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Sorption of C_6 Alkanes in Aluminophosphate Molecular Sieve, $AlPO_4$-5

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Abstract. Sorption of C_6 alkanes viz., *n*-hexane, 2-methylpentane, 2,2-dimethyl butane, 2,3-dimethyl butane, cyclohexane and methyl cyclopentane in $AlPO_4$-5 is studied and sorption capacity and thermodynamic parameters (ΔH^0, ΔH, ΔG, ΔS and S_a) at various sorption coverage for these sorbates have been estimated. The initial heat of sorption (ΔH^0) is found to increase with the degree of branching in the alkane chain. The sorbate-sorbate interactions are found to be more prominent during the sorption of doubly branched alkanes and cyclic alkanes and a higher sorption capacity has been observed for cyclic alkanes. Based on the results obtained, a packing model has been proposed for various C_6 alkanes inside the $AlPO_4$-5 channel.

Keywords: $AlPO_4$-5, C_6 alkanes sorption, sorption energetics

1. Introduction

The advent of aluminophosphate molecular sieves has offered many novel microporous frameworks that can be subjected to potential applications (Wilson et al., 1982). $AlPO_4$-5 is a member belonging to this family and being neutral in nature, its framework offers a unique opportunity to understand the role of structure type as well as size and shape of molecules, on sorbate-sorbent interactions. Therefore, it is of interest to investigate the sorption of non-polar sorbates like linear, branched and cyclic alkanes on $AlPO_4$-5. In this respect, studies reported so far have mainly dealt with the sorption of linear alkanes (Stach et al., 1986; Choudhary et al., 1988; Santilli et al., 1993; McCullen et al., 1993). Recent investigation (Eder and Lercher, 1996) on the sorption of linear and isoalkanes on $AlPO_4$-5 and its all-silica analogue SSZ-24 have shown a similar sorption energetics for both the molecules. In contrast, theoretical calculations (Santilli et al., 1993) have suggested an increased sorbate-sorbent interactions for isoalkanes. Furthermore, no report has appeared on the sorption of cyclic (except cyclohexane) and substituted cyclic alkanes on $AlPO_4$-5. In this context, we have initiated a systematic study on the sorption of various alkanes. The sorption study of C_5 alkanes (Newalkar et al., 1997) viz. namely *n*-pentane, 2-methyl butane and cyclopentane, has shown a higher interaction between 2-methyl butane and $AlPO_4$-5 surface which is in contrast to the results reported earlier (Eder and Lercher, 1996). Furthermore, a higher sorption capacity is obtained for cyclopentane over

n-pentane and 2-methyl butane, which has suggested a stacked type molecular orientation for the sorbed phase of cyclic alkane along the $AlPO_4$-5 channel. In order to confirm these observations in terms of the effect of branching and molecular packing, we have investigated the sorption of linear, branched and cyclic C_6 alkanes at several temperatures. In the present paper, the results of this study are reported and discussed.

2. Experimental

2.1. Materials

$AlPO_4$-5 was synthesized hydrothermally from a gel with a composition of $1.5Pr_3N : 1.0Al_2O_3 : 1.0P_2O_5 : 40H_2O$ at 423 K, using tripropyl amine as the template (Wilson, 1991). Pseudoboemite (Catapol B, Vista Chemicals, USA) and phosphoric acid (85 wt%, Riedel-de Häen, Germany) were used as aluminium and phosphorus source respectively. The synthesized sample of $AlPO_4$-5 was calcined at 813 K for 12 h under air flow (100 ml/min) to remove the occluded template molecules. Thus obtained sample was characterized with respect to crystallinity, purity and morphology using X-ray powder diffraction (Ni filtered CuK_α radiation, Rigaku Dmax III), water sorption (McBain gravimetric balance) at 298 K and scanning electron microscopy method (Jeol, JSM-35C). The recoded X-ray diffraction pattern ensured the high crystallinity as well as purity of the sample and showed the complete absence of undesired phases. Similarly, the water sorption capacity of 12.2 mol/kg obtained for synthesized sample at $p/P^0 = 0.4$ was found to be in close agreement with the literature data (Wilson et al., 1983). A polycrystalline nature of the sample with platelet like morphology was observed from SEM study (Fig. 1).

n-Hexane (n-C_6); 2-Methylpentane (2-MP); 2,2- and 2,3-Dimethylbutane; (2,2-DMB; 2,3-DMB); Cyclohexane (CH) and Methyl cyclopentane (MCP) used in this study were procured from Fluka A.G. (>99% purity,) and were used without further purification. The molecular dimensions of these sorbates are compiled in Table 1. All sorbates were pre-treated by freeze-pump-thaw cycles before use to remove air or other dissolved gases, if any.

Table 1. Molecular dimensions of C_6 alkanes used as sorbates.

Sorbate	Critical diameter (Å)	Molecular length (Å)
n-C_6	4.9	10.36
2-MP	5.4	9.40
2,2-DMB	6.3	8.10
2,3-DMB	6.1	8.10
CH	6.9	6.90
MCP	6.4	7.50

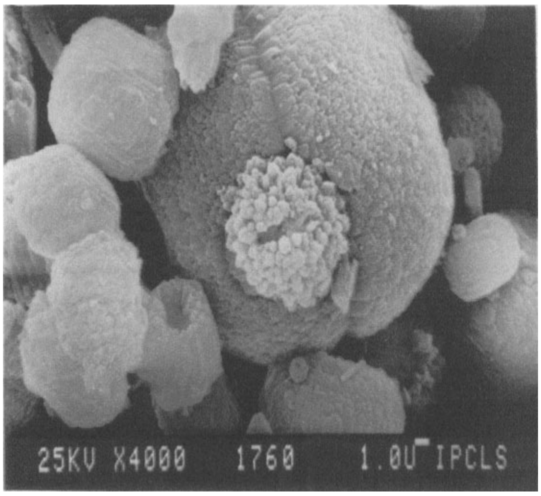


Figure 1. Scanning electron micrograph of $AlPO_4$-5 sample.

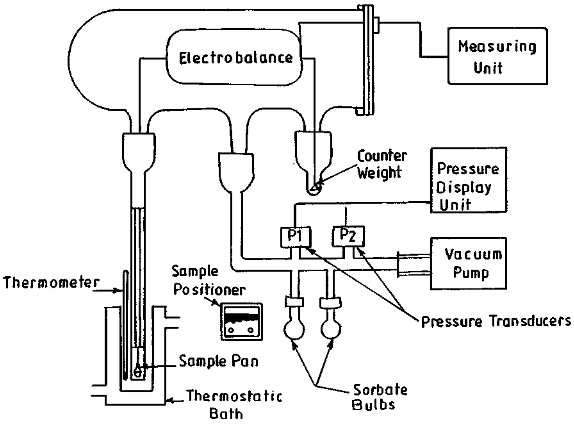


Figure 2. A pictorial representation of experimental set up.

