CHAPTER 6

CATION SELECTIVITY AND INFRARED SPECTRA
OF CATION-EXCHANGED HEULANDITE

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PART I: CATION SELECTIVITY

6.1 Introduction

In Chapter 5 interpretation of exchange isotherms was considered, and it was shown that the explanation is reasonable. In the present chapter aspects of ion exchange selectivity are discussed. This is one of the areas in which ion exchangers have potential applications.

Zeolites may prove particularly useful in biological systems in which ion selectivity controls vital life processes\(^1\). The observations that ion specificity in zeolites can be correlated with structural parameters and that selectivity reversals can occur when there are two or more crystallographically different cation positions in the crystals may eventually lead to conclusions about local order and the presence of polyfunctionality in amorphous materials, such as biological materials where certain kinds of ion specificity and selectivity reversal occur.

6.2 Ion Selectivity

For ideal exchange involving uni-univalent ion pairs, the selectivity will be independent of the
composition of the zeolite and it can sometimes be very large for the entering ion, e.g., Ag in Na-, Li- or K-sodalite hydrate\(^2\). In many other zeolite exchangers the selectivity is strongly dependent upon cationic composition\(^3\). This is the case for almost all sigmoidal isotherms. The selectivity may differ among the ions for different degrees of exchange. Among the factors which influence selectivity may be included: (i) framework topology, (ii) ion size and shape, (iii) charge density of anionic framework, (iv) ion valency, (v) electrolyte concentration in the aqueous phase.

6.2.1 **Framework topology and ion size**

The framework topology, together with ion size, often determines whether a given ion can fit readily into the framework and the stability of the product\(^4,5\).

Among the open zeolite structures considerable regularity has been observed in the selectivity, when due allowance is made for the incomplete exchange sometimes encountered. Certain site groups may prove inaccessible to the entering ion and are then not included in formulating the equilibrium on the remaining accessible site groups. The sequences for mordenite\(^6\), phillipsite\(^7\), gismondine Na-p\(^8\), faujasite type Na\(^9,10\), faujasite type Na\(^{11}Y\),
zeolite A\textsuperscript{12,13}, chabazite\textsuperscript{14,15} and chabazite type zeolite K-G\textsuperscript{16} illustrate the point. Although there are irregularities the trend is very much striking; the heavy polarizable alkali metal ions of large ionic radius tend to be preferred by the zeolite and the smaller alkali metal ion by the aqueous phase.

Frequently encountered dependence of selectivity upon cationic composition of the zeolite makes it more difficult to present generalization. However, for low concentrations of the entering ion within the zeolite, the ion of greater size tends to be concentrated in the exchanger crystal. This means that zeolites such as mordenite are effective in concentrating Cs over Na or K, and K over Na in chabazite\textsuperscript{14}.

6.2.2 Charge density

In zeolite exchangers it is often possible to vary the SiO\textsubscript{2}:Al\textsubscript{2}O\textsubscript{3} ratio of a given framework, either by synthesis or by finding natural occurrences of different components. This represents a large change in the charge density which could affect the selectivity shown towards the given ion pair. This behaviour has been examined in aluminous and siliceous forms of faujasite\textsuperscript{9,11,15,17} and of chabazite\textsuperscript{14-16}. For exchange of pair of ions
between the aluminous (high charge) and siliceous (low charge) forms of the given zeolite the larger ion preferred by the low charge form and the smaller by the high charge one.

6.2.3 Ion sieving

As the size of the cation increases, in many zeolites, ion sieving can become clearly defined as molecular sieves. Ions must traverse the same channels as molecules, and may not be able to penetrate some or indeed any parts of the framework. Because many inorganic cations are considerably smaller than molecules, ion sieve effects for such ions were observed in compact frameworks. For organic ions, however, ion sieving is found among open frameworks. As a rule high temperature will offset the effect of larger ion radius. Thus, at $\approx 200^\circ C$, $Cs^+$ begins to migrate in analcime or sodalite. Double ion sieve effects are also observable in zeolite structures where small cages with restricted windows coexist with wider channels and windows in other parts of the same framework.

