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Sorption of water in aluminophosphate molecular sieve AlPO$_4$-5

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Abstract

The water sorption isotherm over AlPO$_4$-5, in which a low sorption capacity in the initial region followed by a steep rise in sorption is observed, is different from those obtained for polar molecules, namely acetonitrile, ammonia and methanol. An attempt has been made to explain the water sorption behaviour on the basis of a condensation phenomenon using the structural characteristics of AlPO$_4$-5. © 1998 Elsevier Science B.V.

Keywords: AlPO$_4$-5; Water sorption; Condensation phenomenon

1. Introduction

AlPO$_4$-5, a member of the aluminophosphate molecular sieve family, has a structure comprising of alternating tetrahedra of Al and P linked together to form a microporous structure with unidimensional 4-, 6- and 12-membered ring channels [1,2]. Unlike zeolites, AlPO$_4$-5 has a neutral framework with mild hydrophilicity [2]. Generally, sorption isotherms of water in microporous solids like zeolites are of type I as per BDDT classification. This is attributed to the hydrophilic nature of these solids. However, water sorption on AlPO$_4$-5 is unusually low up to the relative pressure of 0.25 followed by a near isobaric rise in the relative pressure range of 0.25 to 0.30. Such a sorption isotherm for water has also been reported for other AlPO molecular sieves, viz. AlPO$_4$-11,

-17, -20 and -31 [3]. Wilson et al. [2] have attributed such behaviour to the mild hydrophilicity, whereas Thamm et al. [4] have proposed a capillary condensation phenomenon in secondary pores of the AlPO$_4$-5 structure to explain the observed behaviour. Goldfarb et al. [5] have investigated the water sorption using solid state NMR and have shown a reversible conversion of tetrahedral Al to octahedral coordination upon hydration. Furthermore, they have recognized two types of water molecule, namely the sorbed water molecules as those coordinated to framework Al and physisorbed molecules reorienting isotropically within the channel of AlPO$_4$-5. However, the unique shape of the water sorption isotherm is still not clearly explained. So, to understand this unusual sorption behaviour of water, we have carried out a systematic water sorption study on AlPO$_4$-5 and AlPO$_4$-11. The sorption of polar molecules, namely acetonitrile, ammonia and methanol, on AlPO$_4$-5 has also been studied.

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2. Experimental

AlPO$_4$-5 and AlPO$_4$-11 samples were synthesised hydrothermally using gel compositions of R:Al$_2$O$_3$:P$_2$O$_5$:H$_2$O of 1.5:1.0:1.0:40 and R:Al$_2$O$_3$: P$_2$O$_5$:H$_2$O of 1.0:1.0:1.0:40 respectively using pseudoboehmite and ortho-phosphoric acid (85 wt%) as aluminium and phosphorus sources [6]. Tri-n-propyl amine (Pr$_3$N) and di-n-propyl amine (DPA) respectively were used as a templating agents (R) for AlPO$_4$-5 and AlPO$_4$-11 syntheses. The hydrothermal crystallizations of the prepared gels were carried out in stainless steel autoclaves for 8 h and 19 h at 423 K and 443 K for the crystallization of AlPO$_4$-5 and AlPO$_4$-11 respectively. After the specified time intervals, autoclaves were quenched with running cold water and the crystallized products were filtered, washed, dried and finally calcined in air at 813 K for 10 12 h in order to remove occluded amine. The crystallinity and the purity of the crystallized products were estimated using the X-ray powder diffraction method (Rigaku Dmax III, Japan. Cu Kα radiation, $\lambda = 1.548$ Å) and water sorption measurement (McBain Bakr Gravimetric Balance) at p/p $= 0.4$ at 298 K respectively and compared with the literature data [2]. The recorded X-ray diffraction patterns for the crystallized samples ensured the high crystallinity as well as purity of the samples. Similarly, the water sorption capacities of 12.2 mmol g^{-1} and 6.6 mmol g^{-1} obtained for AlPO$_4$-5 and AlPO$_4$-11 respectively, at p/p $= 0.4$, were found to be in close agreement with the literature data [2]. The morphology of the crystallized samples was also investigated using scanning electron microscopy (SEM; Jeol, JSM-35C) and was found to be polycrystalline in nature [2].