2.2. Sorption Measurements

Gravimetric sorption measurements were made using a Cahn 2000 vacuum electrobalance (Fig. 2) at 303, 313, 323 and 333 K. Prior to sorption measurement, about 25 mg of $AlPO_4$-5 sample was activated under high vacuum (ca. 10^{-4} Pa) at 623 K for >24 h. The temperature of the sorbent during sorption measurement was controlled to ±0.1 K by circulating water from a constant temperature water bath (Julabo model F30 Ultra Temp 2000). 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 accuracy of ±0.5% of the reading. The time required to achieve sorption equilibrium was found to vary from 0.5 to 3 h depending on the shape and size of sorbate and sorption coverage. Equilibrium was assumed to be attained when the weight of the sample was held constant within ±0.01 mg for at least 30 min.

3. Results and Discussion

3.1. Sorption Isotherms and Capacities

The measured sorption isotherms for *n*-hexane; 2-methylpentane; 2,2-dimethylbutane; 2,3-dimethyl butane; cyclohexane and methyl cyclopentane at 303 K are shown in Fig. 3. A sharp rise in uptake in the low pressure region is observed which indicates the presence of micropore filling phenomenon. However, sorption isotherms did not attain a plateau (as expected for microporous solid) even at relative pressure value exceeding 0.2 and showed an increasing trend in the sorption uptake. A similar observation was made earlier for polycrystalline $AlPO_4$-5 sample and is attributed to the sorption in mesopores present in the sample (Chiang et al., 1991). Consequently, the micropore sorption capacity of $AlPO_4$-5 could not be estimated from any limiting value in the sorption isotherms. However, micropores are expected to be fully occupied by sorbate at $p/P^0 < 0.2$ (Gregg and Sing, 1982). So, micropore sorption capacities of $AlPO_4$-5 were estimated by fitting the sorption isotherm data, into Langmuir isotherm,

$$p/W = 1/B + p/V_{\mathrm{m}} \tag{1}$$

and Dubinin-Radushkevich isotherm

$$\ln[W] = \ln[W_0] - D \cdot (\ln[P^0/p])^2 \tag{2}$$

where p and P^0 are equilibrium and saturation pressures of sorbate at experimental temperatures, W is the amount sorbed, B and D are constants, V_{m} and W_0 are the sorption capacities. D is a constant consisting of $B \cdot T/\beta^2$, where B is a characteristic of sorbent pore structure and is independent of temperature and β is the affinity coefficient. T is the experimental temperature. In both these cases sorption data points are considered only up to $p/P^0 \approx 0.2$ by which all the micropores are expected to be occupied. The values of sorption capacities V_{m}, W_0 and constants B, D obtained from the intercept and slopes respectively along with standard deviation values are given in Table 2. A good corelation is observed between the two estimated sorption capacities values. However, in the case of Dubinin-Radushkevich isotherm, a better fit was observed than Langmuir isotherm. Hence, the sorption capacities derived from Dubinin-Radushkevich constants are used for discussion in the present study.

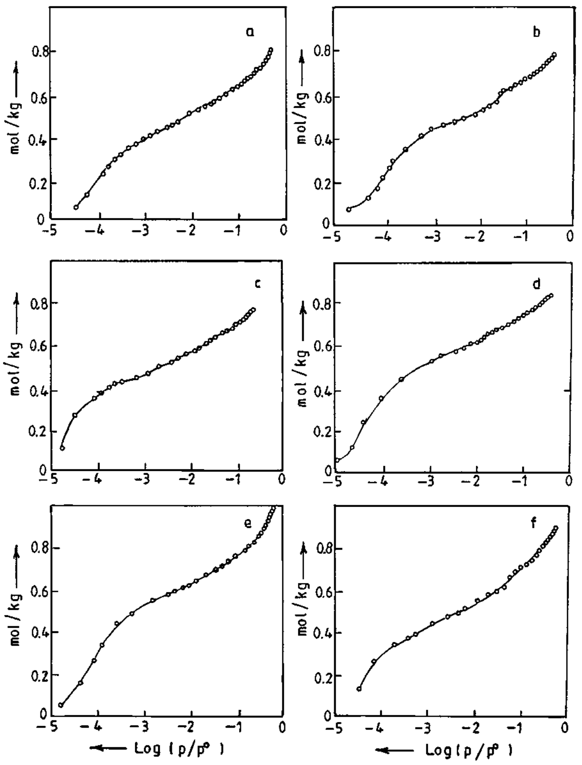


Figure 3. Sorption isotherms of *n*-hexane (a); 2-methyl pentane (b); 2,3 dimethyl butane (c); 2,2 dimethyl butane (d); cyclohexane (e) and methyl cyclopentane (f) at 303 K.

The following trend was observed for sorption capacities at 303 K,

$$\begin{aligned}\text{CH} > \text{2,2-DMB} \approx \text{2,3-DMB} > \text{2-MP}\\ \approx \text{MCP} > n\text{-C}_6\end{aligned}$$

This trend, except for methyl cyclopentane, is noticed at all experimental temperatures. The sorption capacities for methyl cyclopentane at 313, 323 and 333 K are

Table 2. Estimated sorption capacity of $AlPO_4$-5 and fitted Langmuir and Dubinin-Radushkevich parameters for various C_6 alkanes.

Temperature	Langmuir			Dubinin-Raduskavich		
(K)	V_m (mol/kg)	B (K Pa^{-1})	Std. dev	W_0 (mol/kg)	$D \times 10^2$ (mol/kg/K)	Std. dev
			n-Hexane			
303	0.67	15.2	0.12	0.67	1.25	0.014
313	0.62	18.8	0.10	0.65	1.40	0.015
323	0.60	12.2	0.09	0.64	1.58	0.019
333	0.61	6.65	0.07	0.66	1.85	0.022
			2-Methylpentane			
303	0.71	10.5	0.14	0.72	1.19	0.027
313	0.69	8.25	0.12	0.69	1.01	0.013
323	0.68	7.71	0.11	0.71	1.29	0.020
333	0.64	6.27	0.08	0.69	1.31	0.014
			2,3-Dimethylbutane			
303	0.74	14.7	0.11	0.75	0.76	0.013
313	0.69	25.7	0.09	0.72	0.72	0.011
323	0.67	17.9	0.09	0.73	0.96	0.013
333	0.68	10.5	0.11	0.71	1.41	0.032
			2,2-Dimethylbutane			
303	0.76	24.5	0.15	0.76	0.75	0.014
313	0.70	20.6	0.13	0.75	0.84	0.009
323	0.71	10.2	0.12	0.76	0.99	0.022
333	0.67	14.3	0.08	0.73	1.37	0.034
			Cyclohexane			
303	0.85	9.29	0.17	0.82	0.98	0.033
313	0.77	9.36	0.136	0.76	0.99	0.022
333	0.67	8.48	0.12	0.70	1.16	0.098
			Methylcyclopentane			
303	0.74	10.5	0.14	0.72	1.18	0.029
313	0.94	11.2	0.20	0.95	1.12	0.027
323	0.87	11.7	0.15	0.91	1.23	0.018
333	0.85	9.55	0.12	0.89	1.43	0.034

