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Experiment#8 – Synthesis and Analysis of a Nickel Salt $[\text{Ni}(\text{en})_x(\text{H}_2\text{O})_{6-2x}]\text{SO}_4 \cdot y\text{H}_2\text{O}$

D. Calculation

In this experiment, unknown salt A and B were synthesized and analyzed in part I and part II. The part II analysis would determine the mass percent of Ni^{2+} , en, SO_4 , and water. With the mass percent of each component, the mole ratio and chemical formula of the unknown salts could be determined. With the chemical formula, the percent yield of the two salt in Part I could be calculated.

Sample Calculation for Salt A trial 1

Part I – % Yield of Nickel Salt

$$\% \text{ Yield} = \text{Actual yield (g)} / \text{Theoretical yield (g)} \times 100\%$$

$$\% \text{ Yield} = \text{mass of unknown salt (g)} / (\text{moles of Nickel in part I (mol)} \times \text{mwt salt (g/mol)}) \times 100\%$$

The moles of Nickel in part I come from the reactant $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$,

$$\text{Moles of Ni}^{2+} = \text{Moles of } [\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4 = \text{mass}[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4(\text{g}) / \text{mwt}[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4(\text{g/mol})$$

$$= 1.27\text{g} / 263\text{g/mol}$$

$$= 4.83 \times 10^{-3} \text{mol}$$

The other value was determined in Part II's calculation

Part II – Analysis for Salt A trial 1

A. Ethylenediamine Analysis

1. Excess HCl was added to the solution of Salt A. Ethylenediamine in the complex salt can be detached by HCl. Therefore,

$$\text{HCl reacted (mol)} = \text{HCl original (mol)} - \text{HCl unreacted (mol)}.$$

Figure out the amount of unreacted HCl by the moles of NaOH used in the titration

$$\text{Mol NaOH} = \text{Conc NaOH (M)} \times \text{volume NaOH (L)}$$

$$= 17.6 \text{mL} \times 10^{-3} \times 0.107 \text{M}$$

$$= 1.88 \times 10^{-3} \text{mol}$$

$$\text{Mol HCl unreacted} = \text{Mol NaOH} = 1.88 \times 10^{-3} \text{mol}$$

$$\text{HCl original (mol)} = \text{Conc HCl} \times \text{volume HCl (L)}$$

$$= 0.208 \text{M} \times 10.0 \text{mL} \times 10^{-3}$$

$$= 2.08 \times 10^{-3} \text{mol}$$

$$\begin{aligned} \text{HCl reacted(mol)} &= \text{HCl original(mol)} - \text{HCl unreacted(mol)} \\ &= 2.08 \times 10^{-3} \text{ mol} - 1.88 \times 10^{-3} \text{ mol} \\ &= 2.00 \times 10^{-4} \text{ mol} \end{aligned}$$

- Since one mole of en react with 2 moles of HCl,

$$\begin{aligned} \text{Mol en(mol)} &= \text{HCl reacted(mol)} \times (2 \text{ mol HCl} / 1 \text{ mol en}) \\ &= 1/2 \times 2.00 \times 10^{-4} \text{ mol} \\ &= 1.00 \times 10^{-4} \text{ mol} \end{aligned}$$
- Mass of en could be calculated using the moles and molar mass of en

$$\begin{aligned} \text{Mass en(g)} &= \text{mwt en(g/mol)} \times \text{mole en(mol)} \\ &= 60.1 \text{ g/mol} \times 1.00 \times 10^{-4} \text{ mol} \\ &= 6.01 \times 10^{-3} \text{ g} \end{aligned}$$
- Mass percent of en could be calculated using the total mass of sample salt A in trial 1

$$\begin{aligned} \% \text{ mass en} &= \text{mass en(g)} / \text{mass salt(g)} \times 100\% \\ &= 6.01 \times 10^{-3} \text{ g} / 0.0500 \text{ g} \times 100\% \\ &= \boxed{12.0\%} \end{aligned}$$
- Mass of en in 100 grams of salt A

$$\begin{aligned} \text{Mass Ni}^{2+}(\text{g}) &= 12.0\% \times 100 \text{ g} \\ &= 12.0 \text{ g} \end{aligned}$$
- Mole Ni²⁺ = 12.0g / 60.1g/mol

$$= 0.200 \text{ mol}$$

B. Nickel Analysis

- Since in the complex $[\text{Ni}(\text{en})_x(\text{H}_2\text{O})_{6-2x}]\text{SO}_4 \cdot y\text{H}_2\text{O}$, 1 mole of Nickel cation paired with 1 mole of sulfate anion, $\text{mol Ni}^{2+} = \text{mol SO}_4^{2-}$
 Moles of Ni²⁺ could be found from the concentration reading of Cary 50 and the volume of the salt solution

