Synthesis and ion-exchange behaviour of acrylamide zirconium(IV) phosphate: A novel crystalline and Hg(II) selective hybrid inorganic ion exchanger

K G Varshney*, Vandana Jain & Namrita Tayal
Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, India

Received 17 September 2001; revised received 25 November 2002; accepted 14 December 2002

A new phase of hybrid material, acrylamide zirconium(IV) phosphate, has been synthesized and characterized with the help of ion exchange, IR, TGA and XRD studies. The ion-exchange and distribution studies indicate that the material is highly selective for mercury. On this basis some binary separations have been performed on its column thus exploring its analytical potential.

The organic ion exchangers are well-known for their uniformity, chemical stability and for the easy control over their ion-exchange properties through synthetic methods. Inorganic ion-exchangers have established their place in analytical chemistry due to their resistance to heat and radiation and their differential selectivity for metal ions. In order to get a combination of these advantages and to increase the interlayer distance of layered inorganic ion-exchangers so that large species or complexes could be exchanged, many hybrid type exchangers have been developed by incorporation of a polymeric material into inorganic matrix, by way of pillaring or by other non-pillaring methods.

Zirconium based ion-exchangers have received attention because of their excellent ion-exchange behaviour and some important chemical applications in the field of ion-exchange, ion-exchange membranes, solid state electrochemistry and phase transition etc. They possess good stability towards temperature, ionizing radiations and oxidizing solutions.

The present study is an extension of earlier studies in this direction on the materials based on zirconium. An acrylamide based zirconium phosphate has been synthesized and characterized which has shown a promising behaviour as ion-exchanger. The results are presented in this paper.

Experimental Procedure

Reagents and chemicals

Zirconiyl oxy chloride (ZrOCl₂·8H₂O) and acrylamide (CH₂=CHCONH₂) were the CDH (India) products while ortho phosphoric acid (H₃PO₄) was a Qualigens (India) product. All other reagents and chemicals were of AnalaR grade.

Instrumentation

Spectrophotometric determination were carried out on an Elico SL 171 spectrophotometer, while X-ray diffraction studies were performed on a Philips analytical X-ray B.V. diffractometer type PW 1710. pH measurements were performed using an Elico model LI-10 pH meter and IR studies were carried out by the KBr disc method. For thermogravimetric analysis a Cahn thermobalance model 2050 was used.

Preparation of the reagent solutions

Solutions of zirconiyl oxy chloride, acrylamide, phosphoric acid, and hydrogen peroxide were prepared in demineralized water (DMW).

Synthesis of the ion-exchange material

A number of samples were prepared by adding 0.05 M zirconiyl oxy chloride, 0.1 M acrylamide, 2 M ortho phosphoric acid and 0.5% H₂O₂. The pH of the resulting gel was maintained 0-1 by adding concentrated HNO₃ with constant stirring. The resulting slurry obtained under these conditions was stirred for 2 h at a temperature of 70±5°C, using a magnetic stirrer. The slurry was then filtered, and washed with demineralized water (pH ~6). The material was finally dried at 45°C. The dried gel was then cracked into small granules by putting in DMW and converted into the H⁺-form by treating with 1 M HNO₃ for 24 h with occasional shaking and intermittently replacing the supernatant liquid with fresh acid. The material thus obtained was then

*For correspondence (E-mail: romu_gopal@rediffmail.com)
washed with demineralized water to remove the excess acid, dried at 45°C, and sieved to obtain particles of size 50-70 mesh. Tables 1 and 2 give the experimental details of the synthesis of the various samples of the material. Thus, on the basis of its ion exchange capacity sample 1 of Table 2 is selected for further studies.

**Ion-exchange capacity (i.e.c.)**

This was determined by the column process taking 1 g of the material (H⁺-form) in a glass tube of internal diameter of ~1 cm, fitted with glass wool at its bottom. 250 mL of 1 M NaNO₃ solution was used as eluent, maintaining a very slow flow rate (~0.5 mL min⁻¹). The effluent was titrated against a standard alkali solution to determine the total H⁺-ions released. Table 3 summarizes the ion-exchange capacity of the material for various metal ions.

**Effect of eluent concentration on the ion-exchange capacity**

The extent of elution was found to depend upon the concentration of the eluent. Hence a fixed volume (250 mL) of the NaNO₃ solution of varying concentrations was passed through the column containing 1 g of the exchanger and the effluent was titrated against a standard alkali solution for the H⁺-ions eluted out. Fig. 1 shows the variation of the H⁺-ions eluted out with the different concentrations of the eluent. The optimum concentration of the eluent for a complete elution of H⁺-ions in 250 mL NaNO₃ solution was found to be 1 M.

