### CHAPTER 6

**STRUCTURAL CHANGES IN STILBITE AND HEULANDITE DUE TO ION-EXCHANGE : X-RAY STUDIES**

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CHAPTER 6

STRUCTURAL CHANGES IN STILBITE AND HEULANDITE DUE TO ION-EXCHANGE : X-RAY STUDIES

6.1 Introduction

The changing of the nature of the cations in a zeolite structure is a relatively simple task, and a variety of homoionic or mixed-ionic forms can be prepared using different cations. The fact that such alterations in ionic composition may produce some marked changes in properties such as thermal stability\(^1\), sieving\(^2\), sorption\(^3,4\) and catalysis\(^5\) is, from the purely practical point of view, one of the most important aspects of zeolite chemistry. In contrast to other ion-exchange materials like clays and organic resins, it is a distinctive feature of many zeolites, as established by X-ray diffraction, that the exchangeable cations may take positions in widely different crystallographic positions. The number of possible sites generally exceeds the crystal charge deficit which in turn may lead to a pattern of charge neutralization, which is characteristic for a given ion or a group of ions and which is quite sensitive to the state of hydration of the samples\(^6-10\).
It is well established that ion-redistributions occur in the course of an ion-exchange reaction\textsuperscript{6,11,12}.

Recent years have witnessed a spectacular revival of interest in X-ray powder techniques. Formerly, powder data were used only for identification purposes, and never for structure determination. Renaissance of powder diffraction and structure determination, from powder data by X-ray profile analysis, have been discussed in detail by Manohar\textsuperscript{13} recently. Several workers\textsuperscript{14,15} have employed powder diffraction to determine the structure and cation positions of synthetic zeolites.

This chapter includes observations and interpretations of X-ray powder diffractographs of various cation-exchanged forms of stilbite and heulandite. The changes observed in lattice parameters, unit cell volume and crystallinity of samples of different ionic compositions are discussed in relation to the positions of cations and other structural features of these zeolites.

Except earlier studies by Barrer et al\textsuperscript{16,17} on changes in lattice parameters and unit cell volumes of various cationic forms of analcime and chabazite, no reports are found on natural zeolites. Such studies are reported here for the first time on stilbite and heulandite.
6.2 Experimental

Ion-exchanged samples of stilbite and divalent cations are prepared as described earlier (section 5.2). X-ray powder diffraction patterns of the original samples (Ca-forms) of stilbite and heulandite and their different ion-exchanged forms are recorded with an X-ray diffractometer using CuKα radiation. The samples are scanned over a 2θ range of 4 to 45°, at a rate of 1°/min. Sufficient care is taken in preparing the powder samples and in recording X-ray diffraction patterns so as to maintain identical conditions.

The diffraction maxima are indexed by comparing the d-spacings with those of the original samples of stilbite and heulandite. By feeding observed θ values and the assigned hkl values, the lattice parameters a, b, c and β are refined with the help of a cell parameter refinement programme.

6.3 Results

X-ray powder diffraction pattern for the original Ca-form of stilbite is shown in Fig. 6.1. Figures 6.2 to 6.8 represent X-ray powder diffraction patterns for samples of stilbite ion-exchanged with
K, Cs, Ag, NH$_4^+$, Mg, Sr and Ba ions respectively. Figures 6.9 to 6.15 depict X-ray diffractographs of Ca-form and Li, K, Cs, Ag, NH$_4^+$ and Ba exchanged forms of heulandite.

The values of $a$, $b$, $c$ and $\beta$ obtained after 5 cycles of refinement are listed in Table 6.1 for stilbite and in Table 6.2 for heulandite, along with the corresponding unit cell compositions.

6.4 Discussion

It has been proposed by Mortier and Bosmans$^6$ that the ingoing ions may lead to a rearrangement of the other ions in the zeolite structure during ion-exchange reaction. Such a proposition is supported by some recent structural data on monoionic and biionic hydrated zeolites$^{6,11,12}$. A further indication of such an ion-redistribution is shown in an X-ray study of K-alkylammonium zeolite$^{19,20}$. The main cause for such repositioning of cations during ion-exchange is the presence of excess of possible neutralization points as compared to the number of exchangeable cations$^{21,22}$.