found to be higher than that of the value obtained at 303 K. Interestingly, the observed trend in the sorption capacity for linear and branched alkanes has shown the influence of molecular length i.e. the sorption capacity is found to increase with a decrease in molecular length of the alkane molecule (Table 2). Like cyclopentane (Newalkar et al., 1997) a higher sorption capacity for cyclohexane is also observed. These results have reflected the role of molecular dimensions, shape and orientation for having a stacked type of packing for the sorbate molecule. Such roles are discussed in the following sections.

3.2. *Heat of Sorption at Zero Coverage (ΔH^0)*

The heat of sorption values at zero coverage or the initial heat, ΔH^0 (Table 3) for C_6 alkanes were estimated using the Henry constants, (K), in the temperature

Table 3. Estimated Henry constants, (K) and initial heat values (ΔH^0) for C_6 alkanes.

	Henry's constants, K (mol/kg/Pa) Sorbates					
Temperature (K)	n-C_6	2-MP	2,2-DMB	2,3-DMB	MCP	CH
303	12.3	15.8	—	25.1	21.0	29.0
313	7.02	9.12	13.0	12.0	9.97	9.25
323	3.38	4.46	6.0	4.53	5.88	—
333	2.33	2.39	2.8	2.03	3.40	3.50
	Initial heats of sorption (ΔH^0, kJ/mol)					
	56.5	62.2	67.8	66.5	53.6	57.2
C.C.[a]	0.989	0.995	0.999	0.995	0.996	0.985

[a]Correlation coefficients.

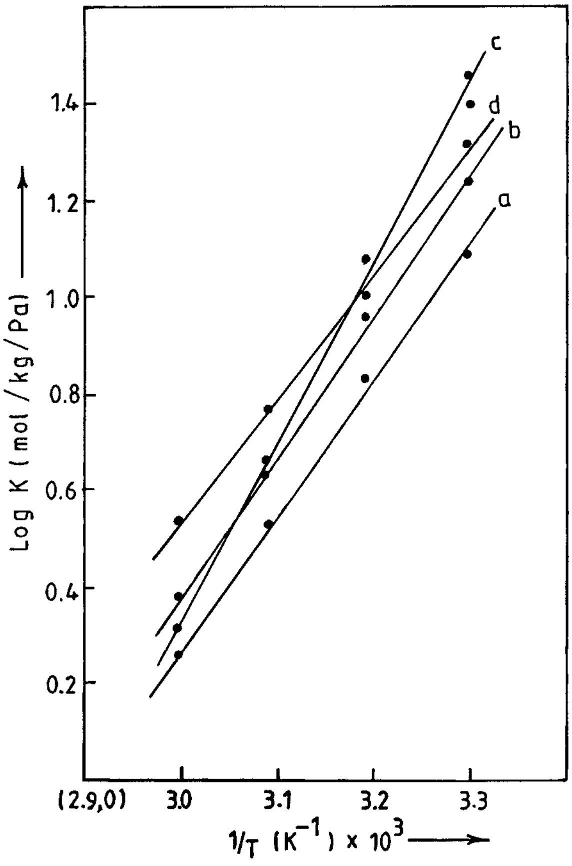


Figure 4. van't Hoff plot of n-hexane (a); 2-methyl pentane (b); 2,3 dimethyl butane (c); and methyl cyclopentane (d) on $AlPO_4$-5.

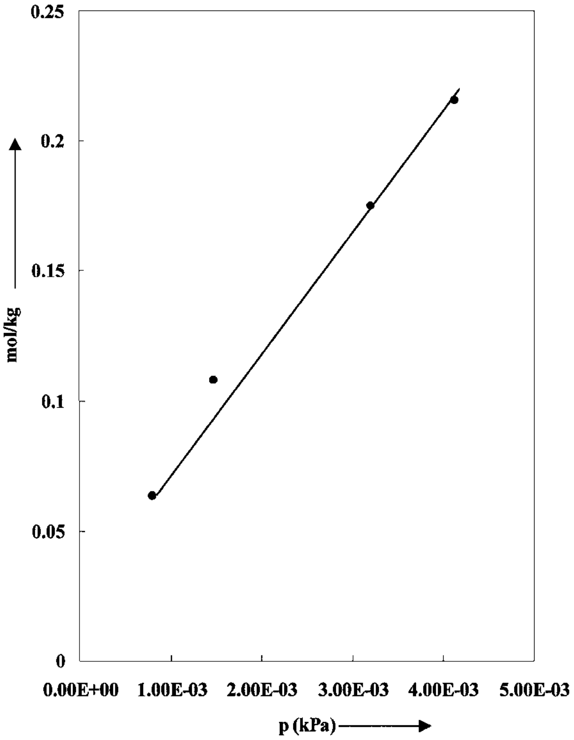


Figure 5. A plot of low pressure sorption data against sorbed amount for n-hexane at 303 K.

range from 303 to 333 K by linear regression of van't Hoff equation (Fig. 4),

$$K = K_0 \exp(-\Delta H^0/RT), \tag{3}$$

where R is a gas constant, K_0 is the pre-exponential factor for sorbate and T is the experimental temperature in Kelvin. The Henry constants were determined graphically (Fig. 5) from the low pressure sorption data and using the relation

$$W = K \cdot p \tag{4}$$

where W is the amount sorbed in mol/kg, p is the equilibrium pressure in pascal and K is the Henry constant.

The estimated $-\Delta H^0$ values for various C_6 alkanes are compiled in Table 3 along with the correlation coefficients and are found to be of the following order,

$$2,2\text{-DMB} \approx 2,3\text{-DMB} > 2\text{-MP} > \text{CH} \approx n\text{-}C_6 > \text{MCP}$$

This trend is in agreement with the observation made earlier on C_5 alkanes sorption in $AlPO_4$-5 where initial heats of sorption for n-pentane (49 kJ/mol) is found to be less than that of 2-methylbutane (54 kJ/mol) and is comparable with cyclopentane (51 kJ/mol) (Newalkar et al., 1997). Furthermore, the initial heat for methyl cyclopentane is found to be higher than that obtained for cyclopentane by 3 kJ/mol. Interestingly, the affinity for branched alkanes is found to increase with degree of branching, as seen from the higher heat of sorption values for 2,2-dimethyl butane and 2,3-dimethyl butane compared to 2-methyl pentane.

