Synthesis and Analytical Applications of a New Chelating Ion-Exchanger

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A new iron-chelating ion-exchanger has been synthesized from iron(III) nitrate and diethanolamine. The ion-exchanger shows selective uptake of some metal ions based on the coordination with the lone pair of electrons of nitrogen. The quantitative separations achieved are: Cu(II)-Hg(II), Cd(II)-Hg(II), Zn(II)-Hg(II), Mn(II)-Pb(II), Mg(II)-Cd(II) and Zn(II)-Pb(II).

Interest in chelating ion-exchangers has increased greatly in recent years. The chelating ion-exchangers polysiloxane-based oxime-divinyl benzene resin, thioglycolate chelating resin, N-arylphenylhydroxamines and tin(IV) diethanolamine have been synthesized and studied for their utility in separation science. Iron(III) diethanolamine (IDEA) has not been studied so far. This paper summarizes the studies on the chelating ion-exchanger IDEA.

AR grade chemicals were used. Measurements were made with an ultraviolet-visible spectrophotometer (Perkin Elmer Model 552) and a Systronics digital pH meter Type 335. An electric rotary shaking machine IEC-56 was used.

The chelating material was prepared by mixing 0.1 mol/dm$^3$ solution of iron(III) nitrate and 0.4 mol/dm$^3$ of diethanolamine in different ratios. The mixture was kept standing for 24 hours. The brown precipitate so obtained was filtered and washed with deionized water and dried at $60 \pm 2^\circ C$ in air oven. The product broke into small particles when immersed in water. The material was redried at $40 \pm 2^\circ C$.

Sorption for different metal ions was studied by batch process in 0.25 mol/dm$^3$ hydrochloric acid containing 0.25 mol/dm$^3$ sodium acetate (adjusted to pH 1-6). Breakthrough capacity was determined for Cu(II) and Hg(II): Rate of sorption was determined for 0.042 m mol of Cu(II) in the solution (pH 6).

For separation studies a column containing 1 g of the chelating material in a glass tube of 0.4 cm i.d. was used. The flow rate in all the separations was about 0.2 ml/min.

The precipitation was found maximum when iron(III) to amine ratio was 1:1. Iron(III) and diethanolamine were determined by potassium dichromate and Kjel method respectively. The mole ratio of Fe(III): diethanolamine was found to be 3:1. The results of chemical stability reveal that the material is fairly stable in HCl up to 2 mol/dm$^3$ and in ammonium hydroxide up to 4 mol/dm$^3$. The exchanger was found least stable in sodium hydroxide. It is because sodium hydroxide releases amine from the material. The sorption capacity of the exchanger was found to be 0.52 m mol/g for Cu(II).

The results of Fig. 1 for sorption capacity of IDEA may be explained on the basis of chelate formation between metal ion and the amine group available in the material. The metal ions were taken up from the solutions between pH 3-6 (except Mg(II) which was taken between pH 4-6) and were released when the pH of the column was brought below 3. Nitrogen atom present in amine group offers sites for the chelation with the metal ions. Since the stability of the metal-ligand depends upon the pH of the solutions, any variation in pH leads to detachment of the metal from the ligand. Comparison of sorption of metal ions at different pH values reveals that the sorption behaviour can be divided into three groups: (i) Hg(II) and Pb(II) are highly sorbed by the material and stay at all pH; (ii) Cu(II), Cd(II) and Zn(II) are less sorbed at pH 1; (iii) Mn(II) and Mg(II) are not sorbed at pH 1 and 3 respectively. The sorption behaviour is analogous to that shown by tin(IV) diethanolamine. The results of breakthrough capacity further confirm that IDEA is more selective for Hg(II) than for Cu(II) as evident from Fig. 1.

Fig. 1—Sorption of metal ions at different values of pH
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Fig. 1—Sorption of metal ions at different values of pH.
Ligand Exchange Chromatography and Recovery of some Metal Ions on PAN Sorbed Tin(IV) Silicate Columns

Dhruv Kumar Singh and Rishi Raj Bhatnagar

Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-208002, India

In the ligand exchange column-chromatographic separations of metal ions developed, an inorganic ion-exchanger [tin(IV) silicate] sorbed with PAN [1-(2-pyridyl-azo)-2-naphthol] is utilized. Tin(IV) silicate was prepared [1] by mixing 0.04 mol/l stannic chloride and 0.15 mol/l sodium silicate in the volume ratio 4:1 at pH 8.5. The exchanger (60–100 mesh) was sorbed with PAN (0.1%) for 24 h. Rate of sorption studies for Cu$^{2+}$ and Fe$^{3+}$ reveal that equilibrium is attained within 5 min only due to the chelating agent (PAN). The results of distribution studies of 12 metal ions in different pH-systems are presented in Table 1. The exchanger has been found to be selective for Ni$^{2+}$. The reason for selective sorption and desorption of certain metal ions can be attributed to large differences in stability constants of metal-PAN complexes at certain pH values. The elution is based on the stability constant of the metal eluting ligand complex. The quantitative separations possible (Table 2) include Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Pt$^{4+}$, Fe$^{3+}$, Ag$^{+}$, Cu$^{2+}$, Mn$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$, Cd$^{2+}$. The recovery of Pt$^{4+}$ and Ag$^{+}$ (1–5 mg) from dilute solutions in the presence of Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$ (5 mg each) has also been studied at pH 2.

