COMPLEX ION COMPOSITION BY JOB'S METHOD

1. Introduction

The nickel(II) ion in aqueous solution forms complexes with 1,2-Diaminoethane (ethylenediamine) whose ligand replaces two water molecules in the hydrated complex, i.e. acts as a chelate.

$$Ni(H_2O)_6^{2+} + en \xrightarrow{K_1} Ni(H_2O)_4en^{2+} + 2H_2O$$

$$Ni(H_2O)_4en^{2+} + en \xrightarrow{K_2} Ni(H_2O)_2en_2^{2+} + 2H_2O$$

$$Ni(H_2O)_2en^{2+} + en \xrightarrow{K_3} Nien_3^{2+} + 2H_2O$$

The relative values of k_1, k_2 and k_3 will determine the relative proportions of the complexes. If $k_3 >>> k_2 >>> k_1$, then addition of ligand will result in formation of $Nien_3^{2+}$. If $k_3 <<< k_2 <<< k_1$, then all four complexes (or three, depending on the absolute magnitude of the constant) will co-exist in appreciable quantities at equilibrium. The application of Job's Method is limited to situations where one stage predominates.

In the method, the total molar concentration of nickel(II) plus ligand is kept constant and the ratio varied from zero to infinity. Initially in a solution containing no nickel(II) ion (ratio = 0), no complex will be present and the absorbance of the solution is due solely to diaminoethane. As the concentration of nickel(II) is increased, absorbance will increase *(due to formation of complex)* until the molar ratio of nickel(II) to ligand equals the ratio in the complex. Under the Job conditions, i.e. total molar concentrations of the two species is constant, this represents the maximum possible concentration of complex. Further increases in nickel(II) concentration (with corresponding decreases in ligand concentration) will cause a decrease in absorbance until a solution containing no ligand (ratio = 4) has an absorbance due to nickel(II) ions alone. A plot of absorbance against ratio of molar concentration of nickel(II) ion to ligand will show a maximum where the ratio represents the composition of the complex.

Reference

The Job Method outlined above can be justified rigorously, see *Synthesis and Technique in Inorganic Chemistry* by R. J. Angelici.

2. Procedure

Using solutions of $NiSO_4 \cdot 6H_2O$ (0.4 M) and ethylenediamine (0.4 M) prepare solutions having a total volume of 10 ml in which the mole fraction of ethylenediamine, X, is 0.0, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9. Determine the absorbance of each solution at the following wavelengths: 530, 545, 578, 622 and 640 μm.

By appropriate graphical methods, obtain a possible formula to represent the predominant species present in nickel(II)-1,2-diaminoethane solutions.

Post-lab Questions

1. Write structural formulas for the three possible products of reaction of ethylenediamine with $Ni(H_2O)_6^{2+}$.
2. What does the absorption spectrum of the ligand, ethylenediamine, look like in the visible region which you used in this experiment. Assign the absorption maxima you used in this experiment to individual species in the system, where this is possible.
3. What would happen if the values of K_2 and K_3 were larger than K_1 ? Could you still use Job's method?
4. From the observed changes in the spectra and a knowledge of the complexes present in the solutions, what can be said about the relative ligand field strengths of en and H_2O?

Answer① Three possible products reaction of ethylene diamine with $Ni(H_2O)_6$ are

$$Ni(H_2O)_6^{2-} + en \xrightleftharpoons{K_1} Ni(H_2O)_4 en^{2+} + 2H_2O$$

$$Ni(H_2O)_4 en^{2+} + en \xrightleftharpoons{K_2} Ni(H_2O)_2 en_2^{2+} + 2H_2O$$

$$Ni(H_2O)_2 en_2^{2+} + en \xrightleftharpoons{K_3} Nien_3^{2+} + 2H_2O$$

Answer 3 If instead of opposite direction if $K_3 >>> K_2 >>> K_1$. Actually the relative values of K_1, K_2, K_3 will determine the relative proportions of the complexes. If the case is above then addition of ligand will result in formation of $Nien_3^{2+}$. And as the order is reversed all the 3/4 complexes depending on the absolute magnitude of the constant will ~~result~~ not coexist in appreciable quantities at equilibrium. And because of this there will be no formation of any particular ligand complex which will dominate the rest. Therefore, Jobs method will no longer be applicable.

