DIFFERENT ALTERNATIVES FOR STABILITY CONSTANT DETERMINATION OF Zr AND Hf 2-METHYL LACTATE COMPLEXES BY CATION EXCHANGE

H. F. ALY, M. A. EL-HAGGAN, A. A. ABDEL-RASSOUl

Atomic Energy Establishment, Cairo (Egypt)

Three different alternatives are applied for the determination of the stability constants of zirconium and hafnium complexes with 2-methyl lactic acid using cation exchange. Calculations based on the exchange equilibria of the highly charged metal cations and the positively charged ligand complexes rather than that of the hydrolysed complex species are worked out according to SCHUBERT and FRONAEUS, respectively. The third alternative adopted in this work, is principally based on the consideration of all complexed species produced by hydrolyses in the aqueous phase. The B-values obtained by the different methods are intercorrelated and discussed.

Introduction

Tetravalent zirconium and hafnium ions show a great tendency to coordinate with oxygen donor ligands.\(^1\)\textsuperscript{-3} Although the complex equilibria of Zr(IV) and Hf(IV) with several oxygen donor ligands is reported,\(^4\) data concerning the stability constants of 2-methyl lactate complexes with both elements are not available yet. In this work, the stepwise formation constants of Zr(IV) and Hf(IV) complexes with 2-methyl lactic acid have been determined using a cation exchange resin distribution technique at an ionic strength of 2.0M (HClO\(_4\)). Different alternatives are used in the treatment of the equilibria encountered.

Experimental

Materials

2-Methyl lactic acid (Eastman-Kodak Chemical Co., USA) was purified as reported in a previous work.\(^5\) \(^{96}\)Zr (T = 65 d) was prepared from neutron irradiated zirconyl chloride and was further purified and freed from the \(^{95}\)Nb daughter by ion exchange.
chromatography directly before use. $^{181}$Hf (T = 42 d) was obtained by the neutron activation of spec. pure HfO$_2$ (1 mg), processed and adjusted to be ca. 10$^{-4}$M of hafnium in 2M HClO$_4$.

The Dowex-50X8 cation exchanger (100–200 mesh), was converted to the H$^+$-form, washed repeatedly with distilled water and thoroughly dried before being stored under vacuum.

**Procedure**

The distribution data were obtained by adding suitable known weights of the resin to different aliquots of an aqueous phase containing different concentrations of the complexing ligand together with the radioactive tracer (~10$^{-4}$M). The aqueous phase was previously adjusted to a total ionic strength of 2.0M (HClO$_4$). Equilibration was achieved through mechanical shaking within 6 hrs, at 25 ± 2 °C.

The distribution coefficient D, was derived from the following expression:

$$D = \frac{A_0 - A}{A} \cdot \frac{v}{m}$$

where $A_0$ and $A$ — the counting rates for a given volume of the aqueous phase before and after equilibration,

$v$ — the volume of the aqueous phase (ml),

$m$ — weight of the resin (mg).

**Results and discussion**

Both Zr(IV) and Hf(IV) are known to have small ionic radii and large ionic potentials, and as a result of their charge densities, these ions have a tendency towards hydrolysis. The calculated distribution percentage of the various hydrolytic species encountered in a medium kept at constant ionic strength of 2.0M (HClO$_4$), shows that hafnium is mostly in the free cationic form, while zirconium is susceptible to a considerable degree of hydrolysis.

<table>
<thead>
<tr>
<th></th>
<th>M$^{**}$</th>
<th>[M(OH)]$^{2+}$</th>
<th>[M(OH)$_2$]$^{3+}$</th>
<th>[M(OH)$_3$]$^{4+}$</th>
<th>[M(OH)$_4$]$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium</td>
<td>10.6</td>
<td>14.90</td>
<td>34.0</td>
<td>27.0</td>
<td>13.50%</td>
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<tr>
<td>Hafnium</td>
<td>52.44</td>
<td>34.87</td>
<td>10.3</td>
<td>2.1</td>
<td>0.35%</td>
</tr>
</tbody>
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