Precipitation and Hydrolysis of Metallic Ions in Sea Water. I. Ionic State of Zirconium and Thorium in Sea Water

H. Bilinski and M. Branica

Department of Physical Chemistry, Institute »Ruđer Bošković«,
Zagreb, Croatia, Yugoslavia

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The tyndallometric method is a very suitable and promising experimental method for the determination of solubility and precipitation in a broad concentration range. The critical concentrations of the precipitating components and the charge on the ions present in the solution in equilibrium with the solid phase can be determined. The precipitation diagrams of zirconium and thorium in 50% sea water are shown. The influence of the sea water concentration on the solubility product K_{s4} has been investigated for thorium. Both elements are, under sea water conditions, probably entirely hydrolized without charge. One could therefore expect very effective fixation of the studied elements on other solid particles and the surface in sea water.

INTRODUCTION

The physical chemistry of sea water has been the subject of recent investigations, and the literature has been reviewed by J. P. Riley and G. Skirrow[1]. In one of his papers[2], L. G. Sillén tabulates the amounts of various elements found per liter of average sea water, compiled from the literature. The data available for determining which species is likely to predominate in solution is especially limited for the heavy metal ions. On page 174 of reference 1, E. D. Goldberg suggests that thorium enters the oceans as a particulate phase but is rapidly deposited onto the sea bed. This indicates a small charge on the thorium particles. Lengweiler[3], as quoted in Sillén's paper[2], studied the solubility of FeOOH at various pH's and indicated the possible existence of uncharged $Fe(OH)_3$, or a polymer of it, in sea water. Sillén[2] emphasized the need for investigations into the solubilities of metal hydroxides in sea water in order to obtain evidence for uncharged species, which may be the prevalent form of many elements in the ocean. The complexibility of divalent Zn and Cd ions with hydroxy and chloride ions in sea water has already been studied polarographically in our laboratory[4].

In the investigation into the state and solubility of heavy metals in sea water, we applied the method of solubility limits, which has been utilized previously in investigations dealing with heavy elements in distilled water and sodium perchlorate[5,6,7]. By varying the concentration of sea water in some experiments, the conditions at the river mouth were simulated.

EXPERIMENTAL

Reagents

Zirconium oxychloride $ZrOCl_2(H_2O)_8$, (*Merck pro analysi*) was used to make a stock solution, the concentration of which was determined gravimetrically by adding excess NH_3, igniting the precipitate, and weighing the ZrO_2 so formed.

Thorium nitrate (*Hopkin* and *Williams* Analar $Th(NO_3)_4$) was used to make a stock solution. The concentration of thorium was determined by an ion exchange technique with *Dowex* 50[8].

Hydrochloric acid was standardized against Na_2CO_3 (s) and used to titrate the solution of sodium hydroxide.

The sea water sample was taken at Rovinj on the Adriatic coast, and its salinity was $36.45^0/_{00}$.

Procedure

The samples were prepared in glass tubes, always to a total volume of 10 ml. In one set of experiments, 5 ml. of sea water was mixed with 5 ml. of diluted zirconium or thorium solutions to obtain the »titration curve« of the sea water with these elements. In another set of experiments, towards lower pH values of the »titration curve« HCl was added to the solution of the metals before mixing with sea water, but always so that the final volume amounted to 10 ml. In the third set of experiments, the points plotted above the »titration curve« were obtained by adding NaOH solution partly to the sea water and partly to the metal solutions, so that the final volume was again 10 ml. after mixing. The concentrations plotted in the diagrams are always given for the total volume.

The glass tubes were kept in a thermostated bath at 20^0 C. 24 hours after mixing, the pH of the solution was measured with a glass electrode against calomel on a *Pye* pH-meter. The pH-meter was calibrated against a buffer solution of pH 6.99, which was prepared by dissolving a buffer solution tablet ('SOLOID' brand N. B. S. Formula Burroughs Wellcome and Co., England) in 100 ml. of distilled water.

RESULTS AND DISCUSSION

Fig. 1 shows a general precipitation diagram of zirconium oxichloride in $50^0/_0$ sea water (S = $18.29^0/_{00}$). The pH values were plotted against the logarithm of the metal concentration. Curve 1 is the solubility limit, determined by tyndal-
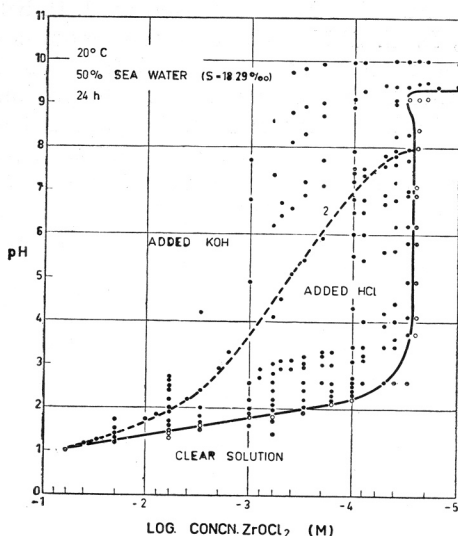