Ion sieving can result in some notable selectivities.$^{18}$ Thus Ag-analcime can readily and quantitatively remove Na-salts from admixture with Cs-salts.
6.2.4 Steric limitations

A further profound effect upon exchange of large ions in open tectosilicates is imposed by the rigid nature of the zeolite framework and hence the nearly fixed pore volume in zeolite. The effect is wholly distinct from ion sieving. Faujasite is one of most porous zeolites with approximately 55% of the volume of each crystal accessible to water molecules. However, faujasite is saturated when it has sorbed $\approx 30$ neopentane molecules per unit cell. Tetramethy lammonium (NMe$_4^+$) and neopentane (CMe$_4$) have about the same volume, so that about 30 NMe$_4^+$ ions would also fill the accessible pore volume in faujasite. However, in aluminous synthetic faujasite (zeolite X) there may be $\approx 90$ framework charges per unit cell. It follows that exchange for steric reasons not associated with molecule sieving must be limited when Na$^+$ is replaced by NMe$_4^+$ or other large organic cations.

6.2.5 Electrolytic concentration

For exchanges involving only univalent ions the concentration of the external electrolyte need have no large effect upon the selectivity. However, when the ions have different charges, the situation becomes more complex. The behaviour to be expected has been investigated
quantitatively\textsuperscript{6,19}). It has been shown that:

(i) selectivity becomes progressively greater for the ion of higher valence the more dilute the exchanging solution, and

(ii) isotherms without inflections and convex upwards may change with increasing dilution to sigmoid curves and finally back once more to curves without inflections but with the opposite curvatures.

6.3 \textit{Equilibrium Ion Specificity}

Cation selectivity refers to the preference order of a zeolite for cations based on the energetics of distance between anionic sites, cation radii and cationic hydration energies.

Eisenmann\textsuperscript{20}) has shown that the specificity of a surface containing fixed charges exhibits for alkali metal ions, when placed in an aqueous solution of these ions, can be accounted for, solely, in terms of ion hydration and electrostatic ion binding energies. It was assumed that anionic sites and the cations form ion pairs with no water interposed between the sites and the cations. Thus if a zeolite (cation exchanger) is placed in an aqueous solution
of the salts, AC1 and BC1, the preference of the exchanger for ion $A^+$ or ion $B^+$ depends on whether the difference in their hydration free energies or their coulombic energies of interaction with the fixed anionic exchange sites predominates.

Consider the reaction

$$A_s^+ + B_{ex}^+ \rightleftharpoons A_{ex}^+ + B_s^+$$

where $ex$ denotes the exchanger phase and $s$ the solution phase. The free energy change for this reaction can be written as

$$\Delta F_{AB}^0 = (F_{el}^A - F_{el}^B) - (F_{hyd}^A - F_{hyd}^B) \quad (6.1)$$

To evaluate $\Delta F_{AB}^0$ one needs to know the partial molar free energy of hydration of the ions, $F_{hyd}$, and the coulombic energy of interaction between the ions and anionic sites, $F_{el}$. Eisenmann has, as a first approximation, expressed the electrostatic free energy of ion site interaction by internal energies calculated with Coulomb's law by widely spaced sites.

$$F_{el} = -\frac{33.3}{(r_+ + r_-)} \quad (6.2a)$$
The Born-Lande equation for the internal energy of alkali metal halide crystals\(^21\) has been used for closely spaced sites.

\[ F_{el}^{el} = -1.56 \frac{(33.2)}{(r_+ + r_-)} \]  \hspace{1cm} (6.2b)

where
\( r_+ \) = radius of cation, nm
\( r_- \) = radius of anion, nm
\( F_{el} \) = electrostatic contribution to free energy, kcal/mole.

