ALUMINUM COMPLEXES OF 2-METHYL-8-HYDROXYQUINOLINE

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SCOPE AND CONTENTS

The complex between Al(III) and 2-methyloxine has been prepared from various aqueous and aqueous-acetone solutions, both in the presence and the absence of acetate ion as an auxilliary complexing agent. The effect of pH on precipitation of the complex from 20% v/v acetone-water medium has been determined. Solid-phase hydrous aluminum oxide has been converted to the tris complex by the addition of a dioxane solution of 2-methyloxine. Infrared spectral evidence has been found for some degree of complexation from reactions in the melt between Al(III) and 2-n-propyl-, 2-n-butyl-, and 2-phenyloxine.

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I. Introduction

The organic reagent, 8-hydroxyquinoline (8-quinolinol, oxine) is widely used in analytical chemistry, with applications in gravimetry, titrimetry, spectrophotometry, fluorimetry, polarography, amperometry, solvent extraction and chromatography.[1]

Despite the usefulness and versatility of this ligand, it has a major drawback in that it is unselective in its reactions with metal ions. The selectivity of oxine has been increased, however, by control of pH and by the use of auxilliary complexing agents to mask interfering ions.

There are several factors that govern the selectivity of such a chelating ligand and the stability of its metal chelates. Such factors include metal ion properties such as charge, size and polarizability and properties of the ligand such as basicity of the donor atoms, polarizability of the donor atoms, and of particular interest in this thesis, steric interactions arising from substituent groups in the parent ligand.[1,2]

One of the early striking discoveries regarding selectivity was reported in 1944 by Merritt and Walker.[3] They noted that while 2-methyloxine resembled oxine in giving water-insoluble chelates with a large number of metal ions, it differed singularly from oxine in that it did not precipitate Al(III). This property was exploited for the determination of Zn(II) or Mg(II) in the presence of Al(III). Merritt and Walker explained this lack of reactivity in terms of steric interaction between ligand molecules - the grouping of three 2-methyloxine molecules around the small Al(III) ion would be sterically inhibited.

Irving and co-workers[4,5] pursued this work further and showed that

reaction with Al(III) was also inhibited by other 2-substituted oxines (e.g., 2-phenyl and 2-(1-ethylpropyl)oxine, 1-hydroxyacridine, and 9-hydroxy-1,2,3,4-tetrahydroacridine) but was not inhibited by alkyl or other substituents in the other ring positions of oxine. They also showed that Ga(III), In(III), and Tl(III) (crystallographic ionic radii 0.62, 0.81 and 0.95 Å, respectively, compared to 0.50 Å for Al(III)) formed normal solid tris complexes with 2-methyloxine in aqueous solution. These observations were explained on the basis that the packing of 2-substituted oxines around the small Al(III) ion created . interligand repulsions, and that in aqueous solution, Ga(III), In(III) and Tl(III) are less electropositive than Al(III) (i.e., have more positive reduction potentials) and thus form more covalent bonds with the ligand donor atoms.

Although interligand steric repulsion should not prevent the formation of a 1:1 complex between Al(III) and 2-methyloxine, formation of the 1:1 complex could not be detected in aqueous solution.[6,7] Irving and Pettit,[8] in acknowledging that they also could not detect the 1:1 complex, stated that in addition to potential interligand steric inhibition in the complex, other factors played a role in determining the non-reactivity of Al(III) with 2-methyloxine. Two important factors are: (a) the 2-methyl group must reduce the stability of its Al(III) complexes, in analogy with measured stability decreases observed in the reactions between 2-methyloxine and divalent transition-metal ions; and (b) the increased basicity of the anionic ligand (pK_{OH} = 11.0 and 10.8 for 2-methyloxine and oxine, respectively, in 50% v/v water-dioxane, 0.3 M $NaClO_4$ salt background, $20^{\circ}C$) required that a higher pH than for oxine must be reached to cause ionization of the same fraction of reagent. While no aluminum hydroxide is observed to precipitate with increasing pH in the reaction between Al(III) and oxine, it is obtained when the pH is raised

in aqueous systems containing Al(III) and 2-methyloxine. The two factors above, in juxtaposition to the stability of aluminum hydroxide, prevent the formation (and subsequent precipitation) of the tris aluminum 2-methyloxinate.

The discovery by Merritt and Walker[3] and the early work by Irving, Butler and Ring[4] stimulated wider investigations of the reaction of 2-methyloxine with other metal ions, and of the complexing behaviour of other 2-substituted oxines. Freiser et al[9-12] and Irving et al[13] reported that while transition-metal and other ions formed complexes with 2-methyloxine in solution, their solution stabilities were lower than those of the corresponding oxinates (in spite of the enhanced basicity of the 2-methyloxinate anion), and attributed these reduced stabilities to steric factors. Similar studies involving other 2-substituted oxines were reported by Ueno and Kaneko[14] and by Corsini and Billo,[15] who provided evidence that the incoming first ligand (substituted in a position adjacent to a donor atom) meets strong steric hindrance from the coordinated water molecules on the metal ion. This interaction reduces the _first_ stability constant (i.e., for the 1:1 complex). Thus, a strategically located substituent group can give rise to two kinds of steric interactions - between the substituent group and coordinated solvent on the metal-ion and/or between the chelate ligands bound to the metal-ion ("interligand" interactions). In further studies, oxine ligands with 2-substituents containing a potential donor atom were synthesized to determine whether the substituent acts as a sterically-hindering group or a complexing group (to yield a terdentate ligand). Work by Corsini and Billo[16,17] showed that rigid ligands such as 4,5-disubstituted acridines could be regarded as 2-substituted oxines and that both the 2-substituted steric effect and chelate ring-strain in closing the second chelate ring may be important in determining chelate stability. Other studies by Stevenson and Freiser[18] and by Corsini

and Cassidy[19] showed that if the 2-substituent containing the potential donor atom was non-rigid, very stable terdentate complexes can be formed provided the second chelate ring is strain-free.

The first concrete evidence that a complex between Al(III) and 2-methyloxine could be formed was provided by Ohnesorge and Burlingame[20] who proved the existence of a 1:1 complex in absolute methanol. The extraction into an organic phase of an Al(III)-2-methyloxine complex was also reported.[21,22] Horton[23] prepared the tris chelate from molten 2-methyloxine (in the absence of water) and Fernando et al[24-26] characterized a number of Al(III) complexes of 2-methyloxine prepared from non-aqueous media.

Although Merritt and Walker[3] and Irving and co-workers[4,8] obtained no evidence for the formation of the complex in aqueous media, Cardwell[27] reported the precipitation of the tris complex from basic aqueous solution in the presence of acetate or tartrate as auxilliary complexing agents. He explained that these secondary ligands complex with the Al(III), preventing hydrolysis of the metal ion as the pH is raised to the level where metal-chelate formation can occur. However, the report did not contain fully described conditions of the experiments, making repetition of the work difficult. For example, it is reported that a "four-fold excess" of ligand was added to the Al(III) solution; this could be interpreted as a ligand:Al(III) molar ratio of 4:1 or of 12:1. Furthermore, Cardwell stated the precipitation is quantitative over the range 5-50 mg of Al(III) but reported no analytical data as evidence. The pH range over which precipitation might be quantitative was not reported, and the temperatures of digestion and drying of the precipitate were not given.

Since this initial work, Cardwell et al[28] have reported on the reactions of other 2-substituted oxines with Al(III) in aqueous solution. Evidence is

given for the formation of tris chelates with 2,5-dimethyl- and 2-methyl-5-chloro-oxine. Ligands with a substituent in the 3-position as well as the 2-position (2,3-dimethyl- and 2,3,4-trimethyloxine) gave bis chelates (oxygen-bridged dimers). No reaction was reported between 2-phenyloxine and Al(III).

The purpose of the present research is threefold:

(a) to define the conditions of Cardwell's work more precisely (e.g., an appropriate ratio of 2-methyloxine:Al(III) and pH of precipitation for both the preparation and quantitative precipitation of the tris complex), and to determine if complexes of Al(III) can be readily formed with 2-substituted oxines containing bulky groups (e.g., 2-n-propyl, 2-n-butyl and 2-phenyl);

(b) to explore other conditions under which the tris complex might be prepared from aqueous solution; and

(c) to re-examine the titration system of Al(III)/2-methyloxine for evidence of complexation not earlier observed by Irving and Pettit.[8]

II. EXPERIMENTAL AND RESULTS

II.A. Apparatus

Calibrated volumetric ware was used when appropriate.

Weighings were made on a Mettler semi-micro, constant-load analytical balance (Type B-6).

Infrared spectra were recorded with a Beckmann I.R.-5 spectrophotometer.

Measurements of pH were made with a Radiometer Model pHM4 pH meter, fitted with a Beckmann E-2 glass electrode (low sodium ion-error) and a Beckmann calomel reference electrode with a ceramic junction.

The potentiometric titration apparatus consisted of a jacketed titration cell, the pH meter, either two ten-millilitre microburets or two fifty-millilitre burets, and a constant-temperature water bath for circulation of water through the jacket of the titration cell.

A heated vacuum desiccator (P5, Precision Scientific Company) was used for drying prepared compounds under reduced pressure.

II.B. Reagents

All common laboratory chemicals were either reagent-grade, or sufficiently pure for the purpose intended.

Aluminum nitrate nonohydrate (J. T. Baker) was used without further purification. Stock solutions of aluminum nitrate containing about 3 mg Al(III)/ml (i.e., about 0.1 millimole/ml) were prepared from the nonohydrate salt and standardized gravimetrically with 8-hydroxyquinoline, as described by Vogel.[29] The concentrations of the standard solutions used were 3.144 mg Al(III)/ml (1.162×10^{-4} moles/ml) and 2.921 mg Al(III)/ml (1.083×10^{-4} moles/ml).

Hexachloro-1,3-butadiene (Eastern Chemical Corporation) used to prepare

mulls for infrared studies, was vacuum-distilled over barium oxide and then stored over molecular sieves (Type 4A, B.D.H. Laboratory Chemicals, Toronto).

The following chemicals and solutions were used in potentiometric titration studies. Reagent-grade 1,4-dioxane (Fisher Scientific Company) was purified by continuous refluxing over sodium, followed by fractional distillation through a one-meter column packed with glass helices. The fraction boiling in the range 100.5-101.0°C was collected as required and used within 24 hours. Carbonate-free sodium hydroxide was prepared according to the procedure of Vogel[30]. Solutions of the base (0.1 M and 1.5 M) were standardized potentiometrically against known weights of potassium hydrogen phthalate. Perchloric acid (0.01 M) containing sodium perchlorate (0.19 M) was used in the potentiometric titrations with 0.1 M sodium hydroxide solution and 0.11 M perchloric acid was used in titrations with 1.5 M sodium hydroxide. Both perchloric acid solutions were previously standardized by potentiometric titration with standard sodium hydroxide (0.1 M and 1.5 M, respectively). A standard Al(III) solution (0.3 mg Al(III)/ml) was prepared by appropriate dilution of aliquot volumes of the stock solution.

