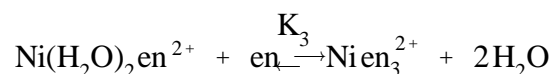
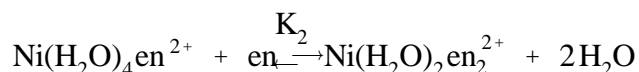
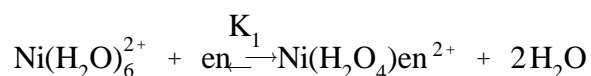


COMPLEX ION COMPOSITION BY JOB'S METHOD

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.



The relative values of k_1 , k_2 and k_3 will determine the relative proportions of the complexes. If $k_3 \gg k_2 \gg k_1$, then addition of ligand will result in formation of $\text{Ni}\text{en}_3^{2+}$. If $k_3 \ll k_2 \ll k_1$, 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 = ∞) 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 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (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 $\text{Ni}(\text{H}_2\text{O})_6^{2+}$.
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 ?