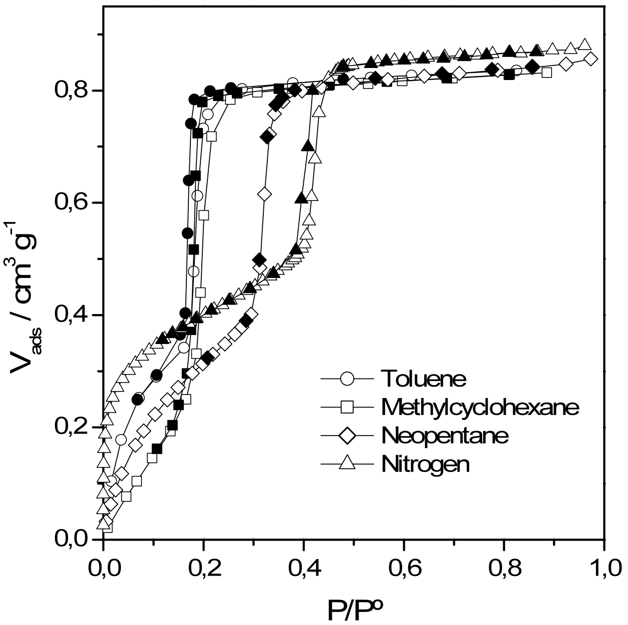

Fig. 7 Adsorption-desorption isotherms of nitrogen at 77 K and of toluene, methylcyclohexane and neopentane determined at 273 K on a MCM-41 sample with pore size ~4.5 nm (*closed symbols*—desorption)

3.4 Final comments

It is noted that there are some similar features for the three adsorptives, but also differences were observed. In particular neopentane seems to be an interesting adsorptive to study in more detail due to the lack of hysteresis observed in the temperature range it was possible to study. Considering that this will obviously depend on pore size, wider pore size samples were also studied. For instance, in Fig. 7 are shown the isotherms similar to those in Fig. 2 but for an MCM-41 sample prepared in the same way but with octadecyltrimethylammonium bromide as structure directing agent, possessing therefore larger pore width ($d_p \sim 4.5$ nm). Now at 273 K the isotherms of toluene and methylcyclohexane already present hysteresis, as with nitrogen at 77 K, but neopentane is still reversible, as also found at lower temperatures. Only for wider pore materials, such as SBA-15, was hysteresis obtained with neopentane. These findings will be further explored as it may be eventually of use for determining the correct branch of the hysteresis loop for the determination of pore sizes in mesoporous materials.

4 Conclusions

In this work the effect of temperature on the adsorption and on the capillary condensation and evaporation processes of toluene, methylcyclohexane and neopentane on a MCM-41 material of pore size ~3.4 nm was investigated.

The adsorption isotherms of toluene and neopentane were found to be type IV, similar to that of nitrogen but those of methylcyclohexane didn't show a knee at low p/p^o, indicating weak adsorbate-adsorbent interactions. It was found that neopentane adsorbs reversibly in the range of temperatures studied (258 to 278 K). On the other hand, at the lowest temperatures the isotherms of toluene and methylcyclohexane exhibited a hysteresis cycle. It was found that these two organic adsorptives have very close hysteresis critical temperatures (between 268 and 273 K), although the stepwise capillary condensation occurs at different p/p^o on pores of the size analysed.

The isosteric enthalpy of adsorption was found to vary in a different way with the amount adsorbed for each one of the adsorptives. Nevertheless, for all the organics the adsorption enthalpies were always higher than the condensation enthalpy of the bulk. At low adsorbed amounts the toluene isosteric enthalpy is high, reflecting a strong interaction of this molecule with the surface of the pores, and decreases gradually reaching a constant value during capillary condensation. The adsorption enthalpy of methylcyclohexane confirmed the very weak interaction of this hydrocarbon with the silica surface. An intermediate behaviour was obtained at low adsorbed amounts for neopentane. With these two adsorptives a slight increase of the adsorption enthalpy occurred at the beginning of the capillary condensation, indicating stronger adsorbate-adsorbate interactions.

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