The characteristics of the ions as well as the ion-exchanger determine the selectivity of an exchanger for a certain ion. Maes and Cremers$^{23,24}$ have
### Table 6.1 Unit cell parameters of different cationic forms of stilbite.

<table>
<thead>
<tr>
<th>Unit cell contents</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>( \beta )</th>
<th>( V ) (( \text{Å}^3 ))</th>
<th>( \omega ) (degrees)</th>
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<tr>
<td>Ca₄.4 Al₂.8 Si₁₂.2 O₁.72</td>
<td>13.49</td>
<td>13.85</td>
<td>13.52</td>
<td>13.56</td>
<td>2252.85</td>
<td>11.24</td>
</tr>
<tr>
<td>Ca₄.2 Li₂.0 Al₄.8 Si₁₂.2 O₁.72</td>
<td>13.51</td>
<td>13.52</td>
<td>13.58</td>
<td>13.62</td>
<td>2252.85</td>
<td>11.24</td>
</tr>
<tr>
<td>Ca₃.3 (Li₂.4 Al₄.8 Si₁₂.2 O₁.72</td>
<td>13.51</td>
<td>13.52</td>
<td>13.58</td>
<td>13.62</td>
<td>2252.85</td>
<td>11.24</td>
</tr>
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<td>13.62</td>
<td>2252.85</td>
<td>11.24</td>
</tr>
<tr>
<td>Ca₂.0 Al₁.0 Si₁₂.2 O₁.72</td>
<td>13.58</td>
<td>13.62</td>
<td>13.62</td>
<td>13.62</td>
<td>2252.85</td>
<td>11.24</td>
</tr>
<tr>
<td>Unit cell contents (anhydrous)</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>β (°)</td>
<td>Volume (Å³)</td>
<td></td>
</tr>
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<td>-------------------------------</td>
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<td>-----</td>
<td>-----</td>
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<tr>
<td>Ca₄.23 Al₈.45 Si₂₆.8 O₇₂</td>
<td>17.73</td>
<td>17.82</td>
<td>7.43</td>
<td>116.2</td>
<td>2106.31</td>
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<td>Ca₃.88 Li₀.70 Al₈.45 Si₂₆.8 O₇₂</td>
<td>18.70</td>
<td>17.21</td>
<td>7.44</td>
<td>114.5</td>
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<td>Ca₃.15 K₂.16 Al₈.45 Si₂₆.8 O₇₂</td>
<td>18.14</td>
<td>18.08</td>
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<tr>
<td>Ca₃.09 Ca₂.28 Al₈.45 Si₂₆.8 O₇₂</td>
<td>17.83</td>
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<tr>
<td>Ca₂.51 (NH₄)₃.44 Al₈.45 Si₂₆.8 O₇₂</td>
<td>18.52</td>
<td>17.64</td>
<td>7.34</td>
<td>110.3</td>
<td>2241.64</td>
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<tr>
<td>Ca₂.24 Ba₁.99 Al₈.45 Si₂₆.8 O₇₂</td>
<td>18.20</td>
<td>17.68</td>
<td>7.32</td>
<td>110.1</td>
<td>2211.94</td>
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argued that cation positioning in small cages influences the selectivity in the large cages and vice versa.

One of the common features in most ion-exchange work in zeolite is that the selectivity is mostly referred to the Na ions, the Na form being generally used as a starting material. However, in the present investigations the Ca forms of stilbite and heulandite are used as starting materials, and various monovalent and divalent cations are substituted for Ca ions. Before proceeding to interpretation of variation in lattice parameters etc, it is necessary to discuss the cation sites in structures of stilbite and heulandite.

6.4.1 Cation sites in stilbite

In the structural model of stilbite proposed by Galli\(^{25}\) the exchangeable cations and water molecules have been found to occur completely inside the cavities formed at the intersection of the larger channels, which are parallel to \(a\), with the smaller channels parallel to \([102]\) direction. The Ca atom lies nearly on the screw axis at \(z/c = 0\). It is surrounded by and bonded to eight water molecules. Essentially there is a spheroidal hydrated Ca-\(\text{Si}_2\text{O}_5\) group. The biggest channels
surrounded by 10-member rings are filled by Ca-SH$_2$O spheroids. Between these spheroids and channel walls there are cavities; other cations are statistically distributed over these sites. These positions are surrounded by three water molecules and two framework oxygens. The coordination of the water molecules in stilbite is complex and varied (varies from triangular to octahedral).

