

Behaviour of Indium in sea water

by

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Introduction

The investigation of constituents, particularly microconstituents, of sea water is very important in the explanation of physico-chemical and biological processes in sea water. In this connection the determination of ionic state of microconstituents and their concentration in sea water is of most importance [BRANICA *et al.* -1968].

Sea water is a solution containing many inorganic salts and substances, which are often not in thermodynamic equilibrium. The ionic state and maximum ionic concentration of some microconstituents cannot be simply postulated from the thermodynamic data. Therefore, these calculation should have been verified by experimental data [BARIĆ & BRANICA-1967].

According to the literature data the concentration of indium in sea water is reported to be less than 20 µg per liter [GOLDBERG-1965]. Its ionic state, however, has not been the subject of any study reported so far.

With the aim to determine the most probable concentration range and ionic state of indium present in sea water, the present investigations were performed using anodic stripping polarography and pulse polarography techniques.

Experimental

Solutions containing from 10^{-4} to 10^{-6} M ionic indium were analyzed by pulse polarography. A Southern Harwell MK II pulse polarograph was used. Solutions of lower concentrations of ionic indium (10^{-5} to 10^{-9} M) were analysed by anodic stripping polarography. Hanging mercury drop electrode according to KEMULA and KUBLIK (1963). Was used, and the polarographic curves were recorded with a Radiometer PO-4 or Radelkis OH-102 polarographs.

Reagent-grade chemicals were used for the preparation of solutions. Sea water samples were collected in the vicinity of Rovinj at 1 m depth, filtered through 0.45 µ Millipore filter, and stored in polyethylene bottle at -10°C . The pH was determined by a Radiometer pH Meter PHM-4 with a glass electrode and a calomel electrode.

Measurements of precipitation of indium were performed in 0.54 M sodium chloride solutions containing borate buffer, and in sea water with added sodium hydroxide. All samples were prepared 4 days before the measurements had been performed by adding the corresponding quantities of stock solution of indium chloride to mentioned solutions.

Results and discussion

The pH and the concentration of ionic indium which was in equilibrium with the precipitate in sodium chloride solution or sea water was measured. Fig. 1. gives the dependence of ionic indium concentration upon the pH values in sodium chloride solution. When the initial concentration of indium was

10^{-4} M, the precipitation started at pH 4.2. The dependence of the concentration of ionic indium on the pH in the pH range between 4.2 and 5 gives a straight line with the slope of one. At pH 5, and the indium concentration about 10^{-5} M, the concentration further decreases with an increase in the amount of sodium hydroxide added, whereas the pH values are irreproducible. When the concentration of indium falls below 10^{-6} M, its dependence upon the pH becomes linear, and the straight line shows again slope of one.

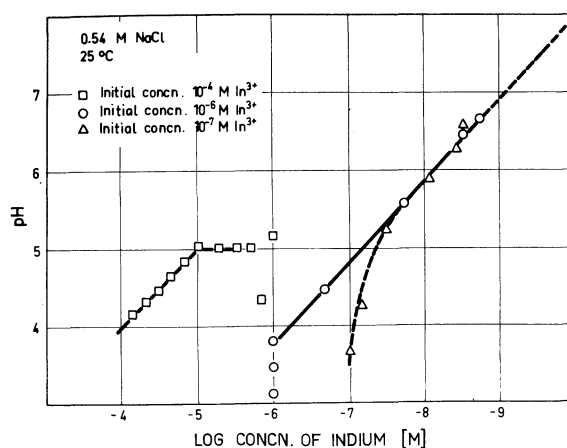
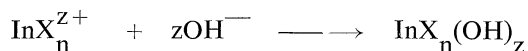


FIG. 1. — Dependence of ionic indium concentration on pH in 0.54 M sodium chloride solution.

At initial concentration of 10^{-6} M the precipitation of indium started at pH 3.8, and the dependence of ionic indium concentration on the pH is linear with the straight line slope of one. Similar results were obtained at 10^{-7} M initial concentration of indium.

If the reaction of precipitation is given by the expression :



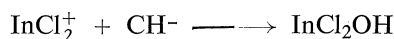
then the solubility product can be expressed in the logarithmic form as :

$$\log K_{sp} = \log [\text{InX}_n^{Z+}] + z \log [\text{OH}^-]$$

where InX_n^{Z+} is free or complexed indium ion.

The slope of the graphical plot $\log \text{InX}_n^{Z+}$ vs. $\log \text{pH}$ gives z , the number of hydroxide groups consumed by one indium ion during the precipitation reaction. If the composition of the soluble complex InX_n^{Z+} is known, then the composition of precipitate can be determined, and vice versa. However, the ionic form of the complex InX_n^{Z+} and the composition of the precipitate InX_nY_z cannot be determined by standard analytical methods.

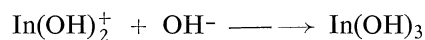
In 0.54 M sodium chloride solution and in sea water at pH 3 or lower indium is present as the InCl_2^+ complex [BARIC & BRANICA-to be published]. In the concentration range between 10^{-4} M and 10^{-5} M z is equal to one, and most probably, the precipitation takes place according to the equation :



The solubility product was calculated from the experimental data given in Fig. 1. and has the value :

$$K_{sp} = [\text{InCl}_2^+][\text{OH}^-] = 10^{-13.9}$$

At concentration of indium lower than 10^{-6} M, one hydroxyl ion is consumed during precipitation, and most probably the mechanism of precipitation is not the same as that at higher indium concentrations. It is highly probable that at higher pH values $\text{In}(\text{OH})_2^+$ is the predominant ionic form of indium in solution, and thus the precipitation can be ascribed to the hydrolyzation process :



The corresponding solubility product was calculated as :

$$K_{\text{sp}} = [\text{In}(\text{OH})_2^+][\text{OH}^-] = 10^{16.2}$$

In the concentration range of indium between 10^{-5} and 10^{-6} M, where a discontinuity of the concentration vs. pH plot was found to exist, InCl_2^+ and $\text{In}(\text{OH})_2^+$ are most probably present in the solution in equal concentrations and precipitation takes place according to both mechanisms. Irreproducibility of the results in this range is ascribed to the illdefined conditions of mixing. Similar results are obtained in sea water.

Conclusion

According to our experimental data it can be concluded that the soluble form of indium in sea water at pH about 8 is present predominantly as $\text{In}(\text{OH})_2^+$, and its concentration cannot be higher than 10^{-10} M.

References

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