Oxine, obtained from the Aldrich Chemical Company, was steam-distilled and recrystallized from absolute ethanol to give white needles, m.p., 72-73°C (lit. values ranging from 72-74°C to 75-76°C[31]).

2-Methyloxine, obtained from the Aldrich Chemical Company, was steam-distilled and recrystallized from absolute ethanol to give white needles, m.p. 71.5-73°C (lit. values ranging from 72° to 74-75°C[32]).

2-n-Butyl- and 2-n-propyloxine were synthesized by the procedure of Kaneko and Ueno[14]. After hydrolysis to yield the free base, the ether layer was separated and hydrogen chloride gas was passed through the solution

to give a pale yellow precipitate in each case. The solid was filtered, washed with dry ether, and recrystallized from absolute ethanol by the addition of ether to give pale yellow crystals. For 2-n-butyloxine hydrochloride, m.p. 172-175°C (lit. value 165.8-167.3°C$^{(14)}$). Calculated for $C_{13}H_{16}NOCl$: 65.68% C, 6.78% H, 5.89% N, 14.91% Cl; found: 65.69% C, 6.70% H, 6.06% N, 15.10% Cl. For 2-n-propyloxine hydrochloride, m.p. 171.5-175.5°C (lit. value 161.5-163.0°C$^{(14)}$). Calculated for $C_{12}H_{14}NOCl$: 64.43% C, 6.31% H, 6.26% N, 15.85% Cl; found: 64.31% C, 6.44% H, 6.28% N, 15.78% Cl.*

2-Phenyloxine, available in the laboratory, had been previously synthesized by the method of Irving, Butler and Ring$^{(4)}$. M.p. 58°C (lit. value 58-59°C$^{(4)}$).

In addition to melting points and elemental analysis, infrared spectra were also used to characterize the 2-n-butyl- and 2-n-propyloxine hydrochlorides. The spectra showed absorption bands characteristic of the -OH and $\gtrsim NH^+$ groups, and of the aromatic and aliphatic -CH groups.

II.C. Determination of % 2-methyloxine and % Al in precipitates

The 2-methyloxine content in the Al(III) complexes was determined by the bromination method described by Corsini and Graham$^{(33)}$, with a slight modification (the use of 1N HCl instead of 2N HCl as solvent). The procedure was initially standardized in experiments with pure 2-methyloxine. These experiments yielded data ranging from 99.7% to 100.2% recovery of the 2-methyloxine taken.

The % Al in the precipitates was determined by ignition to Al_2O_3 at 1200°C$^{(34)}$.

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*Elemental analyses reported in this thesis were done by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

II.D. Al(III) complexes of 2-methyloxine

(a) Precipitation of the 2-methyloxine complex in acetate-buffered aqueous solution.

The complex of Al(III) and 2-methyloxine was prepared using Cardwell's procedure[27]. Exactly 2.00 ml of the standard Al(III) solution (i.e., about 6 mg or 0.23 millimoles Al(III)) were diluted to 100 ml with distilled water, and then glacial acetic acid (5 ml) containing 140 mg (0.95 millimoles) of 2-methyloxine (i.e., a 4:1 ligand: metal molar ratio) was added, followed by 25 ml of 2 M ammonium acetate. The pH of the resulting solution was 4.5 (not neutral as reported by Cardwell). After heating to 60°C, 60 ml of a 2 M ammonium acetate-2 M aqueous ammonia solution was added dropwise with rapid stirring. At about pH 6.3 the yellow solution became cloudy, and addition of base was continued to pH 8.6. A few particles of oily material could be seen on the bottom of the beaker along with a small amount of yellow precipitate. The mixture was digested at 60°C for one hour. The precipitate appeared to be slightly gelatinous in nature and clogged the filtering crucibles (fritted glass, porosity M). The collected precipitates were dried for at least three hours in the vacuum desiccator ($40-45^\circ$C, about 3 mm Hg pressure). The yield on each of six attempts was about 50% of that expected on the basis of quantitative formation of $Al(C_{10}H_8ON)_3$. The low yield necessitated combination of samples for bromometric analysis and for ignition to Al_2O_3. Data obtained from these analyses are in Table I.

The procedure was repeated using a 12:1 ligand:metal molar ratio. However, only a very small amount of precipitate, along with a much larger amount of the oily material, was obtained. Ashing of the oily material produced no residue.

Repetition of the procedure using 30 mg of Al(III) (1.1 millimoles) and

a 4:1 ligand:metal ratio gave a yellow precipitate and some very sticky, oily material. An error was introduced in the bulk analysis of the material collected in that it was not possible to completely remove all of the gummy solid from the beaker. The collected solid was dried and the 2-methyloxine and Al(III) contents determined as above. The percent yield was 86-90% based on quantitative formation of $Al(C_{10}H_8OH)_3$. Analytical data are in Table I.

The same procedure was used to precipitate about 45 mg of Al(III) (1.6 millimoles). A yellow precipitate was obtained, with only a small amount of the oily, gummy material. The solid was dried and the 2-methyloxine and aluminum content determined as described above. The percent recovery as $Al(C_{10}H_8ON)_3$ was 99-100%. Analytical data are in Table I.

TABLE I

Analytical Data for Precipitates Obtained in Acetate-buffered Aqueous Solutions

Al(III) taken (mg)	Ligand:Al(III) molar ratio	% Al found*	% 2-methyloxine found*	% yield based on $Al(C_{10}H_8ON)_3$
6	4:1	8.92	83	about 50
30	4:1	5.95	91.0	86-90
45	4:1	5.53	93.4	99-100
6	12:1	**		
Calculated for $Al(C_{10}H_8ON)_3$		5.38	94.62	

*At the 6 mg level of Al(III), three precipitates were combined for analysis which gave the data shown.

At the 30 and 45 mg level, data represent the average of three and four results, respectively.

**When a 12:1 molar ratio was used, only a very small amount of yellow precipitate and a large amount of a gum-like substance were obtained.

(b) Precipitation of the 2-methyloxine complex in aqueous acetone solutions.

   (i) Precipitation from acetate buffered solutions. To eliminate the precipitation of the oily material described above, the experiments were repeated in aqueous solutions containing 20% by volume acetone. Three different volumes of Al(III) solution were taken and diluted to 80 ml with water, followed by addition of 20 ml of acetone. After addition of each of the ligand solution, buffer solution, and base, an appropriate volume of acetone was added to maintain the composition at 20% v/v acetone-water. The temperature of precipitation and digestion was $40^{\circ}C$ in these experiments, and the solution was allowed to cool to room temperature before filtering. At the lowest Al(III) concentration (about 0.2 millimoles), only a trace of yellow precipitate (slightly gelatinous in appearance) was obtained. At the two higher levels of concentration (about 30 and 45 mg), the yield of yellow precipitate (calculated as $Al(C_{10}H_8ON)_3$) was about 80%. The 20% shortfall is due mainly to the solubility of the complex in acetone (see Section II. E.(a)). The amount of sticky material present was greatly reduced, but was not entirely eliminated. The complexes were analysed for 2-methyloxine and aluminum as previously described, and elemental-analysis data obtained. The data are given in Table II.

   (ii) Precipitation from HCl solution. The preparation of the complex was repeated in the absence of acetate by using a hydrochloric acid solution of the ligand without the addition of acetate buffer. Exactly 15.00 ml of the Al(III) stock solution (47 mg, 1.7 millimoles Al(III)) were taken, 25 ml of a solution of 2-methyloxine (1102 mg, 6.96 millimoles 2-methyloxine) in 6 M hydrochloric acid were added and the total volume diluted with 20 ml of acetone and 40 ml of water. The solution was heated to $40^{\circ}C$ and the pH was adjusted by the dropwise addition of 4 M aqueous ammonia (about 45 ml). Acetone was added with the base to maintain the solvent composition at 20% v/v acetone-

TABLE II

Analytical Data for Precipitates Obtained
in Aqueous-Acetone Media

Al(III) taken (mg)	% Al found*	% 2-methyloxine found*	% C found	% N found	% H found
30	6.26	90.5	65.62	7.84	4.89
45	6.54	90.6	68.76	8.00	4.98
45			69.02 ⎫	7.94	4.73
45			70.02 ⎭ **	8.35	4.97
Calculated for Al(C$_{10}$H$_8$ON)$_3$	5.38	94.62	71.85	8.38	4.82

* At 30 mg and 45 mg levels, data represent the average of two and five results, respectively.

** Elemental analysis on complexes obtained in pH studies (Section II.E.(b)). Final pH of the solutions were 9.20 and 9.08, respectively.

water. At about pH 5, the yellow solution became cloudy; the final pH of the solution was 8.0. The mixture was allowed to digest for 1 hour at 40°C. The yellow solid was filtered and dried as before. The solubility of the precipitate in aqueous acetone reduced the yield to 76%, based on Al(C$_{10}$H$_8$ON)$_3$. Analytical data for this complex are given in Table III.

In the absence of acetone in solution, a very gummy yellow solid was obtained which could not be filtered.

(iii) Precipitation from HNO$_3$ solution. The preparation of Al(C$_{10}$H$_8$ON)$_3$ was attempted using nitric acid solutions of the ligand. Since it was found that the ligand decomposed quite rapidly, even in 1 M HNO$_3$, the procedure used was as follows: 15.00 ml of the standard Al(III) solution (1.7 milli-moles) were pipetted into a beaker followed by the addition of 20 ml of 1 M HNO$_3$ and 45 ml of water. Then, in rapid succession were added 20 ml of acetone

in which were dissolved 1100 mg (about 7 millimoles) of 2-methyloxine and 4 M aqueous ammonia (about 20 ml) to raise the pH to 8.5. Acetone was added with the base to maintain the solvent composition at 20% v/v acetone-water. The mixture was heated to 40°C for 1 hour, and after cooling to room temperature, the yellow precipitate was filtered and dried as before. Solubility of the precipitate restricted its yield to 79% based on $Al(C_{10}H_8ON)_3$. Analysis of this complex gave the corresponding data in Table III.

(iv) Precipitation from NaOH solution. A 15.00 ml aliquot of the standard Al(III) solution (1.7 millimoles) was dilluted to 80 ml followed by the addition of 20 ml of acetone. Then 2 M NaOH (about 2 ml) was added dropwise to precipitate and redissolve aluminum hydroxide. The ligand (1100 mg, 7 millimoles) was added as a solid and more 2 M NaOH (10 ml) was added to raise the pH to 13.5. At this pH, the ligand was fully dissolved. The mixture was heated to 40°C and then 2 M HCl was added dropwise with good stirring. Acetone was added with the acid to maintain the solvent composition at 20% v/v acetone-water. Between pH 11.0 and 10.5, the solution grew increasingly cloudy and at the final pH (8.5), a yellow precipitate was present. The precipitate appeared to be more clumpy and darker than that obtained by Cardwell's method. After standing at 40°C for one hour, the solid was filtered and dried as before (yield = 85%). Analytical data are given in Table III.