The radius of the anion is chosen so that it makes the field strength of the assumed monopolar anion equal to that of the actual multipole.

Eisenmann basically designed the model very successfully to determine the specificity for univalent ions and hence their sequences. This model is very well extended to obtain the specificity of divalent ions.

Consider the exchange of a divalent cation for a monovalent cation in a cation exchanger

\[
\frac{1}{2} A_s^{2+} + B_{ex}^{+} \rightleftharpoons \frac{1}{2} A_{ex}^{2+} + B_s^{+}
\] \hspace{1cm} (6.3)

The free energy of reaction is given by

\[
\Delta F_{AB}^\circ = \left( \frac{1}{2} F_A^{el} - F_B^{el} \right) - \left( \frac{1}{2} F_A^{hyd} - F_B^{hyd} \right)
\] \hspace{1cm} (6.4)
and has the units of kcal per gram equivalent of ions. The free energy of reaction is evaluated by using free energy of hydration cited in the literature$^{22}$.

The interaction of a divalent cation with the fixed uninegative charges whose centers are separated by a distance $d$ is considered. If the divalent cation is on line between the fixed charges at a distance $x$ from one of them, the electrostatic free energy, neglecting entropy contributions, as a first approximation, is given by

$$F_{el} = -\frac{2e^2}{x} - \frac{2e^2}{d-x}$$

$$= -\frac{66.4}{x} - \frac{66.4}{d-x}$$ \hspace{1cm} (6.5)

In eqn. (6.5) $x$ and $d$ are expressed in nm and $F_{el}$ in kcal per gram equivalent ion. Evaluation of first and second derivatives of $F_{el}$ with respect to $x$ indicates that although $dF_{el}/dx = 0$ when $x = d/2$, a cation located at this position would be in metastable equilibrium, because the electrostatic energy is maximum and would prefer being close to one of the fixed charges. Thus the electrostatic energy is given by

$$F_{el} = -\frac{66.4}{r_+ + r_-} - \frac{66.4}{d(r_+ + r_-)}$$ \hspace{1cm} (6.6)
When the intersite distance is equal to or smaller than
\[ 2(r_+ + r_-) \]

\[ F^e_l = \frac{-132.8}{(r_+ + r_-)} \]  
(6.7)

To evaluate \( F^e_l \) Goldschmitt's empirical radii or Pauling radii are used.

6.4 Experimental Details

Ca based heulandite (cf. 5.4.1) is used to carry out ion exchange. 2 g of heulandite is put in 1 M chloride solutions (except for Ag where nitrate solution is used) containing \( \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Rb}^+, \text{Cs}^+, \text{Ag}^+, \text{Mg}^{2+}, \text{Sr}^{2+} \) or \( \text{Ba}^{2+} \) as cations. The volume of the solution used is 100 cc which is more than needed for cent percent exchange (cf. 5.4.2). Ca-based heulandite is in contact with solutions for 72 hrs and the process is carried out at room temperature (30°C).

To decide the selectivity of multivalent cations, in particular, rare earth (like, Th, Ce and Y), weak solutions were used since strong solutions formed turbidity and precipitate in contact with Ca-based heulandite. Strength of the solution used was 0.02 M. Univalent cation exchange using 0.02 M solution was also carried out.
for the sake of comparison. The contact period in all the cases was 72 hrs.

The mixtures were filtered and the filtrates collected were used to estimate the calcium content using flame photometry and EDTA titration (cf. 5.4.4). The residues were washed using acidified distilled water and after drying were subjected to chemical analysis by EDAX.

6.5 Results and Discussion

Comparison of percentage exchange in Table 6.1 shows that exchange is predominant in case of univalent cations. The sequence of univalent cations is

\[ \text{NH}_4^+ > K^+ > Ag^+ > Na^+ > Rb^+ > Cs^+ \]

and for divalent ones is

\[ \text{Sr}^{2+} > Mg^{2+} > Ba^{2+} \].

