Reviews

Sorption properties of hydrogels of transition and p-metal oxide hydroxides

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The experimental data on the sorption properties of hydrogels of FeIll, TiIV, ZrIV, SnIV, NbII, CrII, SmII, CoII, and ZnII oxide hydroxides are summarized. The data were obtained by the point of zero-charge method and by measuring the rates of the indicator reaction, viz., heterogeneous hydrolysis of the chloro complexes of platinum group metals. The compositions of the oxide hydroxides, the pH of the point of zero charge in various ionic media, and the rate constants of the indicator reactions were determined. The values obtained were analyzed in terms of their correlation with the charge, the radius, and the electronic structure of the central ion and with the composition and the preparation conditions of the oxide hydroxide. A data base that allows one to choose an appropriate oxide hydroxide sorbent for extraction of particular complex-forming metals from complexing media is presented. The data obtained confirm the model of the mechanism of heterogeneous hydrolysis and extend its predicting ability. The model was tested experimentally in relation to tin(IV) oxide hydroxide.

Key words: sorption properties, oxide hydroxide, point of zero charge, rate of indicator reaction, hydrogel, ionic media.

Introduction

Inorganic sorbents are used in industrial technologies and environment protection technology, in those cases where contamination of solutions with organic compounds should be avoided and/or radiation-resistant sorbents are required. Freshly prepared gel-like iron, zirconium and titanium oxide hydroxides used as sorbents possess substantial advantages over dry granulated oxides; therefore, at present, wide use of crystalline or granulated inorganic sorbents is no longer justified. Gel-like oxide hydroxide sorbents are highly efficient regarding both the sorption capacity and the rate of sorption; they even permit fairly selective and complete extraction of platinum metals, gold, mercury and copper from complexing media. Since iron and titanium are widespread in nature, gel-like sorbents based on them are cheap and environmentally clean. The synthesis of gel-
like oxide hydroxides is simple, quick, and cheap. Similar sorbents based on zirconium, aluminum, and other metals are less versatile, but certainly, they can also find application in some cases.

As a result of numerous studies, we discovered and investigated a specific type of chemisorption, which applies to the sorption of complex ions; we called it "heterogeneous hydrolysis."3–8

Heterogeneous hydrolysis, which has been described in detail previously,2–3 occurs as aquation* of the complex ions adsorbed on the surface of oxide hydroxides followed by the transformation of the resulting aqua complex into the hydroxide of the central ion of the complex, for example:3

\[
\left[\text{PtCl}_4\right]^{2-} + (\text{Ln}_2\text{O}_3 \cdot n\text{H}_2\text{O})_{\text{surf}} + 2\text{H}_2\text{O} \rightarrow \left[\text{Pt(OH)}_2 \cdot \text{Ln}_2\text{O}_3 \cdot (n\text{H}_2\text{O} \cdot 2\text{H}^+ \cdot \text{surf}) + 4\text{Cl}^{-}\text{aq}.
\]

The new hydroxide phase is firmly bound to the surface of the oxide hydroxide sorbent. The rate of heterogeneous hydrolysis is determined by the basic properties of the surface (i.e., the pH at the point of zero charge), by the supporting electrolyte, and the nature of the complex subjected to heterogeneous hydrolysis itself.3–9

In relation to ferrogels, we observed effects that had not been reported previously, namely, the change of the sorption properties of the gel induced by the short-term or prolonged interaction with an ionic medium.3–9 In order to find out whether this type of behavior is typical of all hydrogels formed by poorly soluble metal oxide hydroxides or it is a specific feature of ferrogels, we studied the sorption properties of titanium and zirconium(IV) oxide hydroxides.10–11 Since these oxide hydroxides were found to exhibit many specific features, the problem was formulated as follows. Based on investigation of a wider range of gels, a theoretical model suitable for predicting the sorption properties of oxide hydroxides in relation to extraction of complexing metals from complex-forming media (aqueous solutions of electrolytes) should be developed. As additional objects of investigation, we chose In(III), Cr(III), Co(II), Zn(II), and Sm(III) oxide hydroxides.12–15

For the latter compound, extensive investigations dealing with the crystalline oxide have been reported.3–16

We attempted to elucidate how the fundamental properties of the metal cation forming the oxide hydroxide sorbent, conditions of the oxide hydroxide synthesis, and its surface properties (the surface and volume charge, and the pH of the point of zero charge on its surface) affect the rate of heterogeneous hydrolysis in the presence of these oxide hydroxides. As the primary fundamental properties that apparently determine the properties of oxide hydroxides, we recognized the charge, the radius, and the electronic structure of the central atom (Table 1). Tentative analysis of some of the available data on the kinetics of heterogeneous hydrolysis from this viewpoint has been carried out in our previous study;17 however, these characteristics seem to be inadequate to provide explanation of all the phenomena observed. A similar approach (except for the electronic structure) has also been used by other researchers.18

The oxide hydroxide sorbents were prepared by alkaline hydrolysis of the corresponding metal salts in aqueous solutions at room temperature. The data on the composition of oxide hydroxides characterize the fast precipitation process. To prepare the sorbent samples, the alkaline hydrolysis was carried out for 5–10 min at a controlled pH of precipitation; then the samples were washed from the mother liquor by decanting and centrifugation for 40 min. The samples obtained in this way were gel-like; they contained the primary water that had not been removed during the gel preparation. These samples were used in the experiments on the determination of the surface charge and on the study of heterogeneous hydrolysis. The pH of precipitation (pHp) served as the main independent parameter determining the properties of oxide hydroxides.

The composition of hydrogels was determined from the curves of drop titration** of solutions of metal salts, used to prepare the hydrogels of oxide hydroxides, with a base. The titration curves were recorded over a period of ~2 h. The samples prepared at specific precipitation pH values (three points, one located in the beginning, one in the middle, and one at the end of the titration curve, were normally chosen) were thoroughly washed, dried in a vacuum desiccator over strong sulfuric acid, and studied by thermal and X-ray diffraction analyses.

The pH value at the point of zero charge (pHpzc) characterizes the pH of an electrolyte solution (in this particular case, an aqueous solution) such that a solid (gel) phase contacting with this solution adsorbs equal numbers of protons and hydroxyl groups. The pHpzc was determined by potentiometric titration in a quartz

** A method of homogeneous titrations,19 which ensures instantaneous preparation of a solution or suspension, homogeneous regarding the composition and pH, is also known.

Table 1. Fundamental characteristics of the central atoms in oxide hydroxides

<table>
<thead>
<tr>
<th>Metal</th>
<th>Goldschmidt radius /Å</th>
<th>Ionic potential, ( I = e/r )</th>
<th>Electronic structure of the outer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(IV)</td>
<td>0.64</td>
<td>6.25</td>
<td>3s^23p^6</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>0.87</td>
<td>4.60</td>
<td>4s^24p^6</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>0.67</td>
<td>5.97</td>
<td>4p^54d^10</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>0.65</td>
<td>4.61</td>
<td>3p^63d^3</td>
</tr>
<tr>
<td>Sm(II)</td>
<td>0.96*</td>
<td>3.12</td>
<td>5s^25p^6</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.67</td>
<td>4.48</td>
<td>3p^63d^5</td>
</tr>
<tr>
<td>In(III)</td>
<td>0.92*</td>
<td>3.26</td>
<td>4p^44d^10</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.83</td>
<td>2.41</td>
<td>3p^63d^10</td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.83</td>
<td>2.41</td>
<td>3p^63d^10</td>
</tr>
</tbody>
</table>

* Replacement of the ligands in the complex by water molecules.

* Templeton and Dauben radius.22

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