The Study of Complexes of Di-n-butyloxamidine with Transition Metals

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Abstract

The determination of solution complexes of di-n-butyloxamidine with Cr(III), Mn(II), Fe(III), Co(III), Ni(II), and Cu(II) was made using Job's method of continuous variation.

Upon investigation of the chemical reactions of aliphatic oxamidines (3, 4), we found that Cu(II) and Ni(II) salts formed solid metal complexes of the general formula,

(R-NH-C-C-NH-R) • MCl_2 • $2H_2O$, whereas the Mn(II) salt formed
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HN NH

(R-NH-C-C-NH-R) • MCl_2 • $4H_2O$. Attempts at that time to obtain
|| ||
HN NH

solid complexes with Co(II), Co(III), Fe(II), Fe(III), and Cr(III) failed. However the color changes with these salts pointed to the formation of solution complexes. Subsequently, a brown Fe(III) solid complex was isolated using benzene as solvent (1).

Recently, we have re-examined the solutions involving the di-n-butyloxamidine with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II). Applying Job's method of continuous variation (2), we have attempted to establish the ligand to metal ion ratio for any complexes that might be formed in these solutions. All the aforementioned metal(II) ions form complexes in solution with the ligand to metal ion ratio of 2:1. The Cr(III) and Fe(III) ions appear to form more than one complex in solution. Thus, Job's (2) method is not applicable.

Assuming a reaction in solution to be $pM + qN = MpNq$ and determining p and q, Job's (2) method shows a plot of change in the absorbance versus mole fraction to yield a maximum or a minimum at the stoichiometric composition of the complex. If the measurements are made at several wavelengths, all should yield the same result. The method of continuous variation can yield reliable results only when the following conditions are observed:

1) Only a single chemical reaction occurs in the solution. There is no association, protolysis, solvolysis, etc., of either the reactants or the products.

2) The law of mass action is applicable in terms of concentration.

3) The reactants form only one complex.

Methods

1) A stock solution of di-n-butyloxamidine of 0.01 M (0.001 for Fe(III)) was made in anhydrous alcohol, either methanol or ethanol. The choice of alcohol made little or no difference in the results. In the case of Mn(II), a water solution of about 0.1 M was prepared. Due to the ready facility of hydrolysis of the oxamidines, water solutions should be avoided except where they can be used immediately.

2) The metal salts were dissolved in the same solvent and made up to the same strength as the corresponding oxamidine solution. The Cr(III), Co(II) and Ni(II) salts were all hydrated. The Mn(II) salt was dissolved in water.

3) The spectra of solvent, metal salt solution, and oxamidine solution were determined using a Beckman DB spectrophotometer. Comparison of these spectra with one of the solution containing both metal ion and oxamidine led to a selection of wavelengths at which Job's (2) method would be applied. The absorbance of the mixtures as the mole fraction of oxamidine varied from 0.00 to 1.00 was read using a Beckman DU spectrophotometer.

4) The room in which the experiments were performed and the instruments housed was held at 68°F and under 30% relative humidity.

5) The wavelengths at which Job's method for each of the salts was applied are listed in Table 1.

6) The plot of A versus wavelength for the Ni(II)-oxamidine system using methanol as solvent is shown in Figure 1.

7) The plot of A versus mole fraction of oxamidine is shown in Figure 2.

Figures 1 and 2 are representative of the types of curves obtained for all the salts with the exception that for Cr(III) and Fe(III), Figure 2 had more than one maximum or minimum or both.

TABLE 1. *Wavelengths for application of Job's Method to salts of transition metals.*

Salt	Wavelengths (mu)
Cr(III)	370, 380, 540, 550
Mn(II)	370, 380, 400
Fe(III)	355, 365, 375
Co(II)	390, 400, 410
Ni(II)	460, 480, 500
Cu(II)	530, 560, 590

Summary

Figure 2, which is typical of the data obtained with the M^{2+} ions, indicates a solution complex of oxamidine/M^{2+} of 2:1. Work is continuing using other methods to determine the nature of the M^{3+} complexes formed in solution.

