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An oxidation-reduction system with chelating properties

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An oxidation-reduction system with chelating properties

by

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I. INTRODUCTION

For several decades, reliable potentiometric methods have been available for the direct determination of pH. The determination generally involves the single measurement of the potential of a cell which consists of a suitable reference electrode and an indicator electrode that is reversible to hydrogen ions. Today, the most widely used indicator electrode is the glass electrode but other more limited, yet reliable, methods are available for determination of pH.

In comparison, the direct determination of the concentration of the ions of metals has not yet reached such a happy state. During the past thirty years many attempts have been made to devise electrodes which are as selective to metal ions as the glass electrode is to hydrogen ions. To date about twenty so-called ion-selective electrodes have been made commercially available. Several of the electrodes have been developed sufficiently to provide selectivity and range for specific cations or anions. Others, however, are quite general in response and are characterized by a drift in potential which necessitates frequent recalibration. The major problem is thus one of building specificity and stability into such electrodes.

Ion-selective electrodes can be classified into two general types: solid (membrane) electrodes, such as the glass electrode for measuring pH; and soluble, reversible oxidation-reduction couples, such as the quinhydrone electrode also used for measuring pH. To date all of the ion-selective electrodes for metals have been of the former (membrane) type. The present thesis deals with an electrode of the

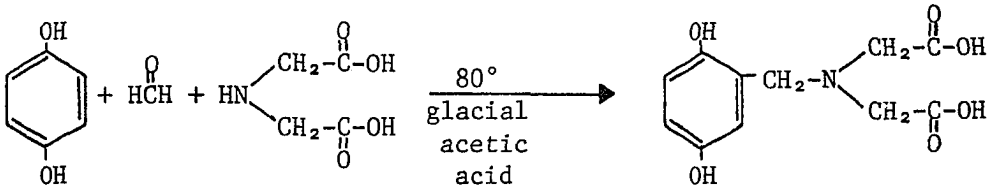
second type.

In this work we have coupled the chelating group methyleneiminodiacetic acid to the oxidation-reduction couple, quinone-hydroquinone, thus conferring on this reversible couple the property of combining with metals. In this way a soluble, reversible oxidation-reduction couple responsive to metal ions should be obtained.

Initial work in this area was carried out by Diehl and Lohman (24) who developed a theory for a metallic ion indicating electrode based on analogy with the quinhydrone electrode but also incorporating chelation. The system involved the quinhydrone of 5,8-dihydroxyquinoline and 5,8-dioxoquinoline. The compound was tested on one metal, nickel, and shown to function as predicted over a limited concentration range, but the quinhydrone proved to be unstable and a functional electrode was never realized.

More recently, Pietrzykowski (30) initiated work on another oxidation-reduction couple by synthesizing 1,4-dihydroxyphenylmethyleneiminodiacetic acid (H_2QMIDA) using the Mannich condensation of hydroquinone, formaldehyde, and iminodiacetic acid.

(1.1)



Although it might be too much to hope that the unique existence and convenient insolubility of the quinhydrone would be duplicated, at least

it would appear possible to obtain a quinone and the corresponding hydroquinone bearing a methyleneiminodiacetic acid group and quite conceivably this couple might respond to metal ions.

Because of the difficulty encountered in working with H_2QMIDA, Pietrzykowski did little beyond synthesizing an obviously impure compound and obtaining preliminary values for a few physical constants. The first efforts in the present work were directed toward synthesis and purification of H_2QMIDA (5). The problems encountered resulted from the insolubility of H_2QMIDA in acidic solutions and the instability of the free acid at high pH and at elevated temperature. The purified H_2QMIDA finally obtained was used in a study of the physical and chemical properties of the material. The infrared, ultraviolet and PMR absorption spectra were obtained, and the behavior on titration with alkali, alone and in the presence of calcium and magnesium, was investigated (5).

In the work being described in this thesis, further study was made of H_2QMIDA, particularly the conversion of it to 1,4-quinone-2-methyleneiminodiacetic acid (QMIDA) and the interaction of the QMIDA-H_2QMIDA system with metal ions.

It was found that H_2QMIDA is fluorescent in the ultraviolet and that the fluorescence is affected by pH and by the presence of calcium and magnesium. Potentiometric titration of H_2QMIDA with eleven chemical oxidizing agents was performed and the results interpreted.

The actual nondestructive oxidation of H_2QMIDA to QMIDA proved to be very difficult to effect. Oxidation of H_2QMIDA to QMIDA by controlled anode potential was attempted. After extensive investigation and method development, QMIDA was finally prepared through the oxidation of H_2QMIDA

with sodium periodate. The QMIDA was purified and the chemical and physical properties determined; ultraviolet, infrared and PMR absorption, melting point, solubility, stability, acid dissociation constants, and oxidation-reduction behavior. An attempt was made to form the quinhydrone of QMIDA and H_2QMIDA. The behavior of the QMIDA-H_2QMIDA system in the presence of thirteen representative metal ions was determined and finally a detailed study of the QMIDA-H_2QMIDA couple as a function of the concentration of aluminum was made.

II. BACKGROUND

A. Organic Oxidation-Reduction Couples

Many organic oxidation-reduction couples are known and many have been thoroughly studied in aqueous and nonaqueous solvents. To say that a couple is reversible is to imply that the electrical potential of a cell, made of two reversible couples, is reproducibly related to the chemical process in that cell. If no current is allowed to flow in the cell, there will be no chemical change of the couples involved. However, when an external voltage large enough to produce current flow is applied, a chemical change proportional to the quantity of electricity passed will occur at both electrodes. If the two electrodes are simply connected (externally, by a wire), current will flow in the opposite direction and the chemical reaction will be exactly reversed. Couples which exhibit such reversibility completely are relatively rare.

Generally, the organic oxidation-reduction systems that are reversible are compounds in which a hydrogen atom is united with an electronegative atom such as oxygen or nitrogen. The most widely known of the reversible organic couples are the aromatic dihydroxy or diamine compounds, the aromatic ring providing stabilization by distributing the charge of the electron or proton added.

The most extensively studied organic oxidation-reduction couple has been that of quinone-hydroquinone. This system is highly reversible and is the basis of a pH indicator electrode, the quinhydrone electrode.

B. The Quinhydrone Electrode

Quinhydrone is a one to one compound formed by the union of quinone and hydroquinone. In 1904 Haber and Russ (18) first established that quinone and hydroquinone formed an oxidation-reduction couple in which the hydrogen ion was involved. Biilmann (2), seventeen years later, realized the potentialities of this discovery and applied the quinhydrone electrode to the determination of the concentration of hydrogen ion. During the next quarter of a century the quinhydrone electrode was widely used for determination of pH.

The theory and operation of the quinhydrone electrode is based on the reaction:

$$(2.1)\quad Q + 2H^+ + 2e^- \rightleftharpoons H_2Q$$

in which Q and H_2Q represent quinone and hydroquinone, respectively. The potential of this half-cell is given by the equation

$$(2.2)\quad E = E^\circ + \frac{0.059}{2} \log \frac{[Q][H^+]^2}{[H_2Q]} \text{ at } 25^\circ$$

in which E° is the standard reduction potential of the quinone-hydroquinone couple. The equation may be rearranged to

$$(2.3)\quad E = E^\circ + \frac{0.059}{2} \log \frac{[Q]}{[H_2Q]} + 0.059 \log [H^+].$$

The potential of a platinum electrode dipping into the solution, measured against a reference electrode, thus varies directly with the logarithm of the hydrogen ion concentration.

The quinhydrone electrode was used extensively for over two decades for the measurement of pH. As the complicated electronic instrumentation necessary for the use of the glass electrode was evolved, the quinhydrone electrode was supplanted by the glass electrode for the routine measurement of pH. By 1950, use of the quinhydrone electrode had ceased.

C. Chelate Rings

A chelate ring compound is defined by Diehl as "a metal derivative of an organic compound in which the metal is attached to the organic molecule through two or more functional groups forming a ring or cage structure" (10). The term "ligand" is used to designate the organic (or other) radical or compound uniting with a metal atom. The term "chelate", according to Diehl (9) is derived from "chela", a Greek word referring to the claw of a lobster and appropriately it carries with it the connotation not only of ring structure but of firmness of binding and of stability.

In the classification of chelate-ring compounds by Diehl (9), ligands are grouped according to the number of sites available for attachment to the metal: thus, unidentate, literally one-toothed; bidentate; tridentate; quadridentate; and sexadentate. The elements through which attachments are made are commonly nitrogen, oxygen and sulfur. These elements are usually incorporated in some functional group, such as the carboxy, hydroxy, amino, and thiol groups. The ligands are further classified according to the functional groups present. The groups may be acidic or basic; the acid groups are -COOH, -OH, =NOH, $-SO_3H$, -SH

and the basic groups, $-NH_2$, =N-, =O, =NOH. The acidic groups lose a proton on union with a metal atom. Chelate rings may be formed by ligands bearing any combination of acidic and basic groups. The charge on the chelate formed is determined by the original charge on the free metal ion and the number of protons displaced from the ligands which become attached.

Chelate rings form chiefly when the positions of the functional groups in the ligand are such that five or six-membered rings are formed with the metal atom. Four and seven-membered chelate-ring compounds are known but the strains in such rings reduce the stability of the compounds. Higher stability is obtained as the number of attachments per ligand increases. A striking example of this is the calcium derivative of ethylenediaminetetraacetic acid; normally calcium does not form coordination compounds but with ethylenediaminetetraacetic acid, a sexadentate ligand, calcium unites through the formation of six bonds forming a highly stable compound.

An application of chelate-ring formation has expanded analytical chemistry in the field of metallochromic indicators by the introduction of a methyleneiminodiacetic acid group, $-CH_2N(CH_2COOH)_2$ (half of the ethylenediaminetetracetic acid molecule), into an acid-base indicator. The initial work of Schwarzenbach, Anderegg and Sallman (37) in this field led to the very useful indicators xylenol orange (21) and Calcein (11). Calcein proved to be an especially useful extension of the concept for in it the acid-base indicator and chelating functions are combined with fluorescence and, as the first metallofluorometric indicator, it has found wide use (8) in the EDTA titration of, and more recently the direct fluorometric determi-

nation of calcium in the presence of magnesium.

While there are no reports in the literature dealing with a quinhydrone oxidation-reduction system in equilibrium with metal ions, it was thought that this condition might be realized if the function of chelation (through the introduction of iminodiacetic acid into the molecules) were added to the couple. Such a system might then provide a potentiometric method for the direct determination of metal ion concentrations.

III. 1,4-DIHYDROXYPHENYL-2-METHYLENEIMINODIACETIC ACID (H_2QMIDA)

A. Introduction

1,4-Dihydroxyphenylmethyleneiminodiacetic acid (H_2QMIDA) was first prepared by Pietrzykowski (30) at Iowa State University. The material was evidently not pure. Because of the difficulty encountered in working with the compound, Pietrzykowski did little beyond measuring a few physical constants. The first efforts in the present work were directed toward perfecting the synthesis and purification of the material (5).

The problems presented in the synthesis and purification of H_2QMIDA arise from the instability of the free acid at high pH and at elevated temperature. Purification yielded a product for which the equivalent weights as determined by neutralization and by oxidation differed by only about 1 per cent. Because further purification could not be effected, the material was used in a study of the physical and chemical properties. The infrared, ultraviolet, and PMR absorption spectra were obtained, and the behavior on titration with alkali, alone and in the presence of calcium and magnesium, was investigated (5).

In the work being described in this thesis, further study was made of H_2QMIDA, particularly the conversion of it to 1,4-quinone-2-methylene-iminodiacetic acid (QMIDA) and a study of the QMIDA-H_2QMIDA system in the absence and presence of metal ions.

H_2QMIDA proved to be fluorescent and the fluorescence as affected by the presence of calcium was studied (Section B. 1).

Oxidation of H_2QMIDA to QMIDA by controlled anode potential was undertaken (Section B. 2). Such a process had already been reported by

Santhanam and Krishnan (35) for the quinone-hydroquinone system. Several different anodes were used.

Really successful oxidation, however, was obtained only by using chemical oxidizing agents, a number of which were tried.

B. Experimental Work

1. Fluorescence of H_2QMIDA with calcium and magnesium

A stock solution of H_2QMIDA, 3.00×10^{-3} M in concentration, in 0.1 M potassium chloride was prepared. Solutions of calcium and magnesium were prepared by dissolving 2.205 g. of calcium chloride dihydrate and 3.050 g. of magnesium chloride hexahydrate in 0.1 M potassium chloride and diluting to exactly 250 ml. with 0.1 M potassium chloride. The resulting solutions were 0.0600 M in metal ion. All buffer solutions were 0.1 M in the respective buffer as well as 0.1 M in potassium chloride. The buffer systems used were: pH 1-2.8, potassium chloride-hydrochloric acid; pH 2.8-7.0 citric acid-potassium hydroxide; 7.0-12.0 boric acid-potassium hydroxide; pH 12-13 potassium chloride-potsssium hydroxide. None exhibited any fluorescence in the region studied. All solutions of pH 7 or greater were deaerated with nitrogen and measured immediately after the buffer was added.

The solutions were prepared as follows: to 10.00 ml. of the stock H_2QMIDA solution in a 25-ml. volumetric flask was added 5.00 ml. of the desired 0.600 M metal solution and enough buffer of the appropriate pH to give a volume of exactly 25 ml. The resulting solutions were 1.20×10^{-3} M in H_2QMIDA and the ones with metal ions added had a tenfold excess of

the metal.

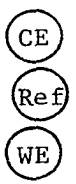
The fluorescence was measured using an Aminco-Bowman spectrophotofluorometer. Both frontal (reflectance) and right angle fluorescence measurements were obtained for comparison. "Blank" runs were made using the respective buffer and metal solutions without H_2QMIDA. Both excitation and emission spectra were obtained. The emission spectrum was obtained using light of 292 nm. for excitation and the spectrum was obtained over the region 250 to 400 nm. The fluorescence of H_2QMIDA from pH 1 to 13 with and without calcium and magnesium present is shown in Figure 3.

2. Electrochemical oxidation of H_2QMIDA

a. Apparatus and solutions A three-electrode polarographic unit constructed from operational amplifiers was used for the rapid scan polarography (cyclic voltametry) of H_2QMIDA. The construction of the circuit and mercury-pool electrolysis cell used are shown in Figure 1. In this circuit a standard fiber-tip calomel reference electrode was used to measure the potential of the working electrode directly at the surface. In this way the voltage error arising from the cell resistance, inherent in a normal polarographic circuit, is avoided. Because of the high input resistance of the operational amplifier circuit, negligible current flowed through the reference electrode. A counter electrode, consisting of a spiral of platinum wire separated from the main solution by a glass frit, was used.

A Leeds and Northrup #62200 Type E Electrochemograph was also used in

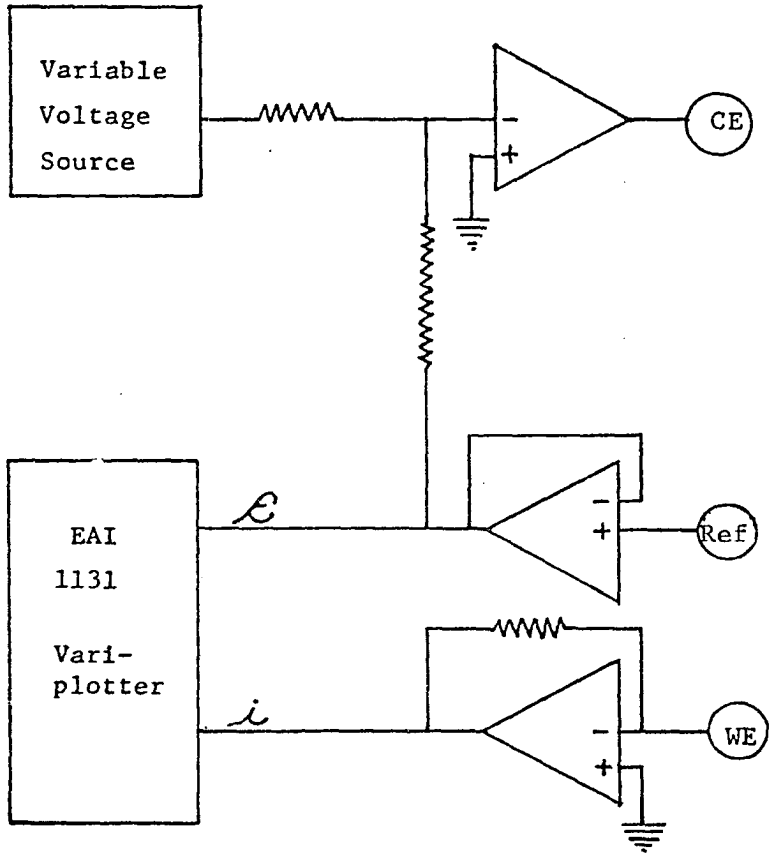
Figure 1. A three-electrode polarographic unit operational amplifier circuitry and a mercury-pool electrode



Counter electrode

Reference electrode

Working electrode


Variable
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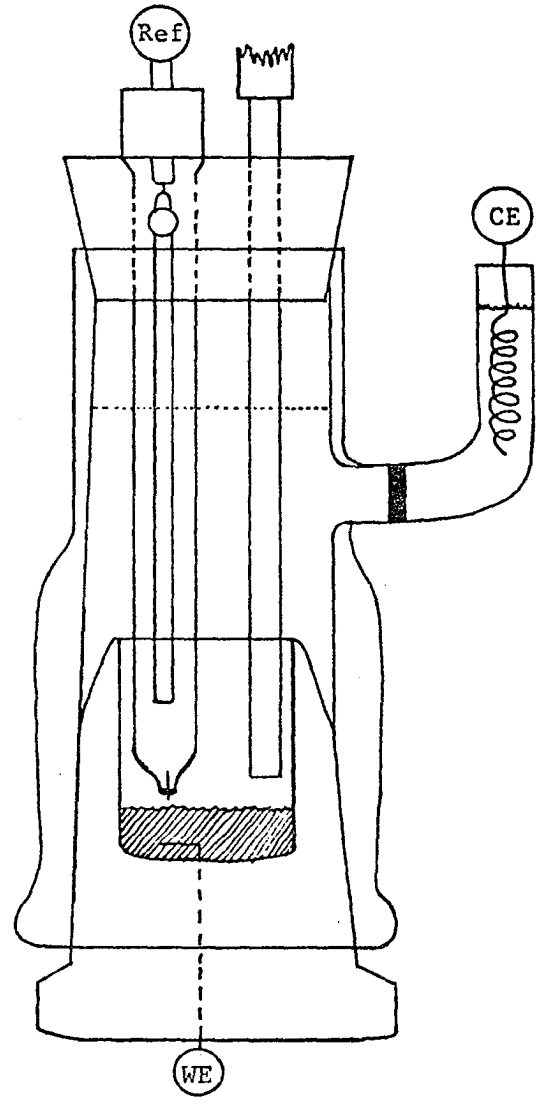
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later experiments. The electrolysis cell used was a Sargent #29392 two-piece polarographic vessel. This cell is provided with a stopcock at the bottom and a removable calomel reference cell connected by a 19/38 standard-taper glass joint with a porous glass frit, Figure 2. An additional side-arm tube was added near the top of the polarographic cell so that nitrogen could be passed over the solution after it had been deaerated.

