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Thermal Behaviour and Adsorption Properties of Natural Stilbite

M. W. KASTURE, S. P. MIRAJKAR[1], V. V. JOSHI, A. L. CHOUDHARI[2] and
V. P. SHIRALKAR[1]
Science college, Nanded - 431 602, Maharashtra, India.

Abstract. Crystals collected from the Ellora valley (Aurangabad, MS, India) of the Deccan traps of India have been characterized as a stilbite (St) by X-ray diffraction, IR spectroscopy and chemical analyses. The thermal behaviour was studied using TG and DTA techniques. The sample was exchanged at reflux temperature with NH_4Cl and NH_4St was prepared. This was further transformed to the H-form of stilbite (HSt) by heating at 573 K for 12 h. The samples so prepared were used for adsorption studies. The comparative study of sorption of these samples shows an increase in the sorption capacity of HSt. The isosteric heat was also computed for these samples.

Key words: Zeolite, thermal behaviour, adsorption, isosteric heats, XRD, IR, TG, DTA.

1. Introduction

Zeolites form a well-defined group of hydrated aluminosilicates of the alkali or alkaline earth elements. The framework structure of zeolites consists of intracrystalline channels and voids. In most of the naturally occurring zeolites, the cations usually present are Ca, Na, K and these extra-framework cations are loosely bound to the framework. Water molecules occluded in the channels are also loosely bound to the extra-framework cations. Zeolites possess the remarkable property of partially dehydrating (reversibly) on heating, and for this reason the thermal behaviour of natural as well as synthetic zeolites has been studied extensively.

Zeolites have been classified into two groups, depending upon their dehydration behaviour. Stilbite, which is commonly found as a vein mineral or locally as a replacement product in volcanogenic rock associated with minerals of the heulandite group or laumontite, belongs to group one.

Stilbite has been investigated in different countries by several workers. Investigation on stilbite from India has been carried out by Sukheswala *et al.* [1]. The crystal structure of stilbite has been reported by Gottardi [2], Slaughter [3] and later refined by Galli [4]. According to these workers, the crystal structure of

Present addresses:
[1] S. P. Mirajkar and V. P. Shiralkar, National Chemical Laboratory, Pune, India.
[2] A. L. Choudhari, Nataji Subhashchandra Bose College, Nanded, India.

stilbite is characterized by large intersecting, relatively open channels of 10- and 8-membered tetrahedral rings.

All the channel cavities and channel openings are occupied by cations. Dehydration studies of stilbite have been reported by Barrer *et al.* [5] and Jacobs *et al.* [6]. A study of the dehydration of stilbite from India has been reported by Joshi *et al.* [7].

Zeolites are specific adsorbents with a large intracrystalline volume associated with a homogeneous system of pores and cavities. Zeolites generally exhibit Langmuir type I adsorption isotherms.

Langmuir coefficients for the adsorption of H_2O and D_2O on zeolite were found to vary with coverage [8]. The adsorption in the zeolite takes place in the cavities, which are uniform throughout the structure. For the adsorption studies, it is necessary that the cavities are retained during any modification or treatment given to the zeolite.

Naturally occurring zeolites display different properties depending on their origin. In the present investigation, zeolite (identified as a stilbite variety) collected from the quarries of the Ellora valley, Aurangabad District, MS, India, has been studied for its thermal and adsorption properties. In addition, the stilbite transformed to the H-form by exchanging with NH_4^+ ion and heating to 573 K, was also studied for its properties using H_2O as the adsorbate molecule. The experimental adsorption data were tested and verified against different adsorption theories.

2. Experimental

2.1. SAMPLE PREPARATION

The crystals separated from rock samples were washed, dried, crushed and sieved to obtain 150 μm size crystals. The powder was refluxed with doubly distilled water to remove soluble impurities. It was then decanted and dried in an oven overnight.

2.2. X-RAY DIFFRACTION STUDIES

The X-ray powder diffractograms were recorded on a Rigaku (model D-Max/III VC) diffractometer using CuK_α ($\lambda = 1.5404$ Å) radiation, scanning at a chart speed of 1°/min in the range of 2θ values from 5° to 65° at room temperature (Figure 1). The observed peak intensities and d values were compared with standard data. All the characteristic peaks of stilbite were found to be present in the X-ray diffractogram, thus confirming its identity.