$$\begin{aligned} \text{Mole Ni}^{2+}(\text{mol}) &= \text{volume(mL)} \times \text{Conc Ni}^{2+}(\text{M}) \\ &= 25.0 \text{ mL} \times 0.0334 \text{ M} \\ &= 8.35 \times 10^{-4} \text{ mol} \end{aligned}$$
- Mass Ni²⁺(g) = mwt Ni²⁺(g/mol) x mole Ni²⁺(mol)

$$\begin{aligned} &= 58.7 \text{ g/mol} \times 8.35 \times 10^{-4} \text{ mol} \\ &= 0.0490 \text{ g} \end{aligned}$$
- % mass Ni²⁺ = mass Ni²⁺ (g) / mass salt(g) x 100%

$$\begin{aligned} &= 0.0490 \text{ g} / 0.0500 \text{ g} \times 100\% \\ &= \boxed{19.7\%} \end{aligned}$$

4. Mass of Ni²⁺ in 100grams of salt A

$$\begin{aligned}\text{Mass Ni}^{2+}(\text{g}) &= 19.7\% \times 100\text{g} \\ &= 19.7\text{g}\end{aligned}$$

5. Mole Ni²⁺ = 19.7g/58.7g/mol

$$= 0.336\text{mol}$$

6. Mole SO₄²⁻ (mol) = 8.35x10⁻⁴mol

7. Mass SO₄²⁻ (g) = mwt SO₄²⁻ (g/mol) x mole SO₄²⁻ (mol)

$$\begin{aligned}&= 96.1\text{g/mol} \times 8.35 \times 10^{-4}\text{mol} \\ &= 0.0802\text{g}\end{aligned}$$

8. %mass SO₄²⁻ = mass SO₄²⁻ (g)/mass salt(g) x 100%

$$\begin{aligned}&= 0.0802\text{g} / 0.0500\text{g} \times 100\% \\ &= \boxed{32.2\%}\end{aligned}$$

9. Mass of Ni²⁺ in 100grams of salt A

$$\begin{aligned}\text{Mass SO}_4^{2-}(\text{g}) &= 32.2\% \times 100\text{g} \\ &= 32.2\text{g}\end{aligned}$$

10. Mole Ni²⁺ = 32.2g/96.1g/mol

$$= 0.336\text{mol}$$

11. The mass percent of the total amount of water in the complex molecule could be found by subtracting the sum of mass percent of other components from 100%

$$\begin{aligned}\text{Mass\% water} &= 100\% - (\text{Mass\%Ni}^{2+} - \text{Mass\%en} - \text{Mass\%SO}_4) \\ &= 100\% - (19.7 + 12.0 + 32.2)\% \\ &= \boxed{36.1\%}\end{aligned}$$

12. Mass of water in 100grams of salt A

$$\begin{aligned}\text{Mass H}_2\text{O}(\text{g}) &= 36.1\% \times 100\text{g} \\ &= 36.1\text{g}\end{aligned}$$

13. Mole H₂O = 36.1g/18.0g/mol

$$= 2.00\text{mol}$$

14. Mole ratio between the different component in the complex could be determined by dividing the moles of every component by the smallest value among them

$$\text{Mole ratio H}_2\text{O} = 2.00/0.202 = 10$$

$$\text{Mole ratio Nickel} = 0.335/0.202 = 2$$

$$\text{Mole ratio en} = 0.202/0.202 = 1.00$$

$$\text{Mole ratio SO}_4 = 0.335/0.202 = 2$$

15. The average mole ratio for the three trials of salt A

$$\text{Avg. Mole ratio H}_2\text{O} = (2.00 + 2.163 + 2.226) / 3 = 2.13$$

$$\text{Avg. Mole ratio Nickel} = (0.335 + 0.320 + 0.321) / 3 = 0.325$$

$$\text{Avg. Mole ratio en} = (0.202 + 0.191 + 0.170) / 3 = 0.188$$

$$\text{Avg. Mole ratio SO}_4 = (0.335 + 0.320 + 0.321) / 3 = 0.325$$

16. Since there was only one Nickel atom in the middle of the complex, all the average mole ratio need to be divided by 2