Several types of working anodes were tried in the course of the study. A standard dropping mercury electrode (DME) was first used. This electrode was constructed in the normal manner using triply distilled mercury.

Next, a mercury pool also shown in Figure 1 was used to provide a higher sensitivity at low concentrations and sufficient capacity for small-scale preparative work. The nitrogen inlet tube was adjustable so that nitrogen could be passed over the solution, or if stirring was desired, bubbled through the mercury or the solution.

A platinum working electrode was also tried. This was constructed by sealing a piece of platinum wire in a soft glass tube and filling it with mercury to make electrical contact. A gold electrode was constructed similarly. In both electrodes about 1 cm. of wire extended into the solution.

A graphite working electrode was prepared using Ultracarbon 101-U spectroscopy electrode graphite. This was sealed into a glass tube, 9 mm. in diameter, with paraffin (17). The end of the electrode was cleaned by rubbing it against fine sandpaper. Electrical contact was made by filling

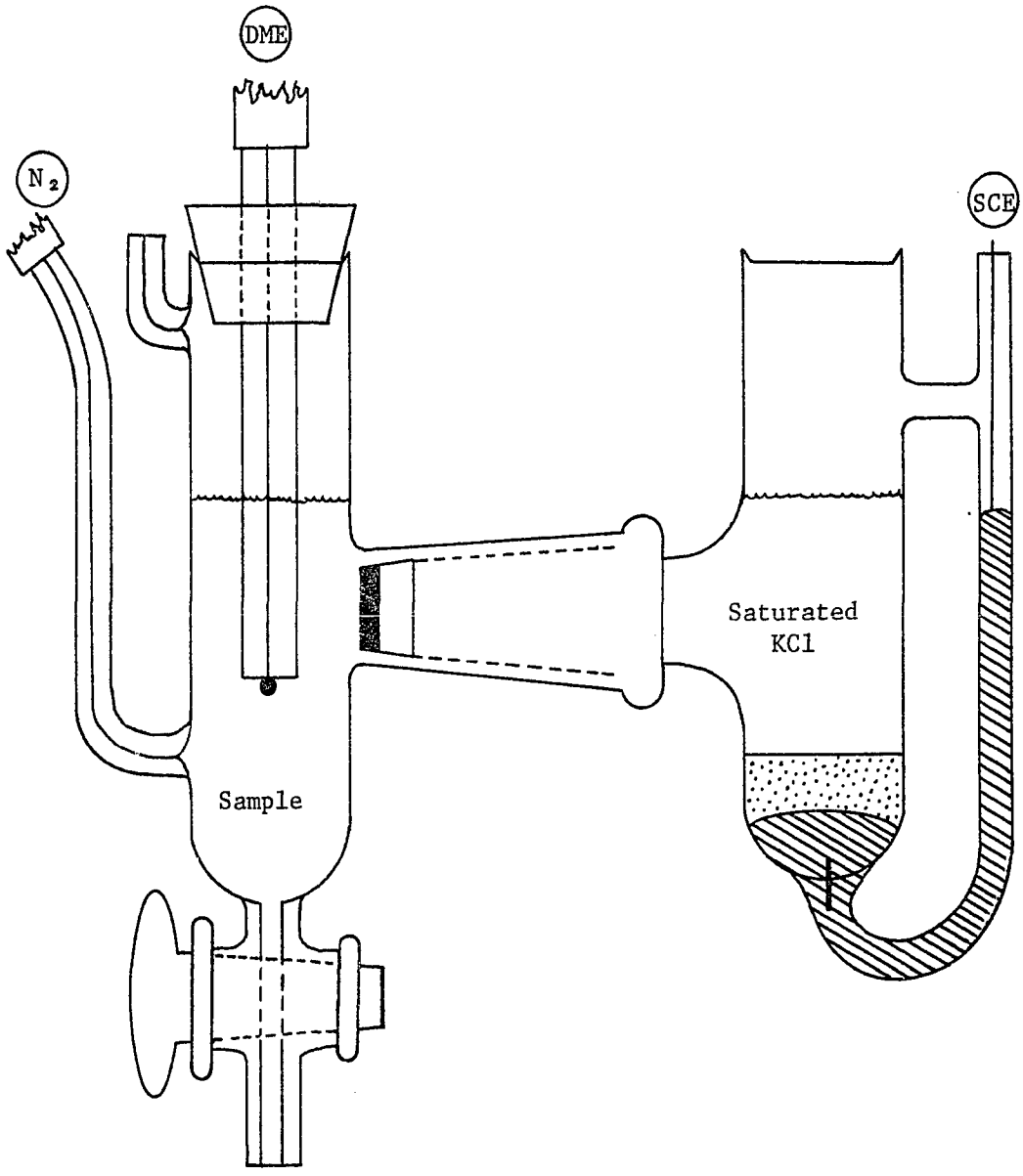


Figure 2. Two-piece, H-type polarographic cell

Mercury

Calomel

the tube with mercury.

Buffer solutions were all 0.1 M and prepared from the respective reagent-grade chemical and deionized water. The pH was determined with a Corning Model 10 pH meter using a Sargent #30070-10 miniature combination electrode that was standardized against Fisher Certified buffers. The accuracy of each lot of the Fisher buffers was checked by comparing them to freshly prepared NBS buffer solutions.

b. Procedure The typical procedure for a voltametric scan of H_2QMIDA is given below. In later work many of the variables in the system were changed one by one, pH, buffers, electrodes, and supporting electrolyte. The changes and the effects obtained are reported in the Results and Discussion section below and only the basic procedure will be given here.

The polarography of H_2QMIDA was investigated in an acetate buffer-supporting electrolyte using the instruments described above. The buffer-supporting electrolyte was 0.1 M and the H_2QMIDA approximately 10^{-3} to 10^{-4} M. The solutions of H_2QMIDA were always freshly prepared unless noted differently. The solutions were deaerated with prepurified tank nitrogen. The voltage scan was normally from -0.5 to +0.6 volts vs. s.c.e. and the 100 microamp current range used. No cell resistance correction was made in the work done with the Leeds and Northrup instrument.

3. Potentiometric titration of H_2QMIDA with oxidizing agents

a. Apparatus and solutions A Corning Model 10 pH Meter was used in these experiments. The electrode system consisted of a #47060 Corning

Platinum Inlay Electrode and a #476010 Sleeve-type Calomel Reference Electrode. A 150 ml. beaker, open to the air, was used as the titration cell. The solutions were stirred with a rotating bar magnet. All solutions were prepared using deionized water.

A 1 N solution of sulfuric acid was prepared by adding 28 ml. of concentrated reagent sulfuric acid per liter of deionized water. Sodium acetate-acetic acid buffer of pH 5.5 was prepared by mixing 0.1 M stock solutions of the respective compounds until the desired pH was attained.

A 10 ml. buret was used for the titrations and the sample size of H_2QMIDA was made so that the end-point should occur when about 7 ml. of 0.1 N titrant was added.

b. Oxidation of H_2QMIDA with potassium dichromate A 0.100 N solution of potassium dichromate was prepared by dissolving 0.475 g. of the reagent salt in 1 N sulfuric acid and diluting to 100 ml. Exactly 0.0897 g. of H_2QMIDA was added to 100 ml. of 1 N sulfuric acid and stirred for 10 minutes before titration. The titration proceeded smoothly, Figure 5, with all the solid dissolving by the time 7 ml. of titrant were added.

A second sample of 0.1 g. of H_2QMIDA was added to 60 ml. of 0.1 M sodium acetate-acetic acid buffer of pH 5.5 and stirred until all the solid material had dissolved. Small crystals of potassium dichromate were slowly added and the potential of the solution was monitored.

c. Oxidation of H_2QMIDA with cerium(IV) A 0.100 N solution of cerium(IV) was prepared by dissolving 6.311 g. of ceric ammonium sulfate dihydrate in 1 N sulfuric acid and diluting to 100 ml. Exactly 0.0897 g.

of H_2QMIDA was added to 60 ml. of 1 N sulfuric acid and stirred for ten minutes before titration. The suspension of the partially dissolved H_2QMIDA was then titrated with 0.100 N cerium(IV). The titration proceeded smoothly until the theoretical end-point region was reached, Figure 6.

A second sample of 0.1 g. of H_2QMIDA was added to 60 ml. of 0.1 M, pH 5.5, sodium acetate-acetic acid buffer and stirred until all of the solid had dissolved. Crystals of ceric ammonium sulphate dihydrate were slowly added to the solution and the potential reading obtained.

d. Oxidation of H_2QMIDA with potassium molybdicyanide Potassium molybdicyanide which is somewhat unstable in aqueous solution was prepared using the procedure of Kratochvil and Diehl (22). Potassium molybdocyanide was oxidized in slightly acidic solution by use of lead dioxide. The excess lead dioxide and lead sulfate formed in the reaction was filtered off and the potassium molybdicyanide filtrate stored in the dark. Anhydrous cobalt sulfate, stored over magnesium perchlorate, was used to standardize the potassium molybdicyanide by potentiometric titration of the molybdenum(V) in ammonium citrate-ammonium hydroxide solution with the 0.100 N cobalt(II) solution.

Exactly 0.417 g. of H_2QMIDA was added to 60 ml. of a 0.1 N solution of sulfuric acid and stirred for ten minutes. The titration with potassium molybdicyanide was then followed potentiometrically.

A second sample, 0.0420 g., of H_2QMIDA was added to 60 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.5, and stirred until all the solid material had dissolved. The H_2QMIDA was titrated as above using the same

0.015 N potassium molybdicyanide solution.

e. Oxidation of H_2QMIDA with periodic acid A 0.100 N solution of periodic acid (assuming a two-electron reduction) was prepared by dissolving 1.1398 g. of the reagent acid in deionized water and diluting to 100 ml. Exactly 0.0897 g. of H_2QMIDA was added to 60 ml. of 1 N sulfuric acid and stirred ten minutes before titration. The suspension of the partially dissolved H_2QMIDA was then titrated with the 0.100 N periodic acid solution. All of the solid H_2QMIDA was apparently dissolved at the point at which 4.00 ml. had been added.

A second sample of H_2QMIDA, 0.0899 g., was added to 60 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.5, and stirred until all of the solid material had dissolved. The H_2QMIDA was titrated as above with the same 0.100 N periodic acid solution.

f. Oxidation of H_2QMIDA with potassium permanganate A 0.020 M solution of potassium permanganate was prepared by dissolving 0.3252 g. of the reagent salt in deionized water and diluting to 100 ml. For a five-electron reduction the permanganate solution would then be 0.100 N; for a three electron reduction, 0.060 N.

Exactly 0.0897 g. of H_2QMIDA was added to 60 ml. of 0.1 M boric acid-potassium hydroxide buffer, pH 8.1. Nitrogen was bubbled through the solution to remove atmospheric oxygen and the mixture was stirred until all the solid had dissolved. A small amount of 0.1 M potassium hydroxide was added after the acid had dissolved to raise the pH of the solution back to 8.0. The solution was then titrated with potassium

permanganate in the absence of air, the reaction being followed potentiometrically.

A second sample of H_2QMIDA, weighing 0.0898 g., was dissolved in 60 ml. of 0.1 M acetic acid-sodium acetate buffer, pH 5.5, and titrated in the same manner as above, except without deaeration.

A third sample of H_2QMIDA, weighing 0.0896 g., was added to 60 ml. of 1 N sulfuric acid solution and stirred for ten minutes. The solution was then titrated as above with the same 0.020 M potassium permanganate. The remaining solid H_2QMIDA dissolved slowly as the titration proceeded.

C. Results and Discussion

1. Fluorescence of H_2QMIDA with calcium and magnesium

The fluorescence spectra of 1.2×10^{-3} M H_2QMIDA, and H_2QMIDA in the presence of a tenfold excess of calcium and magnesium were obtained at pH values from 1 to 13, Figure 3. The pH of the respective measurements was chosen from the neutralization titration curves determined earlier (5, p. 61). In this way fewer solutions were needed and the pH could be selected at which each of the various molecular species, H_4A, H_3A^-, H_2A^{-2}, HA^{-3}, A^{-4}, was at maximum concentration.

The absorption maximum of H_2QMIDA in the ultraviolet spectrum was found to be at 297 nm. However, it was found that if the net fluorescence (total fluorescence minus the "blank") was considered the optimum excitation wavelength was 292 nm. This resulted from a broad Rayleigh scatter band in the spectrum of the blank. The decrease in

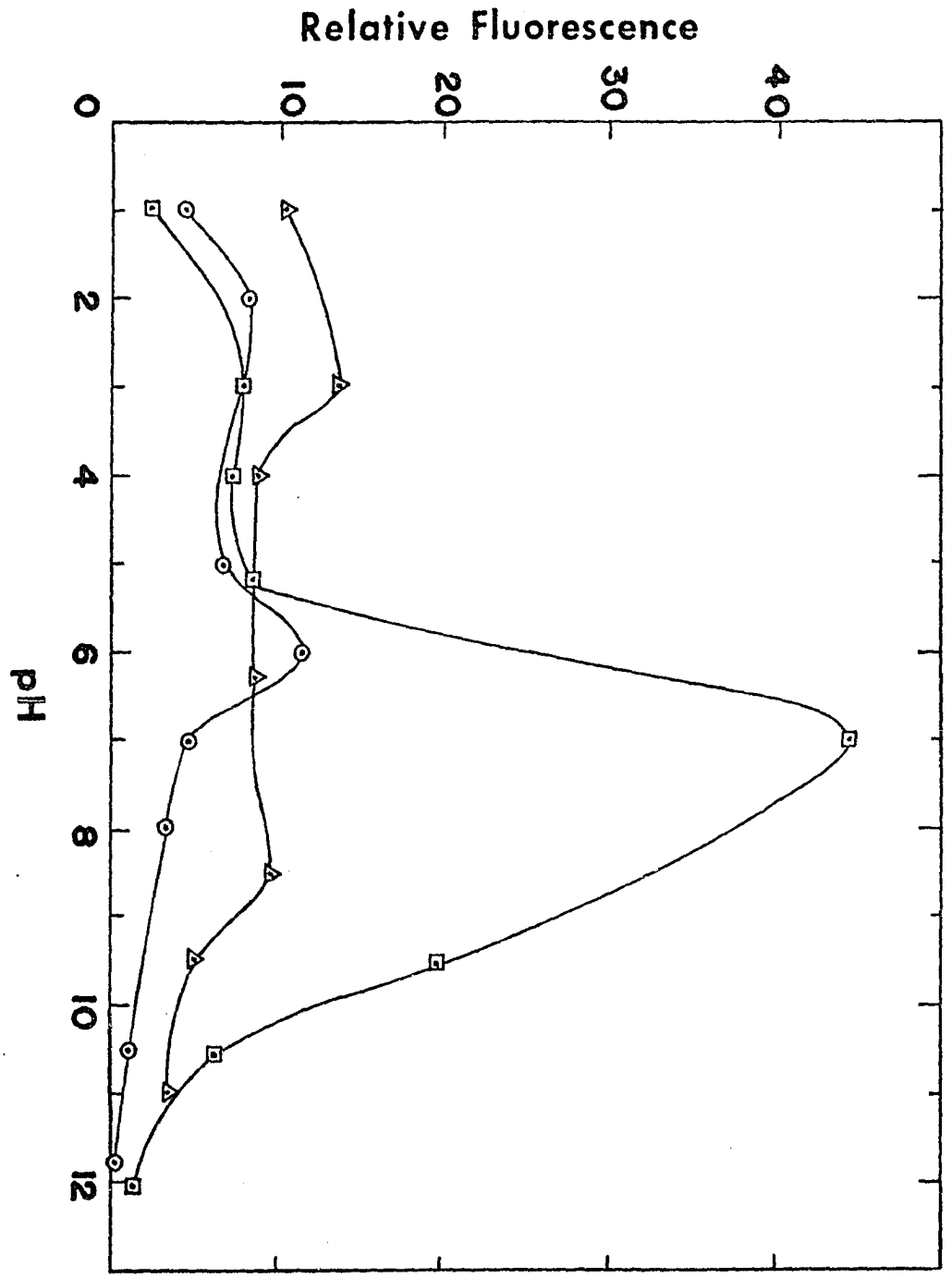
Figure 3. Relative fluorescence of H_2QMIDA, Ca-H_2QMIDA and Mg-H_2QMIDA as a function of pH

λex 292 nm.; λem 352 nm.

○ H_2QMIDA alone

□ + Ca^{++} (tenfold excess)

△ + Mg^{++} (tenfold excess)


Relative Fluorescence
0
10
20
30
40
pH
2
4
6
8
10
12

the excitation wavelength did not appreciably decrease or shift the maximum in the fluorescence emission spectrum.

Only one band, maximum at 352 nm., was present in the fluorescence emission spectrum of free H_2QMIDA and H_2QMIDA in the presence of calcium and magnesium, Figure 3.

As will be seen from the spectra shown in Figure 3, free H_2QMIDA and the nondissociated Mg-H_2QMIDA derivative exhibit a rather low fluorescence, the intensity being little changed with pH. The fluorescence of the Ca-H_2QMIDA compound at pH 7 is eightfold greater. At pH 7 a neutral Ca-H_2QMIDA species is present. Between pH 7 and 10 this species is changed to the Ca-H_2QMIDA$^-$ ion by the removal of the third replaceable hydrogen atom of H_2QMIDA, the intensity of the fluorescence decreasing during the conversion.

Additional work was done on the fluorescence of Ca-H_2QMIDA to optimize resolution and sensitivity. Frontal fluorescence measurements were found to produce less light scattering and were best suited to the relatively high concentration (1.2×10^{-3} M) of H_2QMIDA used. Right angle fluorescence was better at lower concentrations. Several filters were used in an effort to decrease noise and scatter, but with little success. The Aminco-Bowman spectrophotofluorometer used is a single beam, uncorrected instrument, that is, the intensity of the light delivered to the cell containing the solution varies with wavelength in accord with the variation in output of the xenon lamp used. Further work in this area would not be profitable unless an instrument with a constant light flux is used and "corrected" spectra obtained.

2. Electrochemical oxidation of H_2QMIDA

a. Preliminary study Three solutions of 5×10^{-3} M H_2QMIDA at pH 2, 6 and 10 were prepared and deaerated. A polarogram of each was obtained from -0.5 to +0.3 volts vs. s.c.e. Using the same dropping mercury electrode, a quick (about 1 second) cyclic scan over the same voltage range was made on a hanging mercury drop and the current observed.

Only one oxidation wave was observed in the three polarograms. The wave shifted to a lower potential as the pH was increased, the half wave potentials being -0.01, -0.18 and -0.33 volts vs. s.c.e. at pH 2, 6 and 10, respectively. The cyclic voltametry indicated that at pH 2, one product was formed in the oxidation and that this product was reduced on the reverse scan. At pH 6 the cyclic voltamogram indicated again that one oxidation product was formed and then reduced on the reverse scan, this time much more reversibility. At pH 10 there were three products formed in the oxidation process, only one of which was stable or reversible enough to be reduced on the reverse scan.