2.3. CHEMICAL ANALYSES

The chemical analyses were carried out by wet chemical analysis methods. Atomic absorption spectroscopy (Hitachi - 8000) was used to obtain the Na, K and Ca content of the samples. The sample is a calcium-rich variety of stilbite.
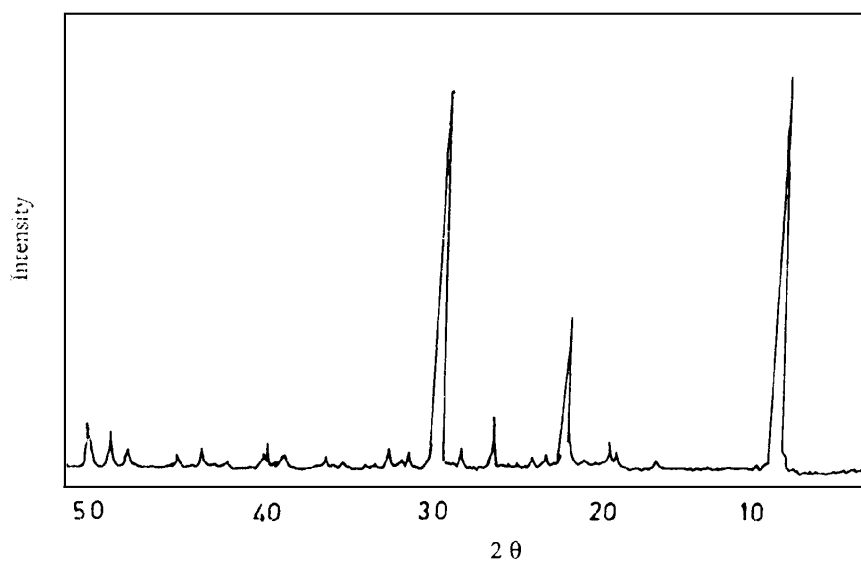
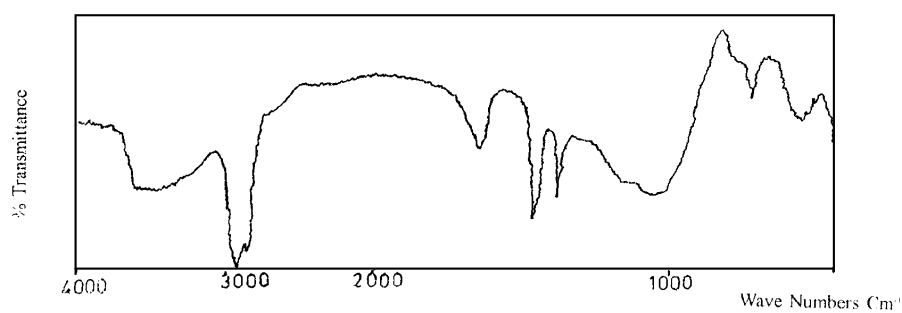*Figure 1.* X-ray diffractogram of stilbite.

Figure 2. IR spectrum of stilbite.

The chemical formula, derived on the basis of oxygen 72, is

$$Na_{0.5}K_{0.07}Ca_{3.37}Fe_{0.04}[Al_{6.69}Si_{24.36}O_{72}]\cdot31\ H_2O$$

with a Si/Al ratio of 3.64.

2.4. IR STUDIES

IR spectra were recorded on a Pye-Unicam SP-300 spectrometer using the Nujol mull technique (Figure 2). The details of the observed IR bands are given in Table I.

Table I. IR data.

External linkages (Structure sensitive)	Wave number (cm^{-1})
Asym. stretch	1099
Sym. stretch	728 Sharp
Double ring	539 Shoulder
Pore opening	490 Shoulder
Internal tetrahedra	Wave number (cm^{-1})
Asym. stretch	1376 Sharp
Sym. stretch	670 Strong
T—O bend	460 Medium strong
Hydroxyl stretch	3293 Medium, 3920 Broad
H_2O bend	1653 Medium strong

Table II. Thermogravimetric analysis.