(c) Infrared spectra of the Al(III) complexes of 2-methyloxine.

Infrared spectra of 2-methyloxine (Figure 1) and of the following preparations were taken (as hexachloro-1,3-butadiene mulls, between sodium chloride plates):

(1) the precipitates prepared from acetate-buffered aqueous solution using 6, 30 and 45 mg Al(III);

(2) the complex prepared from acetate-buffered, 20% v/v acetone-water

TABLE III

Analytical Data for Precipitates Obtained
in the Absence of Acetate Buffer

|	% Al	% 2-methyloxine	% C	% N	% H
Precipitate from HCl solution	7.00	90.3	69.39	8.32	4.88
Precipitate from HNO$_3$ solution	6.96	90.9	66.42	8.31	4.78
Precipitate from NaOH solution	5.46	94.12	70.81	8.42	5.07
Calculated for Al(C$_{10}$H$_8$ON)$_3$	5.38	94.62	71.85	8.38	4.82

medium (at various final pH values, section III.E.(b));

(3) a sample of the sticky solid obtained when the complex was prepared
from aqueous solution;

(4) the complex prepared from HCl solution (no acetate buffer);

(5) the complex prepared from HNO$_3$ solution (no acetate buffer); and

(6) the complex prepared from NaOH solution (no acetate buffer).

Figure 2 is the infrared spectrum of (6), which is representative also of
the spectra of (1)-(5). All spectra except that for the ligand showed strong
absorptions at 1112 cm^{-1} (which has been assigned to the C–O–Al stretching
frequency[25]) and at 1279 cm^{-1} which is characteristic of complex formation
between Al(III) and 2-methyloxine[23]. The spectrum for (6) had one strong
peak not present in the others, at 1020 cm^{-1}.

The sharp peak at 764 cm^{-1} and the strong broad band at 3300 cm^{-1} of the
free ligand were absent in all other spectra. Also, the band of 700 cm^{-1} in
the spectrum of the free reagent was sharply reduced in intensity. In all
spectra except that for the free ligand, there was a weak absorption at about

Figure 1.   Infrared spectra of hexachloro-1,3-butadiene
            (top) and 2-methyloxine (bottom).

WAVENUMBER CM⁻¹
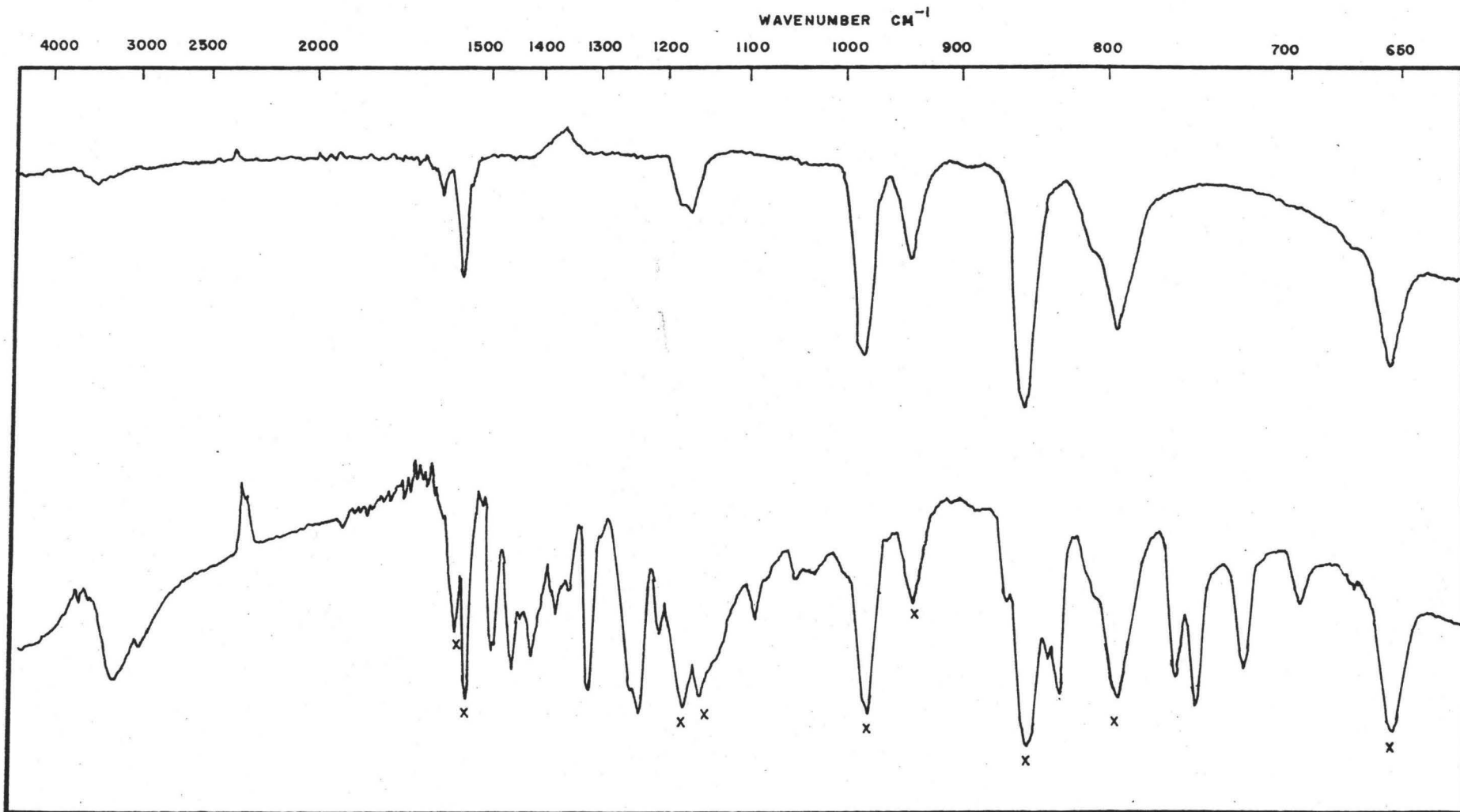
X = hexachloro–1,3–butadiene

Figure 2. Infrared spectrum of $Al(C_{10}H_8ON)_3$ prepared from an initially alkaline solution (pH 13).

WAVENUMBER CM⁻¹
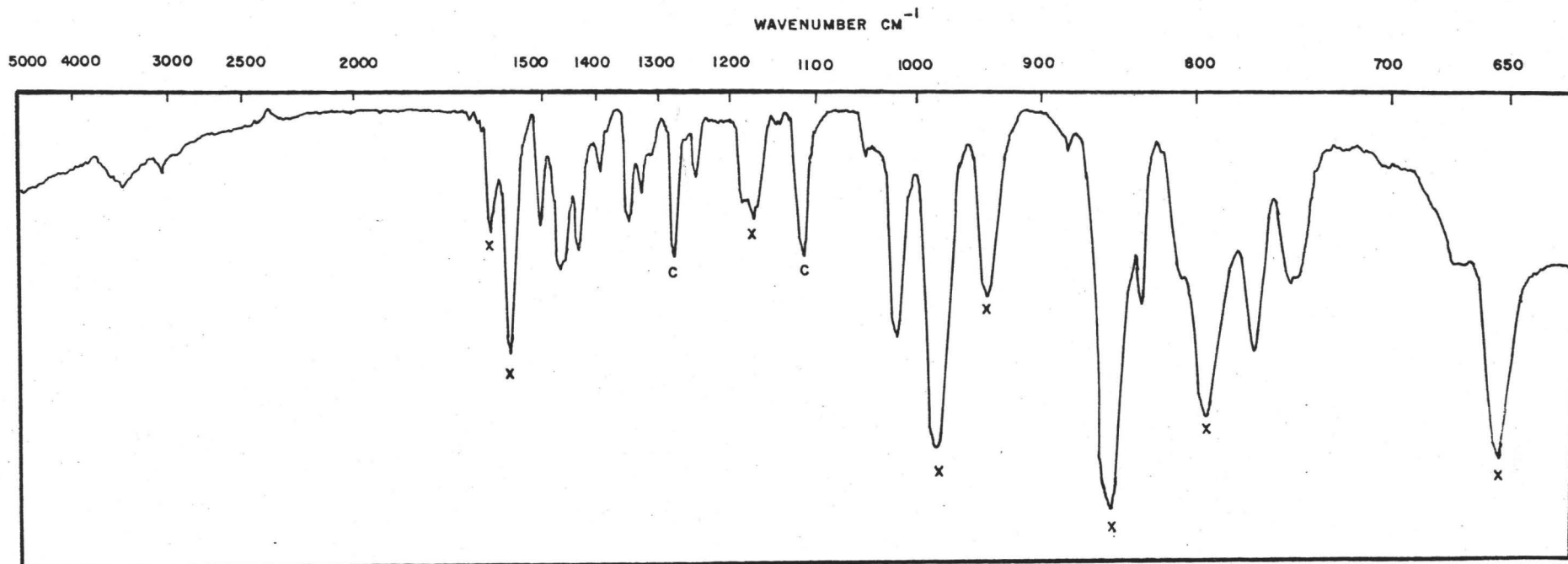
X = hexachloro-1,3-butadiene
C = complex

3500 cm^{-1}, due in part to moisture in the hexachloro-1,3-butadiene and in part to adsorbed or lattice water in the complex.

II.E. Effect of pH on complexation of 2-methyloxine and Al(III)

(a) Solubility of the 2-methyloxine complex in aqueous acetone solution.

The solubility* of Al($C_{10}H_8ON$)$_3$ in 20% v/v acetone-water was determined as follows. Al($C_{10}H_8ON$)$_3$ (100 mg, prepared by procedure III.D.(b)(i), using 45 mg Al(III)) and 50 ml of 20% v/v acetone-water were placed in an erlenmeyer flask. The flask was stoppered and placed on a mechanical shaker for one hour at room temperature (23$^{\circ}\pm$ 2°C), and then allowed to stand at rest for 30 minutes. The undissolved solid was transferred into a previously weighed filtering crucible, washed with water, and dried under vacuum. The determined solubility (0.75 mg/ml) in 20% acetone was used in other experiments to estimate loss of precipitate due to solubility. This solubility was determined at room temperature in a 20% acetone-water mixture having pH 7.01. As described in the following section, maximum precipitation occurs in the pH range 6-10.5, so for accurate estimates of solubility loss, the final pH of the solution should be close to 7, and the solution should be cooled to room temperature.

(b) Preparation and characterization of the precipitate from solutions of
      varying pH.

The effect of pH on the precipitation of the complex from 20% v/v acetone-water was examined. The precipitate was prepared (using 45 mg of Al(III)) as previously described, except that the volume of the ammonia-ammonium acetate buffer was varied to obtain different pH values. The final volume of the solution was adjusted to about 250 ml and kept constant to keep the solubility

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*The term "solubility" is used loosely here since it is not known whether equilibrium conditions prevailed in the experiments.

losses constant. For pH values greater than 9, sodium hydroxide (2 M to 8 M) was used. The precipitates were digested for one hour at 40°C, and then cooled to room temperature before being filtered. The pH values of the filtrates were measured (34 values, from pH 5.7 to 13.75 were obtained; see Figure 3). The precipitates were then washed, dried under vacuum as before, weighed, and the weights corrected for solubility loss. The effect of pH on the percent recovery as $Al(C_{10}H_8ON)_3$ is shown in Figure 3.

