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# The Determination of the Charge of Some Inorganic Thorium Complexes with the Ion — exchange Method

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Chemistry of thorium complexes is now of particular interest but our knowledge is still inadequate. The thorium ion forms various coplexes with a great number of anions and in water solutions the salts of thorium are undergoing hydrolysis already at low pH values (pH > 3.5) giving various products.

In connection with our investigations it has been of great interest for us to know the composition and charge of the thorium complexes of chloride, nitrate, and sulphate in the concentration region from 0.1-5 M. At the same time we wished to know whether presence of other cations has any influence on the formation of these complexes.

Day and Stoughton<sup>1</sup> and Zebroski, Alter and Heumann<sup>2</sup> have investigated the formation of thorium complexes with these anions using the solvent extraction method with thenoyltrifluoroacetone as the chelating agent in the presence of high concentrations of perchlorate ions. They have found that all investigated anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, etc.) form complex thorium

ions of the type  $ThX_n^{m+}$ .

In the present investigation we have applied the ion-exchange method given by Strickland<sup>3</sup> and Kraus and Nelson<sup>4</sup>. Applying the law of mass action to the ion exchange processes Krauss and Nelson obtained a simple relationship

$$\frac{d \log D}{d \log C_r} = -\frac{v}{a}$$

where D is the distribution coefficient, i.e. the ratio between the concentration of the investigated ion in the ion exchanger phase and in the solution phase.

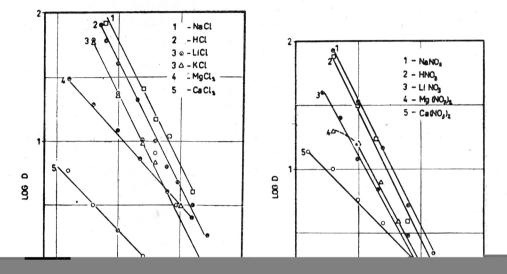
 $C_r$  is the concentration of the known charge ion (the exchanging ion) in the solution at equilibrium.

a is the charge of the exchanging ion.

v is the charge of the complex ion.

#### EXPERIMENTAL

The ion-exchanger used was Amberlite IR-120 (60—100 Mesh) transferred into the exchanging ion form by treatment in the column. The systems were prepared in glass-stoppered reagent bottles of 50 ml., giving a determined volume of the thorium nitrate solution  $1.36 \times 10^{-3} M$  to which had been added the solution of Th<sup>234</sup> (NO<sub>8</sub>)<sub>4</sub> (carrier free) and the solution of the exchanging ion. The total volume was always 10 ml. 0.25 g. of the air dried resin were added, the systems kept for 24 hours at room temperature and then the activity of Th-234 was measured in 2 ml. of supernatant liquid with a G. M. counter. The thorium-234 was isolated from the solution of uranyl nitrate by the method described by Dyrssen<sup>5</sup>.



are also -2 for monovalent ions and -1 for divalent ions, which suggests that the prevalent complex ion has the charge of 2+. The only deviation from the results was obtained with the Mg(NO<sub>3</sub>)<sub>2</sub> solution, where from the slope of -2one may conclude that the charge is 4+.

In the presence of the sulphate ion the slope of the straigh lines for all exchanging ions indicates the charge of 3+ for the complex Th(HSO<sub>4</sub>)<sup>3+</sup> (Fig. 3).

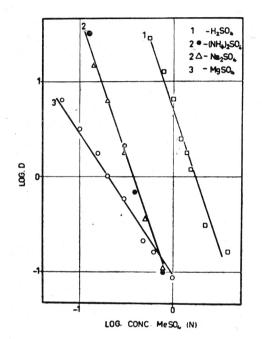


Fig. 3. Determination of charge of thorium sulphate complex ions in solutions of  $H_2SO_4$ . (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>.

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#### IZVOD

#### Određivanje naboja nekih anorganskih torijevih kompleksa primjenom metode ionske izmjene

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Određivan je naboj torijevih kompleksnih iona s kloridom, nitratom i sulfatom u prisutnosti različitih kationa pomoću ionske izmjene upotrebljujući torij-234 kao radioaktivni indikator.

Nađeno je, da torij (IV) s kloridima u danim uvjetima tvori kompleks s 2 pozitivna naboja. S nitratima tvori u većini slučajeva kompleks s 2 pozitivna naboja jedino u otopini magnezijeva nitrata određen je naboj 4+. Sulfatni ion u otopinama svih upotrebljenih elektrolita dao je kompleks s nabojem 3+.

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