Synthesis and characterization of a Hg(II) selective n-butyl acetate cerium(IV) phosphate as a new intercalated fibrous ion exchanger: Effect of surfactants on the adsorption behaviour

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The fibrous ion exchange materials are now well recognized in environmental studies. They are used for the separation of harmful ionic impurities from gaseous and liquid media due to their high sorption efficiency. They can also be used as cloth, conveyor belts, staples and in air filters, water filters and dry scrubbers.

Recently, various hybrid fibrous ion exchangers have been synthesized in these laboratories by combining organic polymeric species such as acrylonitrile, acrylamide, styrene, peetin and cellulose acetate with inorganic ion exchangers. The introduction of organic species into an inorganic fibrous material enhances its reproducibility in ion exchange behaviour and its chemical stability to some extent.

Investigations on a new, intercalated fibrous material, n-butyl acetate Ce(IV) phosphate which possesses promising ion exchange characteristics, are reported here. The effect of anionic, cationic and non-ionic surfactants on its adsorption behaviour has also been studied.

Experimental

Ceric sulphate [Ce(SO₄)₂·4H₂O] was obtained from CDH (India), n-Butyl acetate (C₄H₇O₂) and phosphoric acid (H₃PO₄) were obtained from E. Merck (India) and Qualigens (India), respectively. All other reagents and chemicals were of Analar grade.

X-ray diffraction studies were made on a Philips analytical X-ray B.V. diffractometer type PW 170 B.V. IR studies were carried out by Shimadzu 8201 PC spectrophotometer. For simultaneous TGA/DTA measurements, Sdt 2960 instrument (powdered sample, mass 15-25 mg, heating rate 10°C/min, in flowing air), was used. SEM studies were performed using JEOL JSM 840, SM.

Solutions of ceric sulphate were prepared in 0.5 M H₂SO₄ and those of n-butyl acetate in ethanol. 6 M solution of phosphoric acid was prepared in demineralised water.

Synthesis of the ion exchange material

Samples of n-butyl acetate Ce(IV) phosphate (nBACP) were prepared by adding one volume of 0.05 M ceric sulphate solution to two volumes of a (1:1) mixture of 6 M H₃PO₄ and n-butyl acetate solution (0-20%) dropwise with constant stirring using a magnetic stirrer at a temperature of 60±5°C. The resulting slurry, was stirred for 3½ h at this temperature, filtered and then washed with demineralised water til pH-4 before drying at room temperature to form a sheet. It was cut into small pieces and converted into H⁺-form by treating with 1 M HNO₃ for 24 h, and was finally washed with demineralised water, dried at 45°C and sieved to obtain particles of size 50-70 mesh. Table 1 provides details of the synthesis and ion exchange capacity (i.e.,) of the various samples. Sample nBACP-6 was
selected for further studies because of its highest ion exchange capacity.

Studies on i.e.c. and elution behaviour were done by the column process. The optimum concentration of the eluent for a complete elution of H⁺ ions, was found to be 1 M. The minimum volume of 1 M NaNO₃ solutions for complete elution of H⁺ ions was found to be 190 mL.

Thermal studies
Several 1.0 g of the samples of n-butyl acetate Ce(IV) phosphate were heated at various temperatures in a muffle furnace for 1 h each and their i.e.c. was determined by the column process after cooling them to room temperature. The results are given in Table 2.

Adsorption studies
200 mg of the exchanger in H⁺-form were added to a mixture containing 18 mL of the acid solution and 2 mL of the metal ion solution. The mixture was kept for 24 h, shaking intermittently to achieve equilibrium. The metal ions in the solution before and after equilibrium were determined by the EDTA titrations and the distribution coefficients (Kₐ) were calculated by:

\[ K_a = \frac{1 - F}{F} \frac{V}{M} \text{ (mL/g)} \]

where I and F are the initial and final amounts of the metal ions in the solution phase, V the volume (mL) of the solution, and M the amount (g) of the exchanger.

The above experiment was repeated by replacing surfactant solutions.

