

## DETERMINATION OF PRECIPITATION LIMIT OF Zn (II) ION WITH 2-AMINO-4-CARBAMOYL BUTANOIC ACID

<sup>1</sup>Fatmir Faiku\*, <sup>2</sup>Haxhere Faiku

<sup>1</sup>Department of Chemistry, Faculty of Natural Sciences, University of Prishtina, Mother Teresa Street 5, 10000 Prishtina, Kosova

<sup>2</sup>Department of Natural Science, Association Loyola Gymnasium, Ring Rout, 20000 Prizren, Kosova

\* Corresponding author, e-mail: [f\\_faiku@hotmail.com](mailto:f_faiku@hotmail.com)

**ABSTRACT:** The goal of this research was to investigate the condition for removing of Zn cation from water, through precipitation method with 2-Amino-4-carbamoylbutanoic acid as ligand. In this study we examined the precipitation of Zn (II) ion in water solutions of  $ZnSO_4 \cdot 7H_2O$  ( $3 \times 10^{-3} \text{ mol L}^{-1}$ ,  $5 \times 10^{-4} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$ ) with 2-Amino-4-carbamoylbutanoic acid ( $1 \times 10^{-1} \text{ mol L}^{-1}$ ,  $1 \times 10^{-2} \text{ mol L}^{-1}$ ,  $1 \times 10^{-3} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$ ) in constant ionic strength of  $0.6 \text{ mol L}^{-1} \text{ NaCl}$ . We have determined the concentration region at which Zn (II) start to precipitate. From precipitation diagrams of zinc with 2-Amino-4-carbamoylbutanoic acid in ionic force  $0.6 \text{ mol L}^{-1} \text{ NaCl}$ , we have found that during decreasing the concentration 2-Amino-4-carbamoylbutanoic acid in case of constant concentration of Zn (II) the limit of precipitation is shifted to lower values of pH. Also from precipitation diagrams we can see that when the concentration of zinc decreasing, in case of constant concentration of 2-Amino-4-carbamoylbutanoic acid the limit of precipitation will shift at lower values of pH. From the IR spectroscopic analysis we can conclude that Zn (II) ion can precipitate with 2-Amino-4-carbamoylbutanoic acid.

**Key words:** 2-Amino-4-carbamoylbutanoic acid, precipitation limit, Zn (II) Ion, Environment, ligands, IR spectroscopy.

## INTRODUCTION

Human activities can cause water pollution or can pollute river sediments [1]. 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 [2]. 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 dicarboxylic acids) [3], or can be present from natural humic acids and aminoacids. 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 [4]. 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 [4]. Is investigated the precipitation of Zn (II) ions with 2,3-dihydroxybutanedioic Acid [5], succinic acid [6], citric acid [7], 2-hydroxy-1,2,3-propanetricarboxylic acid [8] and (2S)-2-Aminobutanedioic [9]. Faiku et al. [8] have investigate the precipitation of Zn (II) ions from water solutions of  $ZnSO_4 \cdot 7H_2O$  with 2-Hydroxy-1,2,3-Propanetricarboxylic Acid in constant ionic force  $0.6 \text{ mol L}^{-1}$ . They have found that decreasing the concentration of 2-Hydroxy-1,2,3-Propanetricarboxylic Acid, the level of precipitations will shift in lower values of pH.

Faiku et al. [9] have investigate the precipitation of Zn (II) ions from water solutions of  $ZnSO_4 \cdot 7H_2O$  with (2S)-2-Aminobutanedioic Acid in constant ionic force  $0.6 \text{ mol L}^{-1}$ . They have found that decreasing the concentration of (2S)-2-Aminobutanedioic Acid, the level of precipitations will shift in lower values of pH.

The Aim of this work was to investigate the condition for removing of Zn cation from water, through precipitation method with 2-Amino-4-carbamoylbutanoic acid.

## MATERIALS AND METHODS

In this study we used:  $ZnSO_4 \cdot 7H_2O$ , 2-Amino-4-carbamoylbutanoic acid as a ligand, sodium hydroxide and sodium chloride. For this investigation 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 Tezhak et al. [10].