Figure 3 shows that precipitation begins just beyond pH 6, is essentially 100% between pH 7-10.5, and drops rapidly to zero between pH 10.5-12. Analytical data for precipitates at pH values 9.20 and 9.08 are reported in Table II. Infrared spectra of several precipitates obtained at various final pH values (i.e., 6.70, 7.33, 7.90, 9.06, 9.40, 9.53, 9.77) showed the characteristic bands for the complex at 1112 cm^{-1} and 1279 cm^{-1} (see Section II.D.(c)).

II.F. Potentiometric titrations of 2-methyloxine-Al(III) systems

The solvent for the titrations consisted of 50.0 ml of 0.01 M $HClO_4$ solution (which was also 0.19 M in $NaClO_4$) and 50.0 ml of dioxane (ionic strength of solution, 0.20). The standard Al(III) solution was pipetted into the titration vessel, and the required amount of ligand was weighed out and dissolved in the solvent. During the titration (with 0.1 M NaOH), dioxane was added with each increment of base to maintain the 50% v/v aqueous dioxane composition. The following solutions were titrated:

 (A) 50.0 ml of $HClO_4$ in 50.0 ml dioxane;

 (B) A plus 5.83×10^{-5} moles Al(III);

 (C) A plus 5.83×10^{-5} moles 2-methyloxine;

 (D) B plus 1.75×10^{-4} moles 2-methyloxine (3:1 molar ratio);

 (E) B plus 2.33×10^{-4} moles 2-methyloxine (4:1 molar ratio).

Figure 3. Effect of pH on precipitation of $Al(C_{10}H_8ON)_3$
(impure) from 20% acetone–water medium in presence
of acetate.

(o = pH adjusted with aqueous ammonia
Δ = pH adjusted with sodium hydroxide solution)
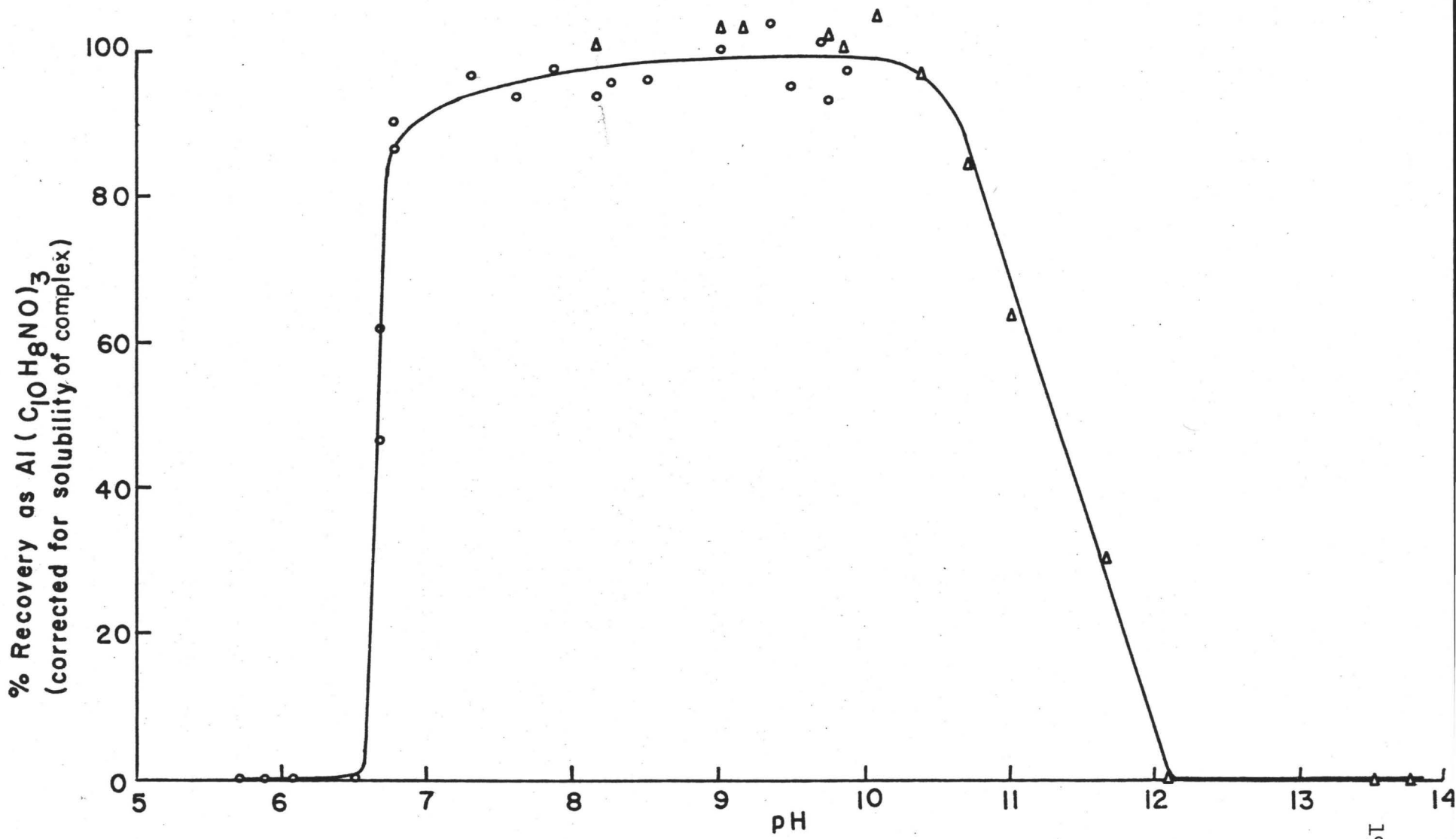
The resulting titration curves are shown in Figure 4.

Since Figure 4 shows no evidence of complexation, the experiment was repeated using increased concentrations of reagents. The solvent consisted of 50.0 ml of 0.11 M $HClO_4$ solution and 50.0 ml of dioxane, and the solutions were titrated as above except that 1.5 M NaOH was used. The following solutions were titrated:

(A) 50.0 ml of $HClO_4$ in 50.0 ml dioxane;

(B) A plus 5.83×10^{-4} moles Al(III);

(C) A plus 6.99×10^{-3} moles 2-methyloxine;

(D) B plus 6.99×10^{-3} moles 2-methyloxine (12:1 molar ratio).

The resulting titration curves are shown in Figure 5. Evidence that complexation has occurred exists in the appearance of a precipitate as noted on curve D. Also, the fact that curve D initially lies lower than curve C is probably due to the fact that complexation has already begun, thus removing some of the 2-methyloxine from the solution resulting in a lower initial pH of the solution.

II.G. Conversion of the hydrous oxide of Al(III) to the 2-methyloxine complex

The Al(III) solution (10 ml containing 31.44 mg, 1.17 millimoles) was diluted to 69 ml and one ml of 4 M aqueous ammonia was added to produce the hydrous oxide precipitate. The solution was buffered at pH 8.5 by the addition of 10 ml of a 0.04 M ammonium nitrate/0.01 M aqueous ammonia solution. Next, 20 ml of dioxane containing 740 mg of 2-methyloxine (4.65 millimoles, a 4:1 ligand:Al(III) molar ratio) was added. The final solution was 20% v/v dioxane-water. A yellow precipitate appeared instantaneously and was immediately filtered into a previously weighed sintered-glass crucible. This experiment was repeated as above, except that individual mixtures were allowed to stand

Figure 4. Potentiometric titration curves of aluminum and 2-methyloxine.

(A) 50.0 ml of $HClO_4$ in 50.0 ml dioxane;

(B) A plus 5.83×10^{-5} moles Al(III);

(C) B plus 5.83×10^{-5} moles 2-methyloxine;

(D) B plus 1.75×10^{-4} moles 2-methyloxine (3:1 molar ratio);

(E) B plus 2.33×10^{-4} moles 2-methyloxine (4:1 molar ratio).
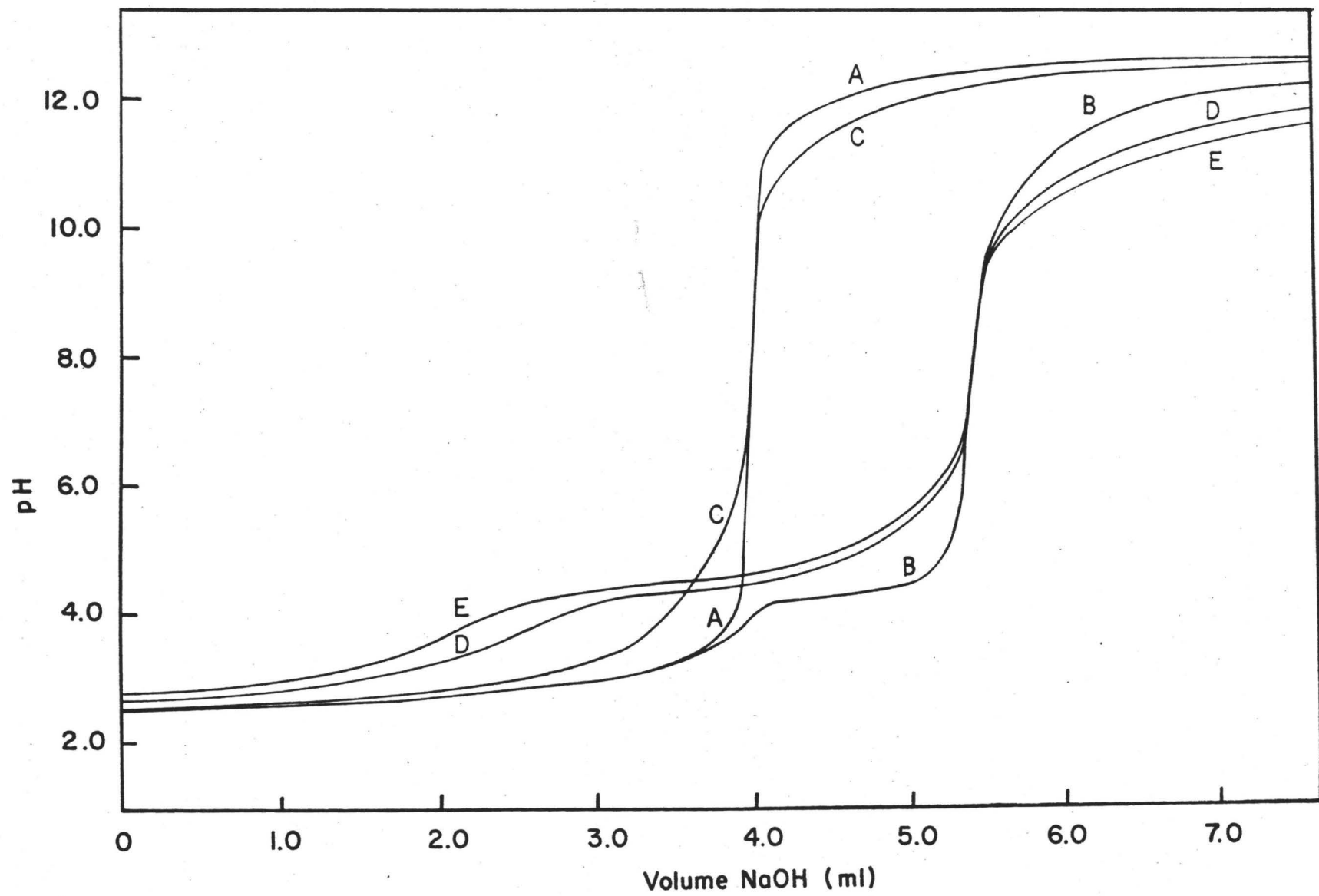
Figure 5. Potentiometric titration curves of aluminum and
2-methyloxine (higher concentrations of reactants).

