## CHAPTER 7

**WATER SORPTION BY HEULANDITE AND ITS DIFFERENT FORMS**

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7.1 Introduction

Adsorption is another distinctive property of zeolites, the first being ion exchange. Ion exchange has been referred to as a "chemical" process in contrast to adsorption as a "physical" one, although this distinction at the first glance is misleading. Usually, in ion exchange, as in redistribution of ions by diffusion, chemical factors are less significant than in adsorption where the solute is held by the sorbent by forces which may not be purely electrostatic.

Various terms have been used to describe the penetration by and containment of molecules in dehydrated crystalline zeolites. These include occlusion, imbibition, intercalation, persorption, sorption and adsorption. Adsorption is the correct term which describes the interaction between a molecule and a surface whether it is the external surface of a solid or the internal convoluted surface of a dehydrated microporous zeolite crystal.

The study of adsorption of gases and vapours on solids dates from Gideon's tests on fleece in 1100 B.C. and the early experiments of Scheele.
and Abbe F. Fontana. Early investigators were attracted by reversible dehydration-hydration phenomenon in zeolite minerals. Much of the early work on adsorption of gases was performed on the stable zeolites which retained their structure upon dehydration.

In 1840 A. Damour observed that crystals of zeolite could be reversibly dehydrated without any apparent change in the transparency or morphology. Friedel first proposed that structure of dehydrated zeolites consists of open spongy framework. He observed that liquids like alcohol, benzene, chloroform, carbon disulphide and mercury were occluded by zeolites, with changes in refractive indices of zeolites. Grandjean in 1909 observed gases like ammonia, air, hydrogen, carbon disulphide, hydrogen sulphide, iodine and bromine are adsorbed by chabazite. Dehydrated chabazite crystals were observed to rapidly adsorb the vapours of water, methyl alcohol, ethyl alcohol and formic acid; however, when exposed to acetone, ether, or benzene, essentially no adsorption occurred. McBain deduced from his observations that the pore opening in the chabazite crystals must be smaller than 0.5 nm in diameter. To describe this phenomenon of selective adsorption, or "persorption" as he termed it, McBain originated the term "Molecular Sieve." He distinguished between zeolite type adsorption and solid solution. The interstices or
ultrapores within the crystal lattice could contain any molecules which are small enough to permeate the crystal. The adsorbed phase dispersed through the internal voids of the crystal without displacing any atoms which make up the permanent crystal structure.

Sorption and diffusion of rare gases by heulandite has been studied by Barrer and Vaughan\(^8\). Sorption and diffusion of water vapours by different zeolites have been studied by Barrer and Fender\(^9,10\), whereas Bikov and Scharbatyuk\(^11\) have reported results of sorption of water vapour on natural zeolites. However, it appears that influence of cation exchange on adsorption of water is not studied. Taking into account these facts, water sorption studies on natural heulandite and its cation exchanged forms are carried out in the present work. For these adsorbents water is used as adsorbate, since it can occupy small channels and voids in the crystal lattice.

This chapter gives the report on estimation of the pore volume, adsorption capacity and their variation for different heulandite forms. Some knowledge regarding zeolitic water is needed in this connection.

### 7.2 Zeolitic Water

Nuclear magnetic resonance (nmr) studies\(^12\) have revealed that the water molecules in the
larger zeolite cavities exhibit the same pattern as the isolated liquid, thus indicating that molecules in the centers of large cavities do not occupy definite lattice sites. In zeolite, with smaller cavities, the molecules of water appear to cluster around the cations. This association of water molecules with cations is consistent with the results of electrical conductivity studies.

During dehydration it appears that the water molecules line the inside of the zeolite structural cages\(^\text{12}\). Cation dipole interactions play an important role in the nature and structure of the zeolitic water. It is also proposed that non-framework water and cation in zeolite behave as a concentrated electrolyte\(^\text{13,14}\). The nmr measurements have shown that the water acts as a viscous liquid. The correlation obtained on several cation exchanged forms, indicates that the water molecules fill the cavity and are localised near the cation\(^\text{15}\).

At temperatures down to about 200° K, the water molecules retain their mobility, below this temperature the immobilization of the water molecules occurs gradually and without a sudden phase change. At 77° K ice-like structure of water molecules is situated in an arrangement resembling the pentagonal dodecahedron.

