

Part I: Removing of Zn(II) from Polluted Water: Determination of Precipitation Limit Of Zn(II) Ion With 2-Hydroxy-1,2,3-Propanetricarboxylic Acid

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Abstract: Problem statement: The goal of this research was to investigate the condition for removing of Zn cation from water, through precipitation method with 2-hydroxy-1,2,3-propanetricarboxylic acid as ligand. **Approach:** In this study we examined the precipitation of Zn(II) ion in water solutions of $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ (1×10^{-2} and 5×10^{-3} mol L⁻¹) with 2-hydroxy-1,2,3-propanetricarboxylic acid (1×10^{-1} - 1×10^{-3} mol L⁻¹) in constant ionic strength of 0.6 mol L⁻¹ NaCl. We have determined the concentration region at which Zn(II) start to precipitate. **Results:** From precipitation diagrams of zinc with 2-hydroxy-1,2,3-propanetricarboxylic acid, in ionic force 0.6 mol L⁻¹ NaCl, we have found that during decreasing the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid, in case of constant concentration of Zn(II), the limit of precipitation is shifted to lower values of pH. The solid phase is analyzed by IR spectroscopy. **Conclusion:** From the IR spectroscopic analysis we can conclude that Zn(II) ion can precipitate with 2-hydroxy-1,2,3-propanetricarboxylic acid.

Key words: Environment, precipitation limit, Zn(II) ion, ligands, 2-hydroxy-1,2,3-propanetricarboxylic acid, IR spectroscopy

INTRODUCTION

Human activities can cause water pollution or can pollute river sediments (Montgomery, 1985). Components from organic or inorganic origin, within time they can sediment in lower part of river. The sediment from river contains heavy toxic metals, organic or inorganic components (Halamic *et al.*, 2001). Water from river can contain ions (Cu, Cd, Zn, Pb, Al and Hg), depends on pollution, which are very toxic for water organisms. If these ions bind with different ligands (organic molecules), the metal toxicity will reduce. Natural water contains a lot of molecules and ions with organic and inorganic origin. Cations in natural water can be present as complex, but anions can be from human activities (phosphates and dicarboksilik acids), (Hammond, 1971) or can be present from natural humic acids and aminoacids (Flaig and Beutelspacher, 1975; Schnitzer and Khan, 1978). Investigation of the interactions between metals and ligands, is very important for Environmental chemistry.

Oceans and seas water contain metals, also zinc and other helate ligands in normal quantity but

sometimes depends on pollution they can contain high level of these metals and ligands. We can find complexes which are not stable with different inorganic ligands, as example chloride ions, or complexes, which are stable and these are formed from metals and helate ligands from organic matters or formed from polluted water (Ibanez *et al.*, 2007).

Toxic metals as zinc are considered as non toxic when it is complexes with helate ligands. Water organisms (fish's) can eat these complexes, but it is not believed that these kinds of compounds can entry to the nutritive chain. But this should investigate very carefully in each case (Ibanez *et al.*, 2007).

The Aim of this work was to investigate the condition for removing of Zn cation from water, through precipitation method with 2-hydroxy-1,2,3-propanetricarboxylic acid as ligand.

MATERIALS AND METHODS

In this study we used $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$, 2-hydroxy-1,2,3-propanetricarboxylic acid as a ligand, sodium hydroxide and sodium chloride. For this investigation

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we have prepared some concentrated solutions which are stored on glass bottles in room temperature. Diluted solution we have prepared fresh for each series of precipitated systems. The precipitated systems are prepared using methods from Tezak *et al.* (1951).

Precipitated system, $ZnSO_4 \times 7H_2O$ with 2-hydroxy-1,2,3-propanetricarboxylic acid, is investigated in the long region of concentration with ionic force of $NaCl$ 0.6 mol L^{-1} .

As example, one series it's prepared in this way:

- The solution was added in two line of test-tube. In the first line of test tubes is added the solution of $ZnSO_4 \times 7H_2O$ with known concentration (as example $1 \times 10^{-1} \text{ mol L}^{-1}$). In second line of test tube we added the 2-hydroxy-1,2,3-propanetricarboxylic acid solution, also with known concentration (as example 1 mol L^{-1}). The second line of test tube we added $NaCl$ in that way that ionic force to be 0.6 mol L^{-1} . After that we added the solution of $NaOH$ to increase the pH value. The total volume in each test tube should be 10 mL. The differences till 10 mL, we have fill with distillate water
- Solution from the first line tubes was added to the solution of second test tube (7 times per 20 sec). All the concentration is calculated on the total volume after mixing, which means at 10 mL. The systems after mixed are stored on thermostat for 24 h in $25^\circ C$. To determine the precipitated diagrams, when the concentration of Zn ions stays unchanged, we have to change the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid. For that we used three deferent concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid for one concentration of Zn(II) ion. We used concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid 1×10^{-1} , 1×10^{-2} and $1 \times 10^{-3} \text{ mol L}^{-1}$ for each concentration of Zn(II). For zinc (II) ion we used two concentration 1×10^{-2} and $5 \times 10^{-3} \text{ mol L}^{-1}$. At all of these systems we added solution of $NaCl$ in that way that ionic force to be 0.6 mol L^{-1} . Also we added the $NaOH$ to change the pH values. Precipitated systems are monitories after 24 h. It is determinate the concentration which cause the difference between clear solution and precipitation. Then it is measured the pH value on the top of precipitate with pH meter, "Metrohm"
- Some precipitates are prepared in large quantity for quantity analysis. Systems have stored in thermostat for 24 h in the temperature of $25^\circ C$ and

then the pH value is measured on the top of precipitate. These systems are filtered (we used filtered paper with blue line for filtration) and are dried on the air. We used the IR spectra to characterize and to find the presence of organic components to precipitate. To record IR spectra we used spectrophotometer, "SHIMADZU 8400 S" with potassium bromide technique

RESULTS

Precipitation of zinc(II) with 2-hydroxy-1,2,3-propanetricarboxylic acid was investigated to concentration of zinc 1×10^{-2} and $5 \times 10^{-3} \text{ mol L}^{-1}$ with different concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid (1×10^{-1} , 1×10^{-2} and $1 \times 10^{-3} \text{ mol L}^{-1}$). We have added the solution of $NaCl$ because we want that general ionic force to be 0.6 mol L^{-1} . In this mixture we added the $NaOH$ solution in that way that pH increase continually and from here to find at which pH values the Zn(II) ion will precipitate.

DISCUSSION

From the precipitation diagram of Zn(II) with 2-hydroxy-1,2,3-propanetricarboxylic acid we can see, that when concentration of zinc is $1 \times 10^{-2} \text{ mol L}^{-1}$ and concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid $1 \times 10^{-1} \text{ mol L}^{-1}$ (Fig. 1) we have not the precipitate,

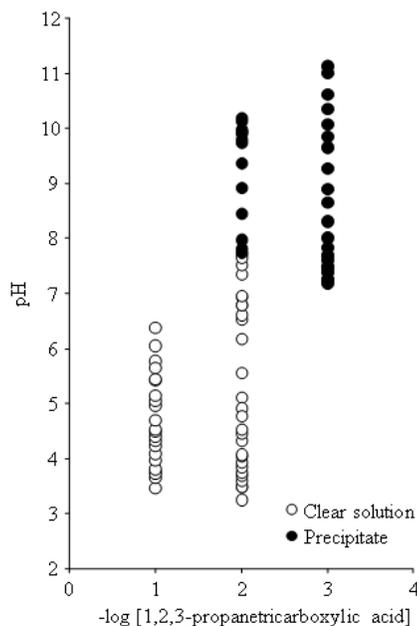


Fig. 1: Precipitate diagram of Zn(II) in concentration $1 \times 10^{-2} \text{ mol L}^{-1}$

but the precipitation start when the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is 1×10^{-2} and 1×10^{-3} mol L⁻¹ at the value of pH = 7.81 and 7.19, respectively. At pH = 10.27 the precipitate start when the concentration of Zn is 5×10^{-3} mol L⁻¹ and concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is 1×10^{-1} mol L⁻¹ (Fig. 2), but when concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is 1×10^{-2} mol L⁻¹, precipitate start at pH = 10.03. When the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid is 1×10^{-3} mol L⁻¹ precipitate start at pH = 6.96.

We have found that diagrams have not changed after a long stored and for that the time of 24 h was approved as time of achieved the equilibrium. To analyze the precipitate, some of test tubes are filtered and are dried in the room temperature. These precipitate are characterized with IR spectra (Fig. 4 and 5).

We have obtained also the IR spectra of 1,2,3-propanetricarboxylic acid (Fig. 3). Comparing the IR specters, we can conclude that we have interaction between Zn and 1,2,3-propanetricarboxylic acid.