(A)   50.0 ml of $HClO_4$ in 50.0 ml dioxane;

(B)   A plus 5.83×10^{-4} moles Al(III);

(C)   A plus 6.99×10^{-3} moles 2-methyloxine;

(D)   B plus 6.99×10^{-3} moles 2-methyloxine (12:1 molar
ratio).

($\dagger$ = appearance of hydrous aluminum oxide
$\mathbf{\dagger}$ = appearance of yellow precipitate)
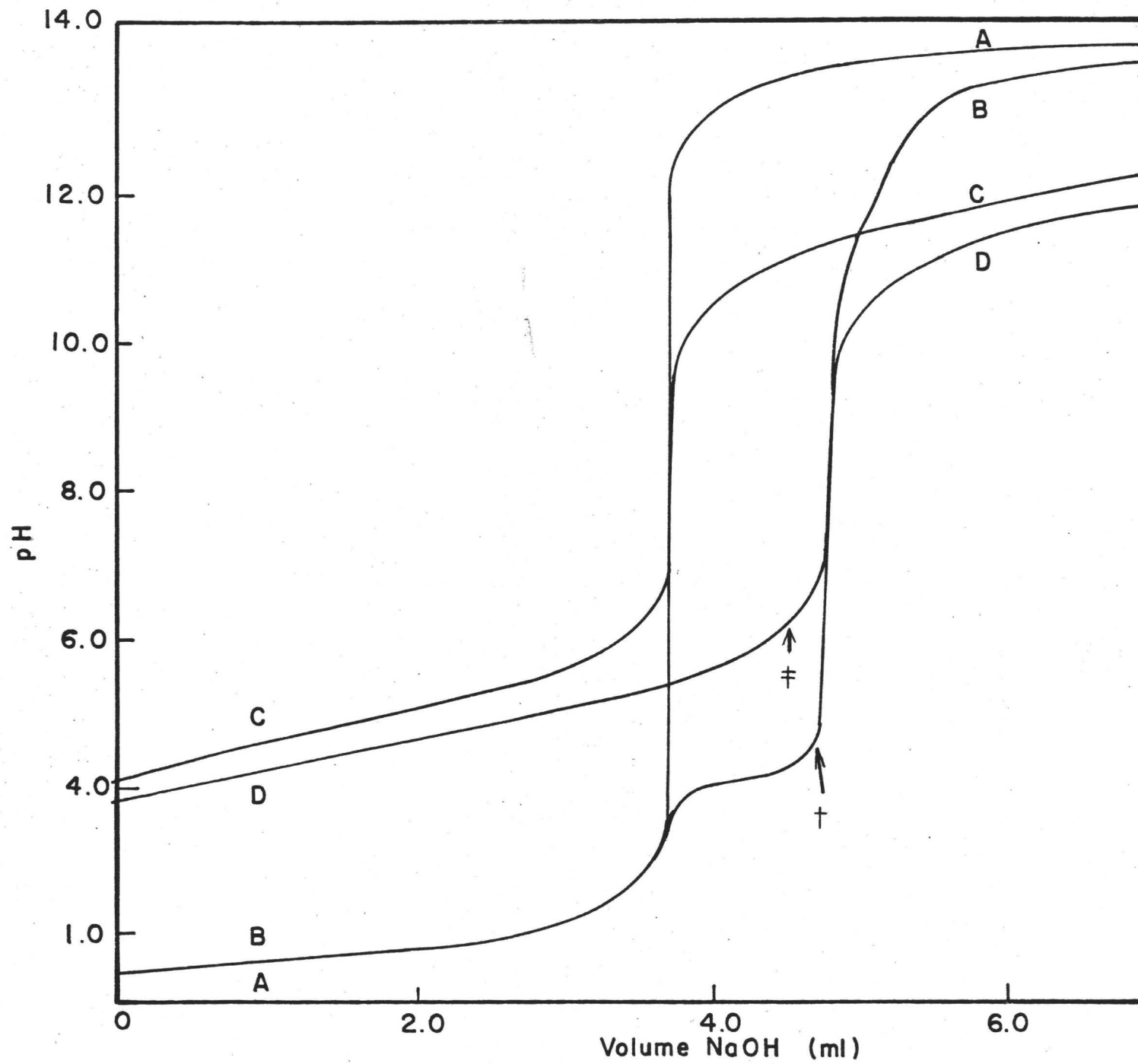
(at room temperature, with constant stirring) for 30 minutes, 5 hours, and 20 hours. Analysis of the precipitates gave the results in Table IV.

TABLE IV

Analytical Data for Precipitates Obtained by the Conversion
of the Hydrous Oxide of Al(III) (4:1 molar ratio)

	% 2-methyloxine	% C	% N	% H
Filtered immediately	80.80	59.83	7.17	4.89
after 1/2 hr.	81.50	64.72	7.58	5.25
after 5 hr.	82.07	64.60	7.36	5.04
after 20 hr.	81.39	66.46	7.35	5.18
Calculated for $Al(C_{10}H_8ON)_3$	94.62	71.85	8.38	4.82

Since the determinations above show that the conversion product is not pure $Al(C_{10}H_8ON)_3$, the experiment was repeated using an increased concentration of 2-methyloxine (i.e., an 8:1 ligand:Al(III) molar ratio). The data for these experiments are given in Table V.

TABLE V

Analytical Data for Precipitates Obtained by the Conversion
of Hydrous Oxide of Al(III) (8:1 molar ratio)

	% 2-methyloxine	% Al	% C	% N	% H
Filtered after 1/2 hr.	93.90	5.41	72.64	8.40	5.51
after 5 hr.	94.8	5.39	71.48	8.39	5.44
after 20 hr.	94.4	5.36	73.20	8.38	5.36
Calculated for $Al(C_{10}H_8ON)_3$	94.62	5.38	71.85	8.38	4.82

Infrared spectra taken on the products of both conversion experiments showed the characteristic bands for the complex (1112 cm^{-1} and 1279 cm^{-1}). The spectra were essentially the same as those described in Section II.D.(c) (see Figure 6).

## II.H. Aluminum complexes of other 2-substituted oxines

Attempts to precipitate an Al(III) complex from aqueous solution with 2-n-propyl-, 2-n-butyl-, and 2-phenyloxine led to mainly aluminum hydroxide. As a result, the preparation of the complexes was attempted from melts, in the absence of water.

2-n-Propyloxine (3.08 millimoles), a brown oil prepared by the neutralization of the hydrochloride, was mixed with aluminum chloride (1.07 millimoles) in an open beaker which was then heated in an oil bath to 185–190°C. The dark brown solution was held at this temperature for three hours, with occasional stirring. On cooling, a brown solid formed whose infrared spectrum showed strong peaks at 1120 and 1275 cm^{-1}, indicating complexation. The presence of uncomplexed ligand was also indicated by shoulders at 833 and 1250 cm^{-1}. Washing the brown product with ether gave a yellow solution which was separated from the undissolved brown material. After evaporation of the ether, a yellow-brown liquid remained which was shown by its infrared spectrum to be free ligand. The undissolved brown material gave an infrared spectrum that showed reduced contamination by free ligand (Figure 7). A sample of this solid was heated to 1100°C in a platinum crucible. The resulting white solid indicated the presence of aluminum in the sample. Also, the solid was dissolved in dilute HCl and tested with alizarin paper[35], which gave a positive test for Al(III).

This experiment was repeated with 2-n-butyloxine (2.73 x 10^{-3} moles,

Figure 6. Infrared spectrum of $Al(C_{10}H_8ON)_3$ prepared from solid-
phase aluminum hydroxide in 20% dioxane-water.

(At pH 8.5; molar ratio of 2-methyloxine:Al(III), 8:1;
reaction time, 30 minutes.)

WAVENUMBER CM^{-1}
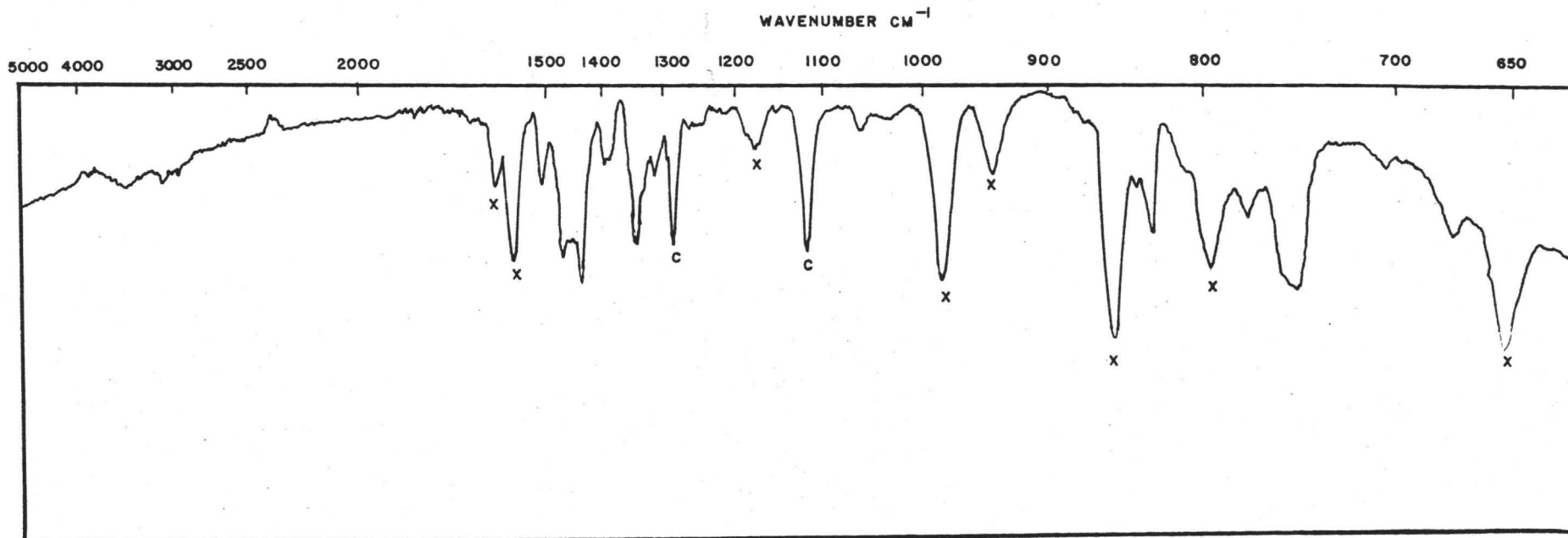
X = hexachloro-1,3-butadiene
C = complex

Figure 7. Infrared spectrum from reaction of aluminum chloride and 2-n-propyloxine in the melt.