Exchange is more in all univalent cation except in Rb^+ and Cs^+. The size of cations decreases in order of \[ \text{NH}_4^+ > K^+ > Ag^+ > Na^+ \]. In all the exchanges Si/Al ratio is not affected much emphasizing that the crystallinity of the material is maintained.

It is observed that at very low concentration of solutions, yttrium and thorium do not exchange at all, whereas cerium exchange is 18.5% with oxide formula for Ce-heulandite \( \text{Ca}_{3.75} \text{Ce}_{0.07} \text{Al}_{7.89} \text{Si}_{28.16} \text{O}_{72} \) and Si/Al
Radius and hydration free energy of cations exchanged with Ca\(^{2+}\) on heulandite using 1 M solutions. Oxide formula and percentage exchange:

<table>
<thead>
<tr>
<th>Radius of cation (nm)</th>
<th>Formula on the basis of 72 oxygens (O(^{2-}) is common to all)</th>
<th>Si/Al</th>
<th>Free energy of hydration (kcal/g ion)</th>
<th>Percent exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.140 Ca(<em>{0.25})(NH(</em>{4}))(<em>{0.75}) Al(</em>{7.53}) Si(_{28.66})</td>
<td>3.81</td>
<td>185.0</td>
<td>93.5</td>
<td></td>
</tr>
<tr>
<td>0.133 Ca(<em>{0.48}) K(</em>{0.52}) Al(<em>{8.42}) Si(</em>{28.11})</td>
<td>3.34</td>
<td>179.9</td>
<td>87.4</td>
<td></td>
</tr>
<tr>
<td>0.126 Ca(<em>{0.79}) Ag(</em>{0.21}) Al(<em>{7.32}) Si(</em>{29.67})</td>
<td>4.05</td>
<td>146.0</td>
<td>79.3</td>
<td></td>
</tr>
<tr>
<td>0.095 Ca(<em>{1.46}) Na(</em>{0.54}) Al(<em>{7.90}) Si(</em>{28.68})</td>
<td>3.63</td>
<td>162.3</td>
<td>61.8</td>
<td></td>
</tr>
<tr>
<td>0.148 Ca(<em>{1.66}) Rb(</em>{0.46}) Al(<em>{7.47}) Si(</em>{29.21})</td>
<td>3.91</td>
<td>185.0</td>
<td>56.5</td>
<td></td>
</tr>
<tr>
<td>0.169 Ca(<em>{2.42}) Cs(</em>{0.83}) Al(<em>{7.36}) Si(</em>{29.02})</td>
<td>3.94</td>
<td>192.7</td>
<td>36.7</td>
<td></td>
</tr>
<tr>
<td>0.113 Ca(<em>{1.53}) Sr(</em>{0.92}) Al(<em>{7.54}) Si(</em>{30.85})</td>
<td>4.09</td>
<td>175.1</td>
<td>60.0</td>
<td></td>
</tr>
<tr>
<td>0.065 Ca(<em>{1.96}) Mg(</em>{0.64}) Al(<em>{7.40}) Si(</em>{28.64})</td>
<td>3.87</td>
<td>65.6</td>
<td>48.7</td>
<td></td>
</tr>
<tr>
<td>0.135 Ca(<em>{3.14}) Ba(</em>{0.05}) Al(<em>{7.51}) Si(</em>{28.77})</td>
<td>3.83</td>
<td>205.9</td>
<td>17.8</td>
<td></td>
</tr>
</tbody>
</table>
Heavy univalent cations like Rb$^+$ and Cs$^+$ over other univalent cations, rubidium having larger percentage of exchange and potassium the least (Table 3). Moreover, the trend in selectivity for NH$_4^+$, Na$^+$, is reversed as compared to selectivity when 1 M solution used. Hence, the series is influenced by strength used. For 0.02 M solution, series for univalent ions is Rb$^+$ > Cs$^+$ > Na$^+$ > Ag$^+$ > K$^+$ > NH$_4^+$. The radii of NH$_4^+$, K$^+$, Ag$^+$ and Na$^+$ respectively 0.14, 0.133, 0.126 and 0.095 nm and a series exhibits weak field selectivity, since in the strongest field pattern, selectivity decreases with increasing radius of the univalent ion considered. Accordingly, the series should have been Cs$^+$ > Rb$^+$ > NH$_4^+$ > K$^+$ > Ag$^+$ > Na$^+$ > NH$_4^+$.