**Elution behaviour**

The column containing 1 g in the H⁺-form was eluted with 1 M NaNO₃ solution in different 10 mL fractions having a standard flow rate of 0.5 mL min⁻¹ and 10 mL fractions of the effluent were collected. They were titrated for the H⁺-ions released against a standard NaOH solution. This experiment was conducted to find out the minimum volume necessary for a complete elution of H⁺-ions, which reflects the efficiency of the column. The result is shown in Fig 2.

**Thermal studies**

1 g samples of the material were heated at various temperatures for 1 h each in a muffle furnace and their ion-exchange capacity was determined by the column process after cooling to room temperature. The results are summarized in Table 4. Fig. 3 shows the TGA curve of the material.

**pH Titrations**

pH titrations were performed by the batch process using the method of Topp and Pepper. 500 mg portions of the exchanger in the H⁺-form were placed

---

### Table 1—Synthesis of various samples of acrylamide based zirconium(IV) phosphate

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Conc. of Zr (M)</th>
<th>Conc. of H₃PO₄ (M)</th>
<th>Conc. of acrylamide (M)</th>
<th>Ion-exchange capacity (meq dry g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>2.0</td>
<td>0.05</td>
<td>0.85</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>1.0</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>1.0</td>
<td>0.1</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>2.0</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

---

### Table 2—Synthesis of acrylamide based zirconium(IV) phosphate by varying the conc. of H₂O₂

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Conc. of Zr (M)</th>
<th>Conc. of H₃PO₄ (M)</th>
<th>Conc. of acrylamide (M)</th>
<th>Conc. of H₂O₂%</th>
<th>Heating time (h)</th>
<th>Ion-exchange capacity (meq dry g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>0.5</td>
<td>2</td>
<td>2.26</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>1</td>
<td>2</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>2</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>3</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>4</td>
<td>2</td>
<td>0.84</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>2.0</td>
<td>0.1</td>
<td>0.5</td>
<td>4</td>
<td>0.44</td>
</tr>
</tbody>
</table>
in each of the several 250 mL conical flasks followed by equimolar solution of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 mL to maintain the ionic strength constant. The pH of the solution was recorded after equilibrium and was plotted against the milli-equivalents of the OH\(^-\) ions added. The results are shown in Fig. 4.

**IR studies**

Figure 5 shows the IR spectrum of the material taken by the KBr disc method.

**X-ray studies**

Figure 6 shows the X-ray diffraction pattern of the material. Table 5 summarizes the results of these studies.

**Distribution studies**

200 mg portions of the exchanger in H\(^+\)-form were taken in 20 mL of the different metal ion solutions in the required medium and kept for 24 h with intermittent shaking to attain equilibrium. The initial metal ion concentration (0.001 M) in the solution was so adjusted that it did not exceed 3% of total ion-exchange capacity of the material. The determinations before and after equilibrium were carried out volumetrically using EDTA\(^-\) as the titrant.

The \(K_d\) values, as summarized in Table 6 were obtained by the formula:

\[
K_d = \frac{I - F}{F} \cdot \frac{V}{M} (\text{mL/g})
\]

where, \(I\) is the initial metal ion concentration, \(F\) is the final metal ion concentration, \(V\) is the volume of the solution and \(M\) is the mass of the exchanger.

**Separations achieved**

Several binary separations were tried using a column of internal diameter ~0.6 cm containing 2 g of the material. The column was washed thoroughly with
deminarlized water and the mixture to be separated was loaded on it, maintaining a flow rate of 2.3 drops min\(^{-1}\) (0.15 mL min\(^{-1}\)). The separation was achieved by passing a suitable solvent through the column as eluent and the metal ions in the effluent were determined quantitatively by EDTA titrations. Table 7 and Fig. 7 give the salient features of the separations.