Neutron scattering experiments\(^\text{16,17}\) have
shown that the water within zeolite cavities, containing sodium ions, is 30 times as viscous as bulk water at room temperature, however, the density is same as liquid water. Moreover, these water molecules have a torsional motion.

In summary, for hydrated zeolites with small and narrow cavities, the positions of the water molecules appear well defined and coordination occurs with cations in the cavities. The cation in the hydrated zeolite seems to be surrounded by as many water molecules as is spatially possible, as long as they do not lie too far away from aluminosilicate framework and the negative charge distribution.

7.3 Pore Volume in Dehydrated Zeolites

Various theories have been advanced to explain the adsorption behaviour of zeolites. Barrer and Ibbitson\textsuperscript{18} have proposed that the adsorbed molecules form a regularly disposed, frequently mobile interstitial component of the dehydrated zeolite crystals. The structurally stable three-dimensional zeolites were able to adsorb a quantity of gas equivalent to the water of hydration on a volume basis.

The quantity of a gas or a liquid (x)
adsorbed by a solid depends upon pressure, temperature, the nature of the gas and the nature of the solid. When exposed to a gas or a liquid, the intracrystalline voids and channels of a dehydrated zeolite fill with the molecular species concerned and when the filling is complete, no more adsorption occurs. This results in an isotherm contour of the Langmuir type or type I as illustrated in Fig. 7.1. Thus, adsorption is a matter of pore filling and the usual surface area concepts as they are applied to other adsorbents are not applicable.

The pore volume of a dehydrated zeolite and other microporous solids, which have type I adsorption isotherm, can be calculated by Gurvitsch's rule.

The adsorption isotherm generally intersects the vertical line at pressure $p/p_0 \approx 1$ at an angle of nearly $90^\circ$ (Fig. 7.1). The quantity of material adsorbed, $x_s$ at this point of saturation is assumed to fill the micropores of the solid as the normal liquid, having a density, $d_a$, of the liquid at that particular temperature. The total pore volume in the micropores $V_p$ is given by

$$V_p = x_s / d_a$$

(7.1)

where $d_a$ is the density of liquid adsorbate in g/cc, $x_s$ is in g/g and $V_p$ in cc/g. The Gurvitsch's rule is
Fig. 7.1 The isotherm type I and relation of the quantity adsorbed at saturation corresponding to complete pore filling, $x_s$ at $p = p_0$.

Fig. 7.2 McBain adsorption balance 1-tube, 2-quartz spring, 3-pan with adsorbent, 4-bulb containing liquid adsorbate, 5-manometer, 6,7-thermostats, 8,9 and 10-cocks.
obeyed by many different adsorbates on microporous adsorbents like silica gel, carbon and to a large extent by dehydrated zeolites.

The total pore volume of the voids in dehydrated zeolites may be calculated from the amount of adsorbed water on the assumption that the water is present as the normal liquid, with the average density assumed to be that of normal liquid water at the temperature concerned. In zeolites which have more than one type of channel size or void, the void spaces available for occupancy by most molecular species are smaller than the total water volume in the zeolite due to the inaccessibility of the small voids to other molecules.

It is possible to calculate the micropore volume of zeolites, unlike the amorphous microporous adsorbents, from the known structure. The measured pore volume can then be compared with calculated value.

The maximum void volume, $V_p$, in a zeolite, is determined from the water contained in the zeolite at $p/p_0$ equal to 1, using eqn. (7.1). One can then calculate the void fraction, $V_f$, by the equation

$$V_f = x_s \left( \frac{d_c}{d_a} \right)$$  \hspace{1cm} (7.2)
where \( V_f \) = total void fraction in the crystal and 
\( d_c \) = the density of the dehydrated zeolite crystal.

The total pore volume, \( V_p \), in units of \( \text{nm}^3 \) per unit cell is given by

\[ V_p = V_f \cdot V \] (7.3)

where \( V \) is the unit cell volume in \( \text{nm}^3 \).