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Reference

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Table 1. Kd$^a$-values of metal ions

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>pH 2</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+}$</td>
<td>27.5</td>
<td>100.2</td>
<td>150.0</td>
<td>208.7</td>
<td>46.2</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>1,375</td>
<td>T.A.</td>
<td>T.A.</td>
<td>T.A.</td>
<td>150.0</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>18.6</td>
<td>132.0</td>
<td>350.0</td>
<td>81.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>78.2</td>
<td>130.2</td>
<td>250.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>0.0</td>
<td>33.6</td>
<td>87.5</td>
<td>98.2</td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>10.2</td>
<td>66.5</td>
<td>75.0</td>
<td>90.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>42.6</td>
<td>83.2</td>
<td>128.7</td>
<td>73.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>20.8</td>
<td>51.3</td>
<td>200.0</td>
<td>203.3</td>
<td>125.0</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>3.0</td>
<td>41.2</td>
<td>80.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$^{3+}$</td>
<td>23.0</td>
<td>160.2</td>
<td>196.2</td>
<td>148.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Pt$^{4+}$</td>
<td>0.0</td>
<td>0.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Ag$^{+}$</td>
<td>90.8</td>
<td>296.8</td>
<td>375.0</td>
<td></td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ Kd: Amount of metal ion in exchanger phase · g$^{-1}$
Amount of metal ion in solution phase · cm$^{-3}$

Table 2. Separations on PAN-sorbed tin(IV) silicate columns

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mixture</th>
<th>Eluent</th>
<th>Eluate (ml)</th>
<th>Amount loaded (µg)</th>
<th>Amount recovered (µg)</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co$^{2+}$</td>
<td>A</td>
<td>50</td>
<td>250.6</td>
<td>253.1</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Ni$^{2+}$</td>
<td>B</td>
<td>90</td>
<td>248.4</td>
<td>243.0</td>
<td>2.18</td>
</tr>
<tr>
<td>2</td>
<td>Cu$^{2+}$</td>
<td>C</td>
<td>40</td>
<td>460.5</td>
<td>468.0</td>
<td>1.63</td>
</tr>
<tr>
<td>3</td>
<td>Fe$^{3+}$</td>
<td>D</td>
<td>50</td>
<td>256.7</td>
<td>252.0</td>
<td>1.83</td>
</tr>
<tr>
<td>4</td>
<td>Pt$^{4+}$</td>
<td>E</td>
<td>70</td>
<td>406.6</td>
<td>414.2</td>
<td>1.87</td>
</tr>
<tr>
<td>5</td>
<td>Mn$^{2+}$</td>
<td>F</td>
<td>60</td>
<td>375.0</td>
<td>365.9</td>
<td>2.42</td>
</tr>
<tr>
<td>6</td>
<td>Zn$^{2+}$</td>
<td>G</td>
<td>60</td>
<td>240.8</td>
<td>244.6</td>
<td>1.58</td>
</tr>
<tr>
<td>7</td>
<td>Pb$^{2+}$</td>
<td>H</td>
<td>80</td>
<td>402.9</td>
<td>413.8</td>
<td>2.70</td>
</tr>
<tr>
<td>8</td>
<td>Cd$^{2+}$</td>
<td>I</td>
<td>80</td>
<td>414.3</td>
<td>406.7</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Abbreviations used: A 0.01 mol/l HCl; B 0.05 mol/l EDTA in 0.01 mol/l HCl; C 4 mol/l NH$_3$; D Demineralized water; E 0.1 mol/l NH$_3$.
PROCEEDINGS
OF THE
SEVENTY FOURTH SESSION OF THE
INDIAN SCIENCE CONGRESS
BANGALORE, 1987

SECTION—CHEMISTRY
President - Prof. J. P. Tandon

INDIAN SCIENCE CONGRESS ASSOCIATION
14, Dr. Bisesh Guha Street, Calcutta-700 017

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Tannin-Cinchonine method has been described for determining the per cent composition of silicon dioxide, tin dioxide, tungsten trioxide. An accurate and reliable gravimetric method has been reported for silicate analyses of rocks and minerals. The chemical reaction for the separation and for the quantitative determination of tungsten is based on the concept of ion transport through the chelate membrane. The experimental method will find applications for different types of concentrations of Si and W. The results for several of the ore samples originating from eastern Himalayan regions show their very high grade. Since the percent amount of silicon and tungsten are low and very much high respectively, an insight into the geochemical structure of the rock ore can be drawn and assigned. Since the chemical distribution and composition of the rock ores would be available for different regions.

15. Synthesis of Tin (IV) Phosphoiodate and its Analytical Applications as an Electrom-Ion-Exchanger.

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Harcourt Butler Technological Institute, Kanpur-208002

A new inorganic ion-exchanger, tin(IV) phosphoiodate has been synthesized and utilized for oxidation reactions. Its composition, chemical and thermal stability, ion-exchange and electron-exchange properties have been investigated and the oxidation of Fe(II), As(III), Sb(III), Sn(II) and Ti(III) to Fe(III), As(V), Sb(V), Sn(IV) and Ti(IV) respectively have been achieved quantitatively on the columns of this material. The mechanism of oxidation is discussed.