By comparing the initial heats for C_6 and C_5 alkanes, one can find the contribution of methylene group in the initial heat values as given below,

$-CH_2-$ in linear and singly branched alkane	≈8 kJ/mol
$-CH_2-$ in doubly branched alkane (present in the side chain)	≈12.5–13.8 kJ/mol
$-CH_2-$ in cyclic alkane (present in the side chain)	≈3 kJ/mol
$-CH_2-$ in the ring in cyclic alkane	≈6 kJ/mol

Above results can be explained based on the structure of $AlPO_4$-5 and nature of molecular interactions occurring within its channels.

The microporous framework of $AlPO_4$-5 consists of uni-directional cylindrical channels of 6 and 12-membered rings having uniform cross-sections of 3 and 7.3 Å respectively, along the C-axis. It has a hexagonal symmetry with unit cell parameters, $a = b = 13.7$ Å and $c = 8.47$ Å (Bennett et al., 1983). So, C_6 alkanes will be sorbed only in the 12-ring channels and are expected to orient in such a manner which would lead to maximization of their interactions with the channel walls of $AlPO_4$-5. Furthermore, owing to the neutral nature of the sorbent surface, the sorption of these molecules would be governed by the non-specific Vander waals forces of attraction with the surface of the sorbent (Barrer, 1978). Such interactions will essentially depend on the number of hydrogen atoms present in the sorbate molecule and hence are expected to be of similar magnitude for linear and branched C_6 alkanes. But, the observed initial heat values for 2-MP; 2,2-DMB; 2,3-DMB and n-C_6 reflect greater non-specific interaction of branched alkane molecules with the surface. This phenomenon can be attributed to the influence of confinement effect of 12-ring channel on the sorbate molecule and is expected to increase as the molecular size of sorbate molecule approaches the channel dimensions or when pore size of the zeolitic framework approaches the molecular dimensions of the sorbate molecule (Derouane, 1993). As a consequence, molecules of 2-MP; 2,3-DMB and 2,2-DMB having critical diameters of 5.4, 6.1 and 6.3 Å respectively (Table 1), will exhibit increasingly higher initial heats of sorption which has been experimentally observed. Similar observations are also reported on SSZ-24 which is an all silica version of $AlPO_4$-5 (Santilli et al., 1992). These results are found to be in contrast to those reported earlier (Eder and Lercher, 1996) but are found to be in close agreement with those obtained on the basis of molecular simulation studies (Santilli et al., 1993).

Likewise, cyclohexane and methyl cyclopentane molecules are expected to sorb in a chair and half chair conformations respectively, along the channel length of $AlPO_4$-5. Furthermore, a lower interaction energy is expected for cyclic alkane as compared to a linear/branched alkane. But the observed initial heat for cyclohexane is found to be similar to that of n-hexane, while it is found to be marginally less than that of n-hexane for methyl cyclopentane. This observation again reinforces the higher influence of confinement effect on cyclohexane molecule (critical diameter 6.9 Å) compared to methyl cyclopentane molecule (critical diameter 6.5 Å). Thus it would result in lower initial heat value for methyl cyclopentane which is experimentally observed.

These observations suggest that the sorption energetics for C_6 alkanes on $AlPO_4$-5 is controlled by the size and the orientation of the sorbate molecule which similar to pore size dependence observed during the sorption of n-alkanes on all silica zeolites like silicalite, mordenite, faujasite, zeolite A, RHO and ferrierite (Bates et al., 1996). In such cases, initial heat values observed for n-alkanes are found to decrease with an increase in pore diameter from ferrierite to faujasite. To understand the role of pore structure and dimensions in controlling the sorption energetics for alkane molecules on neutral zeolitic frameworks, the observed trend is compared with that reported for C_6 alkanes on silicalite-I (Cavalcante Jr. and Ruthven, 1995). In the latter case the values, (kJ/mol), are in the order,

$$n\text{-}C_6(69.9) > 2\text{-MP}(67.8) > \text{CH}(63.2)$$
$$> 2,2\text{-DMB}(54.4) > 2,3\text{-DMB}(54.4) > \text{MCP}(51.0)$$

Silicalite-I has a 10-ring straight and sinusoidal channel system with dimensions of 5.1 × 5.5 Å and 5.4 ×

5.6 Å respectively (Szostak, 1989). Hence, the influence of overlapping potential on the guest molecules is expected to be higher which is indeed observed in the case of *n*-Hexane. But, as the critical dimensions of branched and cyclic alkanes are higher than the dimensions of silicalite-I channel, these molecules are expected to occupy the more open intersections (≈9 Å) of sinusoidal and straight channels (Cavalcante Jr. and Ruthven, 1995). Hence, the influence of confinement effect is expected to be less on the sorbed molecules in the intersections of the channel which explains the low initial heat values. Interestingly, molecular simulations have also indicated stronger interactions of alkane molecules with unidimensional zeolitic frameworks (free of voids/cavities) having pore diameters ranging from 6.4 to 8.0 Å (Santilli et al., 1993). Thus, the above comparison has highlighted the role of pore structure and dimensions in controlling the confinement effect during sorption on a homogeneous zeolitic surface.

3.3. Dependence of Isosteric Heats, Free Energy Change and Sorbed Phase Entropy on Sorption Coverage

Thermodynamic sorption properties namely iso-steric heats (ΔH), free energy (ΔG) and entropy change (ΔS) and entropy of sorbed phase (S_a) were estimated using the following relations

$$\ln(p) = A - \Delta H/RT \quad (5)$$

$$\Delta G = RT \ln(p/P^0) \quad (6)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (7)$$

$$S_a = S_g + \Delta S \quad (8)$$

where R is gas constant, p is equilibrium pressure at constant surface coverage, T is temperature in Kelvin. P^0 and S_g are the standard pressure (101.33 kPa) and gas phase entropy of the respective sorbate at temperature (T) and A is a constant. A typical representation of iso-steres of *n*-hexane is shown in Fig. 6.

Dependence of the ΔH, ΔG and S_a with sorption coverage is shown in Figs. 7(a)–(f), 8(a) and (b), and 9(a) and (b) respectively. The iso-steric heats values for n-C_6 remained constant (56–57 kJ/mol) upto the loading 0.5 mol/kg before approaching its heat of condensation value as seen in Fig. 7(a). This behaviour indicates a homogeneous nature of $AlPO_4$-5 surface and suggests only marginal sorbate-sorbate interaction. A similar trend is observed for iso-steric heat of sorption for 2-MP Fig. 7(b).