Sample mass:	34.790 mg
Sampling rate:	1.4 K/s
Atmosphere:	Air
Crucible:	Platinum

Temperature range (K)	First point selected (K)	Second point selected	Weight change (mg)	Water molecules lost	Percentage weight loss
332–500	332	500	3.13	19	9.0
617–772	517	772	1.86	11	5.3
918–1011	918	1011	0.18	01	0.5
331–774	331	574	5.34	31	15.3

2.5. THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS

The TG and DTA curves for natural stilbite were recorded on a Setaram 92-12 thermal analyser in air using precalcined α-alumina as a reference material (Figure 3). Milligan and Weiser [9] reported that a step occurs in the dehydration isobar for stilbite at about 393 K, followed by irreversible collapse of the structure at about 673 K. The details of the thermogravimetric analysis for the sample are shown in Table II.

2.6. ADSORPTION

Natural stilbite was ion exchanged with NH_4^+ ion using 1 M NH_4Cl solution and 5 g of natural stilbite. The ion exchange was carried out at reflux temperature for 12 h. Every 2 h, a fresh solution of 1M NH_4Cl was added after removing the previous NH_4Cl solution.
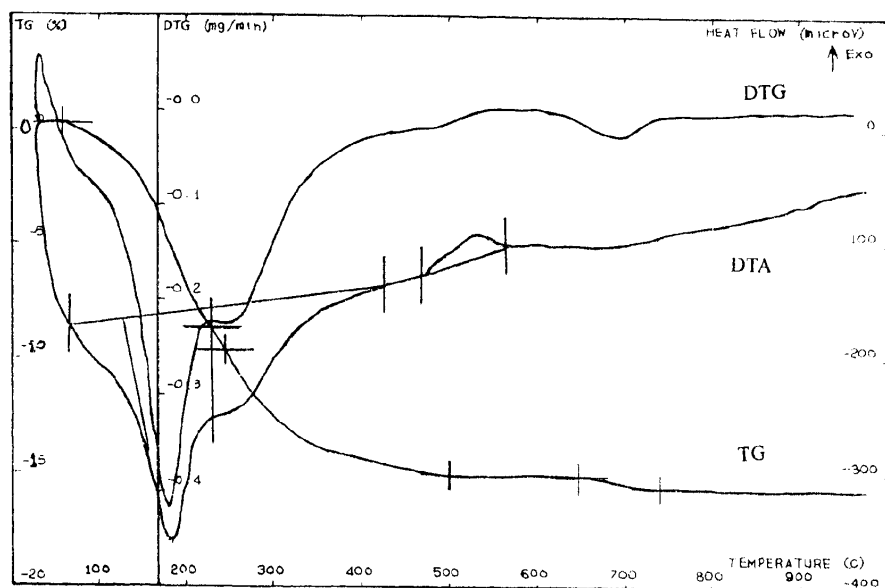
Figure 3. Thermogravimetric and differential thermal analysis curves for stilbite.

The NH_4^+-exchanged stilbite was repeatedly washed with doubly distilled water until it was free of Cl^- ions. The washed material was then deammoniated at 573 K for 4 h to obtain the H-form of stilbite. The degree of ion exchange was verified by atomic absorption spectroscopy (Hitachi - 8000).

The sample was dehydrated at 573 K at a pressure of 10^{-6} torr for 4 h. Water adsorption was studied at five different temperatures (303, 333, 363, 393, and 423 K) using a McBain sorption balance. Adsorption isotherms were obtained up to 24 torr. For each adsorption measurement, the process of dehydration at 523 K and a pressure of 10^{-6} torr was repeated. The structural stability before and after sorption was tested using XRD.

3. Results and Discussion

On the basis of their dehydration behaviour zeolites are classified into two groups as follows.

(1) Those which show no major structural changes during dehydration and which exhibit continuous weight loss as a function of temperature.
(2) Those which undergo major structural changes during dehydration and exhibit discontinuities in their weight loss curve.

Stilbite belongs to group 1, as is evident from the present study. The TG and DTA curve shows that most of the water is lost up to 673 K, the structure of stilbite being stable up to 553 K. The occluded water is lost up to 553 K and the structural

water continues to be lost up to 768 K. There is no further noticeable loss of water above 768 K. The analysis is further supported by the XRD of the sample treated at high temperature. The structural collapse is observed at 823 K, as verified from the absence of peaks in the diffractogram of a sample treated at 823 K.