Results and discussion
n-Butyl acetate Ce(IV) phosphate (nBACP-6) is found to possess a higher ion exchange capacity (2.25 meq/g) than the fibrous Ce(IV) phosphate (1.3 meq/g) (Table 1), perhaps due to the enhanced interlayer distances in the material as a result of intercalation of a polar n-butyl acetate molecule into the layers of Ce(IV) phosphate matrix possessing hydroxyl groups. SEM studies confirm the fibrous nature of the material.

nBACP shows an enhanced adsorption in surfactant media. In anionic surfactants, the adsorption of alkaline earths remains constant throughout the surfactant concentrations used. But for heavy metals, it increases up to CMC, then decreases [except Hg(II) and Mn(II)], while in cationic surfactants, the reverse order is found for both alkaline earths and heavy metals ions. It may be due to a micellar association which can be explained in terms of the electrostatic model, i.e., Gouy-Chapman electrical double layer approximations and the counter ion binding approximation. In non-ionic surfactants, the adsorption of metal ions remains constant up to the CMC value, then increases to maximum [except Mn(II), Cd(II)]. Here, most of metal ions are totally adsorbed perhaps due to the complex formation in the polyoxyethylene shell of the surfactant.

In the electrostatic model, two reactions occur: one entirely at the micellar surface and the other in the bulk phase between the micelles. The micellar/solvent interface consists of Stern layer containing the ionic surfactant heads and a certain amount of adsorbed counter ions resulting a lowering of the apparent charge density of the micelle and of a diffused layer. Therefore, the spatial distribution of the counter ions in the neighbourhood of charged micelles is

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of n-Butyl acetate</th>
<th>Na⁺ ion-exchange capacity (meq/dry g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nBACP-1</td>
<td>0</td>
<td>1.30</td>
</tr>
<tr>
<td>nBACP-2</td>
<td>1</td>
<td>1.45</td>
</tr>
<tr>
<td>nBACP-3</td>
<td>3</td>
<td>1.74</td>
</tr>
<tr>
<td>nBACP-4</td>
<td>5</td>
<td>1.80</td>
</tr>
<tr>
<td>nBACP-5</td>
<td>7</td>
<td>1.90</td>
</tr>
<tr>
<td>nBACP-6</td>
<td>8</td>
<td>2.25</td>
</tr>
<tr>
<td>nBACP-7</td>
<td>8.5</td>
<td>2.15</td>
</tr>
<tr>
<td>nBACP-8</td>
<td>9</td>
<td>2.00</td>
</tr>
<tr>
<td>nBACP-9</td>
<td>10</td>
<td>1.60</td>
</tr>
<tr>
<td>nBACP-10</td>
<td>12</td>
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</tr>
<tr>
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<td>nBACP-12</td>
<td>15</td>
<td>1.25</td>
</tr>
<tr>
<td>nBACP-13</td>
<td>20</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 2—Thermal stability of n-butyl acetate-Ce(IV) phosphate after heating for 1 h

<table>
<thead>
<tr>
<th>Drying temperature (°C)</th>
<th>Na⁺ ion exchange capacity (meq/dry g)</th>
<th>Change in colour</th>
<th>% Retention of i.e.c</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>2.25</td>
<td>Yellow</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>2.10</td>
<td>Light yellow</td>
<td>93.3</td>
</tr>
<tr>
<td>200</td>
<td>1.75</td>
<td>Light yellow</td>
<td>77.8</td>
</tr>
<tr>
<td>300</td>
<td>1.50</td>
<td>Creamy yellow</td>
<td>66.7</td>
</tr>
<tr>
<td>400</td>
<td>0.85</td>
<td>Creamy yellow</td>
<td>38.0</td>
</tr>
<tr>
<td>600</td>
<td>0.31</td>
<td>Off white</td>
<td>14.0</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>White</td>
<td>0</td>
</tr>
</tbody>
</table>

[except Hg(II) and Mn(II)]
influenced by the charge density of the polyelectrolytes. Further, the binding of hydrophilic ions is controlled by the electrostatic interactions. Ions having a charge opposite to the surfactant head groups (counter ions) are attracted to the micelle surface while reverse is true for the co-ions. Binding of amphiphilic ions is governed by hydrophobic and electrostatic effects; additive for counter ions, but opposed for co-ions.