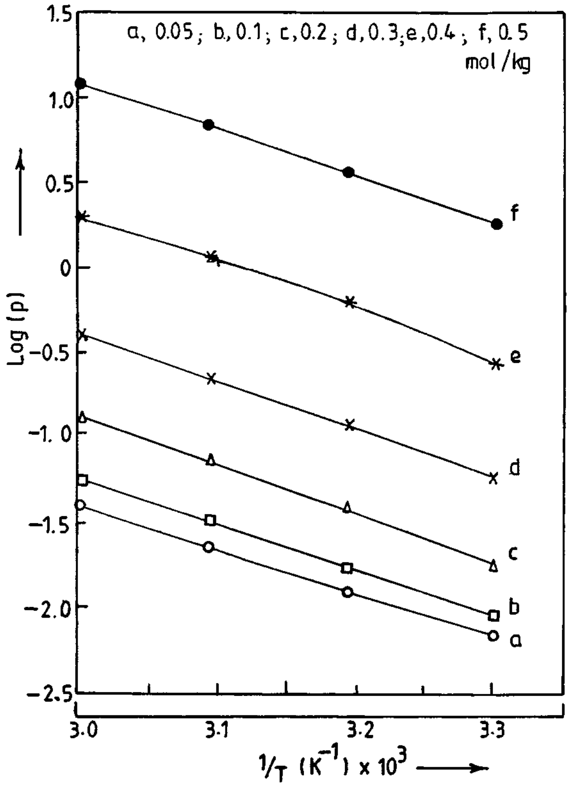
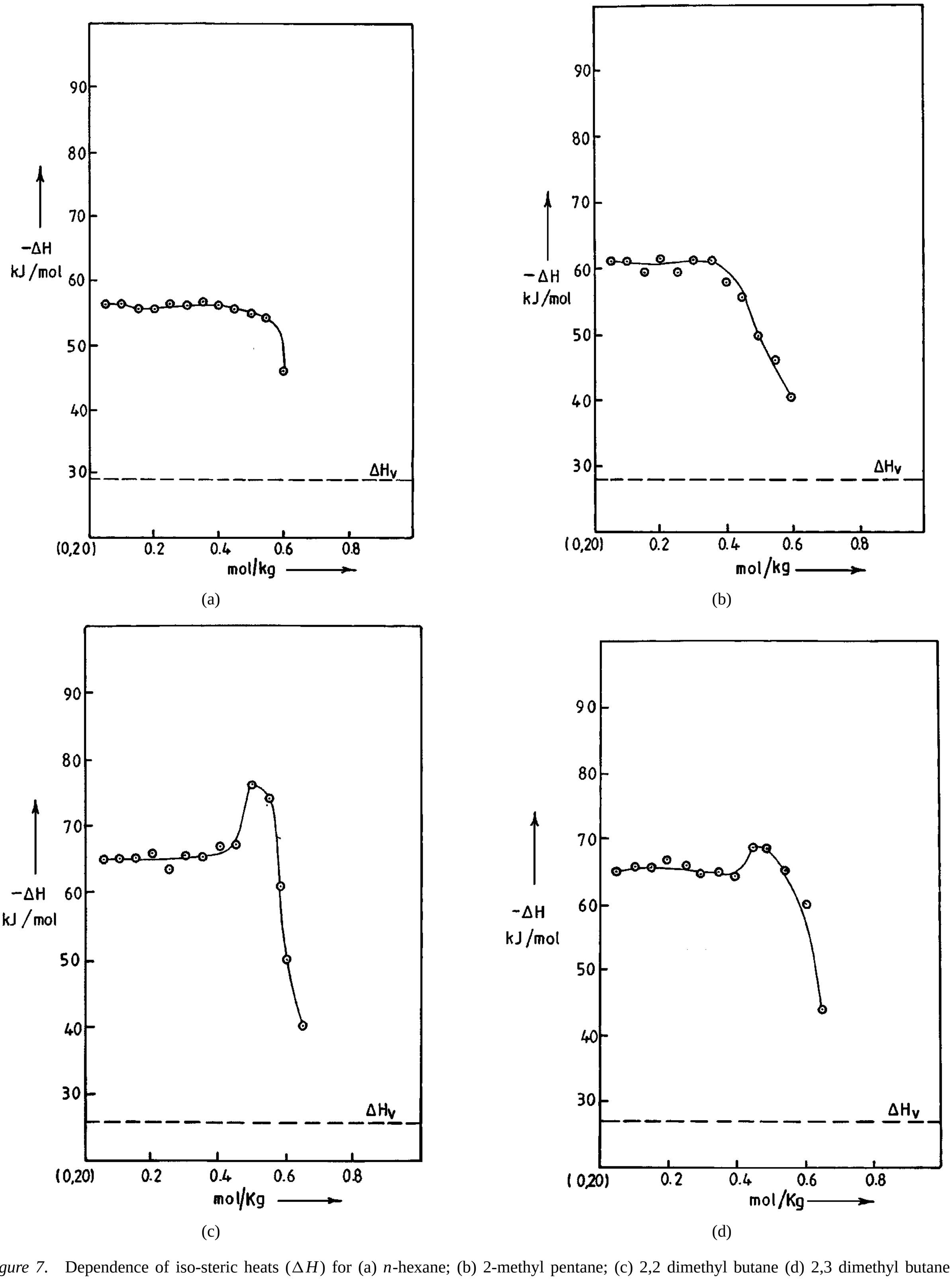


Figure 6. Isosteres of *n*-hexane on $AlPO_4$-5.

$-\Delta H$ values for doubly branched alkanes namely 2,2- and 2,3-DMB remained almost constant upto a coverage of 0.4 mol/kg, followed by an increase of ≈10 and 6 kJ/mol in heat values for 2,2-DMB and 2,3-DMB respectively up to 0.6 mol/kg before approaching the heat of condensation value of respective sorbate (Fig. 7(c) and (d)). This trend in $-\Delta H$ values shows the increasing importance of sorbate-sorbate interactions inside the $AlPO_4$-5 channel.

The heat of sorption for cyclohexane shows a gradual increase up to sorption coverage of 0.40 mol/kg followed by a sharp increase in the sorption coverage in the range of 0.40 to 0.60 mol/kg before falling to the condensation value as shown in Fig. 7(e). A similar behaviour is observed for methyl cyclopentane (Fig. 7(f)) but the value of $-\Delta H$ shows a sharp increase up to 0.65 mol/kg before the steep fall towards the heat of condensation.