WAVENUMBER CM⁻¹
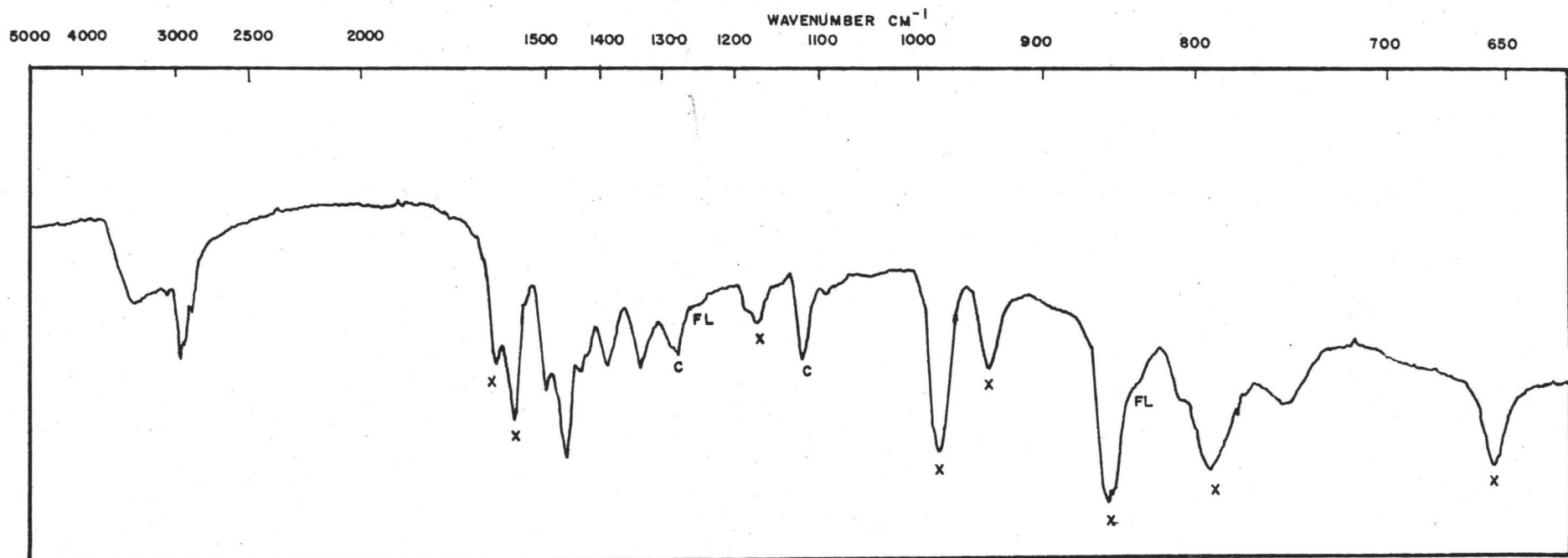
X = hexachloro-1,3-butadiene
C = complex
FL = free ligand

prepared from its hydrochloride) and 0.68×10^{-3} moles of aluminum chloride. The brownish-yellow solid that resulted on cooling gave an infrared spectrum that indicated complexation (strong bands at 1112 and 1280 cm^{-1}). Small shoulders at 833 and 1250 cm^{-1} showed the presence of some free ligand. Washing the solid with ether gave results as before; the yellow-brown oil isolated from the ether gave the infrared spectrum for 2-n-butyloxine, and the undissolved brown solid produced a spectrum very similar to Figure 7. Heating the brown solid to $1100^{o}C$ produced a white solid that indicated the presence of aluminum. Alizarin paper gave a positive test for Al(III) as described above.

The ligand 2-phenyloxine was available as a pale yellow solid; 2.03×10^{-3} moles were mixed with 0.69×10^{-3} moles of aluminum chloride and heated as above. The mixture began to melt at $65^{o}C$ and formed a thick orange-brown paste at $110^{o}C$. An infrared spectrum of a sample of this mixture indicated no complexation had occurred. At $160^{o}C$, a dark brown liquid was obtained. The temperature was raised to $175^{o}C$ and held there for two hours. After cooling, the solid dark brown product was washed with ether and vacuum dried at $150^{o}C$ for 40 minutes. A sharp band at 1112 cm^{-1} in the infrared spectrum suggested that complexation had occurred. The band at 1280 cm^{-1} was obscured by ligand absorption. Heating the product to $1000^{o}C$ produced a white ash, indicating that aluminum was present in the sample. Alizarin paper gave a positive test for Al(III).

III. DISCUSSION

III.A. Al(III) Complexes of 2-Methyloxine

As noted in the INTRODUCTION, the precise procedure used by Cardwell to precipitate 5-50 mg of Al(III) quantitatively from aqueous solution as $Al(C_{10}H_8ON)_3$ is not clear. In particular, one is left to guess whether a "four-fold excess" of 2-methyloxine means a 4:1 or a 12:1 molar ratio of ligand to Al(III). Also, the temperature of digestion of the precipitate appears to have been either 50-60°C or room temperature. After filtration, the precipitate was said to have been dried in a desiccator, but the temperature, pressure and time are not stated.

For the experiments in this thesis in which precipitations were made from aqueous media (i.e., no acetone added), the precipitates were digested at 60°C (for one hour) rather than at room temperature, because the precipitates coagulated more readily at the elevated temperature. For precipitation made from a 20% v/v acetone-water medium, the digestion temperature was lowered to 40°C to reduce the loss of acetone. The precipitates obtained from both solvent media were dried in the same manner, i.e., in a desiccator at 40-45°C, about 3 mm pressure, for at least three hours. These conditions were considered sufficiently vigorous to remove adsorbed water without causing loss of water of crystallization, or decomposition of the metal complex itself.

For precipitations from aqueous media, amounts of Al(III) ranging from 6-45 mg and molar ratios (2-methyloxine to Al(III)) of both 4:1 and 12:1 were used. The data are summarized in Table I. From this table, it is apparent that at a 4:1 molar ratio of reactants, quantitative precipitation of Al(III) as the yellow tris complex was achieved only at the 45 mg level of Al(III). At

the 6 and 30 mg levels, a brown gum-like substance was obtained together with
a yellow precipitate. Both the yellow and the gum-like precipitates contained
complexed Al(III), as evidenced by sharp absorption bands at 1112 and 1279 cm^{-1}
in their infrared spectra. When the molar ratio of reactants was 12:1 (for
6 mg Al(III)), the precipitate appeared to be composed totally of the sticky
material, and no analyses were attempted. It is concluded that quantitative
precipitation from aqueous solution of 5-30 mg of Al(III) as the tris 2-methyl-
oxinate is not as easily achieved as stated by Cardwell[27].

The gum-like material has been previously noted by other investigators [36]
in work with 2-methyloxine and Th(III) in aqueous solution. The substance
appears to occur frequently when the concentration of metal-ion taken for pre-
cipitation is low. This observation has not been explained satisfactorily but
it is speculated that its origin is related to the very low solubility of 2-
methyloxine* in neutral or slightly alkaline aqueous media, and the relative
rates of nucleation of 2-methyloxine and of complexation with the metal-ion
(e.g., slower at lower metal-ion concentrations).

Because of the large amounts of gum-like material precipitated from the
aqueous medium when a 12:1 ratio of reactants was taken, it was decided that
Cardwell must have used a 4:1 molar ratio in his work, otherwise mention of
this problem would have surely been made. Subsequent precipitations discussed
in the present work were thus made with a 4:1 molar ratio. In addition, in
order to reduce or eliminate the formation of the brown sticky material even
at this molar ratio, a 20% v/v acetone-water solvent was used to increase the
solubility of the reagent. The use of this solvent medium has two consequences:

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*In aqueous solution at 25°C, the acid-dissociation constants of 2-methyloxine
are 5.6 (pK$_{NH}$) and 10.1 (pK$_{OH}$)[37]. The solubility in the pH range 7 to 9 is
about 2.46 x 10^{-3} M[38].

(a) the results obtained can no longer be directly compared to Cardwell's results; and (b) because of the appreciable solubility of the tris complex in the solvent (about 0.75 mg/ml at pH 7.0, room temperature), quantitative recovery of Al(III) as $Al(C_{10}H_8ON)_3$ can no longer be expected.

When the procedure for precipitation from aqueous medium was applied to precipitation from the 20% v/v acetone-water medium, only a trace of yellow precipitate was obtained at the 6 mg level of Al(III). At the 30 and 45 mg levels, the yield was about 75-85%, based on $Al(C_{10}H_8ON)_3$, and 95-105% after correction for solubility losses. The amount of gum-like material was greatly reduced. The analytical data for the composition of the precipitates (Table II) is not satisfactory for $Al(C_{10}H_8ON)_3$. Complexation of Al(III) has occurred, however, as indicated by bands at 1112 and 1279 cm^{-1} in the infrared spectra. The precipitate could be a mixture largely of $Al(C_{10}H_8ON)_3$ and of hydrolyzed species such as solid phase aluminum hydroxide and $Al_jL_k(OH)_l$ (poly-nuclear species when $j > 1$, L = 2-methyloxinate anion). Such a mixture would be consistent with the high % Al and low % 2-methyloxine found.

When the precipitations from 20% acetone-water medium were repeated (for 45 mg of Al(III)) in the absence of acetate ion (the 2-methyloxine was dis-solved in dilute HCl or HNO_3 and the pH adjusted to 8.0-8.5 with aqueous ammonia), about an 80% yield based on $Al(C_{10}H_8ON)_3$ was obtained in each instance. Again, correction for solubility losses would raise the yields to about 100%. The analytical data for the composition of the precipitates (Table III) are again not satisfactory for $Al(C_{10}H_8ON)_3$, particularly the data for % Al and % 2-methyloxine. (The data for % N and % H are inexplicably good.) As before, the precipitate is likely mainly the tris complex contamin-ated by hydrolyzed Al(III) complexes. Infrared spectra showed the bands characteristic of complexation. In spite of the fact that pure $Al(C_{10}H_8ON)_3$

was not obtained, it was very surprising to obtain any complexation at all, in view of Cardwell's report that the use of aqueous ammonia alone, in the absence of acetate, precipitates aluminum hydroxide[27].