Water sorption isotherms on AlPO$_4$-5 and -11 were measured gravimetrically in the temperature range of 303 333 K using a Cahn 2000 vacuum electrobalance. About 20 mg of the calcined sample was activated at 623 K under high vacuum ($\sim 10^{-4}$ Pa) for > 24 h prior to sorption measurements. Dissolved air, if any, in double distilled water was removed using freeze–pump–thaw cycles before use. The temperature of the sample during isotherm measurements was controlled to ± 0.1 K using a constant temperature water bath

(Ultratemp. 2000 Julabo, F-30). The equilibrium pressure was measured with high-precision MKS Baratron pressure transducers (Model 122AA, MKS, USA) having ranges of 0–1.33 kPa and 0 13.3 kPa with an accuracy of $\pm 0.5\%$ of the reading. The time required to achieve sorption equilibrium was found to vary with sorption coverage, i.e. equilibrium was achieved only after 120 min in the initial stages, whereas 30 45 min was adequate at higher loadings. (Equilibrium was assumed to be attained when the weight of the sample remained constant within ± 0.01 mg for at least 30 min.)

Sorption isotherms for acetonitrile, ammonia and methanol on AlPO$_4$-5 were measured gravimetrically using a McBain–Bakr quartz spring gravimetric balance (Thermal Syndicate, UK) having a sensitivity of 30 cm g^{-1} at 303 K. About 250 mg of the calcined sample was employed for this purpose. A cathetometer with 0.001 cm precision was used for measuring spring extension. The time required to achieve equilibrium for these sorbates was much shorter (about 20 30 min) than for water. Sorption of ammonia was followed up to a pressure of 101.33 kPa.

Acetonitrile and methanol (purity 99%) were procured from M/S. S.D. Fine Chemicals, India. The polar sorbates, including ammonia gas, were dried over activated molecular sieve 3A before use.

