CHAPTER II

SYNTHESIS AND ION EXCHANGE

PROPERTIES OF STANNIC MOLYBDOPHOSPHATE
The inorganic ion exchangers are used extensively in various fields e.g. in fuel cell, in kidney machine etc. (1-4) due to their superiority over organic resins as they are more stable at high temperatures and in the presence of radiation. In recent years the wide applicability of these inorganic materials as catalysts in organic and inorganic reactions opened a new chapter in the field of inorganic ion exchangers (5).

Among the synthetic inorganic ion exchangers classified by Pekarek et al. (6). The heteropolyacids and their salts have been paid a considerable attention because of some novel selectivities towards metal ions (7).

The various salts of heteropolyacid of molybdenum tungsten and vanadium were synthesised and studied as ion exchangers (previous chapter). Among them, Ammonium molybdophosphate (AMP) was widely used in the separation of inorganic and organic compounds using various chromatographic techniques (8-15). Molybdophosphoric acid (MPA) and its salts were also used as catalysts in organic reactions such as in oxidation of unsaturated aldehydes to the corresponding acids (16-18). However, no studies have been reported on the synthesis and analytical applications of stannic molybdophosphate. It was therefore decided to synthesise this material and to study its ion exchange properties.

This chapter describes the systematic studies under-
taken to prepare stannic molybdophosphate and to study such properties as ion exchange capacity, thermal and chemical stability. The ion exchange equilibria for the systems of alkaline earth metal ion/H⁺ at various temperatures on stannic molybdophosphate is also included in this chapter.

**Experimental**

**Reagents**

Stannic chloride pentahydrate (J.T. Baker Philipsburg New Jersey) sodium molybdate dihydrate (Veb Jena, Germany) and molybdophosphoric acid (BDH Poole England) were used in this study. All other chemicals were of AnalR Grade.

**Apparatus**

The following instruments were used: Elico model LIOT pH meter for pH titration, spekol (Carl Zeiss Jena Germany) for colorimetric determinations, a spectromon 2000 for IR studies and a stanton thermobalance for TGA studies.

**Synthesis of molybdophosphoric acid (MPA)**

This acid was prepared by WU's (19) method by dissolving 100 gm sodium molybdate in 200 ml of distilled water and adding 10 ml of orthophosphoric acid (85 %) and 100 ml concentrated hydrochloric acid. The clear solution was transferred to one litre separatory funnel and shaken well with 150 ml of ether. After cooling and standing for a few
minutes three layers were formed. The lowest layer which contained the whole complex acid was transferred to another separatory funnel, the complex acid was again extracted with fresh ether. It was then transferred to another beaker and evaporated on a water bath where yellow crystals of molybdophosphoric acid were obtained.

*Synthesis of stannic molybdophosphate via free acid (Sample 1)*

10 gms of MPA and 35 gms of stannic chloride were separately dissolved each in one litre of distilled water. The MPA solution was added to stannic chloride solution in different ratios. When a yellowish precipitate was obtained. The precipitate was refluxed into the mother liquor for ten hours. The precipitate was filtered off and washed with distilled water. The product was dried and immersed in water where in it broke into small granules with crackings. To convert the material into the H⁺ form it was kept in 1.5M nitric acid solution for two days. The material was then washed with water and dried at 50°C. The yellow transparent type product was obtained.

*Synthesis of stannic molybdophosphate via sodium salt (Sample II)*

These samples were prepared by mixing the acidic solution of 0.1M stannic chloride to the solutions of 0.1M sodium molybdate and 0.1M sodium dihydrogen phosphate in ratio 2:1:1 at different pHs. The so obtained yellow precipitate was
allowed to stand for 24 hours at room temperature for digestion and aging. The precipitate was washed by decantation and filtered off and dried at 50°C in an electric oven. The material was converted into H⁺ form as usual.