In addition to the above referred two sites, which are designated as the main Ca, Na site and Na(1) site respectively, Maynard Slaughter\textsuperscript{26} has proposed three more sites Na(2), Na(3) and X sites. The positions of all these sites are represented as shown in Fig. 6.16. Ions at Na(2) and X are bound to four water molecules and oxygens. Ions at Na(3) are bound to two oxygens and very loosely bound to one water.

6.4.2 Cation sites in heulandite

In heulandite calcium is distributed over three special positions on the mirror plane\textsuperscript{27}). The sites 1 and 2 are located at the intersection of the 10- and 8-member tetrahedral ring channels. Both Ca 1 and 2 are in 8-fold coordination with three framework
oxygens and five water molecules.

The site 3 occurs at the intersection of two 8-member ring channels. Calcium 3 is also in 8-fold coordination with three framework oxygens and five water molecules. The four water molecules are closely associated with Al-substituted tetrahedra. All calcium ions are coordinated with oxygens in Al-substituted tetrahedra.

6.4.3 Structural changes due to ion-exchange in stilbite

(a) Alkali metal ion-exchange

The selectivity series observed for stilbite with alkali metal ions is Cs⁺ > K⁺ > Na⁺ ≫ Li⁺. The thermodynamic selectivity of the negatively charged framework for alkali metal ions decreases in the order in which the ionic hydration energies increase. This selectivity series is the one that should be observed if the first ions to be exchanged are the mobile hydrated ones. That means, ion-exchange takes place preferentially at the main sites (referred to as Ca, Na site²⁶). The entrance of alkali metal ions into the large cage where two alkali ions exchange for one Ca²⁺ ion requires the momentary dehydration of these alkali metal ions during
migration through the 10- and 8-member rings as well as the stripping of the water molecules from the Ca\(^{2+}\) ions to which they are coordinated. Such a momentary dehydration of the incoming and outgoing ions and the redistribution of the water molecules in the lattice thereafter will produce a rearrangement of the atoms in the unit cell. Consequently, the unit cell dimensions are likely to be altered. As can be predicted from the above considerations the hydration energy of the ions should play an important role in such alterations. The unit cell data listed in Table 6.1 are in good confirmation with these predictions. The changes in the unit cell dimensions are maximum with Li\(^{+}\) ion-exchange. Even though the exchange in this case is very small (only 4\%), the highest hydration energy of Li\(^{+}\) causes maximum disturbance and hence the large changes in unit cell dimensions. K\(^{+}\) and Cs\(^{+}\) ions have lower hydration energies and the alterations in unit cell dimensions are also comparatively smaller in these exchanges.

(b) Ag\(^{+}\) and NH\(_4\)^{+} ion exchange

The deviations in the values of unit cell dimensions in the case of Ag\(^{+}\)-exchange is observed to be minimum. This can be attributed to the high polarizability
of Ag$^+$ ions. The greater polarization energy contribution from Ag$^+$ ions should enable them to occupy even the lesser-hydrated sites and hence the greater selectivity of these ions.

When two NH$_4^+$ ions replace one divalent Ca$^{2+}$ ion, the changes occur not only in cation hydration but also in local charge distributions and electrostatic fields. Such changes are usually more pronounced than those in exchanges between similar valent ions$^{28}$. As can be seen from Table 6.1 the change in unit cell dimensions in Ca$^{2+} \rightarrow$ 2NH$_4^+$ exchange reaction is greater than that observed in di-divalent exchanges.