3. Results

Water sorption isotherms measured on AlPO$_4$-5 at 303, 313, 323 and 333 K are shown in Fig. 1. Initially, at 303 K (Fig. 1(a)), the sorption is low, reaching a value of 2.88 mmol g^{-1} at p/p $=$ 0.24 followed by a point of inflection in the range of p/p $= 0.245$–0.25 leading to the intracrystalline sorption capacity of 11.45 mmol g^{-1} (estimated at p/p $= 0.4$). A similar behaviour is observed at 313 K (Fig. 1(b)) wherein the sorption capacity is found to be 9.60 mmol g^{-1}. However, the point of inflection in the sorption isotherm is observed at p/p $= 0.26$ at a loading of 2.88 mmol g^{-1}. Owing to experimental limitations, sorption data at 323 K and 333 K could not be measured above p/p $=$ 0.34 and p/p $= 0.18$ respectively. However, sorp-
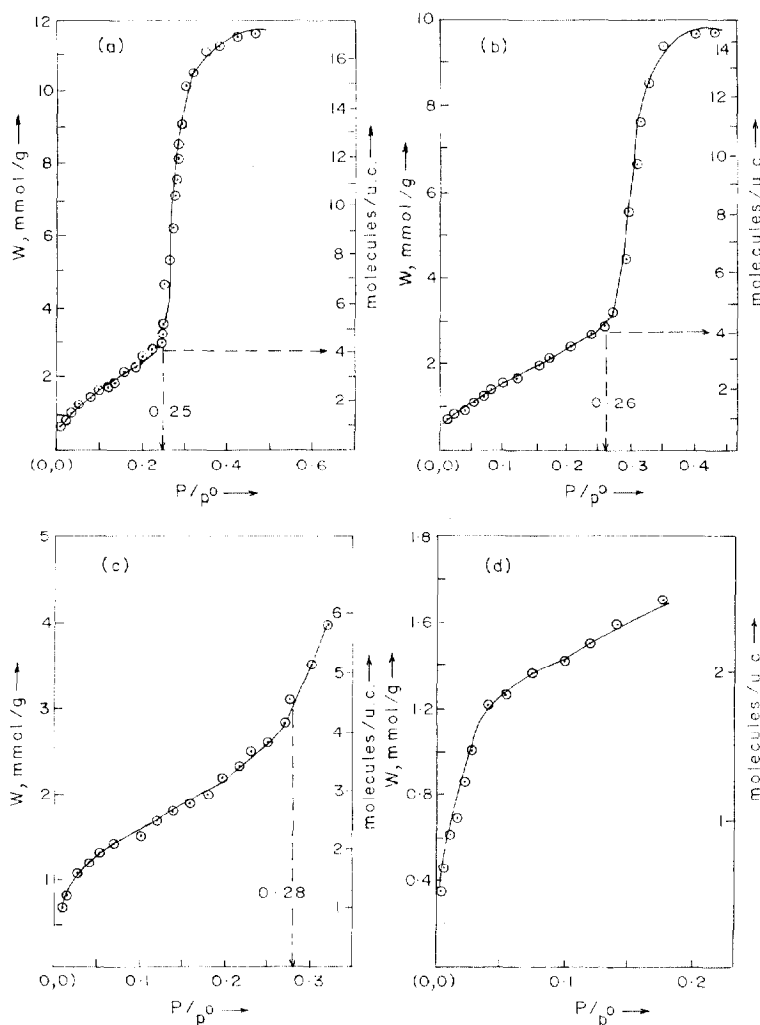
Fig. 1. Water sorption isotherm on AlPO₄-5 at (a) 303, (b) 313 (c) 323 and (d) 333 K.

tion measurements at 323 K indicate the initial stage of inflection at $p/p^\circ = 0.28$ observed at lower temperatures. A sorption capacity of 3.0 mmol g^{-1} at $p/p^\circ = 0.28$ is obtained at 323 K along with the beginning of the inflection (Fig. 1(c)). Similarly, a sorption capacity of 1.71 mmol g^{-1} at $p/p^\circ = 0.18$ is obtained at 333 K, while the inflection is not observed until $p/p^\circ = 0.18$ (Fig. 1(d)).

Isosteric heats of water sorption, ΔH, are estimated by applying the Clausius–Clapeyron equation using the sorption data at 303 and 313 K. The dependence of ΔH on sorption coverage is shown in Fig. 2. The isosteric heat value is high (~ 88 kJ mol^{-1}) at very low coverage and decreases sharply to 50 kJ mol^{-1}, a value closer to the heat of liquefaction of water (≈ 41 kJ mol^{-1}) and then remains more-or-less constant at this value with further increase in sorption coverage. The trend obtained in the isosteric values is found to be in close agreement with those reported [7,8]. The variation in the isosteric heat values for water essentially reflects the presence of surface heterogeneity and the presence of strong hydrophilic sites. However, the number of these sites is apparently small, as the heat values drop sharply and
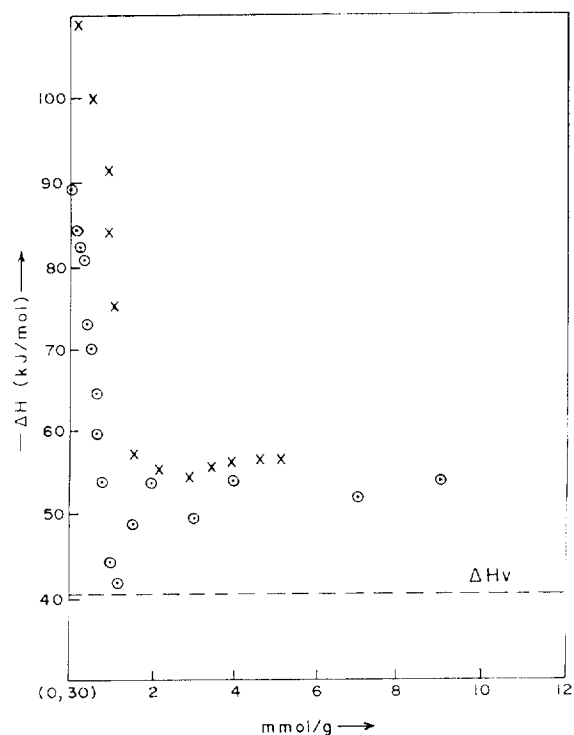
Fig. 2. Dependence of isosteric heats of water sorption $-\Delta H$ with coverage on AlPO$_4$-5 (⊙) and AlPO$_4$-11 (×).