**Chemical composition**

0.3 g exchanger was dissolved in concentrated hydrochloric acid. Molybdenum was determined with α-benzoin oxime (20) as MoO₃. Tin was precipitated by hydrogen sulphide and determined with potassium dichromate after reduction with Lead (21). Phosphorus was determined with magnesia mixture solution (22) gravimetrically in the filtrate.

**Chemical stability**

The exchanger (0.5 g) was kept in different solvents (50 ml) for 24 hours. After removal of undissolved material, tin, molybdenum, and phosphorus were determined spectrophotometrically by haematoxyline (23) acetone (24) and vanadomolybdophosphoric acid (25) methods respectively.

**Ion exchange capacity**

The ion exchange capacity for various metal ions was determined by the column process. H⁺ ions from the exchanger were eluted by 1M alkali metal halide and 0.5 M alkaline earth metal halide solutions. The H⁺ eluted ions were titrated
against standard sodium hydroxide solution. The results are given in Table 2.

**pH titration**

pH titrations were performed by the method of Topp and Pepper (26). The material (0.5 g) in H⁺ was equilibrated with the solution (50 ml) containing alkali metal chlorides/hydroxides for 24 hours. After removing undissolved material the pH of the filtrate was measured. The plots are shown in Fig. 2.

**Thermal studies**

The SMP samples in H⁺ were heated in a muffle furnace at different temperatures for an hour. The effect of heat treatment on the ion exchange capacity of the material along with the effect of heat on other ion exchange materials is presented in Table 3.

The water contents of the SMP in Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ forms were also determined by heating to constant weight in air oven at 200°C. The results are given in Table 5

**IR studies**

IR spectra of the SMP samples and molybdophosphoric acid were recorded using the KBr disc technique. The results are shown in Fig. 1.
Thermogravimetric analysis (TGA)

TGA of the SMP samples in $H^+$ form were performed at a heating rate of 10°C/min. Under atmosphere of $N_2$. The results are shown in Fig. 3.

Equilibrium time

In order to obtain some idea about equilibrium time, 20 ml of solutions of each metal nitrate/nitric acid were equilibrated with the exchanger (0.2 g). The material was withdrawn from the solution at intervals and the pH of the solution was measured. It was found that the equilibrium was attained within two hours in all cases.

Ion exchange equilibria

The ion exchange isotherms were studied at 30, 45, 60°C.

In the forward reaction 0.2 g SMP was equilibrated with 20 ml of a solution of varying ratio of alkaline earth metal nitrate/nitric acid in glass stopped flasks in temperature controlled shaker at 0.1 constant ionic strength. The material was filtered after equilibrium and the concentration of the metal ions and $H^+$ ions in the solution were determined titrimetrically with standard ethylenediamine tetra acetic acid (EDTA) and sodium hydroxide solutions respectively. The concentrations of alkaline metal ions and hydrogen ions in solid phase and in solution phase were deduced from the
change between the initial and equilibrated concentrations in aqueous solution. The mole fractions of $H^+$ and $M^{2+}$ in exchanger phase and in solution phase were calculated on the basis of maximum ion exchange capacity (0.85 meq/g).

Reversibility of the exchange was confirmed by performing similar experiments with the corresponding metal forms of the exchanger.

**Results and Discussion**

Heteropolyacid salts can be prepared either by adding salt solution to the free heteropolyacid solution (via free acid) or by direct precipitation of mixed anion (molybdate, tungstate, vanadate etc.) solutions (via sodium salt). Ammonium molybdophosphate (AMP) shows the same ion exchange behaviour whether prepared via free acid or via sodium salt while tungstophosphate and molybdoarsenate do not show similar behaviour when prepared by these two methods (35).

Stannic molybdophosphate (SMP) a new ion exchange material is also prepared by these two methods. The SMP material was synthesized by the free acid method (Sample I) by adding MPA solution to the solution of stannic chloride at different ratios, whereas the sample II was synthesized by the sodium salt method by adding the 0.1M solution of stannic chloride to the solutions of 0.1M sodium molybdate
and 0.1M sodium dihydrogen phosphate in the ratio 2:1:1 at different pHs. In the latter case it is seen that at higher pH i.e. in alkaline medium no precipitation take place, it is probably due to formation of their respective salt at this pH. The Table 1 shows that the samples are quite stable in nitric acid and ammonium nitrate but it is dissolved in sodium hydroxide solution probably due to the degradation of heteropolyacids into their salts. The chemical composition of these two samples (I,II) is also shown in Table 1.