$$\text{Avg. Mole ratio H}_2\text{O} = 5.7$$

$$\text{Avg. Mole ratio Nickel} = 1$$

$$\text{Avg. Mole ratio en} = 0.5$$

$$\text{Avg. Mole ratio SO}_4 = 1$$

17. Since $[\text{Ni}(\text{en})_x(\text{H}_2\text{O})_{6-2x}]\text{SO}_4 \cdot y\text{H}_2\text{O}$.

$$\text{Avg. mole ratio H}_2\text{O} = 6 - 2X + y$$

$$X = \text{Avg. Mole ratio en} = 0.5$$

$$Y = 5.7 - (6 - 2 \times 0.5) = 0.7$$

Therefore, the chemical formula for salt A was $[\text{Ni}(\text{en})_{0.5}(\text{H}_2\text{O})_5]\text{SO}_4 \cdot (7/10)\text{H}_2\text{O}$

$$\text{The molar mass of salt A} = (58.7 + 0.5(60.1) + 5.7(18.0) + 96.1) \text{g/mol} = 288 \text{g/mol}$$

18. Going back to Part I, the percent yield of salt A could now be determined

$$\% \text{Yield} = \frac{\text{mass of unknown salt (g)}}{(\text{moles of Nickel in part I (mol)} \times \text{mwt salt (g/mol)})} \times 100\%$$

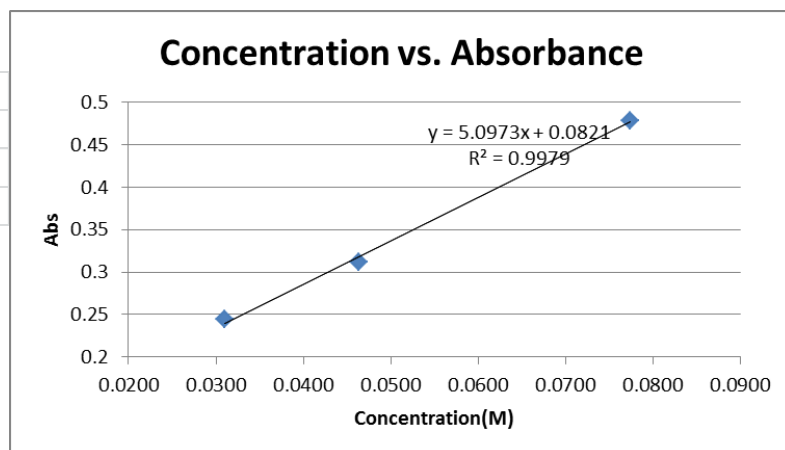
$$= \frac{1.212 \text{g}}{4.83 \times 10^{-3} \text{mol} \times 288 \text{g/mol}}$$