Precipitated system  $ZnSO_4 \cdot 7H_2O$  with 2-Amino-4-carbamoylbutanoic acid is investigated in the long region of concentration with ionic force of NaCl  $0.6 \text{ mol L}^{-1}$ .

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  $ZnSO_4 \cdot 7H_2O$  with known concentration (as example  $3 \times 10^{-3} \text{ mol L}^{-1}$ ). In second line of test tube we added the 2-Amino-4-carbamoylbutanoic acid solution also with known concentration (as example  $1 \times 10^{-1} \text{ mol L}^{-1}$ ). The second line of test tube we added NaCl in that way that ionic force to be  $0.6 \text{ mol L}^{-1}$ . 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 the  $25^\circ$ . To determine the precipitated diagrams, when the concentration of Zn ions stays unchanged, we have to change the concentration of 2-Amino-4-carbamoylbutanoic acid. For that we used three deferent concentration of 2-Amino-4-carbamoylbutanoic acid for one concentration of Zn ion. We used concentration of 2-Amino-4-carbamoylbutanoic acid  $1 \times 10^{-1}$ ,  $1 \times 10^{-2}$ ,  $1 \times 10^{-3}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$  for each concentration of Zn(II). For zinc ion we used two concentration  $3 \times 10^{-3} \text{ mol L}^{-1}$ ,  $5 \times 10^{-4} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$ . At all of these systems we added solution of NaCl in that way that ionic force to be  $0.6 \text{ mol L}^{-1}$ . 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  $25^\circ$  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 AND DISCUSSION

Precipitation of zinc (II) with 2-Amino-4-carbamoylbutanoic acid was investigated to concentration of zinc  $3 \times 10^{-3} \text{ mol L}^{-1}$ ,  $5 \times 10^{-4} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$  with different concentration of 2-Amino-4-carbamoylbutanoic acid ( $1 \times 10^{-1} \text{ mol L}^{-1}$ ,  $1 \times 10^{-2} \text{ mol L}^{-1}$ ,  $1 \times 10^{-3} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$ ). We have added the solution of NaCl because we want that general ionic force to be  $0.6 \text{ mol L}^{-1}$ . 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. From the precipitation diagram (Fig. 1) of zinc (II) with 2-Amino-4-carbamoylbutanoic acid we can see, that when concentration of zinc is  $3 \times 10^{-3} \text{ mol L}^{-1}$  and concentration of 2-Amino-4-carbamoylbutanoic acid  $1 \times 10^{-1} \text{ mol L}^{-1}$  the precipitate start at  $\text{pH}=7.0$ . If we decrease the concentration of 2-Amino-4-carbamoylbutanoic acid ( $1 \times 10^{-2} \text{ mol L}^{-1}$  and  $1 \times 10^{-3} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$ ) the precipitate will formed at lower value of  $\text{pH}=6.2$ ,  $5.5$  and  $4.8$  respectively. From the precipitation diagram (Fig. 2) of zinc (II) with 2-Amino-4-carbamoylbutanoic acid, in constant ionic force  $0.6 \text{ mol L}^{-1}$  NaCl, we can see, that when concentration of zinc is  $5 \times 10^{-4} \text{ mol L}^{-1}$  and concentration of 2-Amino-4-carbamoylbutanoic acid acid  $1 \times 10^{-1} \text{ mol L}^{-1}$  the precipitate start at  $\text{pH}=6.3$ . If we decrease the concentration of 2-Amino-4-carbamoylbutanoic acid ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ,  $1 \times 10^{-3} \text{ mol L}^{-1}$  and  $1 \times 10^{-4} \text{ mol L}^{-1}$ ) the precipitate will formed at lower value of  $\text{pH}=5.4$ ,  $5.1$  and  $4.5$ , respectively.