The ion exchange capacity of the SMP for alkali and alkaline earth metal ions is given in Table 2. The ion exchange capacity increases as the hydrated radius of the cation decreases it means that the counter ions exchange in the hydrated forms.

The variation in the ion exchange capacity of SMP heated to various temperatures is given in Table 3. The ion exchange capacities of other tin based exchangers are also included in this table for comparison. It is seen that the ion exchange capacity decreases with increase in temperature. This decrease in ion exchange capacities is due to the condensation of hydroxyl groups and the conversion of acid phosphate into pyrophosphate. On comparison it is seen that the SMP material can act as a good ion exchanger even at about 400°C. The retention of some ion exchange capacity at 600°C is due to the formation of oxides.
Table 1: Synthesis, ion exchange capacity, composition and dissolution of stannic molybdophosphate

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Synthesis</th>
<th>ion exchange capacity, meq/g</th>
<th>Composition Mo : P : Sn</th>
<th>Dissolution (mg/50 ml) 0.1N HNO&lt;sub&gt;3&lt;/sub&gt; 1N NaOH 1N NH&lt;sub&gt;4&lt;/sub&gt;NO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>DC</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>MPA + Sn(IV)Cl&lt;sub&gt;4&lt;/sub&gt; (1%) (3.5%)</td>
<td>2:1 0.83</td>
<td>1:1:2</td>
<td>0.1-0.8-0.6 0.02-0.01-0.0</td>
<td>DC</td>
</tr>
<tr>
<td>II</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;MoO&lt;sub&gt;4&lt;/sub&gt; + NaH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt; + Sn(IV)Cl&lt;sub&gt;4&lt;/sub&gt; 1:1:2 0.99</td>
<td>1:6:3 0.00-0.1-0.23 0.00-0.19-0.13</td>
<td>DC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D.C. Dissolved completely
MPA = Molybdophosphoric acid
Table 2: Ion exchange capacity of stannic molybdo-phosphate for various cations

<table>
<thead>
<tr>
<th>Cations</th>
<th>taken as (concentration)</th>
<th>Hydrated radii (Å)</th>
<th>Ion exchange capacity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample I</td>
<td>Sample II</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Chloride (1M)</td>
<td>3.40</td>
<td>0.67</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Nitrate (1M)</td>
<td>2.76</td>
<td>0.83</td>
</tr>
<tr>
<td>K⁺</td>
<td>Nitrate (1M)</td>
<td>2.30</td>
<td>0.92</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Nitrate (0.5M)</td>
<td>7.00</td>
<td>0.58</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Nitrate (0.5M)</td>
<td>6.30</td>
<td>0.63</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>Nitrate (0.5M)</td>
<td>-</td>
<td>0.79</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>Nitrate (0.5M)</td>
<td>5.90</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Table 3: Effect of drying-temperature on the ion exchange capacities (meq/g) of various tin (IV) based ion exchangers

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Drying temperature (°C)</th>
<th>SnMoP Sample A</th>
<th>SnMoP Sample B</th>
<th>SnMo(27,28)</th>
<th>SnP(29)</th>
<th>SnAsP(30)</th>
<th>SnMoAs(31)</th>
<th>SnBMo(32)</th>
<th>SnWAs(33,34)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.81</td>
<td>0.99</td>
<td>1.00</td>
<td>1.35</td>
<td>1.75</td>
<td>1.20</td>
<td>1.12</td>
<td>1.18</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>0.58</td>
<td>0.52</td>
<td>0.07</td>
<td>0.82</td>
<td>0.90</td>
<td>0.60</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>0.45</td>
<td>0.46</td>
<td>0.02</td>
<td>0.02</td>
<td>0.20</td>
<td>0.35</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>0.25</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>0.28</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>0.15</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
<td>0.00</td>
<td>-</td>
<td>0.00</td>
<td>0.04</td>
</tr>
</tbody>
</table>