It may be noted that cesium and rubidium have valuable free energy of hydration higher than those of other percentage exchange in these two cases is smaller because of steric hindrances.

To explain the selectivity series for exchange with Ca$^{2+}$ on heulandite, Eisenmann's model was used. As the divalent cation is in exchanger phase

\[ Rb^+ > Cs^+ > Na^+ > Ag^+ > K^+ > NH_4^+ \]
### Table 6.2 Oxide formula and percentage exchange of univalent cations exchanged to Ca$^{2+}$ on heulandite using 0.02 M solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide formula on the basis of 72 oxygens</th>
<th>Si/Al</th>
<th>Percentage exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbH</td>
<td>Ca$<em>{3.5}$ Rb$</em>{0.66}$ Al$<em>{7.98}$ Si$</em>{30.85}$</td>
<td>3.87</td>
<td>45.7</td>
</tr>
<tr>
<td>CsH</td>
<td>Ca$<em>{3.62}$ Ca$</em>{0.11}$ Al$<em>{8.22}$ Si$</em>{29.99}$</td>
<td>3.40</td>
<td>21.3</td>
</tr>
<tr>
<td>NaH</td>
<td>Ca$<em>{3.93}$ Na$</em>{0.54}$ Al$<em>{7.55}$ Si$</em>{28.24}$</td>
<td>3.74</td>
<td>14.3</td>
</tr>
<tr>
<td>AgH</td>
<td>Ca$<em>{4.34}$ Ag$</em>{0.81}$ Al$<em>{8.12}$ Si$</em>{27.54}$</td>
<td>3.39</td>
<td>5.65</td>
</tr>
<tr>
<td>KH</td>
<td>Ca$<em>{4.56}$ K$</em>{0.30}$ Al$<em>{9.20}$ Si$</em>{26.72}$</td>
<td>2.91</td>
<td>0.89</td>
</tr>
<tr>
<td>NH$_4$H</td>
<td>Ca$<em>{4.58}$ (NH$<em>4$)$</em>{0.21}$ Al$</em>{8.15}$ Si$_{27.87}$</td>
<td>3.42</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Percentage exchange = $\frac{\text{Ca}^{2+} \text{ gone out}}{\text{Ca}^{2+} \text{ before exchange}}$ x 100
\[
A^+_s + \frac{1}{2} B^{2+}_{\text{ex}} \rightleftharpoons \frac{1}{2} B^+_s + A^+_{\text{ex}}
\]

and hence the equation (6.4) for free energy changes to

\[
\Delta F^o_{AB} = (F^e_A - \frac{1}{2} F^e_B) - (F^\text{hyd}_A - \frac{1}{2} F^\text{hyd}_B) \quad (6.8)
\]

Cation B is Ca\(^{2+}\) and so

\[
\Delta F^o_{ACa} = (F^e_A - \frac{1}{2} F^e_{Ca}) - (F^\text{hyd}_A - \frac{1}{2} F^\text{hyd}_{Ca}) \quad (6.9)
\]