(c) Divalent ion-exchange

As anticipated the deviations in the values of unit cell dimensions due to divalent cation exchanges are comparatively small. This is so because equal number of Mg$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ ions replace originally present Ca$^{2+}$ ions. Here also, the hydration energy of the ions seems to play a major role. Mg$^{2+}$ ions having the highest hydration energy cause greater changes in unit cell dimensions than changes produced by other ions like Sr$^{2+}$ and Ba$^{2+}$ which have lower hydration energy.
Once again the selectivity series obtained for stilbite \((\text{Sr}^{2+}, \text{Ba}^{2+} > \text{Mg}^{2+})\) indicates that ion-exchange occurs preferentially at the main cation sites situated at the centres of larger 10-member ring channels.

6.4.4 Structural changes in heulandite due to ion-exchange

The structural changes in heulandite due to the exchange of \(\text{Ca}^{2+}\) ions with any other ion is more complicated because of the fact that \(\text{Ca}^{2+}\) ions are more tightly bound in heulandite structure than those in stilbite. The coordination of \(\text{Ca}^{2+}\) ions with the framework oxygen atoms, in addition to coordination with the water molecules would cause more pronounced redistribution of electron densities when these ions are replaced by other ions. Accordingly, the changes in unit cell dimensions are comparatively larger than those in stilbite as can be observed from the values listed in Table 6.2.

It is interesting to note that the maximum variation in unit cell dimensions occurs when \(\text{K}^+\) ions are exchanged. This observation is quite intriguing and cannot be explained on the basis of hydration energies of the cation alone. Some other factors such
as drastic change in the number of water molecules per unit cell and the resulting partial hydration of the cations may also be responsible.

The alteration in unit cell volume for \( \text{Ca}^{2+} \rightarrow 2\text{NH}_4^+ \) reaction is smaller than that for \( \text{Ca}^{2+} \rightarrow 2\text{Cs}^+ \) ion-exchange reaction. The higher preference for \( \text{NH}_4^+ \) ions indicates that these ions will have access to all the three cation sites in heulandite.

The close association of \( \text{Ca}^{2+} \) sites in heulandite with Al-substituted tetrahedra must be one of the major reasons for the complex deviations observed in the dimensions of the unit cell due to the ion-exchange reactions.

6.4.5 Crystallinity changes due to ion-exchange in stilbite and heulandite

The crystallinity of a sample is a measure of degree of periodicity of electron density distributions in the lattice. There have been reports of destruction of zeolite crystallinity due to ion-exchange\(^{29}\). Barrer attributes this reduction in crystallinity in some instances to the removal of a suitable space filling ion which occupied the void. Although no evidence is available,
an alternative explanation might be that with certain ions, which because of their size, are excluded from competing in the exchange, the resulting exchange is actually a hydrogen-ion-exchange.

In the present investigation it is observed that the X-ray diffraction peak intensities decrease markedly in some cases. Figures 6.4, 6.5 and 6.9 illustrate the large decrease in X-ray intensity observed when the Ca$^{2+}$ ions of stilbite are replaced by Cs$^+$, Ag$^+$ and Ba$^{2+}$ ions. Similarly, Figs. 6.12, 6.13 and 6.14 show considerable decrease in intensities of X-ray peaks due to the replacement of Ca$^{2+}$ ions in heulandite by K$^+$, Cs$^+$ and Ag$^+$ ions. The larger sizes of K$^+$, Cs$^+$ and Ba$^{2+}$ ions must be responsible for such distorting effects on the crystal lattice. The non-availability of enough number of electrons required for the proper coordination of these cations with the surrounding atoms or molecules in certain cases may also be one of the influencing factors.

Care must be exercised when interpreting zeolite structural stability from X-ray diffraction measurements alone. Large decreases in intensities can be observed which are not associated with destruction.
of crystallinity. Conversely, a material can be altered to exhibit quite different behaviour with very little observable change in the powder X-ray pattern. As for example, a large decrease in X-ray intensities is observed when the Na$^+$ ions of zeolite X are replaced by rare earth ions$^{2}$. Other measurements indicate little or no change in the degree of crystallinity.