The direction of the shift of the half wave potential with pH was that expected for H_2QMIDA but much less than the 60 mv./pH observed with the quinhydrone system. The value of the half wave potential observed was also much lower than expected. At pH 6 the half wave potential was -0.8 volts vs. s.c.e. Pietrzykowski (30, p. 26) reported +0.13 volts vs. s.c.e. for the half wave potential of H_2QMIDA at pH 6, and the formal potential of the quinhydrone system (on platinum) is reported as +0.10 volts vs. s.c.e. (19, p. 1725) at pH 6. The formation of several unstable oxidation products in alkaline solution was also consistent with

the behavior expected for that of a substituted hydroquinone. The addition of calcium, magnesium and aluminum to the three solutions above resulted in no change in the oxidation potentials.

Although the above work still seemed somewhat promising, later work proved that the oxidation observed was not the desired one, and in fact neither was the one observed by Pietrzykowski. Further purification of the H_2QMIDA resulted in the disappearance of the observed oxidation wave, and Pietrzykowski does not report any purification in his work with the material (30). The most probable explanation of the wave obtained is that it was the oxidation of a readily formed decomposition product of the H_2QMIDA or some impurity produced by a side reaction in the synthesis. This seems all the more probable when it is noted that the diffusion current reported by Pietrzykowski for the oxidation of "H_2QMIDA" is more than a factor of ten lower than the expected value (30, p.28).

It must then be concluded that waves observed in the above work with a DME were not due to the desired two-electron oxidation of H_2QMIDA to QMIDA.

b. Mercury-pool and DME As was discussed in the preceding section, no oxidation waves of very pure H_2QMIDA were found with mercury. No anodic current (other than the residual current) was observed until oxidation of the mercury began. A three-electrode polarograph and mercury-pool electrode were constructed for a more exact study of the behavior of H_2QMIDA toward a mercury anode.

Chloride-free solutions of buffer and H_2QMIDA were prepared so that

the maxiuum positive voltage could be obtained before mercury oxidation started. A cyclic scan of the entire range of voltages from hydrogen evolution to mercury oxidation was made using a fresh solution of H_2QMIDA in acetate buffer of pH 5 over the mercury-pool (Figure 2), using the three-electrode polarograph assembly. No oxidation or reduction occurred between these regions. The acetate was replaced with citrate buffer and the scan repeated--no reaction. To assure that a fast decomposition was not deactivating the species, solid H_2QMIDA was added to the deaerated buffer and scanned as it dissolved to insure that at least some fresh H_2QMIDA would be present at the time of the scan. No oxidation or reduction was observed. The ultraviolet spectrum was found to be normal for H_2QMIDA at this concentration.

The above work was then repeated on the Leeds and Northrup instrument with a DME, in hope that if the lack of oxidation was caused by some sort of surface poisoning of the mercury, that the continuously renewed surface of the DME would allow oxidation to occur. Again, after trying several different buffers (acetate, borate, citrate, phthlate) and pH's, no oxidation was observed except that of mercury at the upper limit. A scan of H_2QMIDA was made without deaerating the solution and an oxygen reduction wave was observed. Solid H_2QMIDA was dissolved without buffer present by slow addition of potassium hydroxide until the pH was 5. A scan of this unbuffered solution yielded no oxidation wave. Potassium nitrate was added as supporting electrolyte and no oxidation was obtained.

In the event that the H_2QMIDA might have undergone some change while being stored as a solid, a new batch of H_2QMIDA was prepared and a sample

scanned immediately--no oxidation. The ultraviolet spectrum of this solution was normal, having the single strong absorption found at 297 nm. produced by H_2QMIDA; the molar absorptivity was also unchanged, an indication that there were no observable changes in environment affecting the hydroquinone ring, which was the group that would undergo oxidation.

Finally, a series of runs were made with all the variations described above, but with all glassware first being boiled in perchloric acid and all solutions made up from triply-distilled conductivity water. A new batch of mercury was also obtained for the DME. In this way if any type of surfactant or contamination were in the water used or on the glassware it would be eliminated.

At pH 10 using borate buffer a very irreversible oxidation wave was obtained that started at -0.15 volts and increased very slowly until the mercury oxidation region at about +0.2 volts vs. s.c.e. However, it was found in earlier work that any reactions, such as oxidation, at pH 10 produce only decomposition. All other work with the described "ultrapure" conditions yielded the same result--no oxidation.

c. Platinum electrode A series of scans from -0.5 to +1.0 volts vs. s.c.e. were made on solutions of H_2QMIDA using a platinum wire electrode and the Leeds and Northrup polarograph. The scan was then reversed and run from +1.0 to -0.5 volts. Concentrations of 3×10^{-3} and 3×10^{-4} M H_2QMIDA were used at pH 5 and 10. Acetate and borate buffer-supporting electrolytes were 0.1 M in concentration. "Blanks were obtained of the buffer solutions in each experiment before the H_2QMIDA was added. Stirring was provided by the nitrogen used for deaeration.

It was evident that no oxidation of H_2QMIDA occurred at the platinum electrode. Several small, nonreproducible waves were observed; these were probably side reactions caused by the oxidation and reduction of platinum.

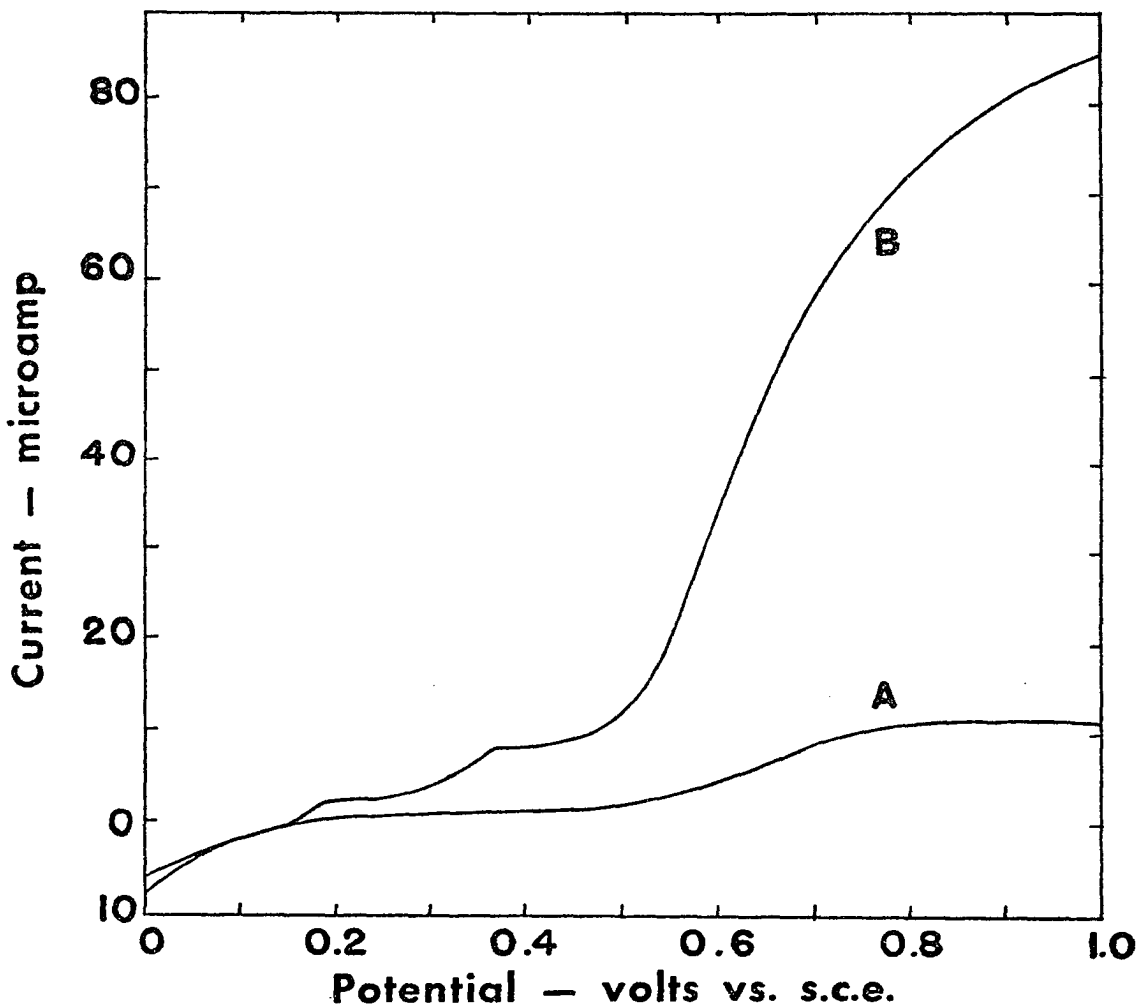
In later work, the oxidation of H_2QMIDA was again attempted using a platinum electrode but using a buffer of pH 4 of 0.1 M potassium acid phthalate. Using the general procedure described above a scan of 1.0 volts vs. s.c.e. was made on the buffer and then repeated after H_2QMIDA was added, Figure 4. In the scan of the buffer alone, only the wave for the oxidation of the platinum surface was observed, the wave falling between 0.4 to 0.8 volts. After H_2QMIDA was added a greater anodic current was noted. The small wave at 0.2 volts could possibly be due to the oxidation of a trace of H_2QMIDA because the formal potential for H_2QMIDA at this pH is about 0.24 volts vs. s.c.e. In the wave starting at 0.4 volts the oxidation of H_2QMIDA, as is the oxidation of many other organic compounds, was catalytically enhanced by the formation of platinum oxide on the anode. Unfortunately, the oxidation was still very irreversible, ranging from 0.4 to more than 1 volt vs. s.c.e. Such irreversibility usually makes direct potentiometry involving the system very difficult and unreliable (cf. Section VII B. 3. b.).

d. Gold electrode A gold wire electrode was prepared in the same manner as was the platinum electrode. All the work of the preceding section was repeated with the gold electrode substituted for platinum. The blanks again showed small anomalous waves but in the scans of the solutions containing H_2QMIDA no waves were observed that could be

Figure 4. Voltamogram of H_2QMIDA using a platinum-s.c.e. electrode system

A. Scan of 0.1 M buffer-supporting electrolyte of potassium acid phthalate; pH 4

B. Scan of same solution after H_2QMIDA was added


80
60
40
20
0
10
Current — microamp
B
A
0
0.2
0.4
0.6
0.8
1.0
Potential — volts vs. s.c.e.

interpreted as the oxidation of H_2QMIDA.

e. Wax-impregnated graphite electrode Three solutions of H_2QMIDA ranging from 3×10^{-3} to 3×10^{-5} M in concentration were prepared in pH 5, 0.1 M, acetate buffer-supporting electrolyte. They were deaerated and scanned from -0.5 to +0.5 volts using a wax-impregnated graphite electrode and the Leeds and Northrup polarograph. Even with the wax covering all but the end of the electrode, the surface of the graphite was large enough to cause very high charging currents. Vigorous stirring, increasing the supporting electrolyte concentration, and use of the lowest concentration of H_2QMIDA did not solve the problem and the current always became excessively large between -0.2 and +0.1 volts during a positive scan. The work was abandoned as offering no hope.

f. Conclusions An irreversible oxidation wave was observed for H_2QMIDA at a platinum electrode but the procedure offered little hope of successful oxidation on a large scale. Because of the irreversibility observed in the current-voltage curves of H_2QMIDA it was concluded that electrochemical oxidation is not a feasible method for the preparation of QMIDA.

3. Potentiometric titration of H_2QMIDA with oxidizing agents

a. Oxidation of H_2QMIDA with potassium dichromate The oxidation of H_2QMIDA with potassium dichromate was successful in 1 N sulfuric acid. A stoichiometric, two-electron oxidation was obtained yielding a stable product, presumably QMIDA. The details of the titra-

tion are given below and the titration curve is shown in Figure 5.

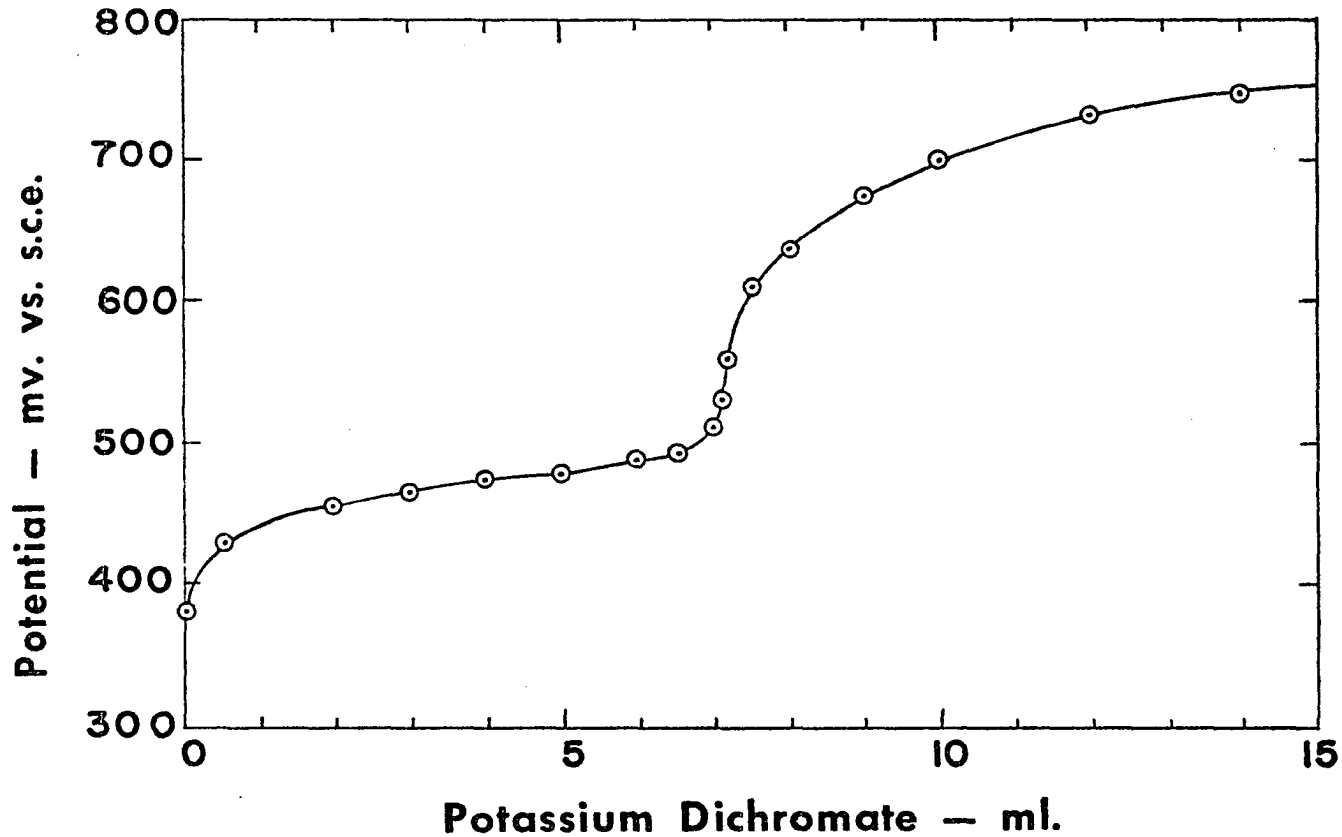
Initially the solution was colorless with some suspended H_2QMIDA. After each addition of titrant the solution became yellow-orange in color and then a clear green (chromium(III) ion). Potential readings stabilized quickly, Figure 5. After the end-point, the unreduced dichromate produced a darkening of the green color. Any color attributable to the desired QMIDA was masked by this dark green color. After two weeks the titrated solution had become slightly cloudy and was dark yellow-green in color. This small change in color was an indication that the oxidation product of H_2QMIDA is fairly stable in the presence of excess potassium dichromate.

The stability of the oxidation product in the presence of excess dichromate results from the small difference between the formal potentials of the QMIDA-H_2QMIDA and dichromate systems in 1 N sulfuric acid. It can be seen from Figure 5 that the formal potential of the dichromate 0.74 volts vs. s.c.e. Potassium dichromate is apparently just strong enough to effect the two-electron oxidation of H_2QMIDA to QMIDA but causes no further oxidation. Unfortunately, the very low solubility of H_2QMIDA in this strongly acidic solution prevents any preparative-scale work but an even more serious problem would be the removal of the chromic ions introduced into the solution.

At pH 5.5 no oxidation of H_2QMIDA occurred on the addition of dichromate. The initial, clear, colorless solution of H_2QMIDA took on the yellow color of the dichromate ion as the crystals of the potassium dichromate dissolved. The potential increased slowly from 140 mv. to

Figure 5. Titration of H_2QMIDA with potassium dichromate in 1 N sulfuric acid

0.0897 g. of H_2QMIDA; 0.100 N potassium dichromate


800
700
600
500
400
300
0
5
10
15
Potential — mv. vs. s.c.e.
Potassium Dichromate — ml.

about 200 mv. and then remained constant as additional potassium dichromate was added. Both the color of the solution and the potential readings were indications that no oxidation had occurred. Twenty-four hours later the potential reading had decreased to 170 mv. and the solution was a clear, dark red.