When precipitation from 20% acetone-water medium was approached from basic solution (the reactants initially present in NaOH solution at pH 13.5) by addition of dilute HCl, an 85% yield based on $Al(C_{10}H_8ON)_3$ was obtained (correction for solubility loss raised this to 96%). The yellow precipitate obtained yielded analytical data (Table III) that corresponded surprisingly well to $Al(C_{10}H_8ON)_3$. The infrared spectrum (Figure 2) showed sharp bands at 1112, 1279 and 1020 cm^{-1}. The latter band was not present in the spectra of the other precipitates or of 2-methyloxine. This experiment illustrates that an auxilliary complexing agent such as acetate is not required to pre-cipitate $Al(C_{10}H_8ON)_3$, and this method represents an alternative to Cardwell's procedure for the preparation of the tris complex.

In addition, this experiment shows that for the analytical concentrations of reactants taken and for the final pH value attained (8.5), $Al(C_{10}H_8ON)_3$ is thermodynamically favoured over hydrolyzed forms of Al(III), including solid phase aluminum hydroxide. Indeed, if $Al(C_{10}H_8ON)_3$ is favoured at pH 8.5, then it should be favoured over the range pH 6-10, since the rate in change in con-centration of the 2-methyloxinate anion (L^-) is the same as that of hydroxide ion over this range (Figure 8). Below about pH 5, the rates are different (due to extensive formation of H_2L^+, i.e., nitrogen protonation), and the concentration of L^- decreases more rapidly than that of hydroxide ion, becoming equal at about pH 3, and less than the hydroxide ion concentration below this pH value. Thus, below about pH 5, one cannot expect the formation of $Al(C_{10}H_8ON)_3$ to continue to be favoured over the formation of hydrolyzed Al(III) species. Experimentally, it was in fact observed that for the analytical con-
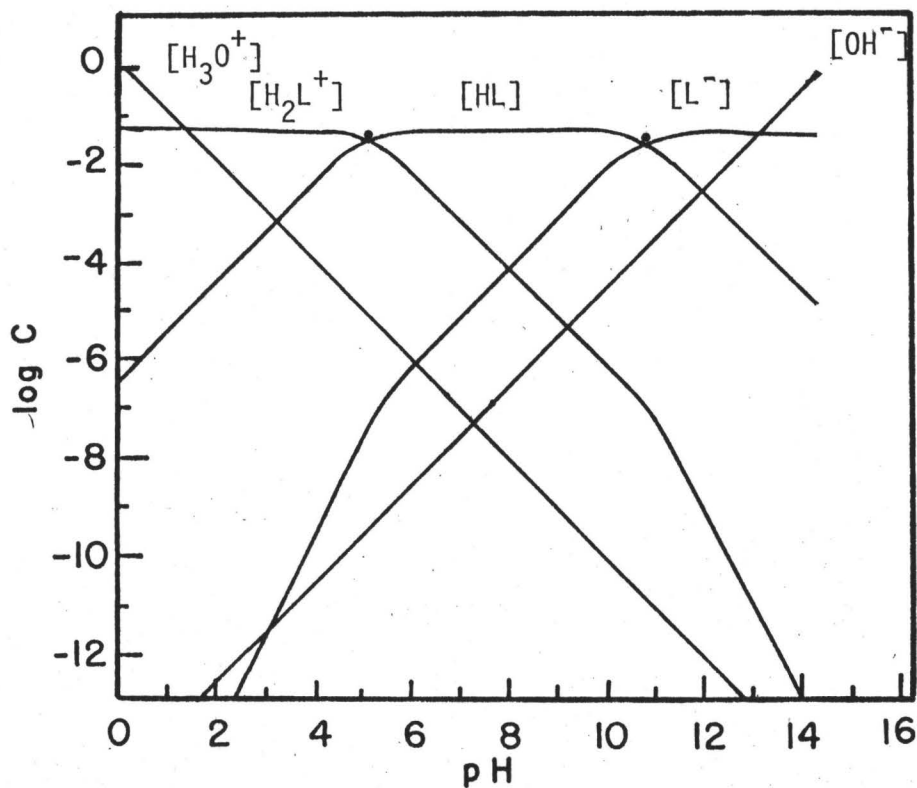
Figure 8. Log concentration diagram for 2-methyloxine species H_2L^+,
HL, L^- in 20% v/v dioxane-water.

(Analytical concentration, 4.7×10^{-2} M; $pK_{NH} = 5.2$;
$pK_{OH} = 10.7$; $pK_W = 14.4^{(39)}$.)

centration of reagents employed (and in the absence of acetate), initial formation of the yellow precipitate did not occur until pH 5 or higher.

The fact that the approach to pH 8.5 from basic solution yielded $Al(C_{10}H_8ON)_3$ in reasonable purity while the approach from acid solution resulted in a product containing some hydrolyzed forms of Al(III), can be accounted for as follows.

It is generally agreed that in dilute aqueous solution (e.g., 10^{-2} – 10^{-4} M), $Al(H_2O)_x^{+3}$ exists below pH 4 and hydroxo complexes above this value[40]. With regard to the general formula $Al_q(OH)_{3q-p}^{p+}$, values of 1, 2, 3, 4, 6, 7, 8 and 13 have been proposed for the polynuclearity factor, q (the hexamer is a major species[41]). Values of +1 to +5, 0, -1, -3, -4 and -6 have been postulated for the charge, p. Compared to the rate of formation of mono-nuclear species, the rate of hydrolytic polymerization is relatively slow but increases as the solution approaches saturation with increasing concentration of hydroxide ion. Eventually, solid-phase aluminum hydroxide is precipitated but redissolves as mononuclear $Al(OH)_4^-$ with increasing hydroxide ion concentration. Above pH 13, the simple mononuclear oxo-anion, AlO_2^- is formed[41].

It has been shown by Turner[42,43] that whereas the parent compound oxine reacts instantaneously with mononuclear Al(III) species, reaction with polymeric species is relatively slow. Cassidy[44] has also found evidence for a similarly slow reaction between 2-(2'-hydroxyphenyl)oxine and polynuclear Al(III) species. If it is assumed that this order of reactivity is the same for 2-methyloxine, then rapid reaction with the mononuclear species $Al(OH)_4^-$ is expected as the pH range is lowered from 13.5 to 8.5. Experimentally, initial precipitation was observed at about pH 11. After the pH had been adjusted to 8.5 and the yellow precipitate allowed to stand for one hour, the tris complex was formed in reasonable purity. When the pH was adjusted to

8.0–8.5 from acid solution, initial precipitation of a yellow complex was
not observed until pH $>$ 5. Below this value and during the upward adjustment
of pH from the initially acidic solution, the formation of both mono- and
polynuclear Al(III) species will have occurred. Since the reaction between
2-methyloxine and the polynuclear species is likely slow, the presence of
hydrolysis products in the precipitate can be anticipated. The experimental
data support this thesis.

As shown above, Cardwell's claim that acetate is required in order to
precipitate the pure tris complex is open to question. The data (Table II)
for precipitation from acid solution in the presence of acetate are no better
than the data (Table III) for the precipitation in the absence of acetate.
Also, reasonably pure $Al(C_{10}H_8ON)_3$ was obtained in the absence of acetate,
starting from basic solution. Indeed, whether or not acetate is present, if
the tris compound is substantially more stable than the hydrolysis products
in the range pH 6–10, conversion to $Al(C_{10}H_8ON)_3$ should occur, given sufficient
time.

That conversion did occur was shown by the experiment in which solid
phase aluminum hydroxide was precipitated at pH 8.5 (in 20% v/v dioxane-
water), and then converted to the tris compound on addition of an 8:1 molar
ratio of 2-methyloxine. Appearance of a yellow precipitate was instantaneous
on addition of the reagent. The data of Table V shows that the conversion
was essentially complete after the precipitate had been allowed to stand for
30 minutes. (The high results for % H cannot be accounted for.)

When the molar ratio of 2-methyloxine to Al(III) was 4:1, immediate
formation of a yellow precipitate was again observed, but after 20 hours the
conversion to $Al(C_{10}H_8ON)_3$ was not complete (Table IV). Either conversion
is very slow after the first few minutes of reaction at this molar ratio of

reactants, or an equilibrium mixture of the products was reached for the dioxane-water medium.

III.B. Precipitation as a Function of pH

In his study, Cardwell[27] did not examine the effect of the pH of the solution on the extent of precipitation. He reported only that adjustment of the pH by an ammonium acetate-ammonium hydroxide solution to pH 8-9 brings about quantitative precipitation of the tris complex in aqueous solution.

In the present study, the effect of pH on precipitation from a 20% v/v acetone-water medium was examined. The solvent was acetonic to reduce the amount of the gum-like material referred to earlier. The amount of Al(III) taken was 45 mg and the solution was buffered with acetate. Figure 3 gives the pH profile of precipitation. The percent recovery was calculated as $Al(C_{10}H_8ON)_3$ although for the steep portions of the curve there is no assurance that the precipitate corresponds to this composition. On the plateau, the composition, as discussed earlier, does not correspond strictly to that of the tris compound because of some formation of hydrolyzed species (Table II). Formation of such species makes reproducibility of the composition difficult, which accounts for the scattering of the data points corresponding to the plateau of the curve.

The data of Figure 3 have been corrected for the solubility of $Al(C_{10}H_8ON)_3$ in 20% acetone-water. The solubility was determined at pH 7.01 so that while the corrections are valid for the plateau region, they probably are an underestimate for the rising portions of the curve. Nevertheless, Figure 3 represents a reasonable profile of the effect of pH on precipitation of the tris complex and is the best that could be obtained under the circumstances.

III.C. Potentiometric Titrations of 2-Methyloxine-Al(III) Systems

Irving and Pettit[8] were unable to obtain evidence for reaction between
Al(III) and 2-methyloxine in 50% v/v dioxane-water by potentiometric titration.
If such evidence were obtained, data from the experiment could be used to cal-
culate the stepwise stability constants for the formation of the series of
complexes in solution. For example, Freiser and coworkers[9-12] have deter-
mined stability constants for the formation of complexes between oxine, 2-
methyloxine, and other derivatives and several divalent metal-ions, and have
shown that the stabilities of the 2-methyloxinates are lower than those of
the oxinates.

Figure 4 shows the titration curves obtained in the present work. Curves
D and E represent solutions in which the molar ratios of reagent to Al(III) are
3:1 and 4:1, respectively. The initial buffer regions of curves D and E cor-
respond to formation of hydroxo species and titration of nitrogen-protonated
2-methyloxine, respectively, as shown by comparison with curve B and curve C.
The buffer region at about pH 10-11 of curves D and E corresponds to titration
of the -OH proton of 2-methyloxine as shown by comparison with curve C in this
region. No evidence for complexation is apparent under the conditions of the
experiment. Yet, since it is now known that 2-methyloxine and Al(III) do
react, conditions must exist in which evidence for reaction can be obtained
potentiometrically. Figure 5 shows titration curves which provide such
evidence. The analytical concentrations of both Al(III) and 2-methyloxine
(5.83×10^{-4} and 6.99×10^{-3} M, respectively) are substantially higher than
those used for Figure 4. Also, the molar ratio of reactants for curve D in
Figure 5 was higher (12:1).