The number of adsorbed molecules \( N_A \) per unit cell can be calculated by

\[ N_A = \chi_s \left( \frac{M_Z}{M_A} \right) \] (7.4)

where \( M_Z \) is unit cell formula weight and \( M_A \) is molecular weight of adsorbate.

### 7.4 Equilibrium Adsorption of Gases and Vapours on Dehydrated Zeolite

The amount of gas or vapour adsorbed by a dehydrated crystalline zeolite depends upon the equilibrium pressure \( p \), the temperature \( t \), the nature of the gas or vapour and the nature of the micropores in the zeolite crystal. This can be expressed by equation
The nature of this function is quite complex and it is very difficult to predict completely on theoretical grounds. At a given temperature, the amount adsorbed \( x \) is experimentally measured as function of equilibrium pressure \( p \). The plot of \( x \) against \( p \) is called the experimental adsorption isotherm. Increase in the temperature of the gas-solid system at a constant pressure will lead to decrease in amount adsorbed \( x \) by the zeolite. A plot of \( x \) versus \( t \), at a constant pressure, is termed as isobar

\[
x = f(p)_t
\]  \hspace{1cm} (7.5)

In the third method, a graph of \( p \) as a function of \( t \) is plotted for a constant value of \( x \). This represents isostere

\[
p = f(t)_x
\]  \hspace{1cm} (7.6)

Since zeolites exhibit type I isotherm, the Langmuir equation has been applied. Contrary to the usual interpretation of type I isotherm, the break in the isotherm corresponds to the filling of the micro-voids and not the completion of monolayer. The Langmuir equation is given by
\[ \frac{x}{x_m} = \frac{Bp}{1 + Bp} \quad (7.8) \]

This can be rewritten in the form

\[ \frac{p}{x} = \frac{1}{x_m} B + \frac{p}{x_m} \quad (7.9) \]

The value of \( \frac{p}{x} \) plotted against \( p \) yields a straight line with a slope of \( \frac{1}{x_m} \). Value of \( x_m \), thus obtained, can be used to determine the pore volume.

Another method to evaluate pore volume is to apply Dubinin-Polanyi theory. Experimentally, it is used in the following form \(^{22,23}\)

\[ \log W = \log W_0 - \frac{E}{2.303 \beta^2} \left[ T \log \left( \frac{P_s}{P} \right) \right]^2 \quad (7.10) \]

where \( W = \) value of adsorption space occupied

\( \text{av}^* \)

where \( a = \) amount of adsorbate in mmole/g.

\( v^* = \) molar volume of adsorbate

\( P_s = \) saturation vapour pressure

\( W_0 \) is a constant and represents the volume of the adsorption space or pore volume, \( \beta \) is a constant which
is independent of temperature and is characteristic of adsorbent porous structure. In order to evaluate $W_0$ and $\beta$, the equation is expressed by

$$\log a = C - D \left[ \log \left( \frac{p_s}{p} \right) \right]^2 \quad (7.11)$$

When $\log a$ is plotted against $\left[ \log \left( \frac{p_s}{p} \right) \right]^2$, the curve is linear and

$$C = \log \left( \frac{W_0}{v^*} \right), \quad D = 0.434 \frac{BT^2}{\beta^2}$$

From the intercept $C$, $W_0$ can be estimated.

7.5 Experimental Details

The amounts of gas and vapour adsorbed by adsorbent and the corresponding isotherm are determined by dynamic or static method. The dynamic method consists in passing a stream of gas through a layer of adsorbent and in registering the gas after the layer of adsorbent, and in measuring the growth of the gas concentration after its passing through the adsorbent layer. This method is widely used while studying mixture of gases. More generally, static method is used. The adsorption unit of this type was fabricated for the present investigation in this laboratory. In this method, often referred to as
gravimetric method, the amount of gas or vapour is measured by weighing the sample in a closed system in a balance generally of quartz spring. This balance was first used by McBain and is commonly referred to as the McBain adsorption balance.