$$= 87.3\%$$

E. Table of Results

Calibration Graph

std	Conc (M)	Abs
1	0.0310	0.2443
2	0.0464	0.3123
3	0.0774	0.4787



Ethy Analysis	Salt A			salt B		
	Trial 1	trial 2	trial3	trial4	trial5	trial 6
Mass salt (g)	0.05	0.05	0.05	0.05	0.05	0.05
Vol NaOH (L)	1.76E-02	1.77E-02	1.79E-02	1.44E-02	1.19E-02	1.20E-02
M NaOH (mol/L)	0.107	0.107	0.107	0.107	0.107	0.107
moles NaOH	1.88E-03	1.89E-03	1.91E-03	1.54E-03	1.27E-03	1.28E-03
M HCL (mol/L)	0.208	0.208	0.208	0.208	0.208	0.208
Moles HCL	2.08E-03	2.08E-03	2.08E-03	2.08E-03	2.08E-03	2.08E-03
moles HCL reacted	2.02E-04	1.91E-04	1.70E-04	5.39E-04	8.07E-04	7.96E-04
mole of En	1.01E-04	9.57E-05	8.50E-05	2.70E-04	4.03E-04	3.98E-04
MW En (g/mol)	60.1	60.1	60.1	60.1	60.1	60.1
Mass En (g)	6.07E-03	5.75E-03	5.11E-03	1.62E-02	2.42E-02	2.39E-02
% mass of En	12.15	11.51	10.22	32.41	48.48	47.84
Nickel Analysis	Salt A			Salt B		
	trial1	trial2	trial3	trial4	trial5	trial6
mass salt (g)	0.249	0.25	0.25	0.255	0.25	0.248
salt soln vol (L)	0.025	0.025	0.025	0.025	0.025	0.025
Ni Concentration (M)	0.0334	0.032	0.0321	0.0294	0.0299	0.0311
moles Ni	8.35E-04	8.00E-04	8.03E-04	7.35E-04	7.48E-04	7.78E-04
MW Ni (g/mol)	58.7	58.7	58.7	58.7	58.7	58.7
Mass Ni	4.90E-02	4.70E-02	4.71E-02	4.31E-02	4.39E-02	4.56E-02
% mass Ni	19.68	18.78	18.84	16.92	17.55	18.40
mole SO4	8.35E-04	8.00E-04	8.03E-04	7.35E-04	7.48E-04	7.78E-04
MW SO4 (g/mol)	96.056	96.056	96.056	96.056	96.056	96.056
Mass SO4 (g)	8.02E-02	7.68E-02	7.71E-02	7.06E-02	7.18E-02	7.47E-02
% mass SO4	32.21	30.74	30.83	27.69	28.72	30.11
% mass H2O	35.95	38.97	40.10	22.99	5.25	3.64
MW H2O (g/mol)	18.016	18.016	18.016	18.016	18.016	18.016
moles H2O	1.996	2.163	2.226	1.276	0.291	0.202
moles Ni	0.335	0.320	0.321	0.288	0.299	0.314
mole En	0.202	0.191	0.170	0.539	0.807	0.796
moles SO4	0.335	0.320	0.321	0.288	0.299	0.314
Mole ratio H2O	9.87	11.30	13.09	4.43	1.00	1.00
Mole ratio Nickel	1.66	1.67	1.89	1.00	1.03	1.55
Mole ratio en	1.00	1.00	1.00	1.87	2.77	3.94
Mole ratio SO4	1.66	1.67	1.89	1.00	1.03	1.55
Avg.Mole ratio H2O	11	5.7		2		
Avg.Mole ratio Ni	2	0.9		1		
Avg.Mole ratio en	1	0.5		3		
Avg.Mole ratio SO4	2	0.9		1		
MWT of Salt(g/mol)	288			371		
actual yield(g)	1.212			1.22		
theo yield(g)	1.39			1.40		
% yield	87.2			87.1		
Chemical Formula	[Ni(en)0.5(H2O)5]SO4*(7/10)H2O			[Ni(en)3]SO4* 2 H2O		

F. Discussion

In this experiment, two kinds of complex nickel salt were synthesized by reacting different amounts of $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ with different amounts of Ethylenediamine. The different amount of reactants introduced lead to different mass percent of nickel and en in the two salts. Salt A was made by reacting 1.27g of $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ with 1.00ml en, while salt B was made by reacting 0.992g of $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ with 3.50ml en. Therefore salt A had greater mass percent of Nickel cation and lower mass percent of Ethylenediamine compared to salt B.

The color of the two salts could also suggest the different constructions of the two salts. According to Crystal Field Theory, ligands in metal complexes causes the d orbitals of the metals to split. The energy gap between the separated d orbitals was the splitting energy. The higher electrostatic interaction the ligand had, the greater the splitting energy. When the splitting energy of the metal complex was large, the complex tended to absorb high-energy light with short wavelength. The rest of the unabsorbed light would be reflected out and determine the color of the complex as the complementary color of the light absorbed. According to the color wheel, the light blue salt A absorbed orange light with wavelength from 580nm to 620nm. Violet salt B absorbed yellow light with wavelength from 560nm to 580nm. The reason for the difference lies in the total electrostatic interaction of all six ligands bonded to the Nickel atom. The reactant $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ had 6 water as ligands while the two synthesized salts had different amount of en as ligands. en had higher electrostatic interaction than water which means the more en the Nickel complex had, the greater splitting energy would have, which would lead to the absorption of shorter wavelength of light. Therefore, the fact that salt A absorbed light of longer wavelength than salt B revealed that salt A had less en than salt B. This corresponded to the synthesizing part where more en was used as reactant for salt B than salt A.

The chemical formula of salt A came to be $[\text{Ni}(\text{en})_{0.5}(\text{H}_2\text{O})_5]\text{SO}_4 \cdot (7/10)\text{H}_2\text{O}$ and the chemical formula for salt B was $[\text{Ni}(\text{en})_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$. The mass percent of nickel and en was consistent with the expected result based on the reaction conditions and the Crystal Field Theory. The number of en in salt B was greater than that in salt A. Therefore salt B absorbed yellow light and was observed as violet while salt A absorbed orange light and was observed as light blue.

G. Conclusion

The goal of this experiment was to synthesize two complex nickel salts and determine their chemical formula by running the Ethylenediamine and Nickel analysis. The Ethylenediamine analysis focused on calculating the percent mass of en while the nickel analysis focused on finding out the percent mass of nickel and sulfate, which all led to the mole ratio between the different components in the compound. The chemical formulas of the salts were determined by the mole ratio, and was consistent with the expectation based on the synthesizing conditions and the Crystal Field Theory. Percent Yield of the synthesis was determined using the molar mass of the salt based on the found chemical formulas.