From the precipitation diagram (Fig. 3) of zinc (II) with 2-Amino-4-carbamoylbutanoic acid we can see, that when concentration of zinc is  $1 \times 10^{-4}$  mol L<sup>-1</sup> and concentration of 2-Amino-4-carbamoylbutanoic acid  $1 \times 10^{-1}$  mol L<sup>-1</sup> the precipitate start at pH=6.0. If we decrease the concentration of 2-Amino-4-carbamoylbutanoic acid ( $1 \times 10^{-2}$  mol L<sup>-1</sup>,  $1 \times 10^{-3}$  mol L<sup>-1</sup> and  $1 \times 10^{-4}$  mol L<sup>-1</sup>) the precipitate will formed at lower value of pH =5.1, 4.7 and 4.2, respectively.

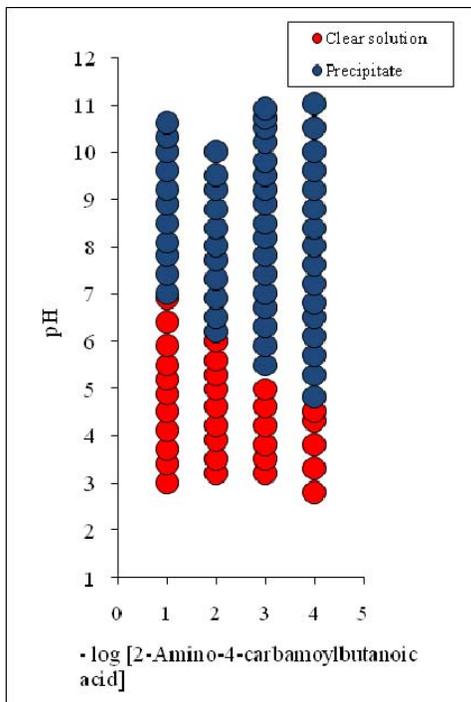


Figure 1: Precipitate diagram of Zn (II) in concentration  $1 \times 10^{-3}$  mol L<sup>-1</sup>

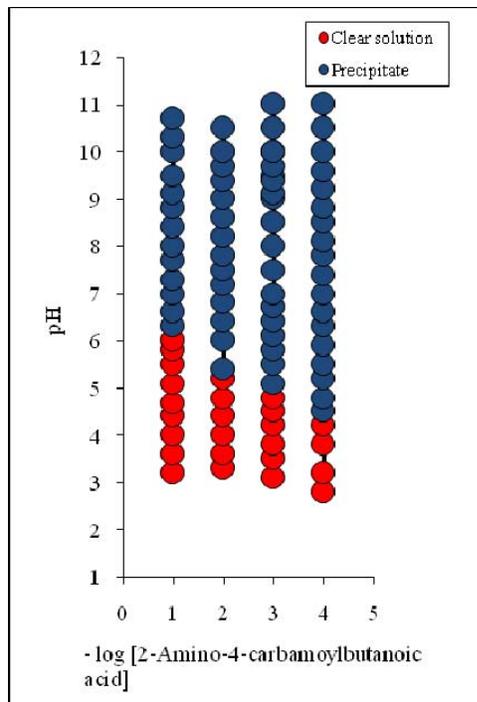


Figure 2: Precipitate diagram of Zn (II) in concentration  $3 \times 10^{-4}$  mol L<sup>-1</sup>

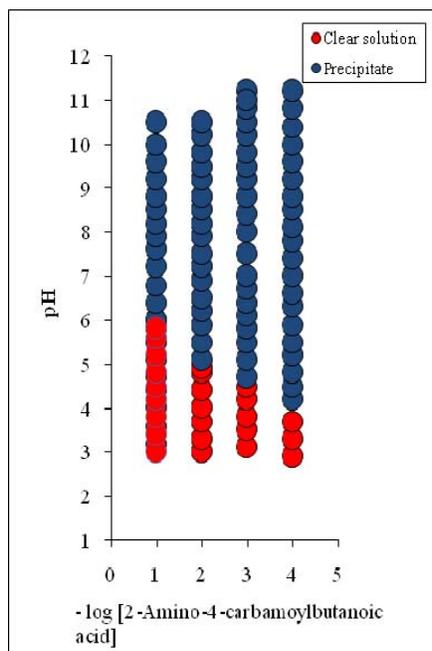


Figure 3: Precipitate diagram of Zn (II) in concentration  $1 \times 10^{-4}$  mol L<sup>-1</sup>

From precipitate diagrams we get a lot of information about the level of pH in which we have the starting point of precipitation of ion Zn (II) with 2-Amino-4-carbamoylbutanoic acid, at ionic force of  $0.6 \text{ mol L}^{-1} \text{ NaCl}$ . The bold cycles, on diagrams, tell us about precipitates and empty cycles show no precipitate.