7.5.1 Fabrication of McBain adsorption balance

Figure 7.2 shows the configuration of the balance fabricated for the present study. 2 is a quartz spring which can bear a maximum load of 1 g. Its force constant is determined by measuring its extension for 100 mg several times. It is 0.0266 cm/mg. This spring is suspended in a glass tube 1 by a hook. At the lower end of the quartz spring a steel pan 3 is fixed by means of very thin platinum wires. The pan accommodates the adsorbent. The thermostat 6 is so adjusted that the pan will be exactly at its centre. The glass column is connected to a bulb containing liquid adsorbate 4 which lies in a thermostat 7, via a T tube. The T tube is further extended to a manometer attachment 5. 10 is a cock opening to a vacuum pump. In the present case, a rotary pump (pressure $10^{-3}$ mm) is used. 8 and 9 are additional cocks. This entire assembly is fixed on a mesh of thick iron bars for support and kept vertical.

The extension of the spring and the manometer
readings (mercury level) are measured by cathetometers; least count of each is 0.001 cm.

7.5.2 Procedure

In the present study, pellets of different forms of heulandite, i.e. Na-, K-, NH\textsubscript{4}-, Ag-, Rb- and Cs-heulandite are used as adsorbents. The composition (Table 6.1) of these samples is as described in Chapter 6. Observations for each pellet are taken at adsorption temperatures 30° and 70° C.

The entire system, after insertion of the weighed sample, is evacuated, using the rotary pump, to \(10^{-3}\) mm. The temperature of the adsorbent is maintained at 200°C. In the case of heulandite, the phase change occurs at 215-230°C. So dehydration at 200°C (activation temperature) is carried out for 5 hrs, the period at the end of which the spring readings are constant and the manometer shows no level difference.

In the evacuation period, cock 9 is kept closed, the bulb is full with double distilled water. After complete evacuation or full dehydration of the pellet, spring reading is recorded, the cock 10 is closed, and the pump is stopped. The temperature of the pellet is adjusted to the required value, 30 or 70°C. Cock 9 is just
opened so that mercury level in manometer shows little movement and the cock is closed immediately. This way a small amount of vapour is admitted to the chamber. It takes almost 12 minutes for equilibrium. After equilibrium mercury levels in the manometer and spring reading are recorded by the cathetometers. Calibration of the spring is used to determine the mass of the vapour (x) adsorbed by the pellet. Manometer readings give pressure p. By opening the cock 9 for a while and immediately closing, successive observations are recorded.

7.6 Results and Discussion

The graphs of amount of water adsorbed against equilibrium pressure for all samples, i.e. natural heulandite and Na-, K-, NH4-, Ag-, Rb- and Cs-heulandite, at adsorption temperatures of 30° and 70° C, are shown in Fig. 7.3. Almost all isotherms, at low pressure, rise sharply and later become flat. They are type I isotherms. The maximum value, \( x_m \), at \( p/p_o \approx 1 \) are shown in Table 7.1. It is found that these values differ from sample to sample. \( x_m \), the void volume obtained from the slope of straight line of \( p/x \) versus \( p \) (Fig. 7.4 and eq. (7.9) ) are also noted in Table 7.1. This table also incorporates the value of void volume (\( W_o \)) obtained from Dubinin-Polanyi theory, i.e. graph of log a versus \( [\log (p_o/p)]^2 \) using
Fig. 7.3 Experimental adsorption isotherms for natural heulandite, Na−, K−, NH$_4$−, Ag−, Rb− and Cs-heulandite at 30 and 70°C.
NATURAL CRYSTALS HEULANDITE
ACTIVATED AT 200°C
△ AT 30°C
□ AT 70°C

Fig. 7.3
Fig. 7.3 (continued)
Fig. 7.4 Plot of $p/x$ vs $p$ for natural, Na-, K-, NH$_4$-, Ag-, Rb- and Cs-heulandite at 30 and 70°C.
HEULANDITE CRYSTALS

ACTIVATED SORPTION

AT TEMP

\( \bigcirc \) 200°C

\( \square \) 200°C

TEMP

30°C

70°C

Fig. 7.4
Fig. 7.4 (continued)
The presence of cation in the zeolite voids may vary the pore volume. In some cases, as typified by zeolite A, a large cation may substantially reduce the pore volume. A glance at Table 7.1 shows that the smallest atom Na containing heulandite has more adsorption capacity and so more pore volume and a larger number of adsorbed molecules per unit cell compared to other forms of heulandite. Cesium ion is the biggest amongst all with radius of 0.167 nm. Radii of ammonium and rubidium ions do not differ much. Consequently, pore volume and the number of molecules adsorbed by unit cell of these forms do not differ significantly. Exceptions to this more general interpretation based on cation size are potassium and silver forms of heulandite.