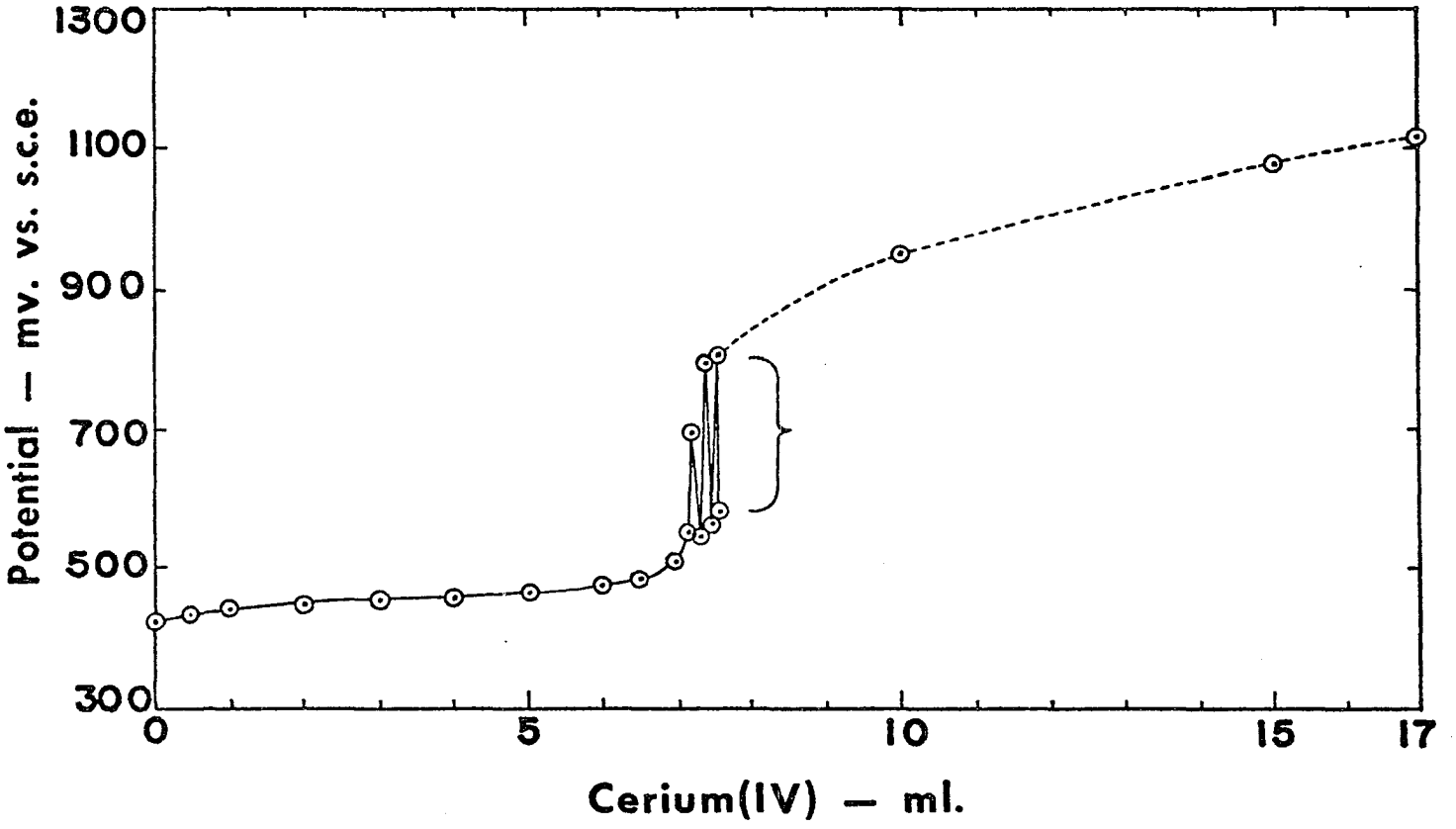
Although the formal potentials of both systems decrease with increasing pH, the larger pH dependance of the dichromate couple makes potassium dichromate too weak an oxidant at pH 5.5 to effect the oxidation of H_2QMIDA.

b. Oxidation of H_2QMIDA with cerium(IV) The titration of H_2QMIDA in 1 N sulfuric acid with cerium(IV) proceeded smoothly until the end-point was reached, Figure 6. At 70 per cent titrated about 99 per cent of the sample had dissolved. The solution was completely clear at the 90 per cent titrated point. As the end-point was passed the potential readings became unstable and decreased rather quickly after each addition of cerium(IV). Finally, as the 200 per cent point was approached, readings were again fairly stable, as a result of the large excess of titrant now present. After standing for twenty-four hours the potential had dropped slightly from 1116 mv. to 1090 mv. Two weeks later the originally yellow-orange solution had darkened to a clear amber solution.

Apparently in this experiment, the initial oxidation product in the titration was oxidized further by the first excess of cerium(IV). The secondary oxidation most likely was further oxidation of the quinone to open the ring. Ring-opening (possibly caused by chelation of

Figure 6. Titration of H_2QMIDA with cerium(IV) in 1 N sulfuric acid

0.0897 g. of H_2QMIDA; 0.100 N cerium(IV)


1300
1100
900
700
500
300
Potential — mv. vs. s.c.e.
0
5
10
15
17
Cerium(IV) — ml.

cerium(IV), cf. Section VII) would also account for the lack of the usual dark brown decomposition product often encountered in the oxidation of H_2QMIDA. Such decomposition of substituted quinones usually produces polymeric humic acids (15; 16; 48), which have a characteristic brown color but which retain the aromatic quinone ring.

The oxidation of the H_2QMIDA with cerium(IV) at pH 5.5 was also unsuccessful. The initial potential of 140 mv. increased slowly as cerium(IV) was added and finally leveled off at 360 mv. After a small amount of cerium(IV) was added, a violet precipitate formed. Twenty-four hours later the potential had dropped to 240 mv. and the solution was a very dark brown and the precipitate was still present. There was no evidence that the desired oxidation product could be obtained from this solution.

c. Oxidation of H_2QMIDA with potassium molybdicyanide Potassium molybdicyanide is a moderately strong oxidizing agent prepared by the oxidation of the molybdocyanide in slightly acidic solution by lead dioxide. The reduction potential of the couple, molybdenum(V)-molybdenum(IV), was reported as 0.73 volts vs. s.c.e., and is not affected by changes in pH (22). The molybdicyanide is somewhat unstable in aqueous solution and was standardized at the time it was used against a standard solution of cobalt(II) sulfate as described in Section III B. 3. d.

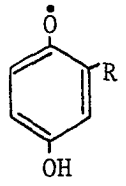
Two titrations of H_2QMIDA were made with the molybdenum(V), one in 0.1 M sulfuric acid and a second in 0.1 M sodium acetate-acetic acid buffer of pH 5.5. No oxidation occurred in 0.1 M sulfuric acid but the H_2QMIDA was successfully oxidized to QMIDA in the solution of pH 5.5.

The standardization of the molybdenum(V) with cobalt(II) gave 0.017 N for the concentration of molybdenum(V). This was appreciably below the concentration of 0.05 N reported by earlier workers (22). As a double check of the standard cobalt solution some of the cobalt sulfate was weighed out and the purity checked by electrodeposition of the metal (45, p. 614). The purity of the "anhydrous" cobalt sulfate as found by electrodeposition was 90.1 per cent. This would make the actual concentration of the molybdenum(V) about 0.015 N, still much lower than expected. It was later found that the problem was caused by the low purity of the potassium molybdocyanide starting material. Omission of the final dilution called for in the procedure used (22) resulted in consistent attainment of the desired concentration, 0.05 M (cf. Section VI), molybdicyanide.

No oxidation of H_2QMIDA was obtained in the titration by molybdenum(V) in 0.1 M sulfuric acid. As the H_2QMIDA was titrated with the 0.015 N molybdenum(V) in the 0.1 M sulfuric acid a slow increase from the initial potential of 423 mv. vs. s.c.e. was noted, but no inflection occurred. After 30 ml. of molybdenum(V) was added the potential had increased uniformly to 501 mv. There was no color change in the yellow titrant solution and some solid H_2QMIDA was still present in the titration cell, indicating that no reaction had occurred.

The titration of H_2QMIDA in buffer of pH 5.5 resulted in a one-electron oxidation of H_2QMIDA. Later work with more concentrated titrant produced the expected two-electron oxidation. The initial potential of

the solution of H_2QMIDA at pH 5.5 was 199 mv. This decrease, compared to 423 mv. above, was representative of the expected decrease in reduction potential with an increase in pH. Potential readings were stable except in the end-point region (11 ± 1 ml.). In this region there was a sharp increase in potential as the titrant was added and then a slow decrease to the recorded value, Figure 7. The two hundred millivolt decrease in the reduction potential made oxidation by the molybdenum(V) possible at pH 5.5. However, the end-point at 11 ml. is evidence that the oxidation involved only one electron. The calculated equivalent weight for a normal two-electron oxidation of H_2QMIDA is 127.6. The approximate equivalent weight calculated for this titration was 254 (theoretical for a one-electron oxidation, 255.2). The formal potentials of the two couples were 0.434 and 0.722 volts vs. N.H.E. for the H_2QMIDA and potassium molybdicyanide, respectively. This small difference in potential combined with other chemical factors was apparently just enough to oxidize the H_2QMIDA to the semiquinone radical:

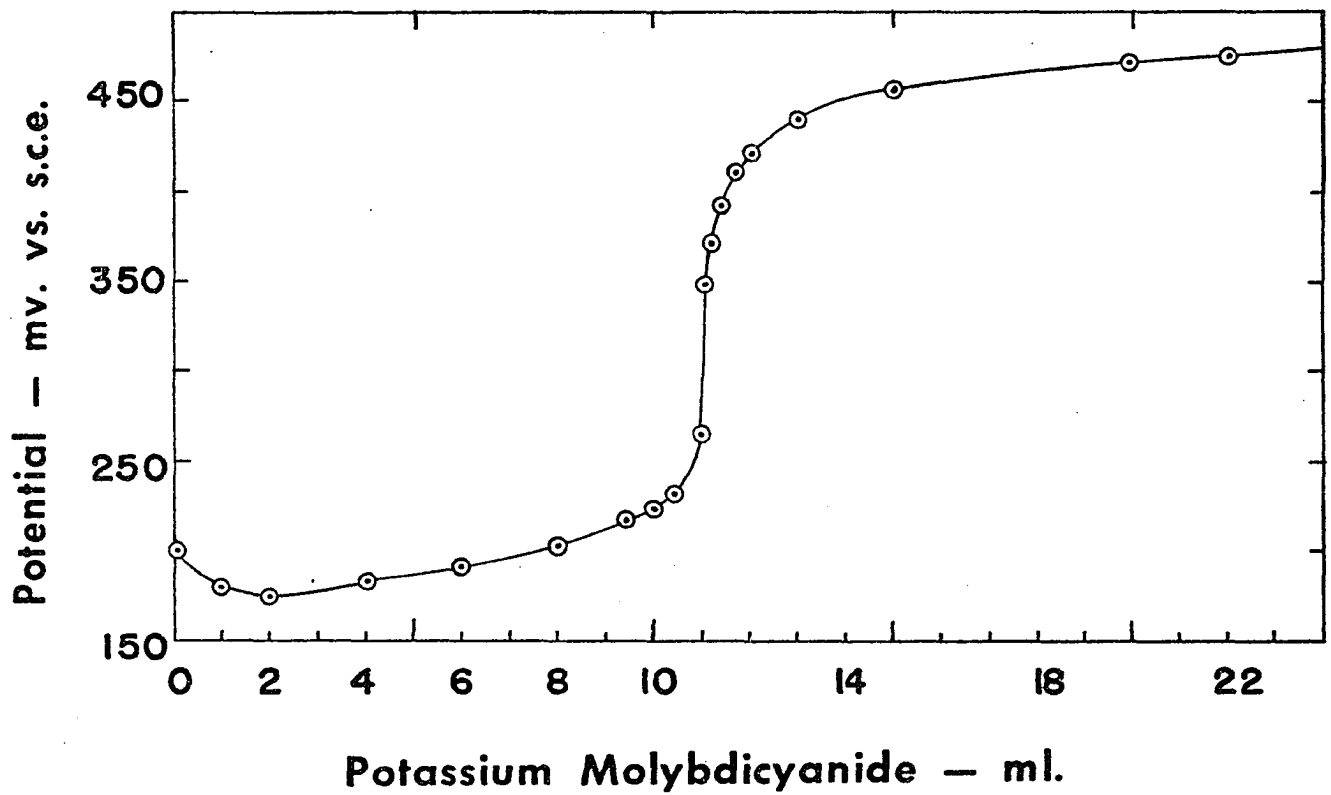


Such products are well known (29; 34; 44), but quite often only as intermediates.

Using higher concentrations of molybdicyanide, 0.05 to 0.1 N a two-electron oxidation of H_2QMIDA was observed. Except for the end-point, the titration curve for this oxidation did not differ significantly from

Figure 7. Titration of H_2QMIDA with potassium molybdicyanide in 0.1 N sulfuric acid

0.0417 H_2QMIDA; 0.015 N $K_3Mo(CN)_8$


Potential — mv. vs. s.c.e.
450
350
250
150
0
2
4
6
8
10
14
18
22
Potassium Molybdicyanide — ml.

that of the one-electron oxidation; it is shown in conjunction with the work of Section VI, Figure 13.

Potassium molybdicyanide is thus quite close to the chemical oxidant desired for the preparation of QMIDA. It is apparently not powerful enough to oxidize H_2QMIDA in strongly acid solution in which the reduction potential of the H_2QMIDA is high, but the oxidation proceeds well in neutral solution. Fortunately, H_2QMIDA (and QMIDA) is quite soluble in neutral solution. Secondly, the metal ion is securely chelated by the cyanide groups and does not form a non-dissociated species with H_2QMIDA or with QMIDA.

Two major drawbacks prevent the use of potassium molybdicyanide in preparative work of QMIDA. The large volumes of potassium molybdicyanide solution needed for the oxidation of even a reasonable amount of H_2QMIDA virtually prevent recovery of any QMIDA. Also the strong absorption in the ultraviolet of the molybdocyanide ion completely obscures the 250 nm. region in which QMIDA absorbs and thus makes it impossible to confirm the presence of QMIDA as the specific product of the oxidation.

Potassium molybdicyanide appears to be more useful for the study of H_2QMIDA in the presence of metals than for a chemical method for the preparation of QMIDA.

d. Oxidation of H_2QMIDA with periodic acid Although periodic acid has been widely used for the systematic degradation of organic hydroxy compounds, it has been shown by Feifer et al. (12) that para-hydroquinone and derivatives of hydroquinones are oxidized to the respective quinones quite smoothly without breakage of bonds or ring-opening.

This anomalous oxidation by periodic acid proved to be the perfect non-metallic, chemical method for the preparation of the QMIDA species.

H_2QMIDA was titrated with periodic acid in 1 N sulfuric acid and in sodium acetate-acetic acid buffer of pH 5.5. The titration in 1 N sulfuric acid produced a one-electron oxidation of the H_2QMIDA. The work at pH 5.5, however, yielded a smooth two-electron oxidation of H_2QMIDA to QMIDA.

In the 1 N solution of sulfuric acid the potential increased sharply from the initial reading of 419 mv. to 500 mv. after 0.20 ml. of titrant was added. From this point to the predicted end-point region there was an increase in potential after each addition of titrant and then a slow drift in the potential on standing. From the 0.20 ml. to 3.00 ml. mark the potential readings decreased at a rate of about 2 mv./min. occurring at 4.00 ml. At 4.00 ml. the suspended H_2QMIDA had completely dissolved. Above the 4.50 ml. point the potential readings were stable and remained in the low eight-hundreds.

After 0.50 ml. of titrant had been added the originally clear, colorless solution developed a brown tinge. This faint brown slowly changed to a clear yellow throughout the remainder of the titration.

The theoretical end-point (assuming a two-electron oxidation and a two-electron reduction) was at 7 ml. The estimated end-point from the data for this titration was around 4 ml. indicating a probable one-electron oxidation of the H_2QMIDA in 1 N sulfuric acid, or a possible (but unlikely) three or four electron reduction of the periodic acid. After standing for one week with the excess periodic acid no decompo-

sition was observed.

In the acetate buffer of pH 5.5 the initial potential of the H_2QMIDA was more negative and oxidation was effected. After the first 0.50 ml. the potential stayed around 150 mv. increasing sharply after each addition of oxidant and drifting back to approximately the same value after several minutes. At the 6.00 ml. point the potential was about 300 mv. and stable. The end-point occurred at approximately 7 ml. and was marked by the absence of drift in the potential reading, 410 mv. Beyond the 7 ml. mark a slow increase in potential occurs after each addition of titrant. At the 200 per cent point the potential was 690 mv. vs. s.c.e. The solution remained clear throughout the titration with a light-orange color slowly developing as the reaction proceeded.

Although the oxidation of H_2QMIDA by periodic acid appears to be rather slow at pH 5.5, the reaction occurs as a two-electron process that yields an end-point at the calculated amount of periodate. The product, presumably QMIDA, is fairly stable in the presence of excess periodic acid, although after standing for a week the brown color of decomposition products was observed. However, the fact that periodic acid nondestructively oxidizes H_2QMIDA in solution of pH 5.5 made further study of this reaction desirable. The solubility of the reduced form (and presumably also the oxidized form) is high enough at this pH for preparative scale work.

e. Oxidation of H_2QMIDA with potassium permanganate Potassium permanganate is a powerful chemical oxidant which has been widely used in the oxidation of organic materials. Although most permanganate oxidations

are destructive in nature, the unusual stability of H_2QMIDA toward periodic acid made investigation of the permanganate-H_2QMIDA reaction worthy of study. The increased oxidizing power of permanganate in neutral and basic solution also made such study promising.

Three titrations of H_2QMIDA using potassium permanganate were performed, in solutions of pH 8, 5.5 and 1 N sulfuric acid. The permanganate proved to be much too powerful of an oxidant in all three cases, however, and no end-points were observed. In fact, the permanganate oxidation of H_2QMIDA was the most destructive oxidation observed in the present work, producing the usual brown decomposition products. So complete was the oxidation that only a clear, colorless solution remained.

At pH 8 the potential of the colorless solution of H_2QMIDA was +80 mv. As potassium permanganate was added it reacted instantly and the potential decreased. At the 6.00-ml. point the solution was brown and the potential -16 mv. Beyond the 6.00-ml. point the potential increased with each addition of potassium permanganate and then drifted lower upon standing. As more permanganate was added the solution became dark brown in color, eventually developing a purple tinge. No permanent potential reading above 100 mv. was ever obtained, even after 20 ml. of titrant (200 per cent excess) had been added.

In the second titration of pH 5.5, the solution of H_2QMIDA was colorless and the initial potential 160 mv. As the potassium permanganate struck the solution it turned colorless and the potential readings decreased. The minumum potential was +155 mv. at 3.00 ml. As more titrant was added the color darkened from a yellow to a light and finally

dark brown. Beyond the 6.50-ml., manganese dioxide appeared briefly as the permanganate reacted, but then quickly disappeared. A check of pH at this point revealed that no change had occurred. As before, no end-point was found. The potential drifted back down to almost the initial reading after each addition of titrant. Here again, the potassium permanganate (and perhaps even the first reduction products, manganese dioxide and manganese(III)), was breaking up the ring and further oxidizing the products.

The third titration, in 1 N sulfuric acid, although more promising because potassium permanganate is a weaker oxidant in acid solution whereas the H_2QMIDA is harder to oxidize, was also unsuccessful.

The initial potential of the suspension of H_2QMIDA was 407 mv. The potential was stable and increased slightly with addition of titrant. At the theoretical end-point, 7 ml., the reading was 442 mv., but no inflection was found. The solution was a clear, very pale yellow with some solid still present. With the addition of more titrant the color darkened slowly and at 20 ml. all of the solid had finally dissolved, but the potential remained about 450 mv. Even at the 40-ml. point, corresponding to a large excess of titrant, the potassium permanganate reacted instantly. After three minutes the potential reading had decreased to 420 mv. The addition of several crystals of potassium permanganate produced brief local high concentrations of the oxidant that deflected the meter up to 900 mv. for a second or two before the permanganate reacted. Then the color of the solution lightened and eventually, after the addition of more potassium permanganate crystals, the solution became perfectly clear and colorless. As the color of the permanganate disappeared

the potential readings decreased to 100 mv. No end-point or permanent excess of oxidant was observed after these additions of large amounts of excess potassium permanganate.

Thus, it was found that potassium permanganate completely oxidized and degraded H_2QMIDA in acid solution. This was, however, the first time that an oxidant was found which actually broke the H_2QMIDA into such small fragments that the solution became completely colorless. Such high oxidizing power in acidic and basic solution proved potassium permanganate to be useless for the chemical preparation of QMIDA.

f. Other chemical oxidants Two additional chemical oxidizing agents, sodium bismuthate and ferric tris-1,10-phenanthroline sulfate, were investigated and found to oxidize H_2QMIDA but were unsatisfactory for other reasons. The procedures used were essentially the same as those given in Section III B., and the experimental procedures are not given.

The first material was sodium bismuthate. Some of the powdered compound was added to a solution of H_2QMIDA in 1 N sulfuric acid and pH 5.5 buffer. No oxidation occurred in 1 N sulfuric acid. At pH 5.5 a degradative oxidation occurred making the solution a very dark brown and causing the measured potential to decrease as the H_2QMIDA decomposed. Here again, as with cerium and dichromate, the oxidation produced a trivalent metal ion that would interfere in later work.