SnMoP = stannic molybdophosphate; SnMo = stannic molybdate; SnP = stannic phosphate
SnMoAs = stannic molybdoarsenate; SnBMo = stannic boratomolybdate
SnWAs = stannic tungstoarsenate
The IR spectra of MPA and SMP samples in the H⁺ forms are given in Fig. 1 and the peak to peak correlation is given in Table 4. It is seen that the peak or band of phosphate group does not come in the range 2200-2400 cm⁻¹ in heteropolyacids and their salts.

The X-ray diffraction patterns of the SMP samples show an amorphous nature. The pH titration curves are given in Fig. 2. The curves reveal the monofunctional acidic behaviour of the SMP samples. For Li⁺, there is gradual increase in pH as we increase the concentration of OH⁻ ions. Hence, the exchanger is partially converted into Li⁺ form. whereas in the case of Na⁺ ion there is steep rise in pH 2.5 to 11. This shows that there is less conversion of exchanger into Na⁺ form at this pH range. On the other hand we may conclude that the exchanger phase prefers Li⁺ than Na⁺ ion in this pH range. No significance difference has been observed in the samples prepared by the free acid method or by the sodium salt method.

The thermogravimetric analysis (TGA) curves are shown in Fig. 3. It is clear from the figures that as the drying temperature is increased the weight is decreased gradually upto about 250°C and more slowly from 250 to 600°C. From 600°C there is no further appreciable decrease. This loss in weight may be due to the loss of external water molecules and, conversion of phosphate into pyrophosphate and
Figure 1. IR spectra of molybdenum phosphoric acid and stannic molybdenum phosphoric acid (MSP).
Table 4: Peak to Peak Correlation of IR spectra of stannic molybdophosphate and molybdophosphoric acid

<table>
<thead>
<tr>
<th>Band (cm⁻¹)(43)</th>
<th>Nature of peak</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molybdophosphoric acid</td>
<td>Tin(IV) molybdophosphate</td>
</tr>
<tr>
<td>3400ᵃ</td>
<td>OH stretching or coordination water</td>
<td>Weak, Broad</td>
</tr>
<tr>
<td>1600ᵇ</td>
<td>Structural water molecule</td>
<td>Weak, Sharp</td>
</tr>
<tr>
<td>1065ᶜ</td>
<td>PO₄, HPO₄, H₂PO₄</td>
<td>Strong Sharp</td>
</tr>
<tr>
<td>960ᵈ</td>
<td>PO₄, HPO₄, H₂PO₄</td>
<td>Strong Sharp</td>
</tr>
<tr>
<td>860ᵉ</td>
<td>Mo-O or Sn-O</td>
<td>Strong Shoulder</td>
</tr>
<tr>
<td>800ᶠ</td>
<td>Mo-O or Sn-O</td>
<td>Strong Broad</td>
</tr>
</tbody>
</table>
Figure 2. pH titration curves for SMP sample 1
Figure 7.6 pH titration curves for SiP Sample II
Figure 3.a TGA curve of SMP Sample I
Figure 1.b TGA curve of SMP Sample II
condensation of hydroxyl groups.