Silver has atomic weight 119 and its percentage exchange in heulandite is 80. Being a heavier ion, it may affect the stability of zeolite structure and
Fig. 7.5  Plot of log a vs $[\log (p_g/p)]^2$ for natural, Na-, K-, NH$_4$-, Ag-, Cs- and Rb-heulandite, at 30 and 70 °C.
Table 7.1 Void volume $V_p$ (or $x_m$ or $W_0$), void fraction $V_f$, total pore volume $V_p'$ and number of molecules $N_A$ per unit cell at 30°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_s = \frac{V_p}{cc/g}$</th>
<th>$x_m = \frac{V_m}{cc/g}$</th>
<th>$W_0 = \frac{W_0}{cc/g}$</th>
<th>$V_f = \frac{V_f}{cc/cc}$</th>
<th>$V_p' = \frac{V_p'}{nm^3}$</th>
<th>$N_A = \frac{N_A}{molecules/unit cell}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural H</td>
<td>0.130</td>
<td>0.136</td>
<td>0.133</td>
<td>0.2567</td>
<td>0.5398</td>
<td>19.9083</td>
</tr>
<tr>
<td>Na-H (0.097)</td>
<td>0.134</td>
<td>0.135</td>
<td>0.135</td>
<td>0.2613</td>
<td>0.5495</td>
<td>20.3087</td>
</tr>
<tr>
<td>K-H (0.133)</td>
<td>0.117</td>
<td>0.119</td>
<td>0.119</td>
<td>0.2252</td>
<td>0.4736</td>
<td>18.0683</td>
</tr>
<tr>
<td>NH$_4$-H (0.133)</td>
<td>0.123</td>
<td>0.129</td>
<td>0.124</td>
<td>0.2413</td>
<td>0.5075</td>
<td>18.3683</td>
</tr>
<tr>
<td>Ag-H (0.126)</td>
<td>0.115</td>
<td>0.117</td>
<td>0.115</td>
<td>0.2239</td>
<td>0.4709</td>
<td>17.7752</td>
</tr>
<tr>
<td>Rb-H (0.147)</td>
<td>0.120</td>
<td>0.124</td>
<td>0.121</td>
<td>0.2315</td>
<td>0.4868</td>
<td>18.3887</td>
</tr>
<tr>
<td>Cs-H (0.167)</td>
<td>0.112</td>
<td>0.115</td>
<td>0.113</td>
<td>0.2194</td>
<td>0.4614</td>
<td>17.0425</td>
</tr>
</tbody>
</table>

The quantities in the brackets are the radii in nm of respective cations.
Table 7.2 Void volume $V_p$ (or $x_m$ or $W_o$) void fraction $V_f$, total pore volume $V_p'$ and number of molecules $N_A$ per unit cell at 70°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_{sp}$</th>
<th>$x_m$</th>
<th>$W_o$</th>
<th>$V_f$</th>
<th>$V_p'$</th>
<th>$N_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cc/g</td>
<td>cc/g</td>
<td>cc/g</td>
<td>cc/cc</td>
<td>nm$^3$</td>
<td>molecules/unit cell</td>
</tr>
<tr>
<td>Natural H</td>
<td>0.100</td>
<td>0.116</td>
<td>0.1152</td>
<td>0.1974</td>
<td>0.4152</td>
<td>15.314</td>
</tr>
<tr>
<td>Na-H</td>
<td>0.100</td>
<td>0.103</td>
<td>0.108</td>
<td>0.1950</td>
<td>0.4101</td>
<td>15.174</td>
</tr>
<tr>
<td>K-H</td>
<td>0.081</td>
<td>0.0897</td>
<td>0.090</td>
<td>0.1559</td>
<td>0.3229</td>
<td>12.509</td>
</tr>
<tr>
<td>NH$_4$-H</td>
<td>0.085</td>
<td>0.0867</td>
<td>0.096</td>
<td>0.1668</td>
<td>0.3507</td>
<td>12.694</td>
</tr>
<tr>
<td>Ag-H</td>
<td>0.088</td>
<td>0.092</td>
<td>0.095</td>
<td>0.1713</td>
<td>0.3603</td>
<td>13.602</td>
</tr>
<tr>
<td>Rb-H</td>
<td>0.098</td>
<td>0.103</td>
<td>0.108</td>
<td>0.1891</td>
<td>0.3976</td>
<td>15.017</td>
</tr>
<tr>
<td>Cs-H</td>
<td>0.088</td>
<td>0.090</td>
<td>0.090</td>
<td>0.1724</td>
<td>0.3625</td>
<td>13.391</td>
</tr>
</tbody>
</table>
consequently greater distortions in pore volume. The availability of space for water molecules around the cation is disturbed and so uniform layerwise pile up of adsorbate molecules may not be possible. Bhomrah and Kulkarni\(^{25}\) have reported similar results for CoX and NiX. Cesium (At. wt. 133) is heavier than silver, but only 38\% exchange had taken place, and so it is the more stable form than Ag-heulandite. The experimental adsorption isotherm for Ag-heulandite at adsorption temperature of 70 °C, as seen from Fig. 7.3, shows distorted type I isotherm and thus supports the above explanation.