The titration to obtain curve D (Figure 5) provided evidence for complex-
ation. In fact, the yellow complex was observed to precipitate at pH 6.1.
Also, curve D initially lies lower than curve C (titration of the free

ligand), which can be accounted for in two different ways: (a) complexation has already begun which would liberate both protons from the (protonated) nitrogen and oxygen atoms of the ligand, resulting in a lower pH than curve C; or (b) precipitation of aluminum hydroxide has begun which would liberate protons from water molecules, resulting in a lower pH than curve C. However, the latter possibility can be eliminated because the initial pH (3.8) for curve D is high enough to precipitate aluminum hydroxide (as observed for curve B), but no haziness was observed in the solution at this pH value or at higher pH values, until the yellow precipitate appeared.

Although these titrations provided evidence for complexation of Al(III) with 2-methyloxine, calculation of stepwise stability constants is not possible because of precipitation of the complex. It would be useful, then, to find conditions under which the complex forms but does not precipitate in order to obtain the stability constants for the complex, which could then be compared to the stability constants for the corresponding aluminum-oxinate complex.

III.D. Aluminum Complexes of Other 2-Substituted Oxines

Cardwell and coworkers[28] reported that 2,5-dimethyl- and 2-methyl-5-chloro-oxine yielded tris chelates with Al(III) in aqueous solution. Dimeric bis chelates containing an Al-O-Al linkage are obtained with 2,3-dimethyl- and 2,3,4-trimethyloxine. No evidence for reaction between Al(III) and 2-phenyloxine was obtained in aqueous solution, in non-aqueous media, or in the melt.

In the present study, attempts to prepare compounds between Al(III) and 2-n-propyl-, 2-n-butyl- and 2-phenyloxine from aqueous solution failed. Solid-phase aluminum hydroxide was the main product. Evidence for reaction was obtained, however, in the melt (i.e., in the absence of water). Well-defined infrared bands characteristic of complexation were observed in the

1112-1120 and 1275-1280 cm^{-1} ranges (Figure 7). The reaction products were brown, indicating some decomposition due to the high temperatures used in the experiments. Also, some contamination from the ligand was apparent from the infrared spectra (Figure 7). Although the reaction products were not isolated and purified, the spectral evidence does suggest some degree of reaction.

From both Cardwell's report[28] and the present work, there appears little doubt that the increased size of the 2-substituent has hindered the complexation reaction in aqueous media. If the lack of reaction in aqueous media is confirmed by further work, it would be tempting to explain the observation on the basis of greatly reduced complex stability due to steric interactions between the bulky substituent and coordinated water.

III.E. Discussion of Errors

The results obtained in analyses of percent aluminum and percent 2-methyloxine are subject to the errors inherent to the methods used for the analyses.

The main source of error in the analysis of aluminum by ignition to Al_2O_3 is the hygroscopic nature of the oxide. The error caused by retention of water has been reported as 0.6 percent of Al_2O_3 at 900°C and 0.3 percent at 1050°C[45]. Water is expelled from the oxide of aluminum at 1100°C, but even after this treatment the residue is hygroscopic. It is recommended that the oxide be heated to 1200°C, where it becomes non-hygroscopic[34]. Determinations of aluminum in samples of pure aluminum oxinate gave results within 2% (relative) of the known percent aluminum. The average relative deviation from the mean values obtained in the aluminum determinations was 0.5-1.0%.

The bromometric determination of 2-methyloxine is very precise and accurate[33] and errors introduced would be in the standard potassium bromate and thiosulphate solutions used, and in the burette readings taken for the volumes of each of these solutions. Determinations of pure 2-methyloxine gave results from 99.7% to 100.2% 2-methyloxine. The average relative deviation from the mean values obtained in the 2-methyloxine determinations was generally about 1%.

III.F. Suggestions for Further Work

(1) Additional experiments should be attempted in which longer digestion periods are allowed for precipitates obtained from 20% acetone-water, both in the presence and absence of acetate ion. These experiments would determine whether or not hydrolyzed species would convert to $Al(C_{10}H_8ON)_3$ to yield a purer tris complex.

(2) Further attempts should be made to find conditions under which the tris complex is formed and remains in solution during the course of a potentiometric titration. The data from such a titration would allow calculation of the stepwise stability constants, and comparison with those of the Al(III)-oxine system would provide a measure of the effect of the 2-methyl group on the stability of the complexes formed.

(3) Further experimentation with 2-n-propyl-, 2-n-butyl-, and 2-phenyloxine and Al(III) in 20% acetone-water should be done to show conclusively whether or not complexation occurs in the presence of a strongly polar solvent. The aluminum hydroxide precipitated in the solutions of these ligands should be left to digest in order to determine whether conversion to metal-ligand complexes will occur. Experiments in less polar non-aqueous solvents would also be of interest.

IV. CONCLUSIONS

(1) Contrary to the claim by Cardwell[27], small amounts of Al(III) (6-30 mg) could not be precipitated quantitatively as $Al(C_{10}H_8ON)_3$ from aqueous solution. If Cardwell actually precipitated pure $Al(C_{10}H_8ON)_3$ with these small amounts of metal ion, then the procedure described by him is lacking. However, starting with 45 mg of Al(III), precipitation as $Al(C_{10}H_8ON)_3$ was essentially quantitative.

(2) For a 20% acetone-water medium containing acetate, the composition of the precipitate obtained did not correspond to $Al(C_{10}H_8ON)_3$. The precipitate is likely largely the tris complex contaminated by hydrolyzed species of aluminum.

(3) For a 20% acetone-water medium containing chloride or nitrate but no acetate, the composition of the precipitate obtained was essentially as stated in Conclusion (2).

(4) As an alternative to Cardwell's procedure, $Al(C_{10}H_8ON)_3$ can be prepared by careful reduction of the pH of an initially basic 20% acetone-water solution of the reactants, in the absence of acetate or other similar auxilliary complexing agents.

(5) Solid-phase aluminum hydroxide can be converted to $Al(C_{10}H_8ON)_3$ simply by adding a dioxane solution of 2-methyloxine. When the molar ratio of reactants is 8:1, the conversion is complete.

(6) The effect of pH on the precipitation of $Al(C_{10}H_8ON)_3$ from 20% v/v acetone-water has been determined. Because of the presence of hydrolyzed species in the precipitate and of the approximate nature of solubility corrections, the profile of precipitation obtained is not exact.

(7) The use of high concentrations and a high molar ratio of reactants enabled the detection of complex formation in 50% v/v dioxane-water by potentiometric titration. The early occurrence of precipitation, however, made the stepwise stability constants unattainable.

(8) No evidence was obtained for reaction in 20% acetone-water between Al(III) and 2-n-propyl-, 2-n-butyl-, and 2-phenyloxine. This conclusion is based on only limited experimental work. Infrared spectral evidence for some degree of complexation was obtained when the reaction was attempted in the melt.

V. APPENDIX

Log Concentration Diagram

The curves in Figure 8 show the change in the log concentration with pH for the species H_2L^+, HL, L^-, H_3O^+, and OH^- (L = 2-methyloxinate anion). These curves were obtained as follows.

The pK_w in 20% dioxane-water medium at 25°C is 14.4[39]. Thus the equations for the species H_3O^+ and OH^- are readily obtained:

(1) $\log[H_3O^+] = -pH$

(2) $\log[OH^-] = pH - pK_w$

$$= pH - 14.4$$

When equations (1) and (2) are plotted as a function of pH, they will have slopes of −1 and +1, respectively, and will intersect at pH 7.2.

At the 45 mg level of 2-methyloxine there are 7 millimoles of the ligand in a final volume of about 150 ml. This gives an analytical concentration (C_A) of 4.7×10^{-2} M, and $\log C_A = -1.33$. The pK_{NH} and pK_{OH} values for 2-methyloxine are 5.2 and 10.7, respectively, in 20% dioxane-water at 25°C[39]. Thus the system points for 2-methyloxine at this concentration are (5.2,−1.33) and (10.7,−1.33) (these are represented by the dots in Figure 8). Equations for each of the ligand species H_2L^+, HL, and L^- are developed from the expressions for K_{NH} and K_{OH}, and the mass balance of the ligand species:

$$K_{NH} = \frac{[H_3O^+][HL]}{[H_2L^+]} \; ; \qquad K_{OH} = \frac{[H_3O^+][L^-]}{[HL]}$$

and $[H_2L^+] + [HL] + [L^-] = C_A.$

The fraction of the total analytical concentration that exists as the species H_2L^+ is given by

$$\frac{[H_2L^+]}{C_A} = (1 + \frac{[HL]}{[H_2L^+]} + \frac{[L^-]}{[H_2L^+]})^{-1}$$

$$= (1 + \frac{K_{NH}}{[H_3O^+]} + \frac{K_{NH}K_{OH}}{[H_3O^+]^2})^{-1}$$

$$= \frac{[H_3O^+]^2}{[H_3O]^2 + K_{NH}[H_3O^+] + K_{NH}K_{OH}}$$

Similarly,

$$\frac{[HL]}{C_A} = (\frac{[H_2L^+]}{[HL]} + 1 + \frac{[L^-]}{[HL]})^{-1}$$

$$= (\frac{[H_3O^+]}{K_{NH}} + 1 + \frac{K_{OH}}{[H_3O^+]})^{-1}$$

$$= \frac{K_{NH}[H_3O^+]}{[H_3O^+]^2 + K_{NH}[H_3O^+] + K_{NH}K_{OH}}$$

And,

$$\frac{[L^-]}{C_A} = (\frac{[H_2L^+]}{[L^-]} + \frac{[HL]}{[L^-]} + 1)^{-1}$$

$$= (\frac{[H_3O^+]^2}{K_{NH}K_{OH}} + \frac{[H_3O^+]}{K_{OH}} + 1)^{-1}$$

$$= \frac{K_{NH}K_{OH}}{[H_3O^+]^2 + K_{NH}[H_3O^+] + K_{NH}K_{OH}}$$

Thus, the following equations have been obtained:

$$(3) \quad [H_2L^+] = \frac{C_A[H_3O^+]^2}{[H_3O^+]^2 + K_{NH}[H_3O^+] + K_{NH}K_{OH}}$$

$$(4) \quad [\text{HL}] = \frac{C_A K_{NH}[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]^2 + K_{NH}[\text{H}_3\text{O}^+] + K_{NH}K_{OH}}$$

$$(5) \quad [\text{L}^-] = \frac{C_A K_{NH} K_{OH}}{[\text{H}_3\text{O}^+]^2 + K_{NH}[\text{H}_3\text{O}^+] + K_{NH}K_{OH}}$$

By substituting the known values for C_A, K_{NH} and K_{OH}, and arbitrary $[\text{H}_3\text{O}^+]$ values into equations (3), (4) and (5), the curves shown in Figure 8 are obtained for each of the species H_2L^+, HL and L^-.

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