H. Sources of Errors

Although the chemical formulas of the two salts were consistent with the reaction conditions and the Crystal Field Theory, the chemical formulas of salt A was not expected to have half an Ethylenediamine group. Roughly according to the amount of en added in the synthesis, the expected chemical formula for salt A should be $[\text{Ni en}(\text{H}_2\text{O})_4]\text{SO}_4$, regardless of the hydrated water molecules. The inaccuracy might be resulted from over-titration in the Ethylenediamine analysis. Since

$\text{HCl}(\text{reacted with en})(\text{mol}) = \text{HCl original}(\text{mol}) - \text{HCl unreacted}(\text{titrated})(\text{mol})$ - - - equation 1

The more NaOH used in the titration, the larger the value of HCl (unreacted) was going to be, which would drag down the value of HCl reacted with en, and the mole ratio of en compared to the other components. Since the light yellow ending color of the titration was very hard to be detected, the titration could easily go over the actual end point, resulting in a lower value of en mole ratio. The same error must have happened to trial 1 titration of salt B, giving the en a coefficient of only 2.

Other than the inaccuracies in the Ethylenediamine titration analysis, the Nickel analysis could also bring in errors. Since the calibration curve for Cary 50, which was used to read concentration of Nickel in the salt solutions, yielded a correlation factor of 0.9979, the reading that it provided should be pretty accurate. The majority of the error might lie in the process of making the salt solutions. Since the stock $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ solution need to be pipetted into smaller volumetric flasks, the volume of solution being drawn out might go up and down due to the inaccurate pipette. This would affect the accuracy of Cary 50 even if it was reading a high correlation factor because the molarity of the $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ might flow up and down in the same direction. When transferring salt A and B from the weighing boat into the volumetric flasks, some of the salt might be left in the boat, making the actual concentration lower.

Other than having systematic errors, the degree of purity of the two salts might also cause inaccuracies. Small amount of reactant $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ residual might be left in salt A and B from the synthesizing process and drag down the mole ratio of en. On the other hand, the synthesis might produce other nickel complex. For example, nickel complex with half attached en group along with salt A and B. this would actually cause the percentage of water to go up because now one en group only occupy one branch of the Nickel atom. The synthesis could also produce salt B while synthesizing for salt A and vice versa. The production of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]\text{SO}_4$ might also cause errors in the mole ratios of the components. The error on the mole ratio of water was always the greatest because it was calculate from the mole ratio of the other components. The level of humidity in the air might also give the percentage of water some errors.

The percent yield of the two salts came up to be both around 87%. The loss of products was most likely caused by the drying process. Part of the product salt must have been vacuumed away. The other factor might be the errors in the cooling process. The cooling process was designed to let the salt crystalize out in the decreasing temperature. However, some salt might not have crystalized out during the cooling and was left in the solution. This would also decrease the percent yield of salt A and salt B.

I. Post-lab Questions

1. a) If the solution was over-titrated, the mass percent of ethylenediamine in the salt will decrease. This is because when the amount of titrant increases, the amount of HCl being titrated will appear to be more. According to equation 1 in the percent error discussion, moles of moles of HCl used to react with en would decrease while titrant amount increases, suggesting a smaller amount of en in the salt.

b) If more than 10.0mL of 0.2M HCl is added to the original solution, the mass percent of ethylenediamine in the salt will not be affected because the amount of en was determined from the difference of the original amount of HCl added in and the amount of HCl that was left unreacted. The more HCl added, the more HCl will be left there, while not maintaining the same difference.

2. It was acceptable to use $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ to establish the calibration curve for the product in part 2 of the experiment because in all complex Nickel salt involved in this experiment, the ratio of Nickel to Sulfate was always 1 to 1 because they have complementary charges of +2 and -2. Since H_2SO_4 solution would be added into the solution of salt A and B, all the en would be detached, leaving $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ as the only responsible ion for the color absorption of the solution. Therefore Cary 50 will be able to give a calibration curve solely based on the concentration of Nickel. Since all three Nickel salts have only one Nickel atom per molecule, it was united in term of the number of Nickel atom in every mole of salt. Therefore, it was acceptable to use $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ to establish the calibration curve for the product in part 2 of the experiment.

3. The mass percent of water found experimentally was subjected to greater error than the other three mass percentages because it was calculated by subtracting the sum of the other percentages from 100%. Since all other percentages involve errors, the percentage of water added up all those errors and therefore was the more inaccurate one.