Ferriin, ferric tris-1,10-phenanthroline, was prepared by oxidizing ferrous tris-1,10-phenanthroline in an 0.05 M solution, with chlorine gas or lead dioxide, in dilute sulfuric acid. Ferriin was found to oxidize H_2QMIDA in 1 N sulfuric acid. A slow decrease in potential occurred after

each addition of ferriin but the method proved unacceptable because of the low solubility of the H_2QMIDA under these conditions. At a higher pH the potential was stable up to the end-point was obtained. It was later found that ferriin was very unstable at pH 4-5.5 and reacted with the buffers used (potassium acid phthalate and sodium acetate-acetic acid). This was probably the main cause of drift as excess oxidant was added.

g. Chemicals producing no detectable oxidation Four reagents, although widely employed in the oxidation of other organic compounds, produced no oxidation of H_2QMIDA in 1 N sulfuric acid or in solutions of pH 5.5: 1) hydrogen peroxide, approximately 0.1 N and 30 per cent; 2) ammonium persulfate with and without silver catalyst; 3) potassium chlorate; 4) ferric chloride.

IV. 1,4-QUINONE-2-METHYLENEIMINODIACETIC ACID (QMIDA)

A. Procedure

1. Periodate oxidation of H_2QMIDA

In a 400-ml. beaker was placed 150 ml. of deionized water and the electrodes, of a pH meter. Nitrogen was passed through the water. With vigorous mechanical stirring, small portions of H_2QMIDA and of sodium hydroxide pellets were added. The H_2QMIDA dissolved slowly and the additions of H_2QMIDA and sodium hydroxide were carefully made so as to maintain the pH of the solution between 4.5 and 6.5. A total of 25.5 g. (0.10 mole) of H_2QMIDA was added. The final solution was light pink in color, slightly turbid and of pH of 5.0. The solution was cooled in an ice bath to 5°. At this point the pH was 5.25 and the potential of a platinum electrode inserted in the solution 55 mv. versus the s.c.e.

To this cold, vigorously stirred solution was slowly added 22.5 g. (0.104 mole) of finely ground sodium periodate. The solution darkened immediately as periodate was added while the pH decreased slowly, and the potential of the platinum electrode increased. As the equivalence point was approached the potential increased rapidly from 200 mv. to 510 mv. The final pH was 4.4 and the final temperature 5°. A precipitate appeared toward the end of the oxidation.

QMIDA was then precipitated and removed in three steps. Concentrated hydrochloric acid was added dropwise until the pH became 3.0. The yellow solid precipitated was filtered and the dark brown filtrate re-

cooled, and more hydrochloric acid added until the pH became 2.8. The second precipitation was then filtered. Hydrochloric acid was again added to the filtrate until a pH of 2.0 was obtained. A final crop of solid was removed. The solids obtained were washed with cold, deionized water, air-dried and then dried in a vacuum desiccator over anhydrous magnesium perchlorate. The total yield was 35 g. of light-yellow material consisting of QMIDA and sodium iodate. The first crop consisted of a mixture of QMIDA and sodium iodate, the second of QMIDA contaminated with some sodium iodate, the third of quite pure QMIDA.

2. Separation of oxidation products on Sephadex column

Dark brown oxidation products obtained in early preparations (lacking the pH, deaeration, and temperature color described in the preceding section) were separated on a column of Sephadex G-10 dextran gel, the column being 1 cm. in diameter and 60 cm. tall. A solution of the product in water was passed through the column and elution was made with water. These bands passed from the column, successively dark brown in color, wine-red in color and orange in color.

As explained below these bands were respectively: 1) highly polymerized material essentially aliphatic in character, 2) polymeric, relatively low molecular weight, unsaturated material, and 3) QMIDA. Sephadex is too expensive and the process too cumbersome to use on a preparative scale and the separation was used only to devise the final procedure given above which yields a product from which the polymeric material, 1) and 2) are absent.

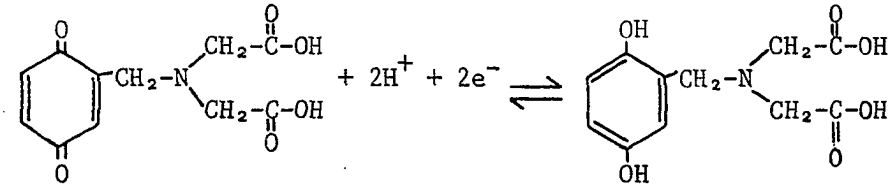
B. Discussion

1. Periodate oxidation and separation on a Sephadex column as a guide to the nature of the oxidation products

Although periodic acid is known to cause degradative oxidations of many organic materials, two papers were found describing the oxidation of hydroquinone to benzoquinone. Feifer and others (12) found that: "The phenols with para oriented hydroxyl groups consumed less periodate than the members of the other two groups of polyhydric phenols. In the case of hydroquinone, only one mole of oxidant was consumed, and there was little further reaction." Alder and Magnusson (1) confirmed this, adding that hydroquinone is instantaneously oxidized by periodate to p-benzoquinone, which unlike o-benzoquinone, is stable in the presence of periodate.

In the present work, the oxidation of H_2QMIDA by periodic acid was first studied on a small scale, using a potentiometric titration, Section III B. 3. e. This work indicated that a stoichiometric two-electron oxidation of H_2QMIDA occurred if the periodic acid was added at pH 5.5,

(4.1)



QMIDA H_2QMIDA

and that the product, presumably QMIDA, was quite stable in the presence of a small excess of periodic acid.

Early attempts to prepare QMIDA by the periodic acid oxidation of H_2QMIDA were unsatisfactory. Final solutions and solid products obtained on acidification were dark in color, although the ultraviolet spectra of the products revealed that some QMIDA was present. Separation of the dark oxidation products was effected by chromatography on a column of Sephadex G-10. The separations effected by chromatography on Sephadex are primarily on the basis of molecular weight and to a lesser extent on the basis of polarity. Until precise conditions for the oxidation were established, the periodate oxidation of H_2QMIDA yielded products which separated into three bands on Sephadex. Ultraviolet spectra were used in establishing the nature of these products, Figure 8.

The first band was dark brown in color, characteristic of decomposition products of H_2QMIDA obtained in earlier work. No bands characteristic of aromatic absorption were present in the ultraviolet spectrum. Because the brown material was the first to pass from the column, presumably it was of high molecular weight and consisted of polymeric material produced by ring-opening and condensation (13; 36; 44).

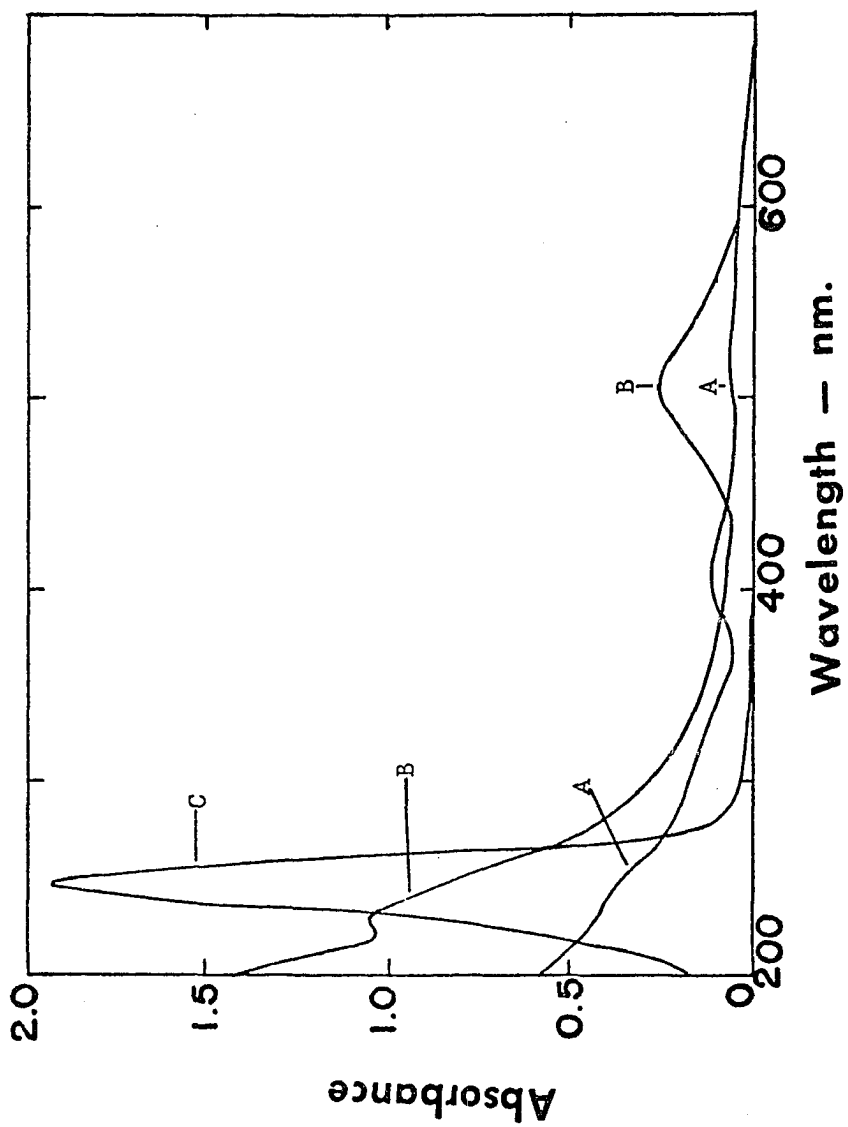
The second band was wine-red in color, and presumably of lower molecular weight. Weak absorption maxima at 230 and 500 nm. were present in the ultraviolet spectrum. H. Musso, in his chapter on phenolic coupling (41; p. 81), states that periodate oxidation produces quinones, hydroquinones and other dimeric products arising from Diels-Alder reactions. Such dimeric and related products have been reported to have an absorbance maximum around 500 nm. (14; 16) but also to have another band at a wavelength equal to or greater than that of the monomeric quinone.

Figure 8. Ultraviolet absorption spectra of the three fractions obtained by passing crude QMIDA through Sephadex G-10 gel

A. Brown band

B. Wine-red band

C. Orange band


Absorbance
2.0
1.5
1.0
0.5
0
200
400
600
Wavelength — nm.
A
B
C
A
B

The maximum in the absorbance of QMIDA falls at 246 nm. The 230 nm. absorption is therefore, too low to arise from an aromatic ring and must result from unsaturated acids (36) produced by ring-opening. That the wine-red band was eluted before the final, orange band indicated that it consisted of material of appreciably higher molecular weight than QMIDA.

The third and final band from the Sephadex G-10 column was orange in color and proved to be QMIDA. A single strong absorption band, at 246 nm., was observed in the ultraviolet spectrum. This agreed well with the wavelengths reported for benzoquinone and substituted benzoquinones, which range from 240 to 250 nm. (3; 42).

2. Optimum conditions for the periodate oxidation of H_2QMIDA

By making semi-quantitative use of the column of Sephadex G-10, an acceptable procedure (given in Section A.) was developed for the oxidation of H_2QMIDA to QMIDA by periodic acid.

The most critical factor in the oxidation proved to be the hydrogen ion concentration of the solution, the optimum pH being 5 to 5.5. At higher pH degradative oxidation is serious; at lower pH precipitation of QMIDA and H_2QMIDA occurs.

The oxidation-reduction potential of the QMIDA-H_2QMIDA couple is pH dependent, the shift being 60 mv. in the negative direction for each decrease of one pH unit. The optimum potential for the periodate oxidation occurs at pH 5 to 5.5 with a striking change in potential when two equivalents of periodate have been added per mole of H_2QMIDA.

Sodium periodate rather than periodic acid was finally used to minimize the amount of sodium hydroxide added during the oxidation and

thus, reducing the detrimental effects of local concentrations of the latter where it entered the solution.

It proved essential to deareate the solution prior to and during the oxidation; otherwise decomposition of H_2QMIDA occurred in the local regions of high pH where pellets of sodium hydroxide entered the solution.

More satisfactory results were obtained when the solution was cooled during the oxidation and the filtration steps.

It was found that QMIDA is about fifty times as soluble as H_2QMIDA (Section V). By starting the oxidation with a concentrated solution of H_2QMIDA, dilution was minimized and the yield of QMIDA improved. The dissolution of H_2QMIDA is very slow so the solution was not cooled until after all H_2QMIDA had dissolved.

Sodium periodate dissolves slowly and it proved best to grind the crystals to a fine powder. An excess of sodium periodate was avoided by employing the potentiometric end-point technique. An excess of periodate promoted decomposition of the QMIDA in the later purification procedure, Section V B. 2.

The low solubility of sodium iodate (produced by the reduction of the periodate) proved to be a problem in later purification. Examination of the ultraviolet spectrum of each of the three precipitations revealed that the first precipitation yielded predominately sodium iodate and the last two mainly QMIDA. Therefore, only the material from the second and third precipitations was saved for purification. The calculated molar absorptivity of the various crops of QMIDA obtained are presented in Table 1.

When appreciable amounts of sodium iodate-periodate were present when the product was being dried, noticeable decomposition of the QMIDA occurred.

V. PROPERTIES OF 1,4-QUINONE-2-METHYLENEIMINODIACETIC ACID (QMIDA)

A. Experimental Work

1. Ultraviolet spectrum of QMIDA

The ultraviolet absorption spectrum of QMIDA was obtained as follows. Three milligrams of QMIDA was dissolved in 100 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.5, and scanned from 800 to 200 nm. using a Cary 14 Recording Spectrophotometer, 1-cm. silica cells, and the buffer solution alone as a reference. Representative data is presented in Table 1 of Section B. 2.

2. Purification of QMIDA

The QMIDA obtained in the second and third precipitations of the procedure given in Section IV was further purified. About 28 g. of crude QMIDA was added with stirring to 150 ml. of deionized water previously deareated with nitrogen and cooled to 2° in an ice bath. To this light tan mixture, pH 1.9, was added slowly concentrated sodium hydroxide (50 per cent by weight). The color darkened to brown as the solid dissolved. When the pH reached about 5 the solution was clear and some white solid which remained was quickly removed by filtration. The clear, dark brown solution was again cooled in ice. Concentrated hydrochloric acid was added dropwise until pH 2 was reached. After a short time precipitation began and more acid was added until the pH of the mixture was stable and between 1.8 and 2.0. The orange-brown slurry was filtered leaving a yellow precipitate which was then washed with small portions of

cold deionized water and air-dried. This procedure was used three times successively. The purity of the QMIDA obtained was determined by measuring the absorbance in the ultraviolet, Table 1.

3. Equivalent weight of QMIDA

a. Neutralization To 30 ml. of deionized, deaerated water was added 0.4780 g. of QMIDA with stirring. After five minutes the mixture was titrated with 0.1022 N sodium hydroxide in a 50-ml. buret. There was a sharp increase followed by a slow decrease in the pH after each addition of base as more QMIDA dissolved. Readings were made one minute after each addition of base. The end-point was determined graphically and the titration curve is shown in Figure 9.

b. Reduction To 40 ml. of 1 N sulfuric acid was added 44.25 mg. of QMIDA with stirring. The clear, amber solution was deaerated with nitrogen for the remainder of the work and was titrated with freshly prepared titanous(III) chloride which was standardized before and after the titration. The titanous solution was prepared by diluting 8.3 ml. of 20 per cent titanous chloride to 250 ml. and was standardized potentiometrically against a standard 0.1 N potassium dichromate solution according to the procedure given by Vogel (45 p. 330). The potentials in both the standardization and equivalent weight titrations were determined using a platinum disk-s.c.e. electrode combination and a Corning Model 10 pH meter. The end-points were determined graphically and occurred at approximately 300 and 500 mv. vs. s.c.e. for the respective QMIDA-

titanium (Figure 10) and dichromate-titanium systems. Because of the instability of the titanous solution three samples of QMIDA, with alternate standardizations, were titrated and the average equivalent weight used.

4. Melting point and contaminants

a. Melting point The melting point of QMIDA was determined using a Thomas Koffer Micro Hot Stage assembly that had been calibrated using melting point standards. A small amount of QMIDA was finely ground, placed between two microscope slip covers and observed while the temperature was increased at a rate of approximately 6°/minute.

b. Residue on ignition Residue on ignition was determined by heating a 0.495 g. sample of the purified QMIDA in a tared, previously ignited platinum crucible for 30 minutes over the full heat of a Fisher burner. Care and low heat were used during the initial charring of the material.

c. Presence of hydrochloride A spatula tip of QMIDA was added to 1 ml. of deionized water and stirred. To this mixture was added several drops of 1 M silver nitrate solution.

5. Proton magnetic resonance spectrum

A proton magnetic resonance spectrum of QMIDA was obtained using a Hitachi Perkin-Elmer R-20B High Resolution NMR Spectrometer. Because of the insolubility or high reactivity of the compound in nonaqueous solvents the spectrum was obtained in deuterium oxide. Use of deuterium oxide was

used to increase the solubility of the QMIDA but it was necessary to add the two materials alternately to prevent decomposition at high pH. The final saturated QMIDA solution was maintained at pH 5 to 6. Sodium-3-(trimethylsilyl)-propanesulfonate was used as the chemical shift standard. The spectrum of QMIDA, along with that of H_2QMIDA, is shown in Figure 11.

6. Infrared spectrum of QMIDA

The infrared spectrum of QMIDA was obtained using the potassium bromide disk technique. A Perkin-Elmer Model 21 Infrared Spectrophotometer was used. The calibration of the wavelength scale of the spectrum was checked at 6.243 microns using a polystyrene film.

7. Solubility of QMIDA in solution

The solubility of QMIDA was determined in deionized water and 0.1 M sulfuric acid. An excess of solid QMIDA (about 0.5 g.) was added to 10 ml. of each solution in a 25-ml. conical flask. The mixtures were placed on a wrist-action shaker and mixed for 12 hours at 28°. Exactly 1.00 ml. of the supernatant liquid was diluted to 200 ml. in a volumetric flask and the ultraviolet spectrum obtained. The solubility was calculated using the molar absorptivity obtained in Section V B. 2. The pH of the equilibrium solutions was measured.

8. Stability of QMIDA in solution

The stability of a solution of QMIDA was studied by changes in the ultraviolet spectrum. A sample of 23.0 mg. of QMIDA was dissolved and

diluted to 1 l. with deionized water. The solution was allowed to stand on the laboratory bench and several spectra were obtained at various times from 0.5 to 371 hours after preparation. Only the region from 400 to 200 nm. was scanned. Selected spectra are summarized in Table 3.

A similar sample of 25.7 mg. of QMIDA was dissolved and diluted to 1 l. as above and stored in the dark. The results of the ultraviolet spectra of this solution are also given in Table 3.

9. Attempted preparation of the quinhydrone of QMIDA and H_2QMIDA

Several attempts were made to prepare and isolate the quinhydrone of QMIDA and H_2QMIDA. About 50 mg. of QMIDA were added to 1 ml. of deaerated water and 10 per cent sodium hydroxide added slowly to dissolve the sample. Then 50 mg. of H_2QMIDA were added and dissolved similarly. An ultraviolet absorption spectrum of the solution was obtained. Concentrated hydrochloric acid was added slowly until the pH remained at 1.8. A brownish-orange precipitate was removed and the ultraviolet absorption spectrum obtained of the filtrate and some of the precipitate, after it had been redissolved. The entire above procedure was then repeated but the H_2QMIDA dissolved first. Additional attempts to prepare the quinhydrone, quite similar to those described above, were also made in acetone and ethanol.