Fig. 3. Sorption isotherm of acetonitrile (□), ammonia (△), methanol (×) and water (⊙) on AlPO$_4$-5 at 303 K.

approach the condensation value of water at a sorption coverage of 1.6 mmol g^{-1}. Furthermore, the initial heat values are found to be comparable with those obtained on highly dealuminated sodium-faujasite-type zeolite [7], indicating a predominantly hydrophobic surface containing isolated hydrophilic sites. While the hydrophilicity of the aluminosilicate zeolite is due to the interaction of water dipoles with the electrostatic field generated by cations and the negatively charged framework, the hydrophilicity in AlPO$_4$-5 can be attributed to the structural defects present in the form of P–OH groups [9].

Sorption isotherms for acetonitrile, ammonia and methanol measured at 303 K are compared with water sorption isotherms in Fig. 3. Unlike for water, all the sorption isotherms are of type I nature as per BDDT classification, reflecting the occurrence of a micropore filling phenomenon. Sorption capacities for acetonitrile and methanol estimated at $p/p' = 0.4$ are found to be 11.8 wt%
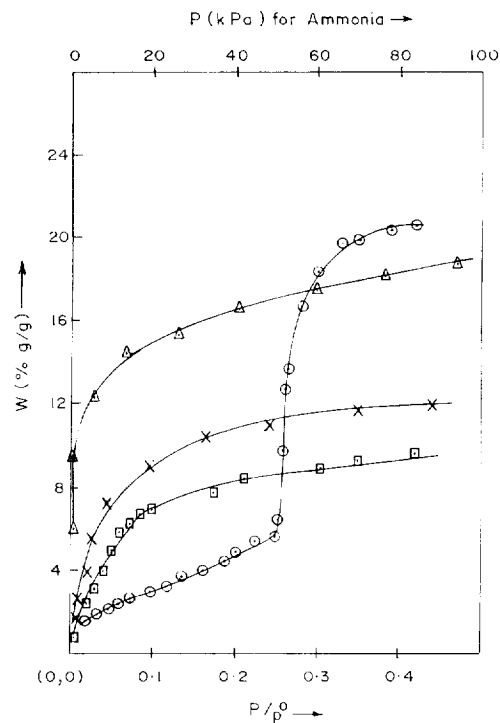
and 9.02 wt% respectively and are much less those obtained for water (21.2 wt%). However, the sorption capacity for ammonia (18.7 wt% at 101.33 kPa) is found to be higher than for other polar sorbates.

4. Discussion

Water sorption on aluminosilicate-type zeolites is often found to be a function of the Si/Al ratio of their framework. Zeolite structures with low Si/Al ratio, like type A, are strongly hydrophilic in nature. This is reflected in a high sorption capacity at very low relative pressure values, resulting in a type I sorption isotherm, whereas for hydrophobic zeolites, like dealuminated zeolites, ultrastable faujasite or silicalite-I, a low water sorption capacity is observed even at high relative pressures.