Substituting eqn. (6.7) for \(F^e\), eqn. (6.9) becomes

\[
\Delta F^o_{ACa} = (- \frac{132.8}{r^+_A + r^-} + \frac{1}{2} \frac{132.8}{r^+_{Ca} + r^-}) - (F^\text{hyd}_A - \frac{1}{2} F^\text{hyd}_{Ca}) \quad (6.10)
\]

where \(r^+_A\) represents cation radius and \(r^+_{Ca}\), radius of calcium ion. \(r^+_{Ca} = 0.099\) nm and \(F^\text{hyd}_{Ca} = 140.2\) kcal/g ion. Hence eqn. (6.10) becomes

\[
\Delta F^o_{ACa} = - 132.8 \left( \frac{1}{r^+_A + r^-} - \frac{0.5}{0.099 + r^-} \right) - (F^\text{hyd}_A - 70.1) \text{ kcal/g ion} \quad (6.11)
\]
Replacing A as \( \text{NH}_4^+ \), \( K^+ \), \( \text{Na}^+ \), \( \text{Ag}^+ \), \( \text{Rb}^+ \) or \( \text{Cs}^+ \) and \( r_+A \) as respective radius in eqn. (6.11) and varying \( r_- \), different values of \( \Delta F_{\text{ACa}}^o \) are obtained for different \( r_- \) for different exchange reactions. Graphs of \( \Delta F_{\text{ACa}}^o \) versus \( r_- \) are plotted for different reactions as shown in Fig. 6.1.

It is seen that there is no intersection of the curves to decide the selectivity series as Eisemann formulated different series for uni-univalent and uni-divalent exchanges. The values of \( \Delta F_{\text{ACa}}^o \) for rubidium and ammonium exchanges are equal for all values of \( r_- \) as their hydration energies are equal and radii nearly equal. Experiment shows total disagreement with this prediction.

The curves obtained in present case have very good similarity with those obtained for exchanges for \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \) and \( \text{Ba}^{2+} \) with \( \text{Na}^+ \) on zeolite under assumption that the sites are infinite distance apart\(^{20}\). This suggests two things: (i) in the present case the assumption that the sites are close may be incorrect, or (ii) this is failure of Eisemann's simple model.

The second suggestion is more probable because in this model Eisemann considers only two factors. They
uni-univalent or uni-divalent exchanges are concerned as in the present case it fails.

It is worthwhile to note here that it has very small influence on exchange, as is seen from the marks on $\Delta F^a_Ca$ axis. Comparison of this value with the value of $\Delta F^a_Ca$ for respective exchanges explains point. This clearly indicates weak-field selectivity. One has to take into account other factors (cf. 6.1) influencing selectivity to interpret the series.

The elution of yttrium and thorium by virtue of the steric hindrances.

Another model is proposed by Barrer and Falconer in which water and zeolite phases are as a continuous dielectric medium with different dielectric constants. As in Eisenmann's model, in this case all changes that are of demonstrable importance are neglected and for these reasons it is perhaps less significant...
heulandite is established. The univalent ion exchange with 
Ca$^{2+}$ on zeolite yields a series $\text{NH}_4^+ > \text{K}^+ > \text{Ag}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$ in strong solution (1 M) indicating weak field pattern. 

It is tried to obtain this series using Eisenmann's model. 

It fails but provides information that contribution of $F^{\text{el}}$ to $\Delta F_{\text{ACa}}$ is very small and selectivity is decided by other factors including hydration energies predominantly.

The concentrations of solution used for exchange have definite influence. 0.02 M solutions used to have exchange with Ce, Y and Th yield exclusions of Th and Y and Ce has 18.47% exchange. The series for univalent cations at this concentration indicates a strong field selectivity except for Rb$^+$ and Cs$^+$ and is $\text{Rb}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Ag}^+ > \text{K}^+ > \text{NH}_4^+$. For divalent cations used, the series is $\text{Sr}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+}$.