B. Results and Discussion

1. Ultraviolet spectrum of QMIDA

An ultraviolet absorption spectrum of QMIDA was obtained at pH 5.5 from 800 to 200 nm. A single absorption band at 246 nm. was observed. This band is attributed to the quinone portion of the molecule and is caused by a $\pi \rightarrow \pi^*$ (K-band) transition (38, p. 161).

The absorption of many quinones is shifted bathochromically when the ring is substituted. The effects of substitution are quite complex and some substituted quinones have been reported that have the same absorption wavelength as the parent compound. There was no appreciable bathochromic shift (from the wavelength of maximum absorption of benzoquinone) observed for QMIDA as a result of substitution of the ring as there was with H_2QMIDA (5, p. 42). The quantitative aspects of the QMIDA absorption are discussed in the next section in conjunction with the purification work.

2. Purification of QMIDA

The primary problem in the purification of QMIDA was the removal of the sodium iodate produced in the oxidation of H_2QMIDA with sodium periodate. The low solubilities of the two materials made a one-step separation impossible. It was found that in mixtures of water and acetone, and of water and ethanol the solubility of the sodium iodate was low enough to allow the removal of most of it. When the QMIDA was reprecipitated from these binary solvents, however, a great deal of decomposition, indi-

cated by the dark brown material recovered, had occurred and overall purity had fallen.

The procedure given involves the use of a simple acid-base reprecipitation in cold, deaerated water. These conditions caused a minimum of decomposition and it was found that if the QMIDA was dissolved quickly with base, some of the sodium iodate, which dissolved more slowly in the cold water, could be filtered off. In the second and third reprecipitations no iodate remained, after the third reprecipitation virtually all of the sodium iodate had been removed. A small but constant decomposition of the QMIDA occurred during each reprecipitation; because of this only three reprecipitations were used.

Appreciable decomposition occurred if the pH was too high during the recrystallization. Loss of QMIDA owing to hydrochloride formation was observed if the final pH was too low. The most expedient method to determine the relative purities of the various QMIDA preparations was the calculation of the molar absorptivity of QMIDA obtained from the ultraviolet absorption at 246 nm. Some of the values obtained are shown in Table 1.

The first data column is from one of the earlier preparations where periodic acid was still being used as the oxidant. The low purity of the dark brown material obtained is evidenced by the low value of the molar absorptivity.

The other four samples were all prepared using sodium periodate as the oxidant. The first of these came from an unpurified batch of QMIDA that was precipitated in one step after oxidation; the major problem here

Table 1. Molar absorptivity of various samples of QMIDA at 246 nm.

Source of QMIDA	H_5IO_6 oxdn. unpurif.	$NaIO_4$ oxdn. unpurif. 1 pptn.	unpurif. 1st of 3 pptns.	unpurif. 3rd of 3 pptns.	purif.[a] 3x
Weight/l. (mg.)	36	30.5	24.5	27.1	25.7
[QMIDA][b]	1.4	1.20	0.97	1.07	1.01
Absorbance (A)	1.40	1.65	0.18	1.70	1.66
Molar absorptivity (Σ)	9000	13,700	1860	15,900	16,400

[a] Purified QMIDA from large-scale preparation used in later work.
[b] Molar concentration x 10^{-4}.

was, therefore, the presence of some sodium iodate. The second sample was from the first precipitation of the recommended three-step process. The very low molar absorptivity confirms the presence of a large amount of sodium iodate in this sample. The third sample is from the last precipitation of the three-step procedure and is quite pure even without any additional purification. The fourth sample in the sodium iodate oxidation was obtained from a large preparative-scale batch of QMIDA that was purified three times using the procedure given in this section. This is the material that was used in the remaining work whenever QMIDA was involved.

Actually, a small amount of even purer QMIDA was obtained once in one of the small-scale experimental prpparations. This sample had a molar ab-

sorptivity of 17,300 but was prepared at a lower concentration which resulted in a large loss of QMIDA by solubility. Such a method would waste too much H_2QMIDA if used on a large scale. Later work revealed that even though the molar absorptivity of the purified QMIDA was slightly lower, this should not cause any difficulty because some of the QMIDA had reverted to H_2QMIDA during the purification process and there were not any appreciable amounts of foreign material present as might be feared.

The molar absorptivity reported for pure quinone is around 22,000 (3; 33). The effects of substitution on the molar absorptivity of quinones cannot be predicted and it cannot be assumed that pure QMIDA would have a value this high. However, the order of magnitude is the same.

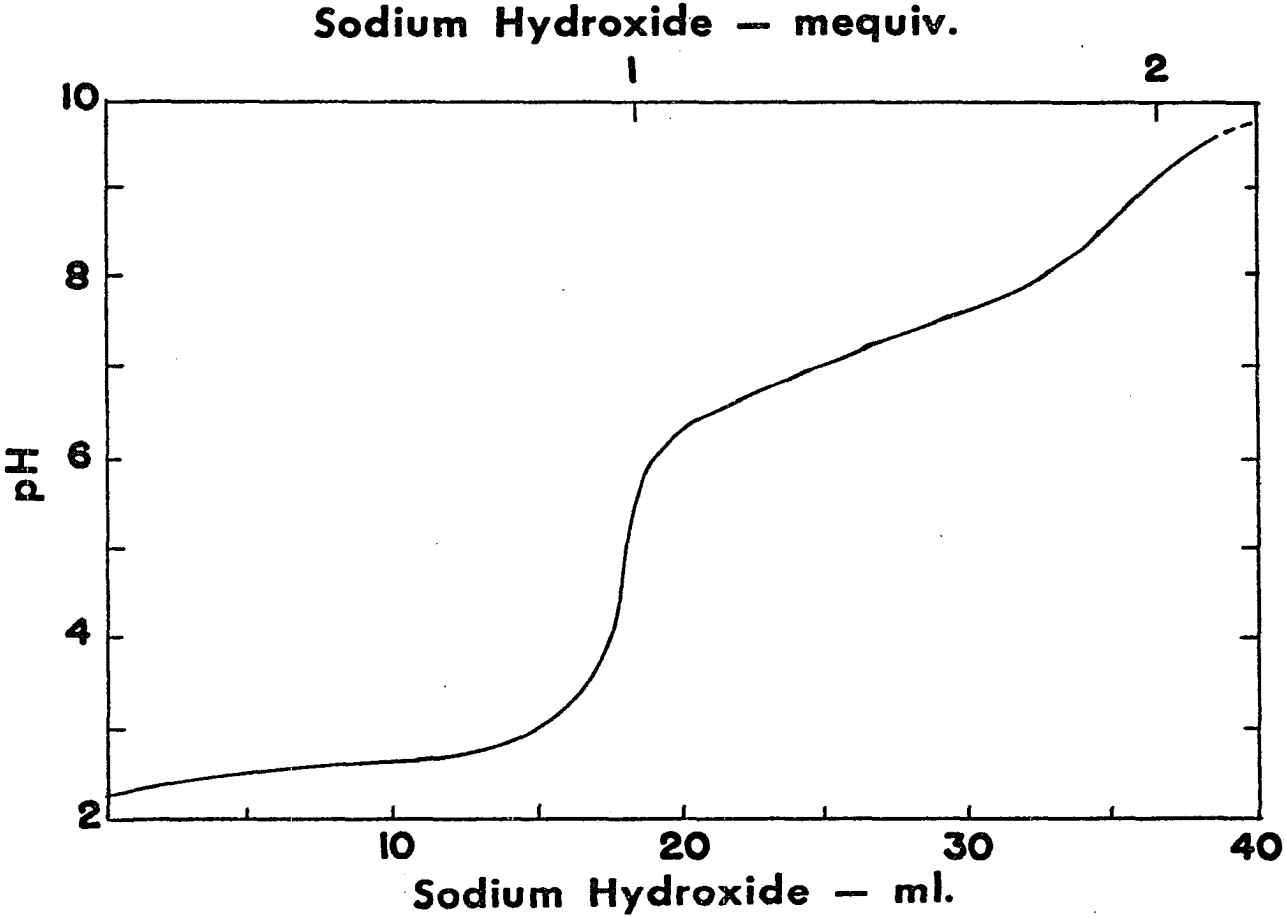
3. Equivalent weight of QMIDA

a. Neutralization The neutralization equivalent weight of the purified QMIDA was obtained by potentiometric titration. The titration curve is shown in Figure 9. The end-point for the removal of the first acidic hydrogen atom occurred at 18.20 ml. This corresponds to an equivalent weight of 257.0; calculated 254.2; 98 per cent purity. The best neutralization equivalent weight purity obtained in the earlier work with H_2QMIDA was 98.2 per cent (5). A second, less distinct end-point occurred at about 36 ml.

The mixture was orange at the beginning of the titration and at the point where the solution cleared, an orange-amber color. The color darkened as the titration proceeded leaving a dark amber solution at the 40 ml. mark. At pH 9.5 the decomposition of the QMIDA became rapid enough to

Figure 9. Titration of QMIDA with sodium hydroxide

0.4780 g. QMIDA; 0.1022 N sodium hydroxide


Sodium Hydroxide — mequiv.
1
2
10
8
6
4
2
pH
10
20
30
40
Sodium Hydroxide — ml.

cause a decrease in the pH after each addition of base making further titration meaningless.

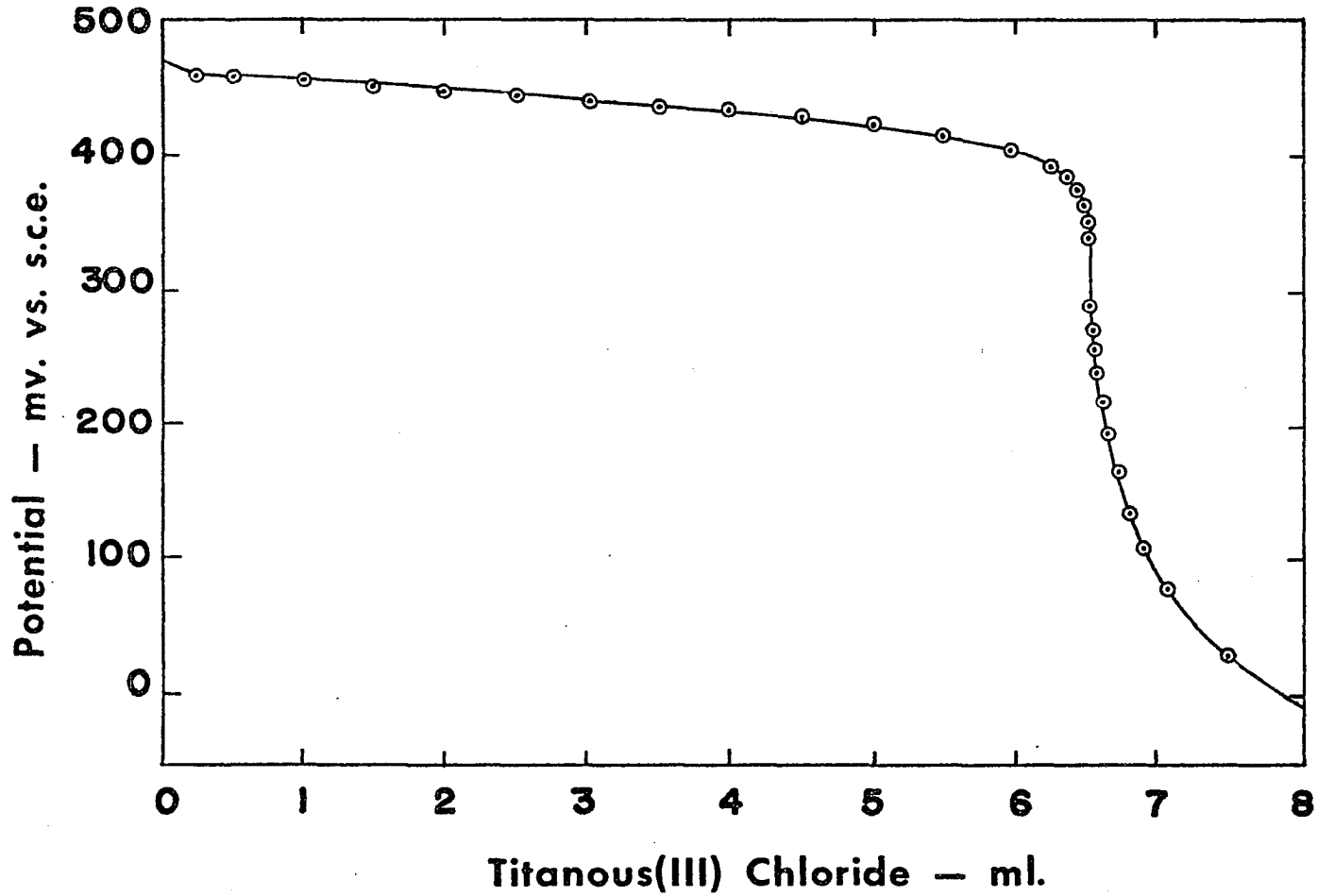
The two hydrogen atoms removed in the titration were the number predicted from the structure proposed. The negative log of the acid dissociation constant, pK_1, for the first hydrogen atom, that of the carboxylic acid, was 2.64 when read from Figure 9. This is probably slightly higher than the true value due to the low solubility of QMIDA (pK_1 for H_2QMIDA was 2.01 (5, p. 50)). The pK_2 for QMIDA corresponds to the removal of the zwitter ion ammonium hydrogen and was 7.31.

b. Reduction The reduction equivalent weight of purified QMIDA was obtained by potentiometric titration with titanous(III) chloride, Figure 10. Rather small samples were used because of the solubility limitations, the H_2QMIDA product of the reaction being of lower solubility than the QMIDA and causing drift in the end-point region at higher concentrations.

The limiting factor was the instability of the solution of titanium(III) even though the titrant was deaerated. Using freshly prepared titanous chloride and alternating between equivalent weight titrations and standardization titrations the following results were obtained after the concentration of the titanium(III) was extrapolated back to the time of each equivalent weight titration: run 1) Eq. wt. 137, N = 0.0495; run 2) 136, 0.0487; run 3) 138, 0.0465. The average equivalent weight found was 137, theoretical: 126.6; 92.4 per cent purity. However, this value of purity was thought to be acceptable because as was discussed

Figure 10. Titration of QMIDA with titanium(III) chloride in 1 N sulfuric acid

44.26 mg. QMIDA; 0.0492 N Ti(III)


500
400
300
200
100
0
Potential — mv. vs. s.c.e.
0
1
2
3
4
5
6
7
8
Titanous(III) Chloride — ml.

in Section 2, some of the QMIDA had reverted back to H_2QMIDA in the purification process and would cause no difficulty in later work.

4. Melting point and contaminants

a. Melting point The behavior of QMIDA on heating was observed through a low power microscope. At 80° a slight darkening of the originally light yellow solid could be detected. The darkening slowly continued with heating along with a gradual collapse of the crystal structure. At 145° the darkening accelerated; the material was a dark brown by 155°. At 159° fusion to a brown liquid was observed, followed by a slow evolution of gas (bubbles formed). Heating was continued to 250° with little change except for the occasional shifting of bubbles in the liquid.

b. Residue on ignition The residue on ignition of a 0.495 g. sample of QMIDA was negligible, 0.1 mg., indicating no inorganic contaminants. However, it was found that fast heating of QMIDA caused fusion of the material followed by the rapid evolution of gas which caused the material to "foam" out of the crucible.

c. Presence of hydrochloride The addition of excess silver nitrate gave a negative test for chloride indicating absence of hydrochloride. On standing overnight, a silver mirror formed on the inside of the test tube. This would indicate that oxidation of QMIDA or its decomposition products had occurred as the silver was reduced.

5. Proton magnetic resonance spectrum

A proton magnetic resonance spectrum of QMIDA was obtained in deuterium oxide. To facilitate a direct comparison, the spectrum of H_2QMIDA was also obtained under similar conditions. The spectra are shown in Figure 11. The respective values of the chemical shifts are listed in Table 2.

Table 2. Summary of proton magnetic resonance spectra of QMIDA and H_2QMIDA in deuterium oxide

Hydrogen atoms of (number)	QMIDA[a]		H_2QMIDA[b]	
	Chemical shift	Integration[c]	Chemical shift	Integration[c]
Ring (3)	7.01 7.11 6.87[d]	2.8	6.88	2.7
Methylene group (2)	4.39	2.0	4.38	2.0
Acetic acid groups (4)	3.92 3.81[d]	4.0	3.81	4.0
Water	4.71	---	4.83	---

[a]pH approximately 4.
[b]pH approximately 5.
[c]Accuracy about ± 0.1 hydrogen atom.
[d]Peaks arising from impurity of H_2QMIDA.