The trend in water sorption behaviour in the initial region of isotherm, i.e. up to $p/p' = 0.24$ at

303 K, is the consequence of the low hydrophilicity in the $AlPO_4$-5 structure. However, a sharp rise in water uptake beyond this stage indicates the incidence of hydrophilic character on the same surface leading to facile water sorption [2]. Such a dual nature of surface characteristics is unique and not commonly observed in the case of zeolites.

One possible cause for such behaviour can be viewed in terms of the transition of crystal phase, as observed in the case of $AlPO_4$-11 upon hydration by Peeters et al. [10]. However, they have ruled out such a possibility for $AlPO_4$-5 from the X-ray diffraction pattern of its hydrated state [10]. We propose that the apparent change from low hydrophilicity to high hydrophilicity is primarily related to a sorption phenomenon, like capillary condensation in the unique framework of $AlPO_4$-5.

An examination of the structural characteristics of $AlPO_4$-5 is useful for understanding the likely mechanism of capillary condensation in the channels.

$AlPO_4$-5 crystallizes in the hexagonal system with $a = b = 13.7$ Å and $c = 8.47$ Å [11]. Its unit cell has a composition of $Al_{12}P_{12}O_{48}$ and contains 12 alternating tetrahedral oxide units each of Al and P. The structure consists of unidimensional 12-, 6- and 4-membered ring channels parallel to the c-axis [11]. The 12- and 6-membered ring channels have pore diameters of 7.3 Å and 3.0 Å respectively [2] and hence are accessible to water molecules having a critical diameter of 2.65 Å. However, water sorption in the six-membered ring channel is expected to be slow owing to the low hydrophilicity of the framework. It is worth noting that the internal space of the 12-membered ring channel (Fig. 4(a)) is created by the network of six 6-membered windows throughout the channel length. Hence, the internal surface of a 12-membered ring channel on which water molecules can be sorbed is generated only after complete, or at least partial, filling of the surrounding six 6-membered ring channels. In other words, for molecules smaller than 3 Å the 12-membered ring channel cannot be considered as a sorption space at the initial stage of the sorption. Alternatively, water molecules can be thought to be sorbed by coordinating themselves with the framework alu-
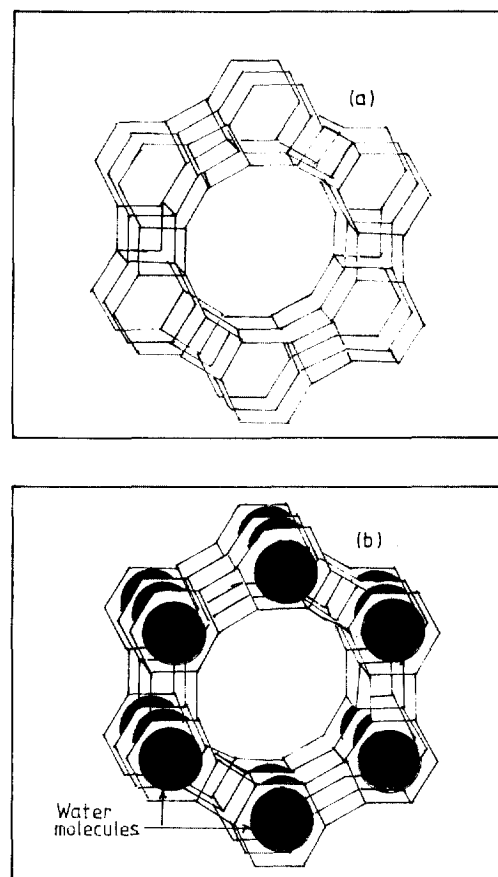

Fig. 4. Pictorial representation of a 12-membered ring channel of $AlPO_4$-5: (a) internal surface at dehydrated state; (b) at a sorption coverage of 3 mmol g^{-1} (about four molecules/u.c.).