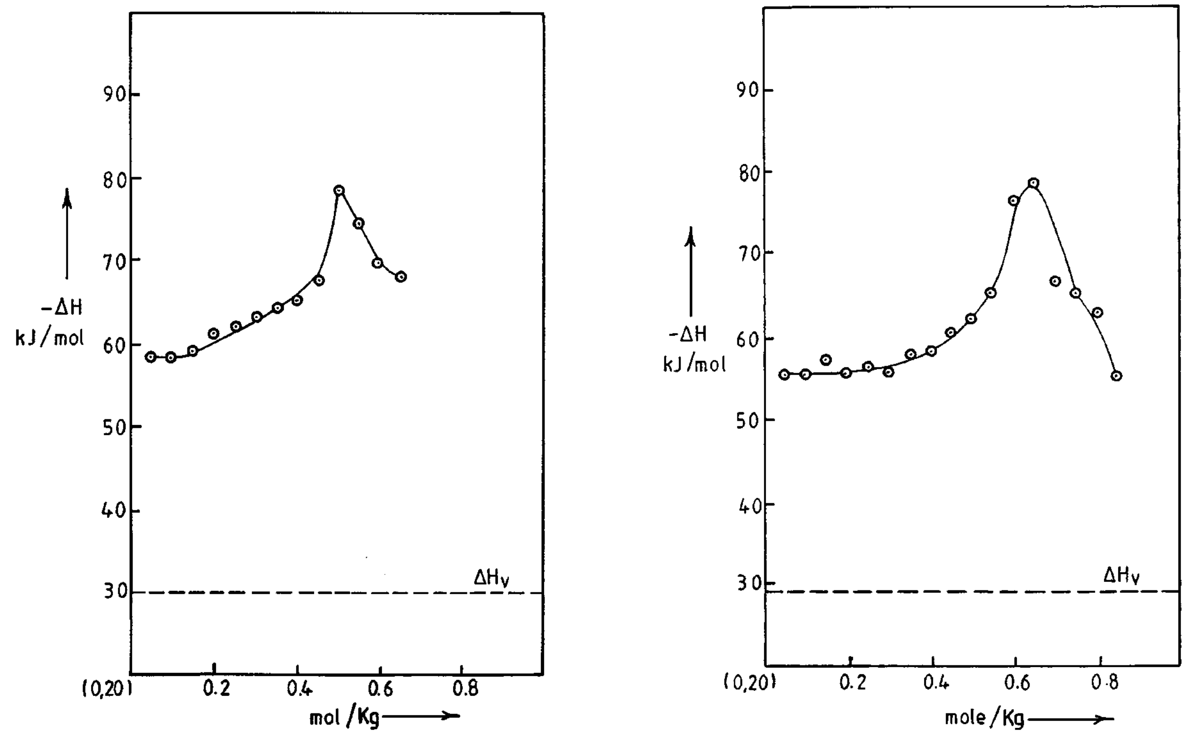
The variation of iso-steric heat value with sorption coverage can be understood in terms of sorbate-sorbate interactions and molecular orientations in the



(a) (b)

(c) (d)

Figure 7. Dependence of iso-steric heats (ΔH) for (a) *n*-hexane; (b) 2-methyl pentane; (c) 2,2 dimethyl butane (d) 2,3 dimethyl butane (e) cyclohexane and (f) methyl cyclopentane on sorption coverage. (*Continued on next page*).



(e) (f)

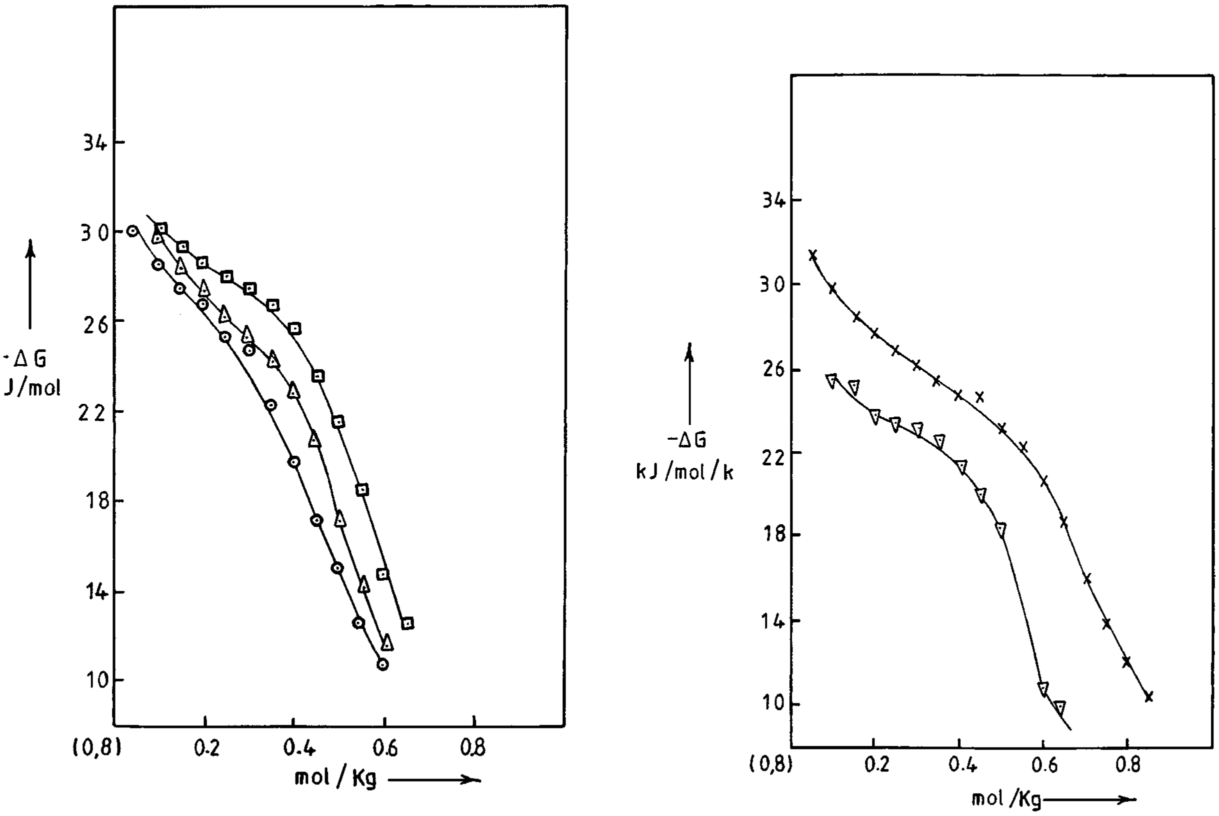
Figure 7. (*Continued.*)

channels of $AlPO_4$-5. Sorbate molecules whose molecular lengths are substantially greater than the channel diameter (7.3 Å) will reside along the channel parallel to C-axis. In such an event the sorbate-sorbate interactions will be minimum and limited to the methyl groups at the terminal positions which is seen from the near constancy in $-\Delta H$ values in the case of n-hexane and 2-methyl pentane. The variation of free energy and sorbed phase entropy for n-hexane and 2-methylpentane with sorption coverage (Fig. 8(a) and 9(a)) also show a gradual decrease supporting the above inference. A similar behaviour is observed for n-pentane sorption in $AlPO_4$-5 (Newalkar et al., 1997).