To the 1,2,3-propanetricarboxylic acid IR spectra (Fig. 3) we see the peaks at 1710 cm⁻¹ which characterize the carboxyl group. At solid phase this peak is shifted at lower values, 1600cm⁻¹ (Fig. 4 and 5). This tells us for the interaction of Zn with 1,2,3-

propanetricarboxylic acid. The breitt peak at 1100 cm⁻¹ is characteristic for the interaction of Zn-OH.

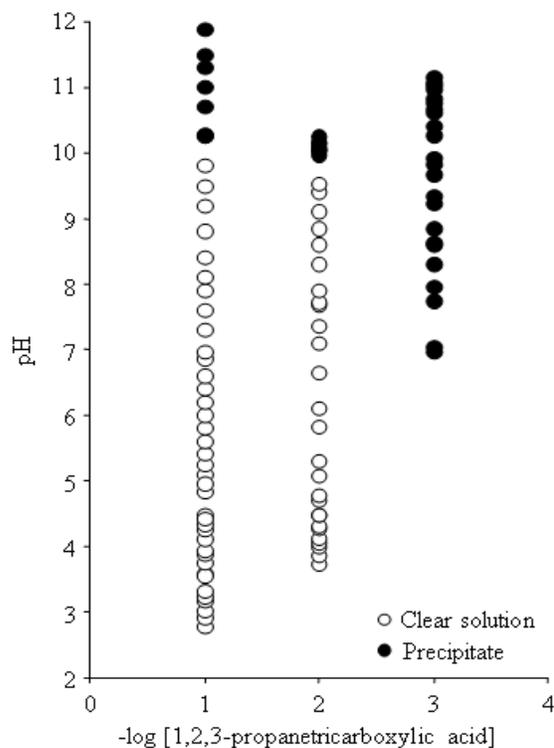


Fig. 2: Precipitate diagram of Zn(II) in concentration 5×10^{-3} mol L⁻¹

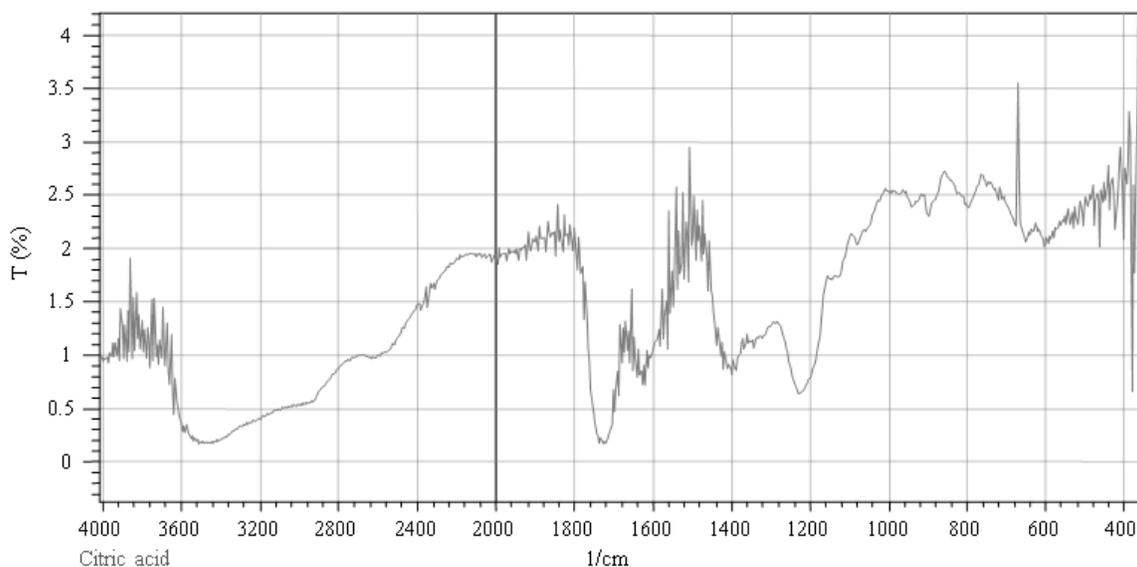


Fig. 3: IR spectra of 1,2,3-propanetricarboxylic acid

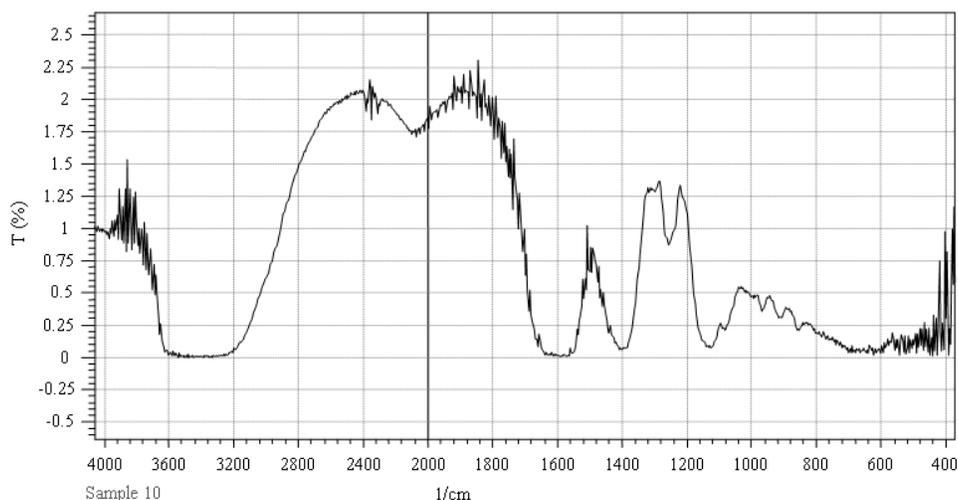


Fig. 4: IR spectra of precipitate which is formed after interaction of Zn(II) with 1,2,3-propanetricarboxylic acid ($c(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}) = 5 \times 10^{-3} \text{ mol L}^{-1}$, $c(1,2,3\text{-propanetricarboxylic acid}) = 1 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 9.46$)

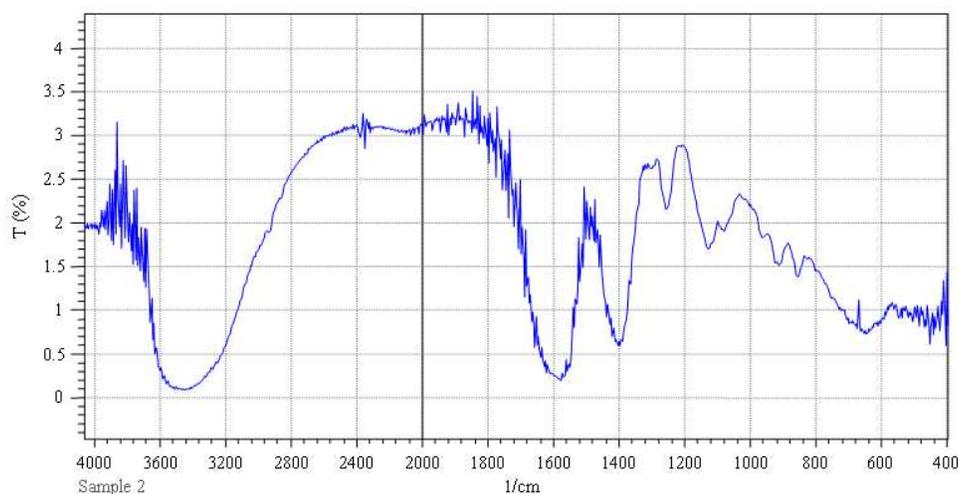