A gradual decrease of the i.e.c. was observed in the material on heating at various temperatures. It retains 93.3% of its i.e.c. on heating up to 100°C, 77.8% up to 200°C and 66.7% up to 300°C. However, on heating up to 400°C, a sharp decrease in i.e.c. is observed (38% retained). At 600°C, it retains only 14% before approaching zero at 800°C. However, on comparing with other fibrous ion exchangers prepared earlier, nBACP-6 is found to be thermally more stable.

The TGA/DTA curves show ~5% weight loss in Ce(IV) phosphate at 99.21°C due to the loss of external water molecules only. Applying the Alberti's equation, number of external water molecules in Ce(IV) phosphate comes out to be ~1 indicating a tentative formula as:

CeO₂. P₂O₅. H₂O. x nBA

Since the %age of carbon in the material has been found to be 0.5%, the value of x is obtained as 0.3, thus pointing to the formula as:

CeO₂. P₂O₅. H₂O. 0.3 nBA

A two step mass loss (7.5% and 7.1%) up to 150°C (Fig. 1) in the TGA/DTA curves also shows the endo effects confirming the removal of external water molecules as well as a partial removal of n-butyl acetate. The third step showing a 3.7% of mass loss due to the removal of strongly coordinated water molecules, showing an endo effect at 321.6°C, which continues up to 400°C where the weight becomes almost constant. It also involves the formation of CeO₂ at 450°C. Finally, a mass loss of about 1.5% between 600 and 800°C, represents a kinetic non-stability of the decomposition products.

The data of thermal analysis (Table 2) points to no effect of the removal of external water molecules (upon heating up to 150°C) on the percentage retention of i.e.c., and, the importance of the temperature interval 200-300°C.

Thermal effects are due to both removal of the part of n-butyl acetate and removal of strongly coordinated water molecules. In this temperature region, the statistically relevant decrease of the percentage retention of i.e.c. occurs (Table 2). Thus, the data suggest that decrease of i.e.c. of materials tested is

![Fig. 1—TGA/DTA curves of n-butyl acetate Ce(IV) phosphate.](image-url)
interrelated with the volatilization of both \((n\)-butyl acetate, co-ordinated water molecules) from the structure of this type of ion exchanger. Full or nearly full retentions are achieved at 400-800°C, due to both CeO\(_2\) formation and disruption of intercalated fibrous structure of studied ion exchanger. These effects/interrelations are similar to that discussed for cellulose acetate based Th(IV) hybrid fibrous cation exchangers\(^{19}\).

The IR studies\(^{17}\) (Fig. 2) confirm the presence of metal-oxygen and metal-hydroxide bonds in addition to the external water molecules, phosphate groups and acetate part in the material. Bands at 536.1 \(\text{cm}^{-1}\) and 1063 \(\text{cm}^{-1}\) are due to the phosphate groups. The metal-oxygen and metal-hydroxide bands are observed at 669.1 \(\text{cm}^{-1}\) while bands at 1630.9 \(\text{cm}^{-1}\) represent the external water molecules in addition to its usual range at 3430.0 \(\text{cm}^{-1}\). The bands\(^{18}\) beyond 3430 \(\text{cm}^{-1}\) are due to the \(-\text{OH}\) groups. The bands at 1723.4 \(\text{cm}^{-1}\), 1529 \(\text{cm}^{-1}\), 1353.9 \(\text{cm}^{-1}\) and 771.6 \(\text{cm}^{-1}\) indicate the presence of \(-\text{C}=\text{C}=\text{O}\) (acetate group) in the material. The X-ray diffraction pattern exhibits weak peaks indicating its poorly crystalline or amorphous nature.

Thus, the addition of \(n\)-butyl acetate to cerium(IV) phosphate enhances its ion exchange capacity. The adsorption behaviour of the material for the metal ions increases in presence of surfactants, an important aspect for the removal of heavy metals from industrial effluents. The exchanger is highly selective for Hg(II), indicating its importance in environmental studies.

Acknowledgement

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References