In the case of doubly branched alkanes, the constancy in the heat values is observed upto 0.4 mol/kg (Fig. 7(c) and (d)), which is similar to that of linear and singly branched alkanes, suggest that the molecules remain isolated with horizontal orientation. Beyond this coverage there is a sharp increase in the heat of sorption associated with a drop in the sorbed phase entropy (Fig. 9(a)), suggesting onset of intermolecular interactions in the sorbed phase.

Hence, it is proposed that the increasing number of methyl groups of the adjacent sorbed molecules participate in this interaction. Interestingly the observed increase in the heat values suggests that three and two pairs of methyl groups of 2,2-DMB and 2,3-DMB respectively participate in the interactions as the estimated dispersion energy between two methyl groups is of the order of $\approx$3 kJ/mol (Atkins, 1982).

In the case of cyclic alkanes, the molecular length is comparable to the diameter of the channel. Hence, molecules have the freedom to adopt a horizontal as well as perpendicular orientation with respect to the channel length (C-axis). The gradual increase in $-\Delta H$ values upto 0.4 mol/kg, suggest the presence of significant sorbate-sorbate interactions and that the number of methylene groups per molecule participating in such interactions increases with the coverage. Such interactions are found to dominate beyond 0.4 mol/kg as a sharp rise in the $-\Delta H$ values is observed (Fig. 7(e) and (f)). A sharp drop in the sorbed phase entropy values of cyclic alkanes beyond 0.4 mol/kg of coverage also indicates the presence of molecular ordering phenomenon



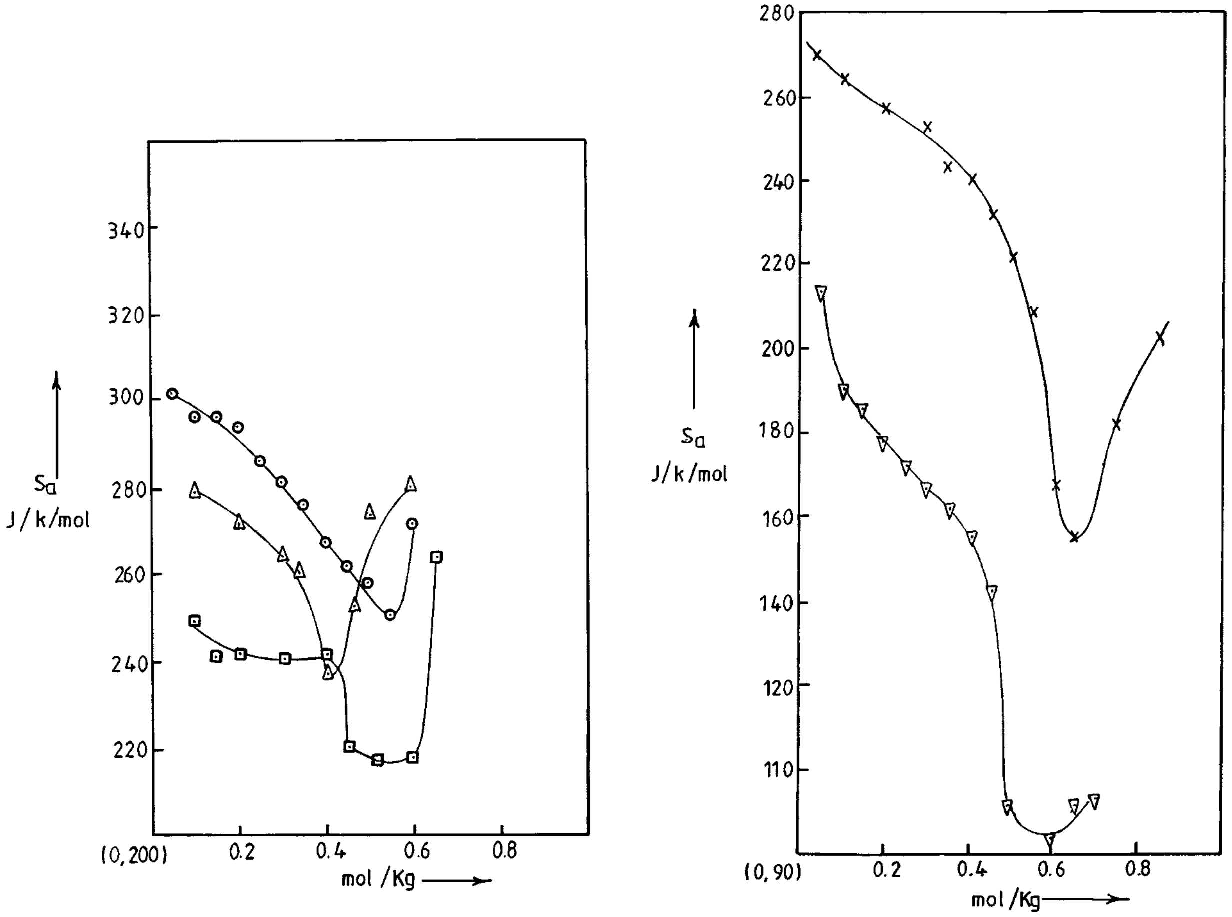
(a) (b)

Figure 8. Dependence of Free energy change ($-\Delta G$) for (a) *n*-hexane (0); 2-methyl pentane (△) and 2,3 dimethyl butane (□); (b) cyclohexane (∇) and methyl cyclopentane (×) with sorption coverage at 303 K.

in the sorbed phase of cyclic alkanes. Furthermore, the observed rise in $-\Delta H$ for cyclohexane and methyl cyclopentane is ≈ 20 and 24 kJ/mol respectively, which is comparable with the cohesive energy densities of these alkanes (i.e. 27 kJ/mol for cyclohexane and 26.5 kJ/mol for methyl cyclopentane) (Reid et al., 1987). Such a situation indicates the occurance of lateral interactions of long range order prevailing among the sorbed phase of cyclic alkanes. Therefore, sorbed phase of these alkanes is proposed to undergo a molecular rearrangement after a sorption coverage of 0.4 mol/kg wherein the molecules are oriented in a stacked manner perpendicular to channel length inside the $AlPO_4$-5. The proposed molecular rearrangement also explains the sharp decrease in S_a (Fig. 9(b)) with coverage and supports the observed high sorption capacity of $AlPO_4$-5 for these alkanes. The proposed molecular orientations for various type of C_6 alkane molecules at various sorption coverage is illustrated in Fig. 10. Thus it can be inferred that the sorption energetics for cyclic alkanes is dominated by intermolecular interaction phenomenon. The role of such interactions is recently addressed (Eder and Lercher, 1997) wherein a prominent role of intermolecular interactions is shown during the sorption of *n*-hexane on high silica-faujasite type of zeolite. Furthermore, the observed rise in the heat values suggests the role of local environment and pore architecture of sorbent on the sorbed phase of cyclic alkanes.