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. 5).

We have obtained also the IR spectra of 2-Amino-4-carbamoylbutanoic acid (Fig. 4). Comparing the IR specters, we can conclude that we have interaction between zinc and 2-Amino-4-carbamoylbutanoic acid. To the 2-Amino-4-carbamoylbutanoic acid IR spectra (Fig. 4) we see the peaks at  $1660 \text{ cm}^{-1}$  which characterize the carboxyl group. At solid phase this peak is shifted at lower values,  $1540 \text{ cm}^{-1}$  (Fig. 5). This tells us for interaction of Zn (II) with 2-Amino-4-carbamoylbutanoic acid [11]. The breitt peak at  $1000 \text{ cm}^{-1}$  is characteristic for the interaction of Zn-OH [12].

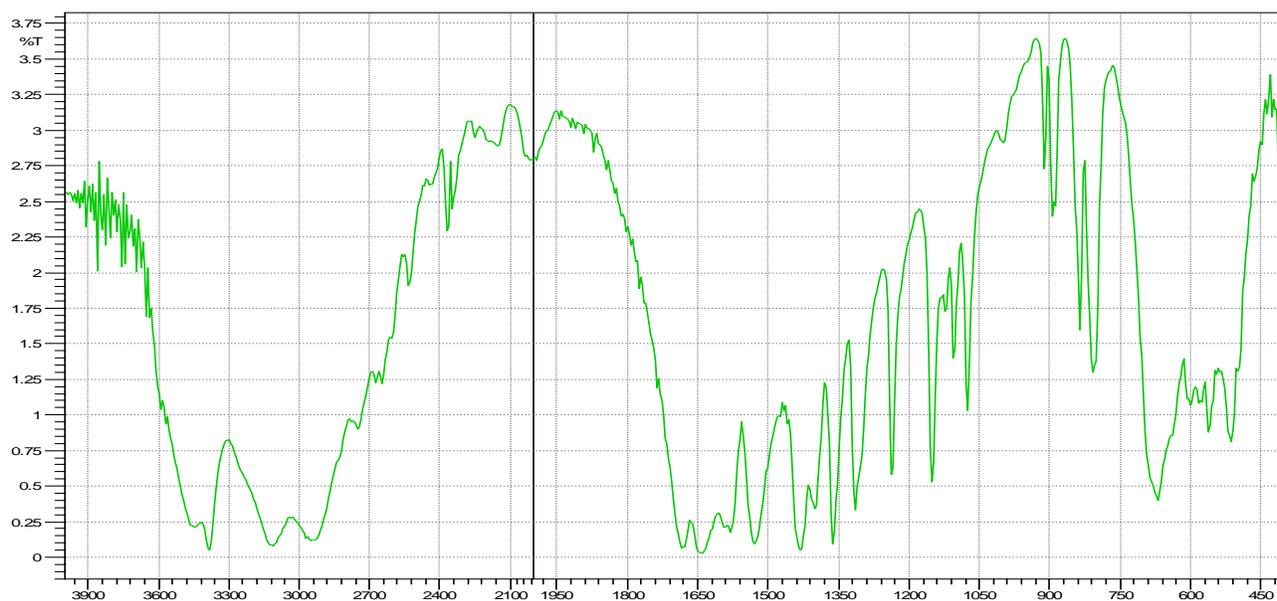


Figure 4: IR spectra of 2-Amino-4-carbamoylbutanoic acid

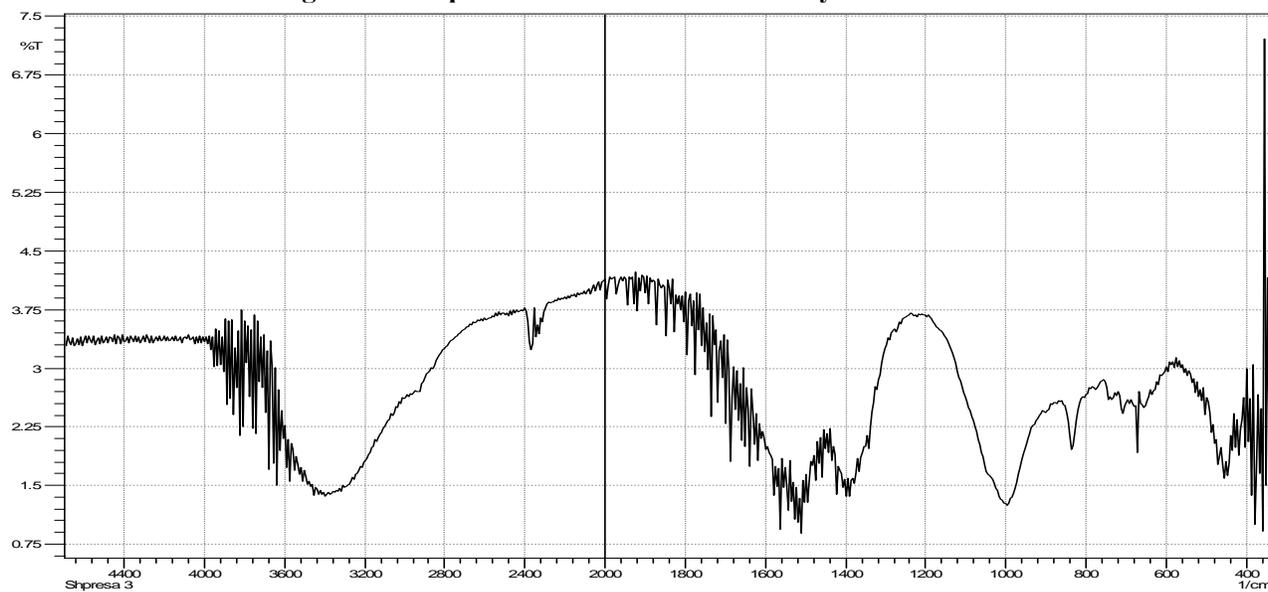


Figure 5: IR spectra of precipitate which is formed after interaction of Zn (II) with 2-Amino-4-carbamoylbutanoic acid

## CONCLUSION

To investigate the interreaction between ligands and metals, which can be present in natural water, is very important for Environment. For that we have analysed the precipitation diagrams of Zn(II) ion with 2-Amino-4-carbamoylbutanoic acid. From our results we can conclude:

1. Also from precipitation diagrams of zinc with 2-amino-4-carbamoylbutanoic acid at ionic force of  $0.6 \text{ mol L}^{-1}$  NaCl, we can see that when the concentration of 2-Amino-4-carbamoylbutanoic acid decrease, in case of constant concentration of zinc, the limit of precipitation will shift at lower values of pH.
2. Also from precipitation diagrams we can see that when the concentration of zinc decrease, in case of constant concentration of 2-amino-4-carbamoylbutanoic acid the limit of precipitation will shift at lower values of pH.
3. Solid precipitates are analyzed by IR spectrophotometer and the IR spectra which we have obtained are compared with IR spectra of 2-amino-4-carbamoylbutanoic acid. From the IR spectra of solid phase and IR spectra of 2-amino-4-carbamoylbutanoic acid we can see that they are not same. From the IR spectra of solid phase we can conclude that zinc can react with 2-amino-4-carbamoylbutanoic acid. The IR spectra of 2-amino-4-carbamoylbutanoic acid and precipitates are not same if we compare in the form and in the intensity peaks. This investigation of interaction between 2-amino-4-carbamoylbutanoic acid and zinc are very interesting for environmental aspects and for that we have investigate the precipitate diagram of zinc with 2-amino-4-carbamoylbutanoic acid.

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