6.5 Summary and conclusions

X-ray powder diffraction studies are carried out on various cation-exchanged forms of stilbite and heulandite. The unit cell parameters of each sample are refined using a computer programme and are compared with those of the original samples. The structural changes observed are explained. It is concluded that the hydration energy of the exchanging ion plays a significant role in effecting the observed structural changes in stilbite due to ion-exchange. The complex ion-exchange behaviour of heulandite is assigned to the special positions of cations in its unit cell. The decrease in X-ray intensities in a few specific cases are explained and correlated to the nature of exchanging ions.
References

1. T. Takaishi, Y. Yatsurugi, A. Yusa and T. Kuratomi
   J. C. S. Faraday I 71 (1975) 97

2. H. Bremer, W. Morke, R. Schodl and F. Vogt
   Adv. Chem. Ser. 121 (1973) 249

3. R. M. Barrer and I. M. Galabova
   Adv. Chem. Ser. 121 (1973) 357

4. T. A. Egerton and F. S. Stone
   J. C. S. Faraday I 69 (1973) 22

5. Kh. M. Minachev and Ya. I. Iskov

6. W. J. Mortier and H. J. Bosmans
   J. Phys. Chem. 72 (1971) 3327

7. P. Gallezot, Y. Ben Taarit and B. Imelik
   J. Catalysis 26 (1972) 295

8. Y. Huang and E. F. Vansant
   J. Phys. Chem. 77 (1973) 663

9. I. A. Maxwell and J. J. deBoer
   J. Phys. Chem. 72 (1975) 1874

10. A. Cremers
    A. C. S. Sym. Ser. 40 (1977) 179
11 D. H. Olson
   J. Phys. Chem. 74 (1970) 2758

12 M. L. Costenbole, W. J. Mortier, and
   J. B. Uytterhoeven
   J. C. S. Faraday I 72 (1976) 1877

13 H. Manohar
   Invited talk VIII 1, XIII National Symposium
   on Crystallography held at Nagpur University,
   March 15-18, 1982

14 M. L. Costenbole and A. Maes
   J. C. S. Faraday I 74 (1978) 131

15 A. Maes, J. Verlinden and A. Cremers
   J. C. S. Faraday I 75 (1979) 440

16 R. M. Barrer and L. Hinds
   J. Chem. Soc. (1953) 1879

17 R. M. Barrer and D. A. Langley
   J. Chem. Soc. (1958) 3817

18 T. P. Singh
   A computer Program to Refine Cell-Parameters
   (1975) Private Communication

19 W. J. Mortier and M. L. Costenbole
   Adv. Chem. Ser. 121 (1973) 125

20 W. J. Mortier, A. Cremers and J. B.
   Uytterhoeven
   J. Phys. Chem. 76 (1972) 650

21 B. K. G. Theng, E. F. Vansant and J. B.
   Uytterhoeven
   Trans. Faraday Soc. 64 (1968) 3370
22 E. F. Vansant and J. B. Uytterhoeven

23 A. Maes and A. Cremers
Adv. Chem. Ser. 121 (1973) 230

24 A. Maes and A. Cremers
J. C. S. Faraday I 21 (1975) 265

25 E. Galli

26 Maynard Slaughter

27 A. B. Merkle and M. Slaughter
Amer. Mineral. 52 (1968) 1120

28 R. M. Barrer, S. Barri and J. Klinowski
J. C. S. Faraday I 76 (1980) 1030

29 R. M. Barrer and D. A. Langley
J. Chem. Soc. (1958) 3804
Captions of the figures

Fig. 6.1  X-ray diffractograph of ST-Ca
Fig. 6.2  "  "  ST-K
Fig. 6.3  "  "  ST-Cs
Fig. 6.4  "  "  ST-Ag
Fig. 6.5  "  "  ST-NH₄
Fig. 6.6  "  "  ST-Mg
Fig. 6.7  "  "  ST-Sr
Fig. 6.8  "  "  ST-Ba
Fig. 6.9  "  "  HUL-Ca
Fig. 6.10 "  "  HUL-Li
Fig. 6.11 "  "  HUL-K
Fig. 6.12 "  "  HUL-Cs
Fig. 6.13 "  "  HUL-Ag
Fig. 6.14 "  "  HUL-NH₄
Fig. 6.15 "  "  HUL-Ba
Fig. 6.16  Projection of cations and water molecules on ac-plane of stilbite structure