On the basis of the chemical composition the TGA and the IR studies tentative formulæ for the SMP samples are proposed with the help of Alberti's equation:\(^{36}\)

\[
\frac{18n}{18n + \text{MW}} = \frac{\text{weight loss (\%)} \times 100}{100}
\]

where \(n\) = no. of external water molecules and
\(\text{MW}\) = Molecular weight of the exchanger

From TGA curves we find that the maximum loss in sample I is about 25 \(\%\) and in sample II it is about 22.4 \(\%\), but it is assumed that at 200\(^0\)C only external water molecules are removed from the exchanger on heating and the weight loss upto 200\(^0\)C for sample I is 14 \(\%\), then the no. of external water molecules will be 3.10 and the tentative formula will be

\[
[(\text{SnO}_2)_{2}(\text{MoO}_3)(\text{H}_3\text{P}_4\text{O}_7)] \cdot 3.10\text{H}_2\text{O}
\]

and formula for sample II will be

\[
[(\text{SnO}_2)(\text{MoO}_3)_{0.33}(\text{H}_3\text{P}_4\text{O}_7)_2] \cdot 5.33\text{H}_2\text{O}
\]

The water contents of the exchanger in the Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\) forms are given in Table 5. The water contents increases as the hydrated radius of the cation increases. A similar behaviour has also been reported for ferric anti-
Table 5: Water contents towards various cations

<table>
<thead>
<tr>
<th>Cationic form</th>
<th>Ionic radii (Å)</th>
<th>Hydrated radii (Å)</th>
<th>Water contents (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>0.80</td>
<td>7.00</td>
<td>14.00</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.08</td>
<td>6.30</td>
<td>13.00</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.21</td>
<td>-</td>
<td>12.00</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1.44</td>
<td>5.90</td>
<td>11.00</td>
</tr>
</tbody>
</table>
monate (37). Plots of $y^0$ vs water contents and hydrated radii vs water contents are shown in Fig. 4. It is surprising that in each case the $\gamma$ water content is double the hydrated radius.

The exchange isotherm for $\text{Mg}^{2+}/\text{H}^+$, $\text{Ca}^{2+}/\text{H}^+$, $\text{Sr}^{2+}/\text{H}^+$ and $\text{Ba}^{2+}/\text{H}^+$ exchange at 30°C are given in Fig. 5. No marked hysterisis loops were observed hence the systems are reversible and suitable for thermodynamic studies. From the above figures it appears that the alkaline earth metal ions are not preferred over hydrogen ions by SMP. These isotherms also indicate the preference of alkaline earth metal ions in order of $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$. The selectivity coefficient of the reaction

$$2\text{RH} + \text{M}^{2+} \rightleftharpoons \text{R}_2\text{M} + 2\text{H}^+ \tag{1}$$

is given by

$$S_H^M = \frac{X_M^2X_H^2}{X_M^2X_H^2}$$

where $X_M$ and $X_H$ refer to the mole fractions of the metal ions and hydrogen ion in the exchanger phase and $X_M$ and $X_H$ to the mole fractions of metal ion and hydrogen ion in solution phase. It is observed that the selectivity coefficient of exchanging ion decreases with the increase in $X_M$.

The thermodynamics equilibrium constant for the
Figure 4(a) Plot of ionic radii ($\frac{r}{r^0}$) vs water contents

Figure 4(b) Plot of hydrated radii vs water contents.
reaction (1) in terms of activity coefficient is given by

\[ K_M^H = \frac{\bar{\gamma}_M \bar{\gamma}_H^2 \cdot \bar{\gamma}_M \bar{\gamma}_H^{2\gamma} \cdot f_M^2 f_H^2}{x_M x_H^{2\gamma} f_M f_H^{2\gamma}} \]  

(2)

where \( f_M \) and \( f_H \) are activity coefficient in the solution phase while \( f_M^* \) and \( f_H^* \) refer to the activity coefficient in the solution phase. The activity coefficients in the solution phase have been calculated by the equation:

\[ \log \frac{\gamma_{H}^2}{\gamma_M} = \log \frac{\gamma_{HNO_3}^4}{\gamma_{M(NO_3)_2}^4} = \frac{2s1}{1+1.5/1} \]  

(3)

\[ s = 1.8252 \times 10^6 (P/\varepsilon^3 T^3)^{1/2} \]

where \( P \) is the density of water, \( \varepsilon \) the dielectric constant of water and \( T \) the absolute temperature of the systems.