PART II: INFRARED SPECTRA OF CATION EXCHANGED HEULANDITE

6.7 Introduction

The geometrical structure of zeolite is discussed considering $\text{SiO}_4^-$ and $\text{AlO}_4^-$ tetrahedra as the basic units linked by common oxygen atoms. Owing to the
fact that coordination number of aluminium exceeds its valency, the AlO$_4$ tetrahedra possess a single negative charge and may be considered as large complexing anion. It is essential feature that the negative charge is not concentrated on the periphery, but is distributed over the internal O-Al bonds of the complex. The compensatory positive cation, however, is concentrated in exchange cations of much smaller radius and at least part of the cations may come into direct contact with the molecules being absorbed. This feature of the chemical structure of the zeolite framework determines the nature of its interaction with molecules of variety of electronic structures. Thus, zeolites are specific adsorbents carrying on the surface concentrated positive charges such as acidic hydrogen atoms of hydroxyl groups, and small cation near distributed negative charges such as exist particularly on complex anions.

Infrared spectroscopy can give useful information about constitution and surface properties of zeolites and how these are modified by various treatments. Changes in the spectra of the zeolite and of molecules adsorbed on the surface can yield direct information about the surface, how adsorbed molecules interact, and where molecules adsorb. There are several reports$^{24-29}$ in literature on applications of infrared spectroscopy to zeolites.
In the present case, infrared absorption bands were assigned to different modes of vibration and attempts were made to explain any changes in these bands as a result of cation exchange.

6.8 Experimental Details

The samples chosen in present investigation are NH$_4^-$, K$^-$, Rb$^-$, Ag$^-$, Cs$^-$ and Na-H. The composition of these samples is as depicted in Table 6.2. The samples with low percentage of ion exchange are used since large percentage of ion exchange influences the water content in zeolite, as shown in following chapter. The infrared patterns are obtained as described in Chapter 3.

6.9 Results and Discussion

Figure 6.2 exhibits infrared spectra for Na$^-$, NH$_4^-$, K$^-$, Rb$^-$, Ag$^-$ and Cs-heulandite. Each of the spectra differs in some respect from others.

6.9.1 Water bands

The absorption bands at frequencies greater than 3000 cm$^{-1}$ correspond to hydroxyl stretch (OH stretch). For NaH the band at 3680 cm$^{-1}$ is distinguishable from broad shoulder at 3480 cm$^{-1}$. According to Uytterhoeven et al.$^{30}$ a band near 3690 cm$^{-1}$ corresponds to water
Fig. 6.2  Infrared patterns of Na-, NH$_4$-, K-, Rb-, Ag- and Cs-heulandite.
The region of 3660 - 3590 cm$^{-1}$ depends upon the type of cation. In present case also the first hydroxyl group is at different frequencies. For NaH it is at 3660 cm$^{-1}$ whereas for NH$_4$H it is at 3660 cm$^{-1}$, for KH at 3640 cm$^{-1}$, for RhH at 3660 cm$^{-1}$, for AgH at 3650 cm$^{-1}$, and for CsH at 3640 cm$^{-1}$.

Bertsch and Habgood$^{32}$ studied the spectra of H$_2$O molecules adsorbed by LiX, NaX and zeolites. In all the cases sharp vibrational bands were observed for OH groups - 3720 cm$^{-1}$ for LiX, 3690 cm$^{-1}$ for NaX and 3648 cm$^{-1}$ for KX, as well as wider bands for OH groups linked by hydrogen bonds (at 3400 cm$^{-1}$). The presence of these absorption bands in the spectrum was interpreted by Bertsch and Habgood as resulting from the interaction of the lone electron pairs of the oxygen atom in the water molecules with the exchange cation of the hydrogen atom of the water molecule with the oxygen atom in the zeolite lattice.

The broader peaks at 3480 cm$^{-1}$ for 3460 cm$^{-1}$ for NH$_4$H, KH, AgH and CsH and 3440 cm$^{-1}$.
belongs to water molecules interacting mainly with the exchange cations\(^{33}\) are stronger in NH\(_4\)H, KH and RbH. The spectrum for NH\(_4\)H shows that peak at 3660 cm\(^{-1}\) is more intense than 3460 cm\(^{-1}\) peak. This may be by virtue of additional OH bands formed by decomposition of NH\(_4^+\) as is reported by Kiselev and Lygin\(^{26}\).