3.4. Sorption of MCP

The sorption capacity for methyl cyclopentane at 303 K is found to be comparable with 2-methyl pentane. However, the sorption capacities of methyl cyclopentane at 313, 323 and 333 K are observed to be higher and are almost comparable with those obtained for cyclopentane (0.95, 0.92 and 0.87 mol/kg respectively) (Newalkar



(a) (b)

Figure 9. Dependence of sorbed phase entropy change, (S_a), for (a) *n*-hexane (0); 2-methyl pentane (△) and 2,3 dimethyl butane (□); (b) cyclohexane (∇) and methyl cyclopentane (×) with sorption coverage at 303 K.

et al., 1997). This is attributed to the different molecular orientation of methyl cyclopentane molecules inside the $AlPO_4$-5 channels. The molecular length of methyl cyclopentane is 7.5 Å which exceeds the channel diameter of 7.3 Å due to which the stacked orientation for methyl cyclopentane molecule inside the $AlPO_4$-5 channel is difficult. So due to steric constraints, methyl cyclopentane molecule is expected to sorb with half-chair conformation along the channel length at 303 K which in turn will result in the observed smaller sorption capacity. However, at higher temperature sorbed phase of methyl cyclopentane may have a stacked orientation due to the combined effect of increased kinetic energy of the methyl cyclopentane molecules and vibration of lattice oxygen atom of $AlPO_4$-5 so as to overcome the steric constraints. So, this trend has shown that the sorption of methyl cyclopentane is kinetically controlled at 303 K, whereas it is thermodynamically controlled at higher temperatures.

The sorption free energy change, $-\Delta G$, for methyl cyclopentane is observed to be higher than that of cyclohexane at all sorption coverages (Fig. 8(b)). On the other hand, $-\Delta H$ of sorption for cyclohexane is found to be more than methyl cyclopentane at all sorption coverages (Fig. 7(e) and (f)). This clearly shows that higher sorption for methyl cyclopentane in $AlPO_4$-5 is entropy driven. Similar sorption behaviour for methyl cyclopentane reported in silicalite-I (Cavalcante Jr. and Ruthven, 1995) has been attributed to greater suppression of molecular rotation of larger cyclohexane inside the silicalite-I channel compared to methyl cyclopentane.

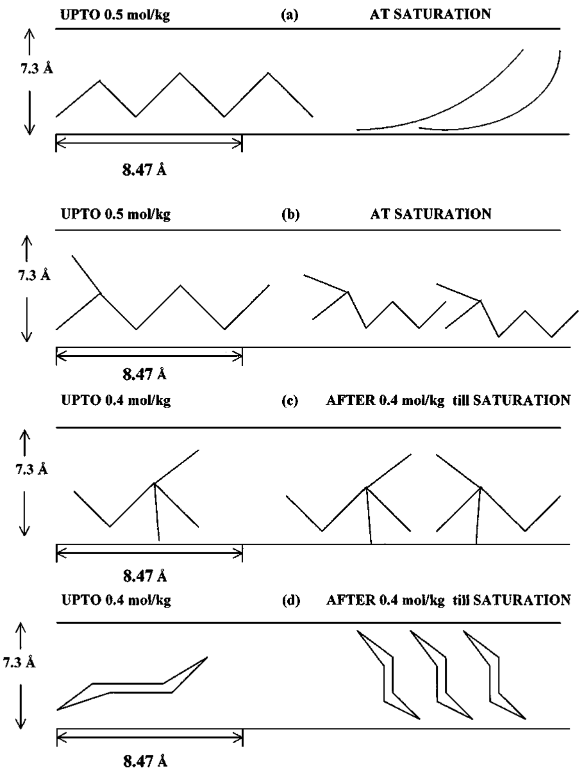


Figure 10. A pictorial representation of molecular orientation of C_6 alkanes viz. (a) linear, *n*-hexane; (b) singly branched, 2-methyl pentane; (c) doubly branched, 2,2-dimethyl butane and (d) cyclic, cyclohexane at various sorption coverage inside the $AlPO_4$-5 channel.

4. Conclusions

From the above study, the following conclusions are drawn:

1. The sorption of branched alkanes is favoured on $AlPO_4$-5 surface and its affinity for branched alkane increases with branching.
2. The sorption energetics for various alkanes is controlled by confinement effect of $AlPO_4$-5 structure and channel dimensions. The strength of such effect in turn depends on the molecular size and shape of the sorbate molecule.
3. The cyclic alkane molecules are packed in a stacked manner along the length of $AlPO_4$-5 Channel and their sorption energetics is strongly influenced by their cohesive energy density.

These results are found to be in close agreement with those obtained for the sorption of C_5 alkanes. Furthermore, these results have clearly reflected the potential of $AlPO_4$-5 for separation of branched alkanes which are the primary constituents used to enhance the octane number of gasoline.

Nomenclature

ΔH^0	Initial heat of sorption, kJ/mol
ΔH	Isosteric heat of sorption, kJ/mol
ΔG	Free energy change during sorption, kJ/mol
ΔS	Entropy change during sorption J/K/mol
S_a	Sorbed phase entropy, J/mol/K
S_g	Gas phase entropy, J/mol/K
p	Equilibrium pressure, Pa
W	Amount sorbed, mol/kg
V_m	Langmuir sorption capacity, mol/kg
W_0	Dubinin-Raduskavich sorption capacity, mol/kg
B	Langmuir constant, Pa kg mol^{-1}
D	Dubinin-Raduskavich constant, mol/kg
K	Henry's constant, mol kg^{-1} Pa^{-1}
K_0	Pre-exponential factor of Henry's constant, mol kg^{-1} Pa^{-1}
R	Gas constant, J mol^{-1} K^{-1}
T	Temperature, K
P^0	Saturated vapour pressure of sorbate, Pa

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