minium atoms. However, this would lead to the formation of penta-coordinated and/or octahedral Al which have been only noticed after 5–6% (3–4 mmol g^{-1}) of water sorption by Meinhold and Tapp [12] from solid state Al NMR studies. Furthermore, a recent study of water sorption by Davis and coworkers [13] based on inelastic neutron scattering and molecular dynamics simulation has also shown that such an event is unlikely to occur in the initial stage of sorption. Therefore, it is logical to believe that the generation of higher coordinated Al is the consequence of water sorption and not the cause for the generation of hydrophilicity. Hence, water molecules are proposed to sorb in the six-membered ring channels at the initial stage of sorption as, in the absence

of specific sites, the sorption in the six-membered ring channel is possible due to energetically favoured conditions [5]. Furthermore, it is expected that the amount sorbed in this region will be small because the pore volume of six-membered ring channel is low ($0.06 \, cm^3 \, g^{-1}$) [11]. Such behaviour is indeed observed at all experimental temperatures. After the six-membered ring channels are occupied, either partially or completely, the sorption in a 12-membered ring channel is expected to occur by capillary condensation, which would set in with the fulfilment of conditions as per the Kelvin equation applicable for a cylindrical capillary having both its ends open:

$$\ln p/p = -\gamma V_1 \cos \theta / r_c RT$$

where γ is the surface tension of sorbate. V_1 is the molar volume of sorbate. r_c is the radius of the capillary. R is the gas constant, T is the experimental temperature in kelvin and θ is the contact angle between the sorbate and sorbent and assumed to be 0.

The estimated relative pressure values, p/p, at which the condensation of water would occur in a 12-membered ring channel of $AlPO_4$-5 are 0.245, 0.263, 0.280 and 0.297 at 303 K, 313 K, 323 K and 333 K respectively. These are in close agreement with the experimentally observed values of 0.250, 0.262 and 0.279 at 303 K, 313 K, 323 K respectively, which confirms the presence of a capillary condensation phenomenon in the 12-membered ring channels of $AlPO_4$-5.

Therefore, it is believed that the point of inflection corresponds to the setting in of the capillary condensation. The unit cell of $AlPO_4$-5 consists of two six-membered ring channels having a pore volume of $120 \, Å^3$. Assuming liquid-like packing of the sorbed phase in the six-membered ring channel and considering a molecular volume of $30 \, Å^3$ (estimated from molar volume), four water molecules are required to saturate the unit cell. It is interesting to note that this value agrees well with the observed sorption value at the point of inflection. Furthermore, a closer look at the construction of a 12-membered ring channel reveals that it is made up of six 6-membered ring channels (i.e. three unit cells). At the point of inflection, the saturation of six 6-membered ring channels will

hydrate the walls of a 12-membered ring channel and facilitate the capillary condensation. In other words, at this stage the 12-membered ring channel can be viewed as an open capillary and lined with water molecules (Fig. 4(b)). This would induce a hydrophilic character throughout the channel length and thus reinforce the presence of a capillary condensation phenomenon beyond a coverage of $3 \, mmol \, g^{-1}$ when six-ring channels are filled with water molecules. It is observed from Fig. 1(a,b) that there is a sharp rise in water sorption at around this coverage.

Thus, water sorption isotherms in $AlPO_4$-5 obtained at 303 and 313 K can be divided into two regions, i.e. a region up to $3 \, mmol \, g^{-1}$ where the sorption essentially takes place in a six-membered ring channel and followed by a sorption in a 12-membered ring channel via capillary condensation. As the sorption isotherm is measured up to $p/p = 0.18$ at 333 K, the condensation phenomenon is not observed at this temperature.

Additional evidence for the proposed mechanism is provided in the form of isosteric heats of water sorption. The dependence of isosteric heats can be explained by considering the proposed two-stage sorption. The initial region in the heat curve is attributed to sorption in a six-membered ring channel. Thus, the high initial heats in the low coverage might be due to the specific interaction of water molecules with P–OH groups present in a six-membered ring channel [9] coupled with a strong influence of overlapping potential of this channel, as sorbate dimensions are very close to the channel diameter. A sharp drop in the heat values up to the heat of condensation of water around $1.6 \, mmol \, g^{-1}$ of loading indicates the absence of specific interactions and the interactions between adjacent water molecules in a hydrophobic environment of the six-membered ring channel.