**Results and Discussion**

The acrylamide based zirconium(IV) phosphate prepared in these studies has some promising ion-exchange properties. A comparison reveals that the prepared acrylamide based zirconium phosphate

![Equilibrium pH titration curve of acrylamide zirconium (IV) phosphate.](image1)

![IR spectrum of acrylamide zirconium(IV) phosphate.](image2)

![X-ray diffraction pattern of acrylamide zirconium(IV) phosphate.](image3)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>DMW</th>
<th>0.01M</th>
<th>0.1M</th>
<th>1M</th>
<th>0.01M</th>
<th>0.1M</th>
<th>1M</th>
<th>0.01M</th>
<th>0.1M</th>
<th>1M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)</td>
<td>1484.6</td>
<td>610.3</td>
<td>564.5</td>
<td>564.5</td>
<td>1616.6</td>
<td>692.3</td>
<td>635.7</td>
<td>796.6</td>
<td>635.7</td>
<td>488.5</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>614.2</td>
<td>589.6</td>
<td>471.4</td>
<td>440.5</td>
<td>1566.6</td>
<td>952.6</td>
<td>809</td>
<td>733.3</td>
<td>506</td>
<td>455.5</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>1850</td>
<td>408.6</td>
<td>333.3</td>
<td>244.1</td>
<td>619.4</td>
<td>265.6</td>
<td>225</td>
<td>963.6</td>
<td>515.7</td>
<td>387.5</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>3333.3</td>
<td>1187.5</td>
<td>1111.7</td>
<td>1111.7</td>
<td>1616.6</td>
<td>1484.6</td>
<td>1484.6</td>
<td>1772.7</td>
<td>1273.3</td>
<td>880.9</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>6400</td>
<td>747.8</td>
<td>712.5</td>
<td>680</td>
<td>875</td>
<td>596.4</td>
<td>509.3</td>
<td>828.5</td>
<td>712.5</td>
<td>596.4</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>2800</td>
<td>2220</td>
<td>1446.6</td>
<td>728.5</td>
<td>1188.8</td>
<td>759.2</td>
<td>673.3</td>
<td>1446.6</td>
<td>1350</td>
<td>1121.0</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>2566.6</td>
<td>1233.3</td>
<td>1100</td>
<td>548.6</td>
<td>1163.1</td>
<td>674.1</td>
<td>485.3</td>
<td>860</td>
<td>531.5</td>
<td>380</td>
</tr>
<tr>
<td>Cr(II)</td>
<td>50</td>
<td>15.38</td>
<td>15.38</td>
<td>15.38</td>
<td>7.14</td>
<td>7.14</td>
<td>7.14</td>
<td>7.14</td>
<td>7.14</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>1366.6</td>
<td>1366.6</td>
<td>1194.1</td>
<td>856.5</td>
<td>4300</td>
<td>2650</td>
<td>1275</td>
<td>3042.8</td>
<td>1733.3</td>
<td>1366.6</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>5750</td>
<td>2825</td>
<td>1200</td>
<td>836</td>
<td>3800</td>
<td>1362.5</td>
<td>1131.5</td>
<td>4580</td>
<td>2027.2</td>
<td>1070</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>11250</td>
<td>11250</td>
<td>11250</td>
<td>7466.6</td>
<td>22600</td>
<td>4440</td>
<td>3683.3</td>
<td>11250</td>
<td>4440</td>
<td>3683.3</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>3371.4</td>
<td>3371.4</td>
<td>1329.4</td>
<td>1250</td>
<td>1635.7</td>
<td>1520</td>
<td>1418.75</td>
<td>4760</td>
<td>2600</td>
<td>2109</td>
</tr>
</tbody>
</table>

**Table 6** - \( K_a \) values of metal ions on acrylamide based zirconium(IV) phosphate in DMW, hydrochloric acid, nitric acid and perchloric acid media.
### Table 7—Binary separations of metal ions achieved on acrylamide based zirconium (IV) phosphate columns

<table>
<thead>
<tr>
<th>S. No</th>
<th>Separation achieved</th>
<th>M$_1$ Amount loaded (µg)</th>
<th>M$_2$ Amount found (µg)</th>
<th>Error (%)</th>
<th>Eluent used</th>
<th>Volume of eluent (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(II)-Hg(II)</td>
<td>4579.94</td>
<td>5504.56</td>
<td>5504.56</td>
<td>Ni: 0.1 M HCl, Hg: 1 M HCl + 1 M NH$_4$Cl</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>Cd(II)-Hg(II)</td>
<td>4858.40</td>
<td>4742.72</td>
<td>5504.56</td>
<td>Cd: 1 M HNO$_3$, Hg: 1 M HCl + 1 M NH$_4$Cl</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>Pb(II)-Hg(II)</td>
<td>4968.15</td>
<td>4968.15</td>
<td>5379.46</td>
<td>Pb: 1 M HCl, Hg: 1 M HCl + 1 M NH$_4$Cl</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Mg(II)-Hg(II)</td>
<td>4038.45</td>
<td>4134.611</td>
<td>5379.46</td>
<td>Mg: 0.1 M HCl, Hg: 1 M HCl + 1 M NH$_4$Cl</td>
<td>70</td>
</tr>
</tbody>
</table>