The TG/DTA curve of stilbite is shown in Figure 3. A sharp endothermic peak is observed at 455 K, which corresponds to dehydration without change of the structure. Nineteen water molecules are lost at this stage. The second endothermic peak, which corresponds to structural rearrangement on dehydration, is observed at 514 K when 11 water molecules are lost. An exothermic peak is also observed in the temperature range of 741 K to 837 K when a single water molecule is lost. Endotherms generally represent physical changes. A sharp endotherm is indicative of crystalline rearrangements. The broad endotherms cover behaviour ranging from dehydration to temperature-dependent phase behaviour of chemical systems. Broad exotherms denote chemical reactions.

In the present study a sharp endotherm at 455 K corresponds to a physical change, because most of the water molecules are lost at this stage. Further, a broad exotherm at 514 K indicates the phase change and the loss of all the water molecules.

The broad exotherm observed in the DTA of the sample indicates a structural collapse (Figure 3). The sluggish nature of these dehydration-induced structural changes occurring in the stilbite is shown by the DTA curve.

Equilibrium isotherms of water molecules on stilbite (St) and the H-form of stilbite (HSt) are shown in Figure 4. The adsorption isotherms of St, and HSt exhibit type I isotherms which are characterized by a long, flat and nearly horizontal portion. In a type I isotherm it is assumed that the adsorbed layer on the interchannel and cavity walls is only one molecule thick and the flat region of the isotherm corresponds to completion of this monolayer. Langmuir assumed an evaporation condensation mechanism to explain equilibrium adsorption isotherms. In this model a dynamic equilibrium exists between the gas phase and the adsorbed phase. The surface of the solid is assumed to have an array of adsorption sites, each molecule being adsorbed at one site. This particular adsorption is also found in the case of stilbite, indicating that the experimental results obtained fit the Langmuir equation

$$\theta_1 = X/X_m = KP/(1 + KP)$$

where

$$K = \frac{k}{n_m \nu_1 e^{-E_1/RT}}$$

and X and X_m are the adsorption capacities at pressure p and at a monolayer coverage, respectively.

Further, this has been tested by plotting a linear Langmuir plot for water adsorption on St and HSt using the equation
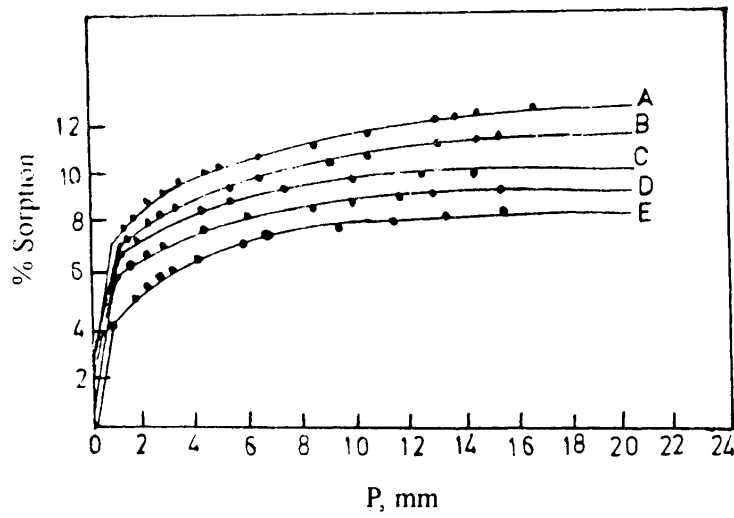
$$P/X = 1/K X_m + P/X_m.$$