Changing the cation in the zeolite may effectively vary the pore openings in both positive and negative directions. In zeolite A, divalent ion exchange opens the aperture to the full diameter, whereas exchange with a larger univalent ion diminishes the aperture size. Potassium ion exchange in zeolite A reduces the effective adsorption pore size to the point where only small polar molecules are adsorbed\(^{26}\).

In potassium heulandite also, the pore size may be reduced and so the sieving effect may take place, with the result that the void volume is smaller than expected from the viewpoint of size of the cation. Distortion of the aluminosilicate lattice is also an important factor. When dehydrated, the aperture of calcium chabazite distorts
from an eventually circular opening, 0.39 nm in diameter, to an ellipsoidal shape, 0.37 x 0.42 nm. In adsorption of polar molecules it is known that the shape of the aperture changes during the adsorption process. These factors may be responsible for the changes observed in adsorption capacity, void volume and the number of molecules for different forms of heulandite in the present investigation. X-ray structural analyses of these samples can be used to confirm these results. However, no such structural analyses for different forms of heulandite are available in literature.

The value of the void fraction for natural heulandite in Table 7.1 is low compared to its value of 0.39 cc/cc. The heulandite being in the mineral form, there may be occluded entities in the channels in the form of oxides. In this context, it should be noted that magnesium is present in heulandite, and may be occupying a position in the channel in the form of oxide. The presence of stacking faults in crystals also causes decrease in adsorption capacity. Stacking faults cause hindrance to mobility of ions (Chapter 5) and so to adsorbate molecules. Consequently, for other forms of heulandite also, the void fraction is smaller.

At higher adsorption temperature 70 °C, the values of pore volume, void volume and $N_A$ (Table 7.2) are
smaller for each sample than those in Table 7.1. This may be because of the distortion in the framework and expansion of liquid adsorbate at this temperature. Distortion in the framework is clearly evident from adsorption isotherm of Ag-heulandite (Fig. 7.3). In other samples also, there may be minor distortions leading to smaller adsorption capacity.

From this it can be concluded that forms of heulandite other than silver have capacity to retain their structure after full hydration, particularly, at adsorption temperature of 30°C. Presence of a heavy ion in a large number in heulandite framework reduces this capacity.

7.7 Conclusions

McBain balance is fabricated to determine the water sorption capacity and consequently the pore and void volumes. These quantities are measured for natural heulandite and its different cation exchanged forms. The values of pore volume obtained from type I isotherm, Langmuir equation and Dabinin-Polanyi theory agree fairly well. The void fraction in natural heulandite is smaller because of occlusions in the channels and presence of stacking faults.
The changes in pore volume are interpreted on the basis of cation size. In the case of Na-heulandite, the pore volume is greater and in case of Cs-heulandite it is the least; for Ag-heulandite it appears that the structure is less stable and has low capacity to retain its structure after distortion and full hydration. K-heulandite might have contracted pores. At higher adsorption temperature, the adsorption capacity of all samples decreases because of framework distortion.
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