Fig. 7—Separation of Ni$^{2+}$ from Hg$^{2+}$; Cd$^{2+}$ from Hg$^{2+}$; Pb$^{2+}$ from Hg$^{2+}$; and Mg$^{2+}$ from Hg$^{2+}$ on acrylamide zirconium(IV) phosphate columns: (a, g) 0.1 M HCl; (b, d, h) 1 M HCl + 1 M NH$_4$Cl; (c) 1 M HCl; (e) 1 M HNO$_3$.

 possesses a better ion-exchange capacity (2.26 meq dry gram$^{-1}$) than the materials prepared earlier$^{10,11}$ such as zirconium(IV) tungstophosphate (1.88 meq dry g$^{-1}$) and styrene supported zirconium phosphate (2.18 meq dry g$^{-1}$). Another most peculiar characteristic of this material is its thermal stability. The material retains 100% of its ion-exchange capacity on heating up to 100°C whereas the materials prepared earlier retain only 95.7% (zirconium(IV) tungstophosphate) and 56.43% (styrene supported zirconium phosphate) of its ion-exchange capacity on heating up to 100°C. Acrylamide zirconium phosphate retains 100% of its ion-exchange capacity on heating up to 200°C whereas in case of zirconium(IV) tungstophosphate, it retains only 90.4% of its ion-exchange capacity on heating up to 200°C.

The elution behaviour indicates that the exchange is quite fast and almost all the H$^+$-ions are eluted out in the first 110 mL of the effluent from a column of 1 g exchanger (Fig. 2). The optimum concentration of the eluent was found to be 1 M (Fig. 1) for a complete
removal of H⁺-ions from the above column. Moreover, the pH titration studies (Fig. 4) reveal that the material behaves as a bifunctional acid for Li⁺-ions showing its theoretical ion-exchange capacity at equilibrium ~3.5 meq g⁻¹. The bifunctional behaviour becomes less prominent in case of the H⁺-Na⁺ exchange. The ion-exchange capacity for this ion is found to be little less (~3.25 meq g⁻¹). However, in case of K⁺ the exchanger appears to be a monofunctional acid i.e., the exchange process is completed in a single step. The value of the ion-exchange capacity further decreases in this case (~3 meq g⁻¹). This discrepancy may be explained on the basis of the hydrated radii of these ions, which are in the order: Li⁺>Na⁺>K⁺. A metal ion with a lower hydrated radii may be exchanged more effectively on the exchanger surface.

The TGA curve (Fig. 3) shows a 16% weight loss upto ~200°C, which may be due to the removal of the external water molecules “n” from the material. The slow weight loss between 200-510°C may be due to the decomposition of the organic part of the material. An abrupt loss of weight between 510-590°C may be ascribed to the condensation of H₃PO₄ to P₂O₇ groups. At 590°C onwards the smooth horizontal curve represents the formation of the pyrophosphate phase.

The number of external water molecules (n) is calculated using the Alberti’s equation with the help of composition of the material which is a separate study under progress.

The IR studies (Fig. 5) confirm the presence of the external water molecules in addition to the O-H and the metal oxide groups in the material. The metal oxide bands are observed at 610 cm⁻¹, while bands at 508 and 1050 cm⁻¹ indicate the presence of PO₄³⁻ group. The presence of external water molecule is indicated by the band at 1600 cm⁻¹, in addition to its usual range at 3000-3500 cm⁻¹. The peak at 2380 cm⁻¹ may be ascribed to the presence of –NH₂ groups in the acrylamide moiety.

The X-ray diffraction pattern (Fig. 6) of the material exhibits very sharp and well-defined peaks indicating a well crystalline character of the material.

The distribution behaviour of the metal ions (Table 6) shows a high selectivity of the material for Hg(II) ions, indicating its importance in environmental studies. It was demonstrated by practically achieving some binary separations involving Hg(II), for example: Hg-Ni, Hg-Cd, Hg-Pb, and Hg-Mg, as summarized in Table 7. The results were found to be quite precise and reproducible.

Acknowledgement
Namrta Tayal wishes to thank CSIR (India) for financial assistance.

References