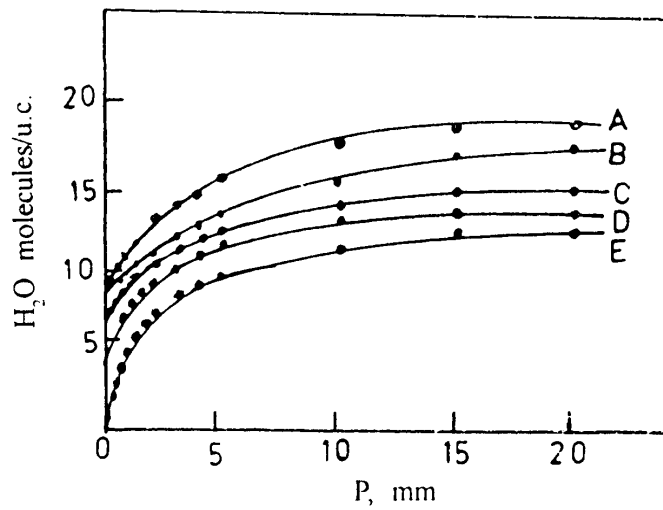*Figure 4.1.* Water sorption capacity for stilbite (St) at: (A) 303 K, (B) 333 K, (C) 363 K, (D) 393 K, (E) 423 K.

Figure 4.2. Water sorption isotherms for stilbite (St) at: (A) 303 K, (B) 333 K, (C) 363 K, (D) 393 K, (E) 423 K.

A plot of P/X vs. P is a straight line with slope $1/X_m$ and intercept $1/KX_m$, as shown in Figure 5, in which X has been replaced by the number of water molecules adsorbed per unit cell (u.c.), a. It is observed that increasing the temperature of the gas–solid system will decrease the quantity adsorbed [4].

The exchangable cations and water molecules of stilbite are located inside the cavities, formed by the intersection of the large channels, which are parallel to
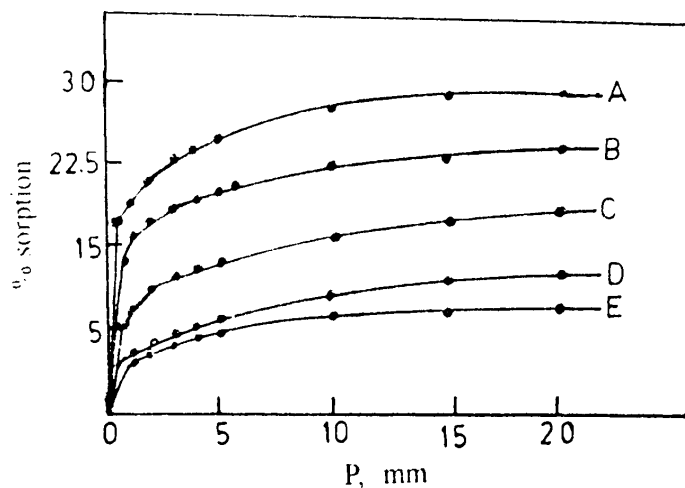
Figure 4.3. Water sorption capacity for H-stilbite (HSt) at: (A) 303 K, (B) 333 K, (C) 363 K, (D) 393 K, (E) 423 K.
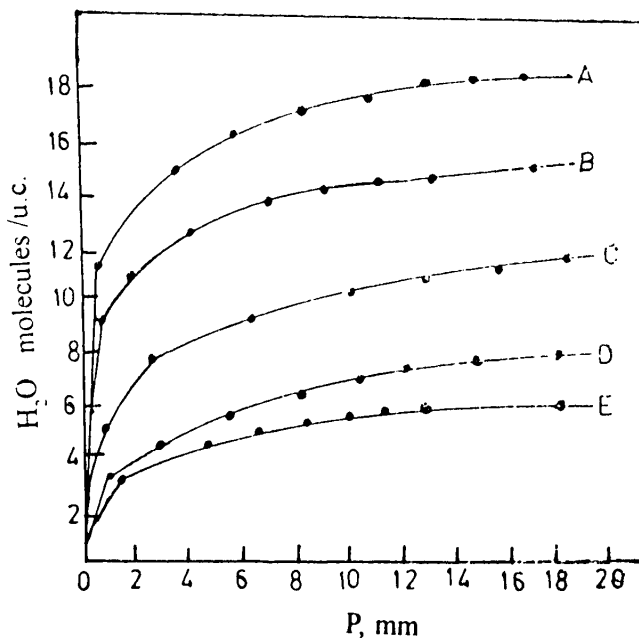