The near constancy in the heat values ($\approx 52 \, kJ \, mol^{-1}$) above $3 \, mmol \, g^{-1}$ indicates the sorption in a 12-membered ring channel and reflects the influence of a condensation phenomenon. However, the heat values are found to be higher than the heat of water condensation value of $40.6 \, kJ \, mol^{-1}$ which is expected when water molecules are confined in a narrow capillary where

overlapping potentials from the walls are experienced.

According to the proposed sorption mechanism, any sorbate with molecular size less than 3 Å is likely to observe a sorption behaviour like water on $AlPO_4$-5. Acetonitrile and methanol (critical diameters >3Å) cannot diffuse inside a six-membered ring channel and are sorbed only into a 12-membered ring channel which provides the sorption space. Thus, the sorption of these sorbates is followed via a pore-filling mechanism and results in a type I isotherm. Ammonia having a critical diameter of 2.65 Å, less than the six-membered ring channel opening, would be expected to sorb into these channels and a similar sorption mechanism to water is expected to prevail. However, the ammonia molecule, being a stronger base and ligand than water, probably coordinates with framework aluminium of 6- and 12-ring channels, thus resulting in a type I isotherm. Solid state NMR studies have also shown the ability of ammonia molecules to coordinate with framework aluminium [5]. Furthermore, the number of ammonia molecules sorbed per unit cell is close to the number of aluminium atoms per unit cell which also reflects the nature of ammonia molecules. The non-facile desorption of ammonia at experimental conditions also reflects the coordinating ability of ammonia molecules. The high sorption capacity for ammonia further confirms the accessibility of six-membered ring channels for ammonia molecules. Furthermore, the absence of an inflection point in the sorption isotherm is expected as ammonia cannot be condensed at experimental conditions.

Our results show that the peculiar water sorption isotherm in $AlPO_4$-5 is related to its structural character, i.e. the presence of unidimensional six- and four-membered ring channels in its structure. In other words, the presence of six- and four-membered ring unidimensional channels is responsible for such mechanism. Hence, such a mechanism is also expected to prevail during the water sorption on $AlPO_4$-11 and VPI-5, as the structural characters of these molecular sieves are similar to that of $AlPO_4$-5 [11]. To investigate this aspect we have measured water sorption isotherms on $AlPO_4$-11 at 303 and 313 K (Fig. 5). Isosteric heats

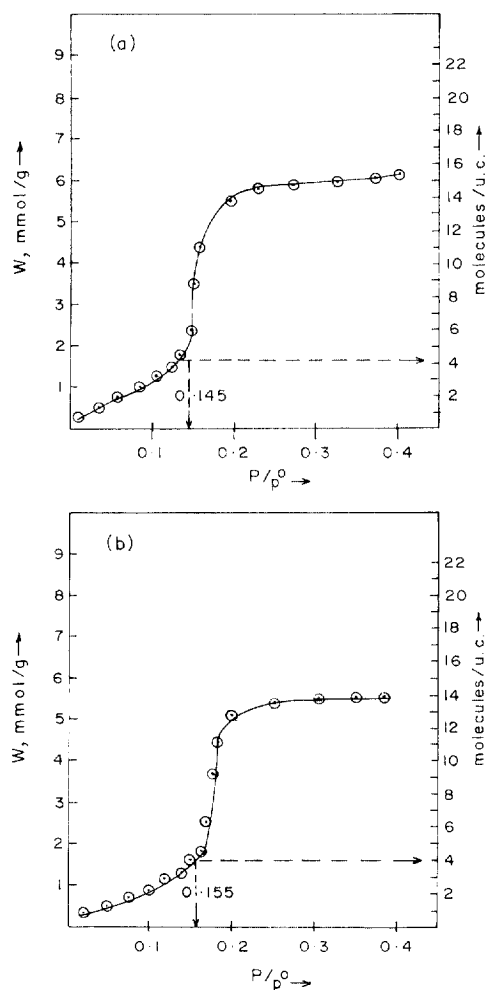Fig. 5. Water sorption isotherm on $AlPO_4$-11 at (a) 303 and (b) 313 K.