The value of \( f_M^* \) and \( f_H^* \) were calculated by Gains and Thomas equation (39).

\[ \ln f_M = (1 - \bar{x}_M) \ln S - \int_{\bar{x}_M}^{1} \ln S d\bar{x}_M \]  

(4)

\[ \ln f_H = -\bar{x}_M + \int_{0}^{\bar{x}_M} \ln S d\bar{x}_M \]  

(5)

The plots of selectivity coefficients (logs) vs \( \bar{x}_M \) are given in Fig. 6. These plots indicate nonlinear relationship for the exchange process.
The calculated values for $K^M_H$ in terms of $\log K^M_H$ vs temperature ($1/T \times 10^3$) are plotted in Fig. 7. It shows that the values of $K^M_H$ increase with increase in temperature.

The free energy change ($\Delta G^0$) for the exchange equilibrium has been calculated by the equation

$$\Delta G = -\frac{RT \ln K^M_H}{Z_M Z_H}$$

where $R$ is the gas constant $Z_M$ and $Z_H$ refer to the valencies of competing ions and $T$ is absolute temperature of the exchange reaction. The results (Table 7) show that $\Delta G^0$ varies with the size of exchanging ions.

The $\Delta H^0$ values have been calculated by the following equation (40)

$$\Delta H^0 = -\frac{R}{Z_M Z_H} \frac{d (\ln K)}{d (1/T)}$$

$\Delta H^0$ values indicate that the exchange taken place with absorption of heat which decreases from Ca$^{2+}$ to Ba$^{2+}$ gradually.

The change in the entropy values has been calculated by the equation $\Delta G^0 = \Delta H^0 - T \Delta S^0$ and the entropy differences between corresponding ion-forms of the exchangers $\Delta S_{ex}$ can be given as (41)
Figure 7: Plot of log $K$ vs. $1/T 	imes 10^3$ temperature.
Table 6: Thermodynamic data for the ion exchange of alkaline earth metals/Hydrogen ions on stannic molybdophosphate

<table>
<thead>
<tr>
<th>Temperature (K°)</th>
<th>Mg^{2+}</th>
<th>Ca^{2+}</th>
<th>Sr^{2+}</th>
<th>Ba^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>lnK</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>-3.117</td>
<td>-3.275</td>
<td>-1.350</td>
<td>-1.190</td>
</tr>
<tr>
<td>318</td>
<td>-2.046</td>
<td>-2.321</td>
<td>-0.820</td>
<td>-0.470</td>
</tr>
<tr>
<td>333</td>
<td>-2.046</td>
<td>-1.233</td>
<td>-0.830</td>
<td>-0.110</td>
</tr>
<tr>
<td>ΔG° (Cal/mole)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>939</td>
<td>887</td>
<td>406</td>
<td>353</td>
</tr>
<tr>
<td>318</td>
<td>647</td>
<td>734</td>
<td>259</td>
<td>147</td>
</tr>
<tr>
<td>333</td>
<td>678</td>
<td>409</td>
<td>278</td>
<td>037</td>
</tr>
<tr>
<td>ΔH° (Cal/mole)</td>
<td>3100</td>
<td>4430</td>
<td>3795</td>
<td>2455</td>
</tr>
<tr>
<td>ΔS° (Cal/deg/mole)</td>
<td>7.1</td>
<td>11.7</td>
<td>11.2</td>
<td>6.9</td>
</tr>
<tr>
<td>ΔS°_{ex} (Cal/deg/mole)</td>
<td>-8.8</td>
<td>5.3</td>
<td>7.2</td>
<td>8.1</td>
</tr>
</tbody>
</table>
\[ \Delta S^0 = \Delta S_{ex} = (S_M^0 - S_H^0) \]

where \( S_M^0 \) and \( S_H^0 \) refer to the aqueous ionic entropies (42). The results are given in Table 7.

\( \Delta S^0 \) decreases from Ca\(^{2+}\) to Ba\(^{2+}\). It shows \( \Delta S^0 \) varies in accordance with hydrated radii of exchanging ions.
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