Figure 4.4. Water sorption isotherms for H-stilbite (HSt) at: (A) 303 K, (B) 333 K, (C) 363 K, (D) 393 K, (E) 423 K.

the a axis, and smaller channels which are parallel to the (102) direction. The Ca^{2+} cations are surrounded by, and bonded to, eight water molecules. The biggest channel surrounded by 10 tetrahedral rings is filled by these water molecules. The cavities in the stilbite structure are occupied by monovalent cations such as K^+
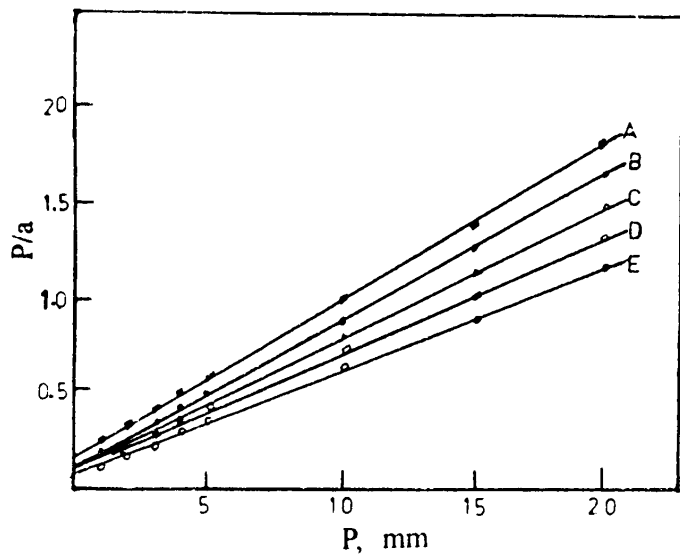
Figure 5.1. Linear Langmuir plots for water sorption on stilbite (St) at: (A) 423 K, (B) 393 K, (C) 363 K, (D) 333 K, (E) 303 K.
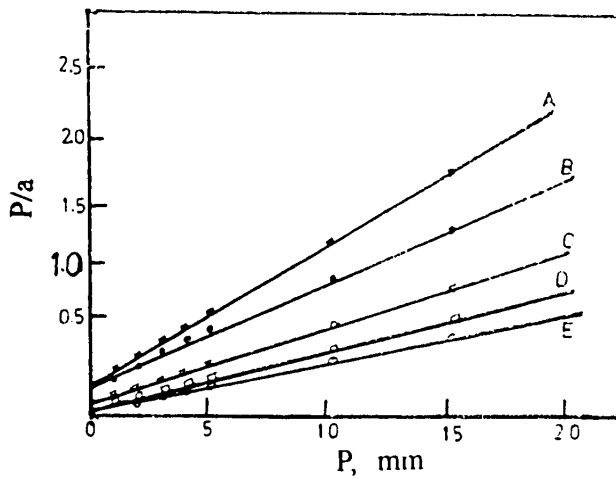

Figure 5.2. Linear Langmuir plots for water sorption for H-stilbite (HSt) at: (A) 423 K, (B) 393 K, (C) 363 K, (D) 333 K, (E) 303 K.

or Na^+. These sites have a statistically lower occupation by other cations, such as Ca^{2+} and Fe^{2+}. These cationic positions are surrounded by water molecules and framework oxygen atoms. The occupancy factor of water molecules in stilbite ranges from 80 to 90% [4].

The percentage sorption and number of water molecules per u.c. in St and HSt are shown in Table III. It is observed that as the temperature increases the number

Table III. Percent sorption and number of water molecules per u.c.

Temperature (K)	Stilbite		H-Stilbite	
	% Sorption	a/u.c.	% Sorption	a/u.c.
303	11.7	17.78	18.00	27.87
333	10.9	16.87	15.00	23.22
363	09.3	14.24	11.70	17.96
393	08.4	13.00	07.90	12.23
423	07.5	11.60	05.90	09.11

of water molecules is found to decrease, which corresponds to a decrease in the percentage sorption. The increase in percentage sorption (water molecules per u.c.) for HSt is much larger than for St. This may be due to the replacement of Ca^{2+} by NH_4^+ and further by H^+, which increases the void volume present in the stilbite channels and cavities.