Large peaks caused by water were observed in the spectra of both QMIDA and H_2QMIDA; these result from a small amount of water in the deuterium oxide used and form proton exchange between the solvent and acidic

Figure 11. Proton magnetic resonance spectra of H_2QMIDA and QMIDA in deuterium oxide

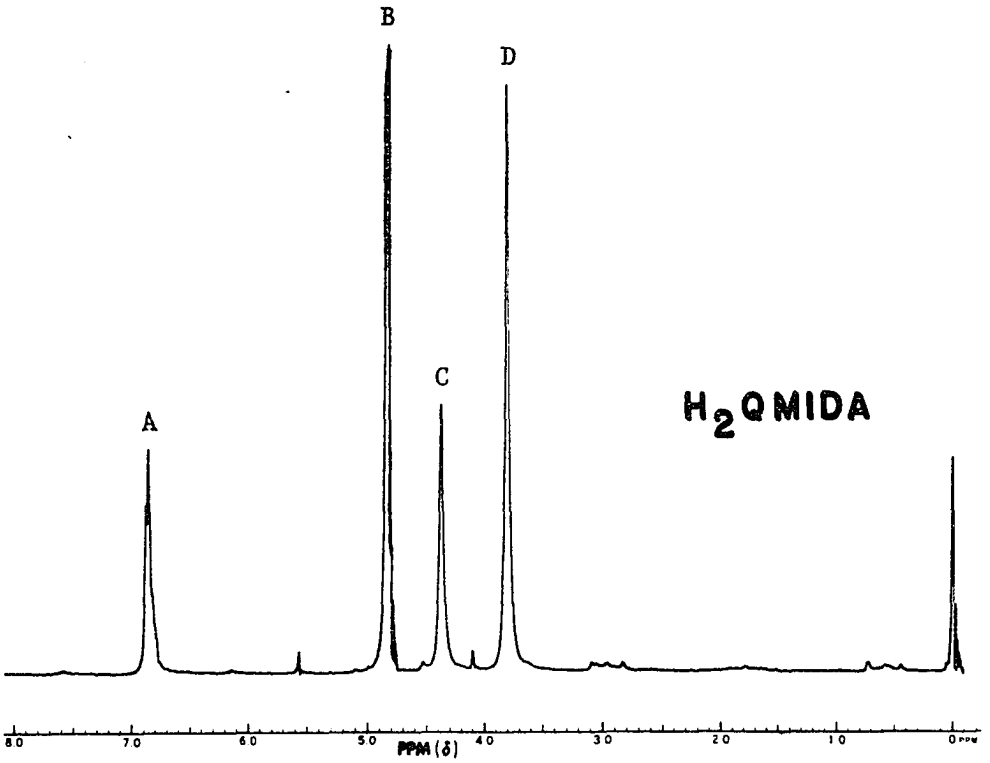
A. Ring hydrogen atoms (3)

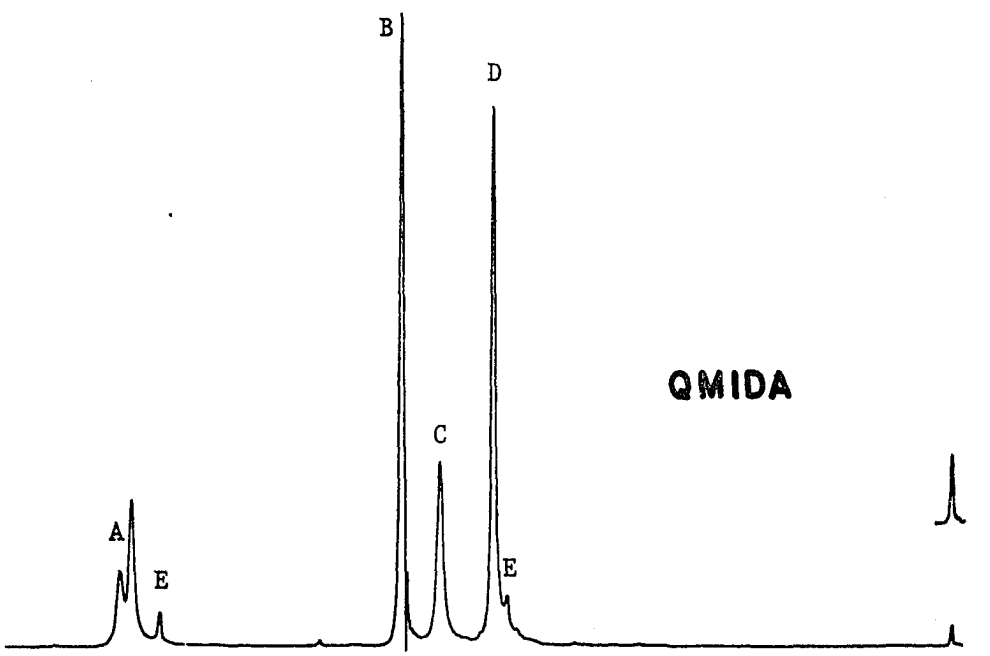
B. Water peak

C. Methylene hydrogen atoms (2)

D. Acid group α-hydrogen atoms (4)

E. Impurity (H_2QMIDA)


B
D
C
A
H_2QMIDA
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0 PPM


B
D
QMIDA
C
A
E
E

hydrogen atoms of the molecules. The small difference in the position of the peak due to water between the two compounds results from a difference in pH and from a difference in concentration of the substances. The interpretation of the H_2QMIDA spectrum was discussed in earlier work (5, pp. 37-41) and only the QMIDA spectrum will be discussed here. Attempts to obtain the spectrum of QMIDA in D_6-dimethylsulfoxide failed because of a reaction with the solvent. The QMIDA was instantaneously reduced to H_2QMIDA as it dissolved in D_6-dimethylsulfoxide. The band at 297 nm. in the ultraviolet spectrum of the reaction product in D_6-dimethylsulfoxide was identical with that of H_2QMIDA.

The spectra of QMIDA and H_2QMIDA were quite similar, as expected. The peaks of the hydrogen atoms of the methylene group appear at the same position. The peaks of the hydrogen atoms of the acetic acid groups of QMIDA are downfield about 0.1 ppm. from those of H_2QMIDA. No simple explanation is offered to account for this shift but it possibly results from the effects of diamagnetic anisotropy on these hydrogen atoms which are near the aromatic ring. The effect of substitution of the ring was more pronounced in the QMIDA spectrum than in that of the H_2QMIDA. A distinct doublet appears for the ring hydrogen atoms of QMIDA but a ragged singlet for H_2QMIDA. This is a result of the lower aromaticity of the quinone ring. The 0.2 ppm. downfield shift of the aromatic protons in the QMIDA is predicted by the tables in Silverstein and Bassler when one considers the replacement of the hydroxyls in the ring with more deshielding carbonyl groups (38, pp. 117, 140). The smaller peak in the doublet of QMIDA results from the hydrogen atom in the 3 position and is

slightly further downfield because of the neighboring, electron-withdrawing zwitter ion; the larger peak represents the 5 and 6 hydrogen atoms.

The small peak at 6.87 (δ) and the shoulder at 3.81 in the spectrum of QMIDA are the result of a small amount of impurity of H_2QMIDA.

The integration of the peak areas of the spectra agreed quite well with the values expected. As was found in the earlier spectra of H_2QMIDA (5), the integration of the aromatic portion of the spectra was slightly low.

6. Infrared spectrum of QMIDA

The infrared spectrum of QMIDA was obtained using the potassium bromide disk technique. Because a detailed interpretation of the infrared spectrum of H_2QMIDA was given in earlier work (5, pp. 29, 32-36) only the salient features of the spectrum of QMIDA will be discussed.

The replacement of the two phenolic groups by carbonyl groups is reflected in the spectrum by a large relative decrease in the size of the hydroxyl bands at 3420 and 1212 cm^{-1}, when compared to the earlier H_2QMIDA spectrum. Conversely, the band assigned to the carbonyl symmetrical stretch, 1656 cm^{-1}, was significantly larger. The bands at 1731 and 1602 cm^{-1} assigned to the carboxylate group remained about the same as would be expected because there was no change in the iminodiacetic acid portion of the molecule. Considerable change appeared in the low-frequency, aromatic region of the spectrum as a result of the change in the aromatic character of the ring.

7. Solubility of QMIDA in solution

The solubility of QMIDA was determined in deionized water and in 0.1 M sulfuric acid. The amount of QMIDA dissolved was determined by obtaining the ultraviolet spectrum of each sample and measuring the absorbance at 246 nm. The ultraviolet spectrum showed that some reduction of the QMIDA to H_2QMIDA occurred while the samples were being dissolved. A sample of known concentration of QMIDA, with the same ratio of QMIDA to H_2QMIDA (cf. next section) as in the sample, used for the solubility measurements, was used as a standard to calculate the exact solubility of the QMIDA. The values found for the solubility were: in deionized water, pH 2.20, 5.62 g./l.; in 0.1 M sulfuric acid, pH 1.38, 6.28 g./l.

The increase in solubility in the more acidic solution is presumably caused by the protonation of the carboxylate ion of the molecule. The solubility of QMIDA is about fifty times greater than that of H_2QMIDA at the same pH (5, p. 49).

8. Stability of QMIDA in solution

The stability of a solution of QMIDA was studied by following the change in the ultraviolet spectrum. Spectra of a 9.08×10^{-5} M solution were obtained from 0.5 to 371 hours after preparation. Selected spectra are shown in Figure 12 and the data from all of the spectra are listed in Table 3.

As can be seen from the data, QMIDA decomposes on standing. The spectra of the product of the decomposition and that of H_2QMIDA are

Figure 12. The ultraviolet absorption spectrum of a 9.08×10^{-5} M solution of QMIDA

A. 0.5 hours after preparation

B. 96 hours after preparation

C. 371 hours after preparation

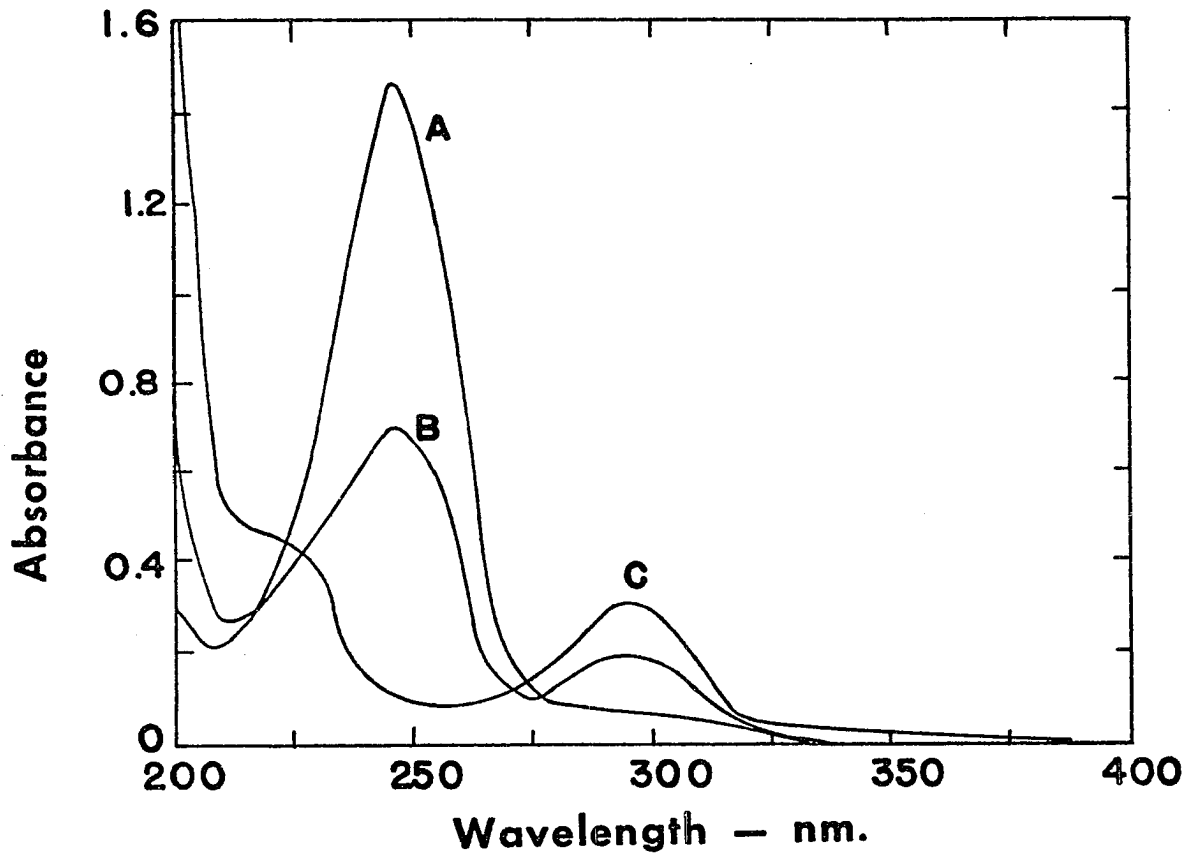

1.6
1.2
0.8
0.4
0
Absorbance
A
B
C
200
250
300
350
400
Wavelength — nm.

Table 3. Decomposition of QMIDA in solution as a function of time

Elapsed time since preparation (hours)	$A^{a}_{246\ nm.}$	%QMIDA[b]	$A^{c}_{297\ nm.}$	$\%H_2QMIDA$[d]
	Stored on bench-top; 9.08×10^{-5} M QMIDA			
0.5	1.47	99	0.06	18
24	1.25	85	0.11	33
96	0.70	47	0.19	58
182	0.28	19	0.28	85
371	0.10	7	0.30	91
	Stored in the dark; 1.01×10^{-4} M QMIDA			
0.5	1.66	100	0.07	19
360	0.46	28	0.29	79

[a]Wavelength of maximum absorbance of QMIDA.

[b]Per cent of QMIDA based on calculation of absorbance expected for the given concentration of QMIDA using the molar absorptivity determined earlier (16,400).

[c]Wavelength of maximum absorbance of H_2QMIDA.

[d]Per cent of H_2QMIDA based on calculation of absorbance expected for a solution of H_2QMIDA, equal in concentration to that of the original solution of QMIDA, using the molar absorptivity determined earlier (3630).

identical, this the decomposition product is probably the reduced form of the couple, H_2QMIDA. The formal reduction potential of QMIDA is about 0.5 volts, too low to allow oxidation of water in this region (pH 5), which would result in a much faster decomposition. The actual mechanism of the decomposition is probably quite complex and not dependent on the usual electrochemical equilibrium considerations (see Section VII C. 2.)

because of the high irreversibility of the QMIDA-H_2QMIDA system.

The data, Table 3, is an indication that there is nearly quantitative conversion of QMIDA to H_2QMIDA in the decomposition process in the presence of light. The two major limitations in the calculations shown in the table are: 1) it was assumed that there was no overlap of the absorption bands of QMIDA and H_2QMIDA; 2) the molar absorptivity used for QMIDA was determined on a sample containing a small amount of H_2QMIDA, thus the calculated per cent values are slightly higher than the true amount of QMIDA present. To a first approximation, however, these limitations are negligible and a smooth, semiquantitative change from QMIDA to H_2QMIDA was observed.

As found in the earlier studies of the stability of H_2QMIDA (5, p. 58), the decomposition of QMIDA is accelerated by light. The ultraviolet spectra of a solution of QMIDA stored in the dark, Table 3, indicated that decomposition of the QMIDA to H_2QMIDA occurs more slowly, in the dark, but apparently by a similar mechanism.

The rapid decomposition of QMIDA by a different mechanism in the presence of aluminum is discussed in Section VII.

9. Attempted preparation of the quinhydrone of QMIDA-H_2QMIDA

Several attempts were made to prepare and isolate the quinhydrone of QMIDA and H_2QMIDA in selected solvents. In deaerated water solutions no difference was noted as a result of changes in the order of addition or dissolution of the QMIDA and H_2QMIDA. The ultraviolet spectrum of the equimolar solutions of QMIDA-H_2QMIDA was the same for all methods of pre-

paration and contained no evidence of quinhydrone formation. After precipitation of the dissolved QMIDA-H_2QMIDA with hydrochloric acid, the ultraviolet absorption spectrum of the filtrate contained a large band corresponding to that of QMIDA and a small inflection at the wavelength of absorption of H_2QMIDA. This is the expected result considering the much higher solubility (Section 7) of QMIDA. The absorption spectrum of the precipitated material contained a large absorption band at the wavelength of absorption of H_2QMIDA and no band for QMIDA. Even if the quinhydrone were formed in solution, the large difference in solubility of the two materials is enough to prevent isolation of the quinhydrone by precipitation methods. The work in the solvents acetone and ethanol showed even less promise and was abandoned.

Little data are available on the spectral properties of quinhydrones in solution. A statement to this effect by Moser and Cassidy (28) was confirmed by a search of the literature. The infrared absorption of quinhydrones have been reported by Brockmann and Franck (4). Tsubomura (43), obtained the charge-transfer spectrum of quinhydrone and interpreted it using molecular orbital calculations.

Quinhydrone was reported to have one additional absorption band that is not observed in the spectra of benzoquinone and hydroquinone. This band occurs at 440 nm. and is not greatly shifted by changes in solvent (26). Water was found to promote quinhydrone formation and the highest molar absorptivity, 890, of the 440 nm. band was found in 0.05 M hydrochloric acid. No band was observed that could be interpreted as suggesting any quinhydrone formation in the present work.

Moser and Cassidy (28) also found that substitution complicates the absorption spectra of quinhydrones. A simple system such as ethylquinhydrone was found to have two additional absorption bands, 360 and 450 nm., rather than the one described above for simple quinhydrone. Also, there are four possible preferred orientational isomers in the ethylquinhydrone system. Such complications in a relatively simple system imply that the absorption spectrum of the quinhydrone of QMIDA-H_2QMIDA were it formed, would be readily detectable but difficult to interpret.

In any case no evidence was found for the existence of a quinhydrone of QMIDA and H_2QMIDA and perhaps in view of the large size of the methyleneiminodiacetic acid group the formation of one should not be expected.

VI. RESPONSE OF THE QMIDA-H_2QMIDA COUPLE TO METALS

A. Introduction

The final phase of the present work was a determination of the behavior of the QMIDA-H_2QMIDA system in the presence of metals, the objective being to devise a direct potentiometric method for the determination of a metal.

In preliminary work it was found by potentiometric titration that the potential of H_2QMIDA was altered by the presence of aluminum, but not by the presence of calcium or magnesium.

In this work a more detailed investigation was made of the behavior of the QMIDA-H_2QMIDA couple in the presence of metal ions. Samples of H_2QMIDA were titrated potentiometrically, alone and in the presence of equimolar amounts of thirteen representative metal ions using sodium periodate and potassium molybdicyanide as the titrants. Aluminum, the metal ion which yielded the most promising results, was chosen for a more intensive study, Section VII.

B. Experimental Work

1. Potentiometric titration of H_2QMIDA with sodium periodate in the presence of metal ions

A sample of 100 ± 0.5 mg. of H_2QMIDA (0.392 mmoles) was added to 25 ml. of deionized water and the mixture deaerated with nitrogen. An appropriate amount of metal salt was added to give an equimolar quantity of the desired metal ion. A solution of 10 per cent sodium hydroxide was

added dropwise, with stirring, until the H_2QMIDA dissolved and pH 6 to 6.5 was maintained. The pH was measured with a Hach Chemical Company Model 2075 pH meter and the potential of the system with a Corning Model 10 pH meter equipped with a platinum-s.c.e. electrode system. The solution was titrated with 0.0500 N sodium periodate (2.675 g./500 ml.) in a 25-ml. buret. The theoretical end-point was at 15.7 ml. The potential and pH of the solution were recorded after each addition of titrant up to the 25-ml. point.

The first titration was performed without any metal ion present so that the formal potential of the QMIDA-H_2QMIDA couple could be obtained under the same experimental conditions for reference. The decrease in pH that occurred during the titration made a second titration of pure H_2QMIDA necessary. In this titration just enough titrant was added to reach the 50-per cent point. Then the pH was varied from 3.5 to 6.5 and the potential recorded. The change in potential as a function of pH was plotted and the formal potentials of each titration corrected to pH 5.8 for comparison. The work was performed at room temperature, 29°. The results of the titrations are given in Table 4.

2. Potentiometric titration of H_2QMIDA with potassium molybdicyanide in the presence of metal ions

The titration was handled as much like the periodate titration as was feasible. To 25 ml. of deionized water was added 100 ± 0.5 mg. of H_2QMIDA (0.392 mmoles) and the mixture deaerated with nitrogen. An appropriate amount of the metal salt was added to give an equimolar quantity of the

desired metal ion. A solution of ten per cent sodium hydroxide was added dropwise, with stirring, until the H_2QMIDA dissolved and a pH of approximately 6 was obtained. Measurements were made as described above and the titrant, potassium molybdicyanide, prepared and restandardized as was described in Section III B. 2. d. The solution of molybdenum(V) was standardized before and after the titrations of the H_2QMIDA. Correction of the formal potential of the couple to pH 5.8 was made as described above. The work was performed at room temperature, 25°. The results of the titrations are given in Table 5.

C. Results and Discussion

1. Potentiometric titration of H_2QMIDA with sodium periodate in the presence of metal ions

The results of the titrations are summarized in Table 4. Of the thirteen metal ions used only three, aluminum, iron(III), and thorium(IV) produced a significant shift in the potential of the QMIDA-H_2QMIDA couple. The potential of the QMIDA-H_2QMIDA system alone was found to be 130 ± 5 mv. vs. s.c.e. at pH 5.8.

