## Stabilities in the Cu<sup>2+</sup> - 1,2-ethanediamine system

Copper(II) form stable complexes with 1,2-ethanediamine (in the following abbreviated as en).

In aqueous solution protons and copper(II) ions compete for the base **en**. At the same time hydroxide and **en** compete for the copper(II) ions:

$$Cu(H_2O)_4^{2+} \leftrightarrow CuOH(H_2O)_3^{+} + H^{+} \qquad pK \sim 7$$

$$Cu(OH)_2(s) \leftrightarrow Cu^{2+} + 2OH^{-} \qquad L= 1.6*10^{-19} M^3$$

These numbers indicate, that the competitive reactions are unimportant relative to the equilibria

 $Cu(H_2O)_4^{2+} + nen \leftrightarrow Cuen_n(H_2O)_{4-2n}^{2+} \log\beta_n > 10 \text{ (n=1 or 2)}$ 

as long as

- 1. pH is below 7
- 2. the concentration of copper(II) ions is not too high and
- 3. the concentration of **en** is not too low.

The aim of this assignment is experimentally to investigate the Cu<sup>2+</sup> - 1,2-ethanediamine system and eventually determine relevant stabilities using pH measurements.

1. The concentration of **en** in the stock solution prepared by weighing 31 g of fairly pure **en** into water to a volume of 500 ml is determined:

To 10 ml of water and two drops of methyl-red indicator solution is added 1000  $\mu$ l of the Stock solution with an automat pipette. Using a 10 ml burette the solution is titrated with 1.000 M hydrochloric acid (yellow to red). The reading should be more accurate than 0.05 ml. Now add another aliquot of 1000  $\mu$ l of the Stock solution and titrate again without refilling the burette. This procedure is repeated until 4000  $\mu$ l of the Stock solution has been titrated. This procedure gives 4 results. Make sure that all individuals in the team has delivered at least one 1000  $\mu$ l aliquot of the Stock solution and has titrated at least once.

Use the average of the results of all teams of the day as the concentration of **en** in the stock solution.

2. The pK's of **en** are determined by pH measurement:

a. All pH-meter readings (format xx.xxx) should be recorded repeatedly at time intervals: make 6 readings with an interval of 10 seconds and use the average

b. Calibrate the pH-meter to standard buffers 10 and 7 and keep the actual readings. Measure the average reading for a standard buffer 4. Measure the temperature in the lab and look up the standard buffer value at the lab temperature.

c. To 8.5 ml of 1 M KNO<sub>3</sub> add 1000  $\mu$ l of the **en** stock solution and 200  $\mu$ l (automat pipette) of a 1.00 M HCl and a magnetic rod. While stirring measure pH as described and record the average reading. Next 100  $\mu$ l (automat pipette) of 1.00 M HCl is added and the pH measured. A new 100  $\mu$ l (automat pipette) aliquot of 1.00 M HCl is added and the pH measured. This procedure is added until a total volume of 2200  $\mu$ l of 1.00 M HCl has been added and the corresponding pH has been determined. Make sure, that all individuals in the team have delivered at least one aliquot of 100  $\mu$ l of 1.00 M HCl using the automat pipette.

3. The  $[Cu^{2+}]$  in a stock solution prepared by dissolving 25 g of pure  $CuSO_4 5H_2O$  in water to a total volume of 100 ml is determined by a iodometric titration:

To 10 ml of water is added 200  $\mu$ l (automat pipette) of the stock solution of copper sulphate and a magnetic rod and .5 g of potassium iodide and ½ ml of starch solution. Using a 10 ml burette titrate with standard 0.100 M sodium thiosulphate (bluish suspension to pure white) and make the reading (x.xx ml). Next add another 200  $\mu$ l aliquot (automat pipette) of the stock solution of copper sulphate and titrate again. The procedure is repeated until 800  $\mu$ l of the stock solution has been titrated without refilling the burette. Make sure, that all individuals in the team have delivered at least one aliquot of 200  $\mu$ l of the stock solution of copper sulphate using the automat pipette. Make an average of the 4 readings. Write the two balanced reaction schemes valid for this titration and calculate the concentration of copper ions in the stock solution. Use the average of the results of all teams of the day as the concentration of copper ions in the stock solution.

4. The logK's in the  $Cu^{2+}$  - **en** system are determined by pH measurement:

a. All pH-meter readings (format xx.xxx) should be recorded repeatedly at time intervals: make 6 readings with an interval of 10 seconds and use the average

b. Calibrate the pH-meter to standard buffers 4 and 7 and keep the actual readings. Measure the average reading for a standard buffer 10. Measure the temperature in the lab and look up the standard buffer value at the lab temperature.

c. To 17.5 ml of 1 M KNO<sub>3</sub> add 1000  $\mu$ l of the **en** stock solution and 300  $\mu$ l (automat pipette) of the stock solution of copper sulphate and 1000  $\mu$ l (automat pipette) of the 1.00 M HCl and a magnetic rod. While stirring measure pH as described and record the average reading. Next 100  $\mu$ l (automat pipette) of 1.00 M HCl is added and the pH measured. A new 100  $\mu$ l (automat pipette) aliquot of 1.00 M HCl is added and the pH measured. This procedure is added until a total volume of 2100  $\mu$ l of 1.00 M HCl has been added and the corresponding pH has been determined. Make sure, that all individuals in the team have delivered at least one aliquot of 100  $\mu$ l of 1.00 M HCl using the automat pipette.