New phosphorus-containing ionites based on allyl-phosphonium salts

T.M. Mirkamilov and B.A. Muhamedgaliev

Translation submitted by E.A. Inglis

Considerable attention has been directed recently at the synthesis of ionites in connection with the expansion in their areas of application as sorbents for purifying industrial waste fluids, in hydrometallurgy of non-ferrous and rare metals etc. It is known that the synthesis of most ion-exchange materials is carried out basically by chemical conversion of polymers and copolymers, but this method is characterised by many stages and complexity of the process, often accompanied by side reactions. In addition, the final products have low chemical and thermal stability, selectivity etc. These disadvantages restrict the spheres of use of ion-exchange resins in practice (refs. 1 and 2).

For this reason it is important to look for the simplest methods of synthesis of ionites with good physico-chemical and thermal properties and with good sorption capacity for metals such as copper, cobalt, nickel, uranium etc. It was therefore of interest to study the sorption properties of products obtained by the copolymerisation of para-tris-phosphate-allyl triphenylphosphonium bromide with acrylonitrile and methyl methacrylate.

The high-molecular products synthesised by copolymerisation of these materials, after treatment with a 5% aqueous alkaline solution for conversion to the OH form, consist of ion-exchange resins having a high exchange capacity and a group of valuable properties.

We studied the selective properties of the synthesised ionites based on p-tris-phosphate-ATPB with acrylonitrile and MMA for bivalent ions in aqueous solutions of nitric acid. From preliminary tests on the sorption under static conditions, the sorption capacity of the ionites for bivalent ions of metals in 0.8 n nitric acid, and it has an affinity with bivalent ions of uranyl, nickel, cobalt, copper and lead, the uranyl being sorbed much more strongly than the other ions. It was established experimentally that as in the case of (ref. 2) the sorption of bivalent ions falls sharply with increase in the concentration of acid in the initial solution. The order of selectivity of the bivalent ions for the synthesised ionites is as follows:

\[ \text{p-t-p-ATPPB} : \text{AN} - \text{UO}_2^{++} > \text{Cu}^{++} > \text{Ni}^{++} > \text{Pb}^{++} > \text{Co}^{++} \]

\[ \text{p-t-p-ATPPB} : \text{MMA} - \text{UO}_2^{++} > \text{Co} > \text{Pb}^{++} > \text{Cu}^{++} > \text{Ni}^{++} \]

As can be seen, the ionites have a clearly pronounced affinity for the uranyl ion, which is due to the fact that UO\(^{++}\) ions are sorbed via the formation of stable complexes as a result of interaction of the unshared pair of electrons of the phosphoryl oxide with the metal ions being adsorbed.

The ion-exchange resins obtained were subjected to physico-chemical and mechanical tests. To assess the effectiveness of the synthesised ionites their sorption properties were compared with analogous properties of other ionites (see Table).

As can be seen from the Table, the synthesised ionites have better sorption properties than ionites obtained from vinylbenzyl-bromide (VBB) with N,N-dimethylaminomethyl methacrylate (DMAEMA) and vinyl pyridine (VP). Vinylbenzyl-bromide, dimethyaminoethyl methacrylate and vinyl pyridine are monomers that are more difficult to obtain.
Considerable interest attaches to studies of the rates of sorption of copper, nickel and cobalt by these ionites from 0.1 n sulphate solutions of these metals. The studies showed that the copper ion has the highest sorption. The synthesised ionites show good sorption of ions of transition metals and can be used in the sorption of metals from solutions. The studied ions can be ranked in the following order in respect of the degree of sorption by the ionites: Cu > Co > Ni. It is known (ref. 3) that resins combining functional amino and carboxyl groups have an affinity for copper ions. This apparently explains the high sorption capacity of the ionites for Cu\(^{++}\) ions.

A study was made of the thermal and mechanical stability of the ion-exchange resins.

The chemical stability of the ionites was determined from the change in exchange capacity, relative loss of mechanical strength and swellability after treatment with 5 n solutions of NaOH and H\(_2\)SO\(_4\). The COE increased somewhat, but decreased in the case of 5 n NaOH. This may be explained by the dissolution of impurities of low-molecular products contained in the ionites and by the partial swelling and dissolution of the ionites. Accordingly the ionites are acid-resistant. One of the main properties of the ionites is thermal stability, which makes it possible to determine in advance the area of application of ion exchange resins and the conditions of their use at elevated temperatures. The thermal properties of the synthesised ionites were studied by differential thermal analysis.

Temperatures of the order of 450 K no appreciable changes take place in the test piece studied. With heat treatment and under isothermal conditions at 473 K the mass losses are 10% of the original value. According to the thermogram the synthesised ionites can tolerate relative high temperatures for a considerable period with minimum mass losses.

Thus, the ionites obtained by copolymerisation of para-tris-phosphate-allyltriphenylphosphonium bromide with acrylonitrile and methyl methacrylate have high sorption properties, and are characterised by high thermal and chemical stability, evidently caused by the branched structure of the ionites.

**REFERENCES**

1. V.V. Korshak and G.S. Geoklenov, Plasticheskie Massy, No. 3, 1979, p. 14

---

**Table 1  Basic physico-chemical characteristics of ionites**

<table>
<thead>
<tr>
<th>Ionite based on</th>
<th>Yield, %</th>
<th>Content of Br for 0.1 AgNO(_3), %</th>
<th>Bulk density, g/Ma</th>
<th>Specific volume of swollen ionite in OH form, ml/g</th>
<th>Cu(^{++}) from solution (5 g/l) of CuSO(_4)</th>
<th>Co(^{++}) from solution (5 g/l) of CoSO(_4)</th>
<th>Ni(^{++}) from solution (5 g/l) of NiSO(_4)</th>
<th>Mechanical strength, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-t-p-ATPPB + AN</td>
<td>94.2</td>
<td>9.4</td>
<td>0.19</td>
<td>2.12</td>
<td>4.0</td>
<td>3.5</td>
<td>2.8</td>
<td>94.0</td>
</tr>
<tr>
<td>p-t-p-ATPPB + MMA</td>
<td>95.0</td>
<td>8.9</td>
<td>0.22</td>
<td>2.3</td>
<td>4.4</td>
<td>3.5</td>
<td>3.4</td>
<td>96.0</td>
</tr>
<tr>
<td>VBB: DMAEMA</td>
<td>92.0</td>
<td>11.4</td>
<td>0.18</td>
<td>2.0</td>
<td>1.8</td>
<td>2.0</td>
<td>2.0</td>
<td>92.0</td>
</tr>
<tr>
<td>VBB: VP</td>
<td>82.0</td>
<td>13.4</td>
<td>0.17</td>
<td>1.8</td>
<td>1.6</td>
<td>–</td>
<td>–</td>
<td>92.5</td>
</tr>
</tbody>
</table>