Answer 4 It is observed that as the concentration of $NiSO_4$ goes on increasing until the equilibrium is established between amount of $NiSO_4$ & EDTA occurs. It is highest at the equilibrium hence it shows highest absorbance at equilibrium. So as the en goes on increasing the field of this ligand goes on increasing. Therefore relative ligand field theory follows following order (in ascending)

$$Ni(H_2O)_4 en^{2+} < Ni(H_2O)_2 en_2^{2+} < Nien_3^{2+}$$

Answer - 2 As the absorption maxima of the ligand ~~goes~~ shows the highest because of its ligand-metal complex reaches the equilibrium. Therefore the absorption spectra of EDTA in visible region will exactly look like that one at the time of equilibrium. Hence, this is possible at equilibrium only (At chelate formⁿ. eqᵐ)

Lab 6 Complex Ion Composition by Job's Method

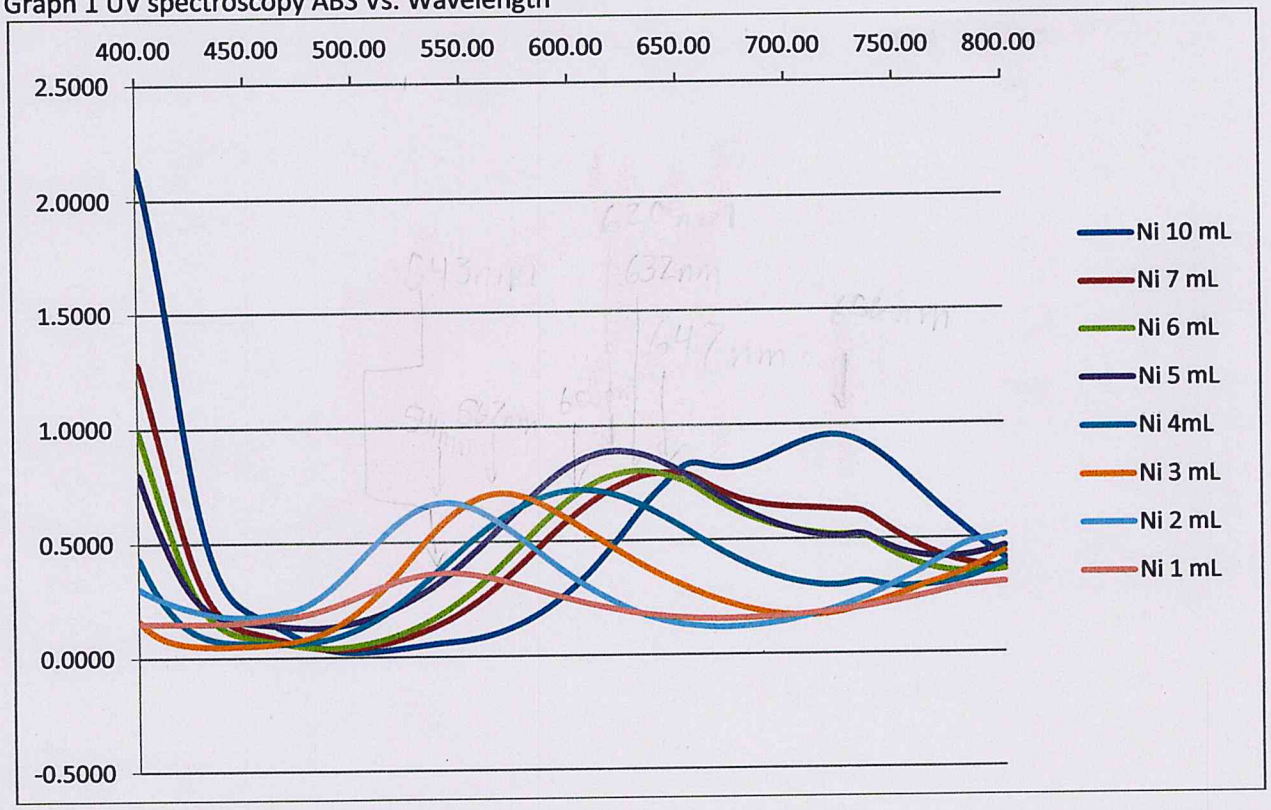
CHEM 481

Introduction

Job's method has been a useful analytical technique used since the early 1900's. This technique is used to determine the extent of comlexation between a metal and a ligand. In this method the total molar concentration of the metal and the ligand are maintained at a constant level. What is changed, however, is the molar ratio of metal to ligand. In a series of analyses with aliquots containing molar ratios from 0.0 (no metal concentration) up to possibly 1.0 (only metal concentration) the composition of the complex equilibrium may be determined. In the data from these analyses a plot of absorbance against the molar ratio is constructed. In this graph the maximum absorbance dictates the position where the ratio is at the composition of the complex.

Data

Graph 1 UV spectroscopy ABS Vs. Wavelength



UV-Vis Lab CHEM 481

INTRODUCTION

The purpose of this experiment is to learn how to operate a UV-Vis instrument and interpret the spectra that it produces

THEORY

The Uv-Vis takes advantage of the characteristics of molecules to absorb light at certain wavelengths to identify them. The peaks in the spectra show up at the wavelength at which the molecule absorbed. This is because light is absorbed at different wavelengths within the spectrum.