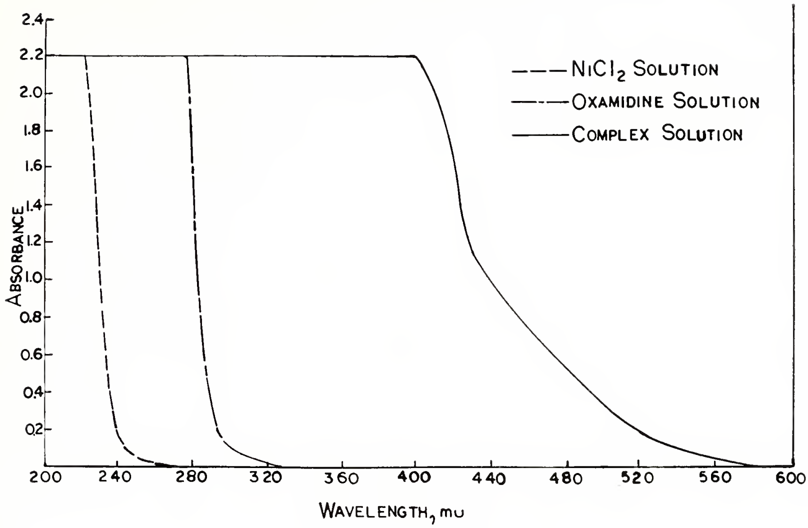

FIGURE 1. *Absorbance vs. wavelength for $NiCl_2$ system.*

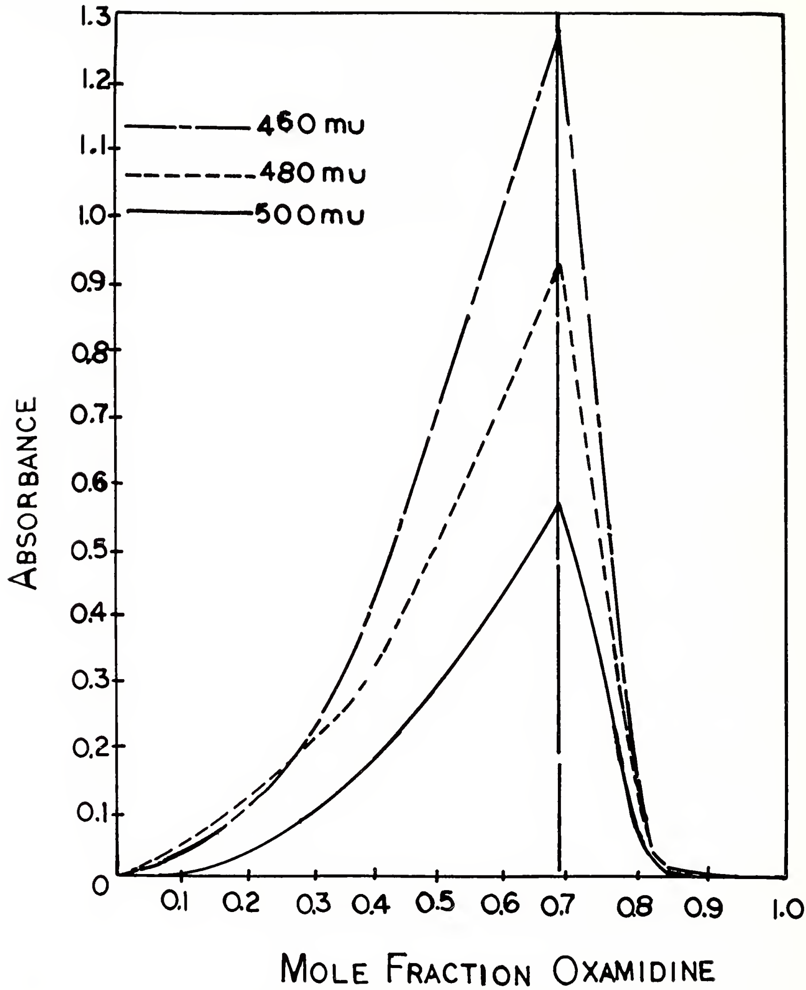

FIGURE 2. *Ni+2-oxamidine complex.*

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