The band at 1640 cm\(^{-1}\) for NaH, NH\(_4\)H, KH, RbH, AgH and CsH corresponds to H\(_2\)O bend. The region around this is also known as deformation region. According to Zhdanov et al\(^{33}\) the intensity of this band depends upon the cation content. As seen from Table 6.2 percentage exchanges of Rb\(^+\), Cs\(^+\) and Na\(^+\) are high. Consequently, the peak at 1640 cm\(^{-1}\) in these samples is less intense compared to corresponding peaks in spectra for other forms of heulandite.

6.9.2 Framework vibrations

In each spectrum, the strongest band occurs at 1200 cm\(^{-1}\) associated with a broader one at 1070 cm\(^{-1}\) or 1060 cm\(^{-1}\). These are fundamental tetrahedral modes in silica, i.e. Si–O asymmetric stretches and so are insensitive to external changes\(^{36-37}\). Si–Si symmetric stretch modes are at 790, 720, and 670 cm\(^{-1}\). The peaks at 720 cm\(^{-1}\) in spectra for NaH, RbH and CsH are weak. This shows that a large number of cations in this framework influences the symmetric stretch vibrations.
These modes discussed are assigned by many workers\textsuperscript{38,39} to pure Si-O vibrations and distinct Al-O vibrations assigned in the region of 715-815 cm\textsuperscript{-1}. Stubican and Roy\textsuperscript{35-37} point out that one should not expect vibrations of pure cation-anion (e.g. Si-O) bonds in aluminosilicate frameworks and introduce Si-O-Al combination frequencies. Kolesova\textsuperscript{40} also uses same notation and assignment. Therefore, instead of assigning SiO\textsubscript{4} or AlO\textsubscript{4} bands distinctly Flanigen et al\textsuperscript{41} use TO\textsubscript{4} unit. The strong band at 460 cm\textsuperscript{-1} corresponds to T-O bend and is insensitive to external changes.

Double rings are absent in heulandite structure. Flanigen et al\textsuperscript{41} associate the peaks in the region 500-650 cm\textsuperscript{-1} to double rings. The peak at 600 cm\textsuperscript{-1} and 525 cm\textsuperscript{-1} in present case, may be the peaks because of the stacking sequences in heulandite. Such stacking sequences exist in phillipsite, chabazite and zeolite W in which such peaks are observed\textsuperscript{41}. These bands are sensitive to external changes. It is seen in spectra for NaH, RbH and CsH that the above mentioned bands are very weak as compared to those for KH, AgH and NH\textsubscript{4}H.

A small peak at 420 cm\textsuperscript{-1} corresponds to pore opening and is sensitive to external changes. Spectra for NaH, RbH and CsH clarify this.
Conclusions

The changes in infrared pattern of heulandite by virtue of presence of cations other than calcium are significant.

Hydroxyl stretch frequency is different for different samples, since the frequency of hydroxyl stretch in the region 3660 - 3590 cm\(^{-1}\) depends upon the type of cation. The peak at 3660 cm\(^{-1}\) in NH\(_4\)H is stronger than that at 3460 cm\(^{-1}\) because additional hydroxyls are formed by ammonium decomposition. In spectra for NaH, RbH and CsH, the 1640 cm\(^{-1}\) H\(_2\)O band is weak.

NaH, RbH and CsH show significant changes in bands at frequencies which correspond to external linkages and so are sensitive to external changes, e.g. the bands at 600, 525 and 400 cm\(^{-1}\). The T-T symmetric stretch peak at 720 cm\(^{-1}\) is markedly reduced in intensity for NaH, RbH and CsH suggesting influences on this mode of vibration because of large ion exchange.
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