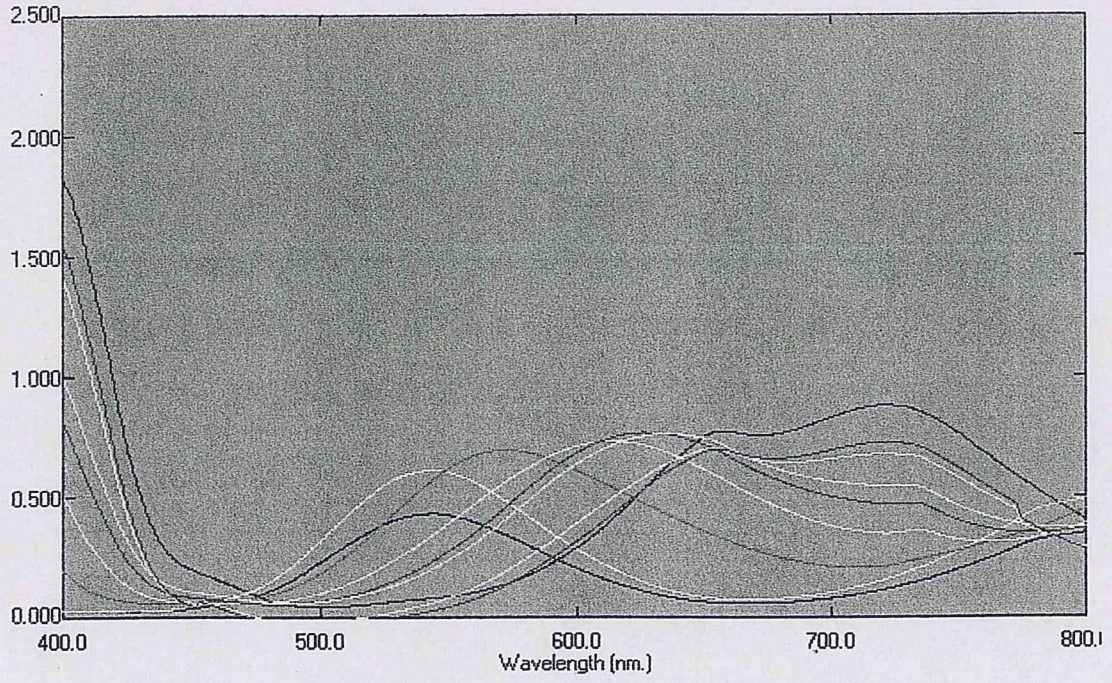
METHODS

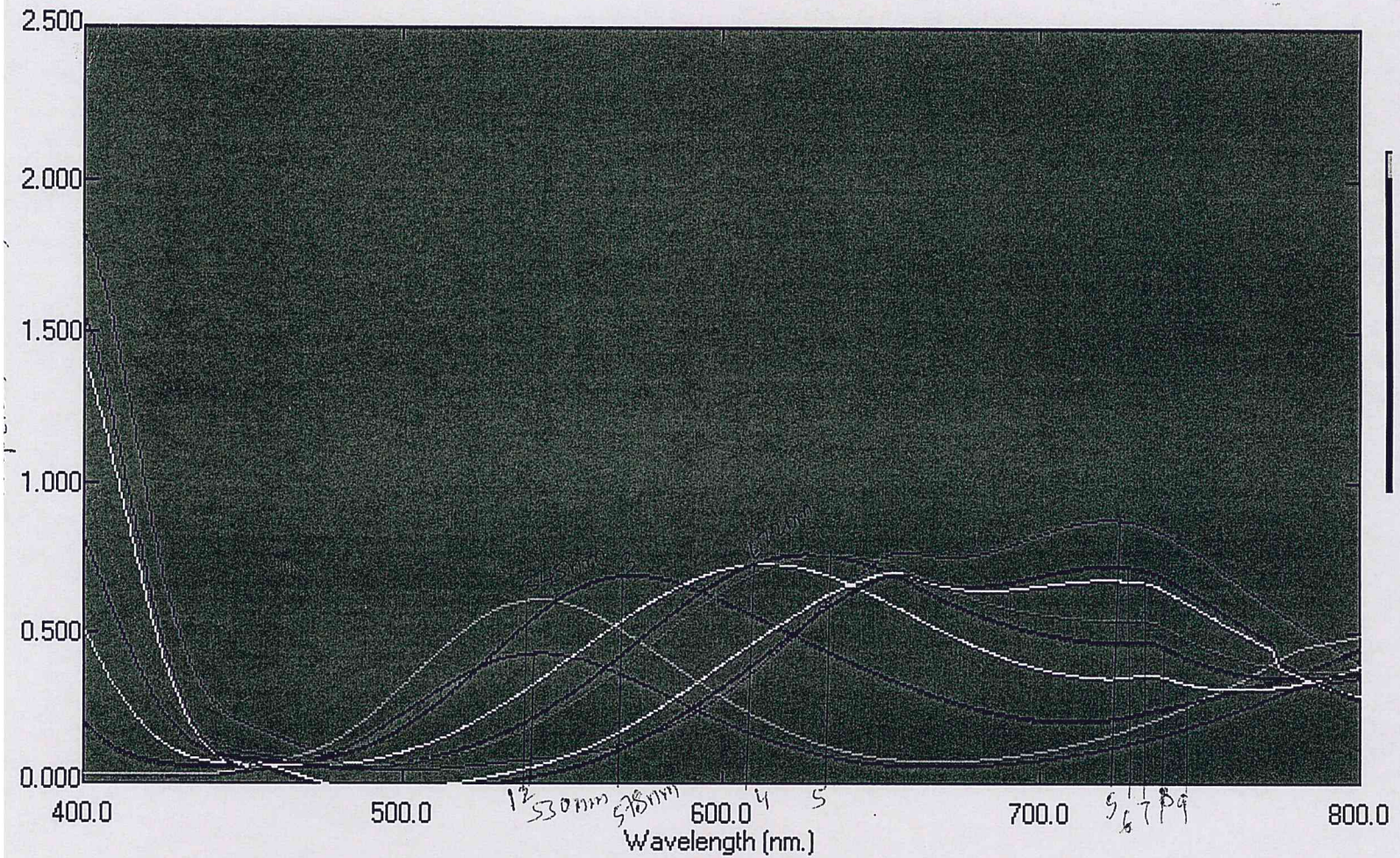
The table below shows the solutions prepared in test tubes. A spectrum was obtained for each one.

Data for NiSO4 and EDTA Solutions	
EDTA (mL)	*NiSO4 (mL)*
0	10
3	7
4	6
5	5
6	4
7	3
8	2
9	1
10	0

RESULTS

The figure below is composed of the spectrum of the samples ran. As the concentration of the EDTA is increased in the test tube the solution has a lower absorbance. This can be seen in the low peaks. The black line is the lowest and it represents the sample with the most EDTA. The blue line has the least EDTA and it is the highest peak.





Chem 481

Tushar

Aim: To obtain & study the UV spectras for different concentrations of $NiSO_4$ + EDTA i.e complex ion composition by Jobs Method.