Fig. 5: IR spectra of precipitate which is formed after interaction of Zn(II) with 1,2,3-propanetricarboxylic acid ($c(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}) = 1 \times 10^{-2} \text{ mol L}^{-1}$, $c(1,2,3\text{-propanetricarboxylic acid}) = 1 \times 10^{-2} \text{ mol L}^{-1}$, $\text{pH} = 6.72$)

CONCLUSION

To investigate the interaction between ligands and metals, which can be present in natural water, is very important for Environment. For that we have analyzed the precipitation diagrams of Zn(II) ion with 2-hydroxy-1,2,3-propanetricarboxylic acid. From our results we can conclude:

- Also from precipitation diagrams of zinc with 2-hydroxy-1,2,3-propanetricarboxylic acid at ionic

force of 0.6 mol L^{-1} NaCl, we can see that when the concentration of 2-hydroxy-1,2,3-propanetricarboxylic acid decrease, in case of constant concentration of zinc, the limit of precipitation will shift at lower values of pH

- Solid precipitates are analyzed by IR spectrophotometer and the IR spectra which we have obtained are compared with IR spectra of 2-hydroxy-1,2,3-propanetricarboxylic acid. From the IR spectra of solid phase we can conclude that zinc

can react with 2-hydroxy-1,2,3-propanetricarboxylic acid

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