of water sorption, ΔH, are also estimated by applying the Clausius–Clapeyron equation using the sorption data at 303 and 313 K (Fig. 2). Interestingly, a similar water sorption behaviour is observed on $AlPO_4$-11. Like $AlPO_4$-5, a sharp rise in the water uptake is observed at a sorption coverage of around four molecules/u.c (1.6 mmol g^{-1}). However, the observed rise in the water uptake is noticed at lower p/p values, i.e. at $p/p = 0.145$ and $p/p = 0.155$ at 303 K and 313 K respectively. This behaviour is readily explained on the basis of the structural characteristics of $AlPO_4$-11, which crystallizes in the orthorhombic

system with $a = 8.37$ Å, $b = 18.5$ Å and $c = 13.5$ Å. It has a ten-membered ring channel which is surrounded by four- and six-membered ring channels and the primary sorption space consists of ten-membered and six-membered ring channels. As in $AlPO_4$-5, water sorption is expected to occur in six-membered rings to begin with, followed by the capillary condensation in the ten-membered ring channel. Therefore, the p/p value required for the condensation phenomenon to occur in the ten-membered ring channel has been estimated using the Kelvin equation, by assuming a mean pore diameter[1] of ~ 5 Å. It is noteworthy that there is good agreement between the estimated (0.135 at 303 K and 0.145 at 313 K) and observed p/p values. Furthermore, the estimated sorption capacity of a six-membered ring channel/u.c. is also found to be around four molecules/u.c., i.e. ≈ 1.6 mmol g^{-1}. Therefore, we believe that the initial sorption (up to 1.6 mmol g^{-1}) occurs in six-membered ring channels followed by sorption in the ten-membered ring channel via a condensation mechanism. The dependence of the isosteric heat of water sorption also provides additional support for the proposed sorption mechanism. The sharp decrease in heat of sorption value (Fig. 2) up to 1.6 mmol g^{-1} can be attributed to the sorption in six-membered ring channels. The higher initial heat of sorption for $AlPO_4$-11 (110 kJ mol^{-1}) compared with that of $AlPO_4$-5 (88–89 kJ mol^{-1}) might result from the higher framework density of the former [11]. The heat of sorption beyond a sorption coverage of 2.0 mmol g^{-1}, which is nearly constant (≈ 56 kJ mol^{-1}), corresponds to water condensation in the ten-membered ring channel of $AlPO_4$-11.

Although the proposed sorption mechanism is expected to prevail on VPI-5, which also contains four-membered and six-membered ring channels, owing to the presence of specific hydrophilic sites in the form of an octahedral framework aluminium atoms [5,13] and the unique structure of water [5] in its microporous framework, water sorption in the six-membered ring channel at the initial stage

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[1]For elliptical pores the mean pore diameter is given by $(l_1 l_2)^{1/2}$, where l_1 (6.3 Å) and l_2 (3.9 Å) are respectively the pore diameters along the major and minor axes of an elliptical pore.

of sorption is unlikely to occur. Thus the water sorption in an 18-membered ring channel is not expected to be driven by a condensation mechanism. The reported water sorption isotherm [14] at 298 K also shows the absence of such a step.

5. Conclusion

We have shown that the typical water sorption behaviour observed in $AlPO_4$-5 is related to its structural characteristics and results from pore filling of six-membered ring channels followed by the capillary condensation in 12-membered ring channels.

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