Fig. 1. Precipitation of zirconium at 20^0 C in $50^0/_0$ sea water; pH range *versus* concentration of $ZrOCl_2$, 24 hours after mixing. Curve 1 is the solubility curve and curve 2 is the »titration curve«.

lometric measurements, and constructed from the first turbid and the last clear system. Curve 2 is the »titration curve« of 50% sea water with zirconyl chloride solution. The solubility limit indicates that in solutions having pH values below 3.5, the predominant species has probably a charge of +2. At a zirconyl chloride concentration of 2.5×10^{-5} M, the solubility is a pH-independent term, which probably corresponds to uncharged $Zr(OH)_4$ or a polymer of it. This value of $\log K_{s4} = -4.6$ is very close to the previously determined value of $\log K_{s4} = -4.36$ for the solubility of zirconium hydroxide in 1M $NaClO_4$ solution[6].

Fig. 2 shows a general precipitation diagram of the solubility limits of thorium nitrate in 50% sea water (S = 18.29%). The solubility curve 1 indicates that in the solutions having pH-values below 5, the predominant species can have a charge of +2. It is probably some hydroxy chloride complex, because the precipitation of thorium hydroxide in sea water is shifted toward higher pH values relative to that in pure water[5]. At a thorium concentration of about 1.6×10^{-5} M, the solubility is independent of pH in the same way as in the case of zirconium. Most probably, under sea water conditions, thorium also exists as some uncharged hydroxide species.

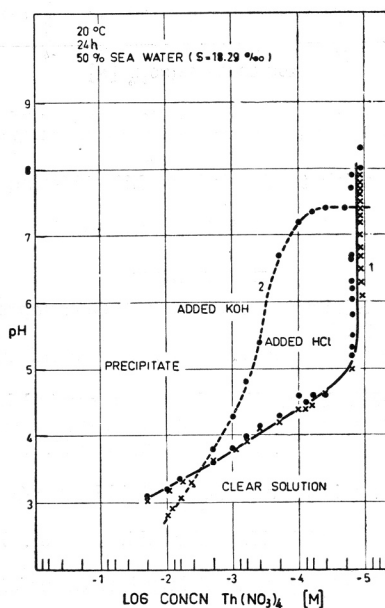Curve 2 in Fig. 2 is the »titration curve« of 50% sea water (S = 18.29%) with thorium nitrate solution.

Fig. 2. Precipitation of thorium at 20° C in 50% sea water; pH range versus concentration of Th(NO₃)₄, 24 hours after mixing. Curve 1 is the solubility curve and curve 2 is the »titration curve«.

Fig. 3 represents the influence of various concentrations of sea water upon the solubility limits of uncharged thorium hydroxide. The solubility does not change considerably with the change of sea water concentration from 10 to 80%, i. e. it is always about 10^{-5} M in the metallic ions and only a little lower than that in distilled water[4].

From these results, we can infer that Th and Zr exist in sea water in the form of uncharged hydroxide associates, in agreement with Lengweiler's results for iron[3]. Owing to this property, one could expect a very effective fixation of thorium and zirconium on other solid particles or on the surface. At the river delta, one could expect an increased precipitation of the elements carried by the river.
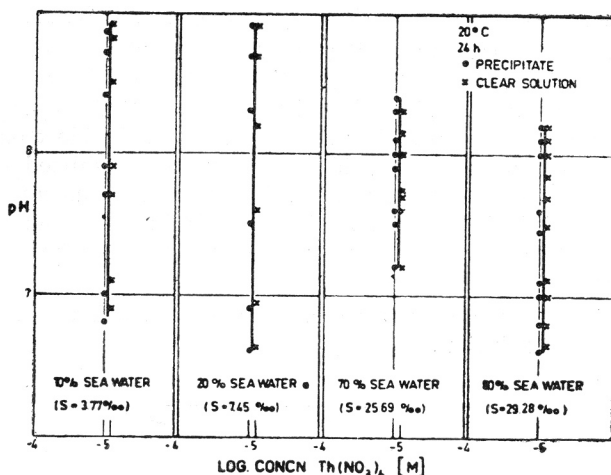

Fig. 3. Solubility boundary under sea water conditions, measured for different concentrations of sea water. The pH value is plotted against the concentration of thorium nitrate.

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IZVOD

Taloženje i hidroliza metalnih iona u morskoj vodi. I. Ionsko stanje cirkoniuma i toriuma u morskoj vodi

H. Bilinski i M. Branica

Tindalometrijska metoda je vrlo pogodna eksperimentalna metoda za određivanje topivosti u širokom koncentracijskom području. Mogu se odrediti kritične koncentra-

cije taložnih komponenata i naboj iona, koji su prisutni u otopini u **ravnoteži s** krutom fazom. Prikazani su taložni dijagrami cirkoniuma i toriuma u 50%-tnoj morskoj vodi (S = 18,29‰). Ispitan je utjecaj koncentracije morske vode na produkt topivosti K_{s4}. Oba elementa se vjerojatno nalaze u morskoj vodi potpuno hidrolizirani i bez naboja. Zbog toga se u morskoj vodi može očekivati vrlo jaka adsorpcija ovih elemenata na krutim česticama ili površinama.

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