However, there is a contradiction in the above observation at elevated temperatures (393, 423 K) i.e. the percentage sorption of water molecules adsorbed per u.c. for HSt is less than for St. This may be due to either Ca^{2+}, which still has an affinity for water molecules at elevated temperatures, or hydrogen loses its affinity towards water molecules at elevated temperatures. Hence, there may be a reduction in the percentage sorption of HSt as compared to St at 393 K and 423 K.

The simple model suggested by Langmuir is found to be in good agreement with stilbite and the H-form of stilbite in the present study.

Using the Clausius–Clapyron equation the isosteric heats of water sorption are computed from the equilibrium at constant sorbate loading:

$$-\Delta H = q_{\text{iso}} = R \left[\frac{T_2 T_1}{T_2 - T_1} \right] \ln \left(\frac{p_2}{p_1} \right)$$

The plots of log p against $1/T$ are found to be linear within experimental error, as shown in Figure 6. Isosteric heats have been calculated using these linear isosters.

As the number of water molecules adsorbed per unit cell increases, the heat of adsorption of water on St and HSt decreases (cf. Table IV and Figure 7). This reaches a minimum of 2.55 kJ mol^{-1} for St and 1.56 kJ mol^{-1} for HSt. In stilbite the biggest channels, surrounded by 10 tetrahedral rings, are filled by eight water molecules and form spheroids. There are cavities between the spheroids and channel walls, and monovalent cations occupy the sites.

These positions are surrounded by five water molecules and three water molecules are attached to the framework oxygen atoms [4]. The large cavities of stilbite are filled with the maximum number of water molecules. These water molecules are associated with weak mutual hydrogen bonds and regroup themselves, gradually forming a dense layer of molecules in the cavities, with oxygen atoms, with cavities in the main channel and with each other. When a layer is formed, the
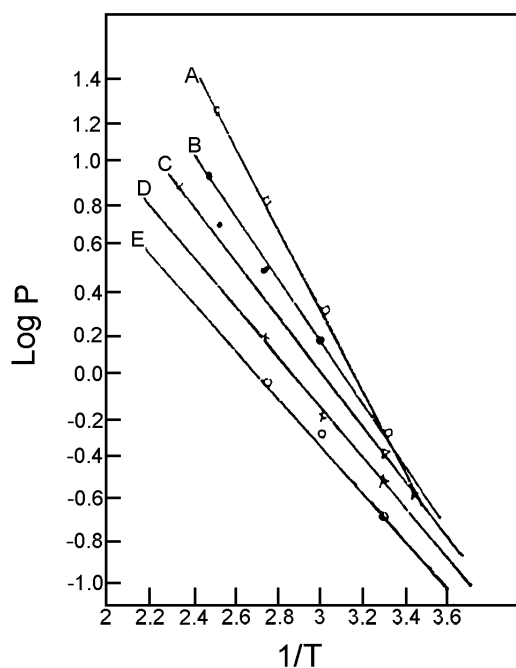
Figure 6.1. Linear isosters for stilbite (St) at: (A) 423 K, (B) 393 K, (C) 363 K, (D) 333 K, (E) 303 K.

heat of adsorption is a minimum and again increases for further filling of water molecules in cavities, wherein the isosteric heat becomes least when the cavities are filled. At this stage, once again, there is a decrease in the value of q_{iso} i.e. when the second minimum appears. Finally the process is complete when it passes the second maximum. The same number of maxima and minima are observed in HSt at almost the same filling per unit cell, indicating that the process of filling follows the same order. The only difference between the two is that the depth of the minima are more pronounced in the case of HSt than for St. This may be due to the increase in the percentage sorption and hence a greater number of water molecules are entering the cavities, channels and framework positions.

4. Conclusion

The sample collected was confirmed as a zeolite, stilbite, of the heulandite family by X-ray diffraction, chemical analyses, IR and TG/DTA. The TG/DTA curve confirmed that most of the water molecules are lost up to 673 K. Further, it confirms the stability of the structure up to 553 K.

Structural collapse takes place at 823 K. Dehydration without change in the structure occurs up to 455 K. The phase change and loss of all water molecules occur at 514 K.
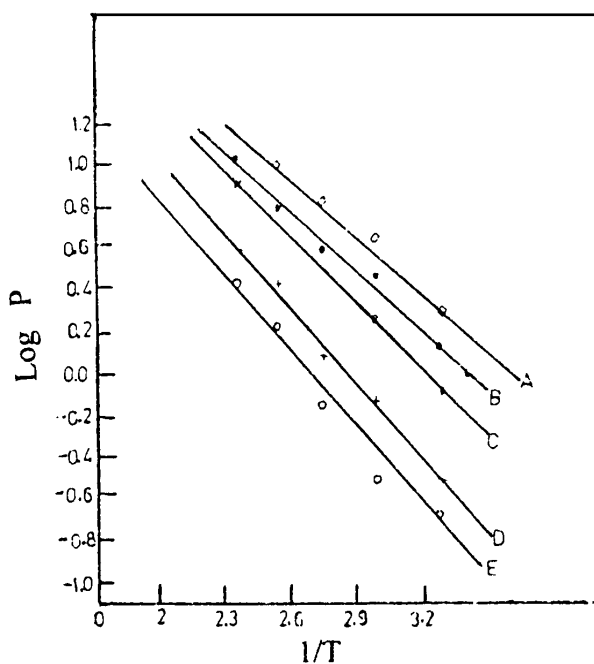
Figure 6.2. Linear isosters for H-stilbite (HSt) at: (A) 423 K, (B) 393 K, (C) 363 K, (D) 333 K, (E) 303 K.

Table IV. Isosteric heat and number of water molecules per u.c.

Stilbite		H-Stilbite	
a/u.c.	q_{iso} (kJ/mol)	a/u..c.	q_{iso} (kJ/mol)
01	6.15	01	6.15
02	3.60	01	6.16
03	2.55	03	3.61
04	3.60	04	4.53
05	4.54	05	5.22
06	3.60	06	1.56
07	4.17	07	4.58
08	3.60	08	4.17

The simple Langmuir model is found to be applicable in the case of stilbite. The percentage sorption in St and HSt is found to be 11.7 and 18.0% (17.7 and 22.8 water molecules per u.c.), respectively. Adsorption studies further reveal that there is much space available in the intracrystalline channels and cavities in the case of H-stilbite as compared to stilbite.
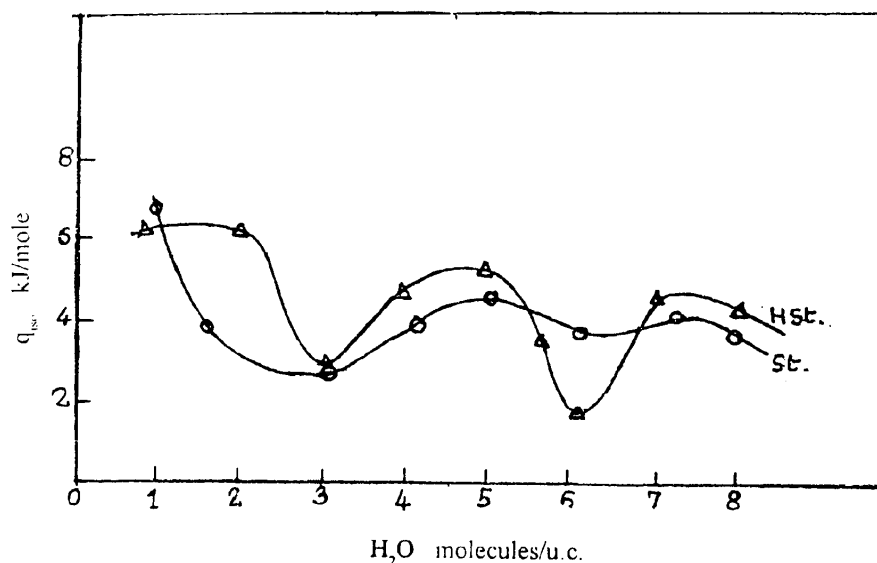
Figure 7. Isosteric heats, q_{iso}, for water sorption: ○, St; △ HSt.

The computation of isosteric heats for St and HSt indicates the distribution of the number of water molecules in the channels, cavities and framework position at the different stages of filling.

Acknowledgements

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