The rather high initial pH, 6 to 6.5, was used so that the titration could be made without further additions of sodium hydroxide. Because no buffer was present, the hydrogen ions produced in the oxidation caused a slow decrease in pH as the titration proceeded. The buffer was omitted to avoid possible preferential chelation of buffer (acetate) and metal. The change in potential of the couple as a function of pH at the mid-point of

Table 4. The effect of different metal ions on the formal potential of the QMIDA-H_2QMIDA system during titration with 0.0500 N sodium periodate; 100 mg. H_2QMIDA, equimolar amount of metal ion

Metal salt used	Weight (mg.)	potential[a] (mv.)	pH (±0.05)	Formal potential[b] (mv.)	Remarks
---	---	135	5.70	130	---
$Al(NO_3)_3 \cdot 9H_2O$	147	160[c]	6.25	187	Turbid soln.
$Bi(NO_3)_3 \cdot 5H_2O$	190	107[c]	6.30	137	Turbid soln.
$Ca(NO_3)_2 \cdot 4H_2O$	93	115	6.05	130	Pos. drift past e.p.
$Cr_2(SO_4)_3 \cdot \simeq 10H_2O$	112	150	5.35	123	Turbid soln.
$Cu(NO_3)_2 \cdot 3H_2O$	95	60[d]	7.00	132	pH increased
$Fe(NO_3)_3 \cdot 9H_2O$	158	136[d]	6.60	184	---
Gd_2O_3	71	113[d]	5.65	104	Turbid past midpt.
$Pb(NO_3)_2$	130	80[d]	6.60	128	pH incr.; turbid
$Mg(NO_3)_2 \cdot 6H_2O$	100	92	6.20	116	---
$Ni(NO_3)_2 \cdot 6H_2O$	110	83[c]	6.70	137	pH incr. past midpt.
$Tl_2(SO_4)_3 \cdot 7H_2O$	161	---	---	---	Tl^{+3} oxidizes H_2QMIDA
$Th(NO_3)_4 \cdot 4H_2O$	216	140[d]	6.65	191	White ppte.
$UO_2(NO_3)_2 \cdot 6H_2O$	197	176[d]	5.10	134	Turbid soln.

[a]Potential at pH given in mv. vs. s.c.e.

[b]Potential in mv. vs. s.c.e. for solution of pH 5.8 calculated from mid-point potential.

[c]End-point observed but the volume of titrant used was greater than theoretical; potential obtained at one-half of end-point value.

[d]No end-point observed; potential obtained at theoretical mid-point.

the titration indicated that the change in potential per pH unit shift over the region pH 4-6 was 60 mv., the potential increasing as pH was decreased. This factor was used to correct all of the mid-point potentials to a common pH, 5.8; thus, comparison of the potentials were placed on the same basis.

In titration in the presence of several metals the volume of titrant required was greater than the volume calculated, and sometime, no end-point was observed; as shown later the latter was shown to result from a disproportionation (decomposition) of QMIDA. A detailed study of the disproportionation of QMIDA following union with aluminum is given in Section VII.

Only one metal, gadolinium, produced a significant decrease in the observed potential of the QMIDA-H_2QMIDA couple. The decrease must be a result of the formation of a stable Gd-QMIDA compound with no (or little) union occurring between the gadolinium and H_2QMIDA.

The end-point in the titration with thallium(III) present occurred at 25 per cent of the calculated volume of titrant. This was an indication that either incomplete oxidation of H_2QMIDA was occurring or that prior oxidation by the thallium(III) might have occurred. The standard reduction potential of thallium(III)-thallium(I) is reported to be 1.25 volts vs N.H.E. (19, p. 1745). Undoubtedly H_2QMIDA was being oxidized by thallium(III).

Further discussion of the respective small variations of each titration curve in this series of titrations is not pertinent to the subsequent work reported in this thesis. Further discussion of the spe-

cifics of the use of sodium periodate in the oxidation of H_2QMIDA is given in Sections III and IV. A study paralleling the titration with periodate described above, using molybdicyanide as the oxidant, is given in the following section.

2. Potentiometric titration of H_2QMIDA with potassium molybdicyanide in the presence of metal ions

The results of these titrations are summarized in Table 5. Although

Table 5. The effect of different metal ions on the formal potential of the QMIDA-H_2QMIDA system during titration with 0.071 N potassium molybdicyanide; 100 mg. H_2QMIDA, equimolar amount of metal ion

Metal ion added[a]	Mid-point potential[b] (mv.)	pH (+0.05)	Formal potential[c] (mv.)	Remarks
---	88	6.85	151	---
Al^{+3}	301	4.40	217	Turbid soln.
Bi^{+3}	220	5.85	217	Turbid soln.
Ca^{+2}	162	5.50	146	---
Cr^{+2}	173	5.50	155	Some Cr^{+3} undissolved
Cu^{+2}	111	6.65	162	Colored species formed
Fe^{+3}	192	6.50	234	---
Gd^{+3}	170	6.15	191	---
Pd^{+2}	150	5.85	153	Turbid past midpt.
Mg^{+2}	132	6.30	162	---
Ni^{+2}	87	6.70	141	---
Tl^{+3}	---	---	---	Tl^{+3} oxidizes H_2QMIDA
Th^{+4}	231	5.50	213	Turbid soln.
UO_2^{+2}	203	6.10	221	Turbid, anomalous behavior vs. pH

[a]Specific metal salt and amount given in Table 4.
[b]Potential in mv. vs. s.c.e. obtained at theoretical mid-point.
[c]Potential in mv. vs. s.c.e. at pH 5.8 as calculated from mid-point potential.

the overall shifts in the potential of the QMIDA-H_2QMIDA couple produced by aluminum, iron(III) and thorium(IV) were found to be quite similar to those found in the periodate titrations, several differences were noted with other metals. The potential of the QMIDA-H_2QMIDA system alone was found to be 150 $\pm$ 20 mv. vs. s.c.e. at pH 5.8. This was about 20 mv. higher than the potential found using sodium periodate. The larger range given for this potential is meant to reflect the wider variations found in potentials here, than obtained with the same metals in the periodate titrations, Section 1.

Because no buffer was used it was necessary to monitor the pH as the titration proceeded details are discussed in Section 1. The shift of the potential of the couple with pH was again found to be approximately 60 mv. per pH unit. As the end-point region was reached a drift in the potential in the negative direction occurred in most of the titrations. In these titrations the theoretical mid-point was used to determine the formal potential.

Titration curves of H_2QMIDA alone and with calcium, magnesium and aluminum present are shown in Figure 13. These titrations were performed in 0.1 M acetate buffer at pH 5.5 so that no correction of the potentials for variations in pH was required. The dilute sulfuric acid present in the solution of molybdicyanide caused a slow, but uniform, decrease in the pH of the solutions as the titrations proceeded. The titrations of H_2QMIDA and H_2QMIDA plus equimolar amounts of magnesium were virtually identical when titrated with the molybdicyanide and are represented by one curve. The titration curve with calcium present differed from those

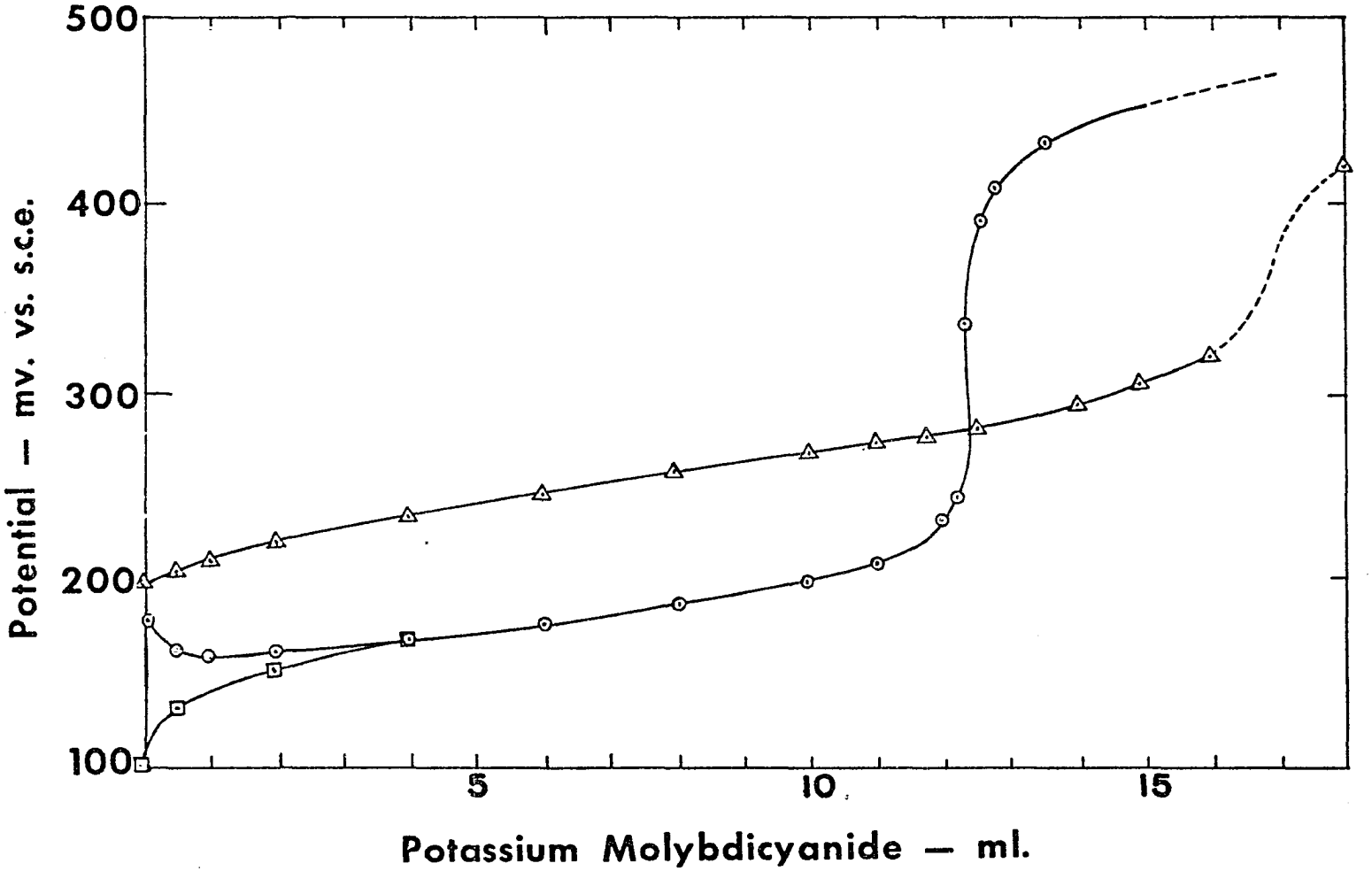
Figure 13. Titration of H_2QMIDA with potassium molybdicyanide in acetate buffer of pH 5.5; no correction of potentials was made for variations in pH during the titration

90 mg. H_2QMIDA; 0.058 N $K_3Mo(CN)_6$

○ H_2QMIDA; H_2QMIDA plus equimolar magnesium

□ H_2QMIDA plus equimolar calcium

△ H_2QMIDA plus equimolar aluminum


500
400
300
200
100
Potential — mv. vs. s.c.e.
5
10
15
Potassium Molybdicyanide — ml.

above only before the 40-per cent point. The curve in the presence of aluminum was displaced toward higher potential. More titrant was required to reach the end-point as a result of the disproportionation of the QMIDA produced in the oxidation. This disproportionation is described in detail in Section VII.

The marked differences in the titrations with molybdicyanide and with periodate were: 1) large shifts in the positive direction were found in the potential using the molybdicyanide as titrant when bismuth(III) and the uranyl ion were present; such shifts were not observed in the periodate titration. 2) A small increase in the potential was produced by the presence of gadolinium, which produced a decrease in the potential in the periodate titration. No further work was done to pinpoint the causes of such discrepancies, but reaction with the titrants, particularly the periodate (and the iodate produced), is probably involved. No potentials significantly lower than that of the QMIDA-H_2QMIDA couple alone were noted in this series of titrations. The addition of the thallium(III) again resulted in oxidation of the H_2QMIDA and is discussed in the preceding section.

D. Conclusions

Three metal ions were found which produced a significant increase in the formal potential of the QMIDA-H_2QMIDA couple in the pH range 4-6: aluminum, iron and thorium. Of these aluminum was selected for further study because of the importance of this metal and because it has only one valence state. In Section VII is presented a detailed study of the effects of aluminum on the QMIDA-H_2QMIDA system.

VII. THE INTERACTION OF THE QMIDA-H_2QMIDA SYSTEM WITH ALUMINUM

A. Experimental Work

1. Potential of the QMIDA-H_2QMIDA couple as a function of the concentration of aluminum added

A solution containing 6.40 mg. of QMIDA and H_2QMIDA was prepared by dissolving both compounds in one 50-ml. portion of 0.1 M sodium acetate-acetic acid buffer, previously adjusted to pH 5.00. The resulting solution, 5.0×10^{-4} M (2.5×10^{-2} mmoles of each material) was placed in a 100-ml. beaker and stirred with an air-driven magnetic stirrer. Nitrogen was bubbled through the solution for the remainder of the work. A Corning Model 10 pH Meter was used for pH control. The instrument was calibrated on the expanded scale using pH 5.00 buffer previously prepared. With this techinque the pH could be easily maintained at 5.00 ± 0.01 by dropwise addition of 10 per cent sodium hydroxide.

Standard solutions of aluminum were prepared by dissolving primary standard aluminum wire in hydrochloric acid and by dissolving reagent-grade hydrated aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ in water; both solutions were standardized by EDTA titration.

In the first study, a solution containing QMIDA and H_2QMIDA, each 5.0×10^{-4} M, was titrated with a 5.0×10^{-3} M solution of aluminum. The potential of the couple was determined to ± 0.1 mv. with a Leeds and Northrup Student Potentiometer calibrated against a Weston standard cell. The electrodes consisted of a Corning #47606 platinum inlay electrode and a Corning #47011 sleeve-type calomel reference, electrode.

The solution of aluminum was then added to the deaerated solution of QMIDA-H_2QMIDA, pH 5.00, using a 10-ml. buret. After each addition the pH was adjusted to 5.00 if necessary and the potential was determined. Aluminum was added until the potential readings became relatively constant or until 2.5 equivalents of aluminum per equivalent of H_2QMIDA had been added.

Runs using concentrations of QMIDA-H_2QMIDA of 5×10^{-5}, 5×10^{-3}, 5×10^{-2} M were also made using the same procedure, equipment and buffer. For the experiment using 5×10^{-5} M only, the buffer concentration was decreased to 0.01 M. The solutions of aluminum were diluted as necessary. The variation of potential with concentration of aluminum is shown in Figure 14.

2. Potentiometric titration with sodium hydroxide of QMIDA and of H_2QMIDA in the presence of aluminum

a. QMIDA Exactly 0.2588 g. (1.22 mmoles) of QMIDA was weighed into a 150-ml. beaker and 40 ml. of deionized water added. Using 0.1022 N sodium hydroxide as the titrant, theoretically, 10.00 ml. (1.022 meq.) of base should have been required for each acidic hydrogen atom. To the acid 4.09 ml. of 0.2500 M standard aluminum solution was added (1.022 mmoles) giving a molar ratio of aluminum to ligand of 1:1. The mixture was stirred for 10 minutes and nitrogen was bubbled through the solution to exclude oxygen. The titration was performed slowly with time being allowed for the pH reading to stabilize when drift was observed. The pH was measured with a Corning Model 10 pH meter equipped with a combination

electrode. The titration curve is shown in Figure 15. The titration curve for pure QMIDA is shown in Figure 9.

b. H_2QMIDA Exactly 0.2608 g. (1.022 mmoles) of H_2QMIDA was weighed and titrated as above. The titration curve is shown in Figure 15. The titration curve of pure H_2QMIDA is reported in earlier work (5, pp. 28, 61).

3. Potentiometric titration of aluminum with QMIDA-H_2QMIDA

a. Titration with equimolar QMIDA-H_2QMIDA A 5.00-ml. portion of a 5.0×10^{-3} M solution of aluminum (0.025 mmoles) was added to 30 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.00. The pH was controlled as described in Section 1. and the potential measured with the same Leeds and Northrup potentiometer assembly. The solution was stirred magnetically and nitrogen passed through it. The titrant, a solution of 5.0×10^{-3} M QMIDA and 5.0×10^{-3} M H_2QMIDA in a buffer of pH 5.00 was added to the solution of aluminum and the potential measured until a "stable" (± 1 mv./min. change) reading was obtained (see Results and Discussion section). A solution of sodium acetate, 0.1 M, was added as necessary to maintain the pH at 5.00. The titration curve is shown in Figure 16.

b. Titration with QMIDA A 5.00-ml. sample of 5.0×10^{-3} M aluminum (0.025 mmoles) was added to 35 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.00. Potential measurements and pH control were carried out as described in Section 1. The aluminum was titrated with a 5.0×10^{-3} M solution of QMIDA (64.0 mg./50 ml.) in sodium acetate-

acetic acid buffer, pH 5.00. Using a 10-ml. buret, the titration could be made to the point at which the ligand-metal ratio was 2:1. Stock solutions of 0.1 M sodium acetate or acetic acid were added dropwise to maintain pH 5.00. The results of the titration are shown in Figure 17.

c. Titration with H_2QMIDA This procedure was the same as that of Section b., with the titrant being 5.0×10^{-3} M H_2QMIDA. The results are also plotted in Figure 17.

4. Ultraviolet absorption spectra of the QMIDA-H_2QMIDA system during titration with aluminum

A 5.0×10^{-5} M solution of QMIDA and H_2QMIDA was prepared by dissolving 64.0 mg. of each material in 50 ml. of 0.1 M sodium acetate-acetic acid buffer of pH 5.00 and diluting an aliquot of this solution one hundredfold by adding buffer of pH 5.00. The ultraviolet absorption spectrum of this solution was obtained using a Cary 14 recording spectrophotometer and 1-cm. quartz cells. A volume, 50.0 ml., of the above solution was titrated with 1.25×10^{-3} M aluminum using a 10-ml. buret. After each addition of aluminum the ultraviolet spectrum of the solution was obtained and the sample returned to the original solution for further titration. The titration was stopped at 8.00 ml., representing a molar ratio of aluminum to total ligand of 2:1, or a molar ratio of aluminum to each respective ligand of 4:1.

Individual ultraviolet spectra were also obtained of QMIDA and H_2QMIDA at pH 5.00. Then, immediately after a large excess of aluminum was added, the spectra were again obtained. The results are given in

Table 6.

5. Potential of the Quinone-H_2QMIDA system as a function of the concentration of aluminum

An equimolar solution containing 27.0 mg. of quinone, Q, molecular weight 108, and 64.0 mg. of H_2QMIDA, molecular weight 255, was prepared by dissolving both materials in 50 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.00, and diluting this solution to exactly 500 ml. with deionized water. Potential measurements were made with a Leeds and Northrup potentiometer as described in Section 1. The pH was kept at exactly 5.00 by the addition of 0.1 M sodium acetate. After deaeration with nitrogen, 5.0×10^{-3} M aluminum was added with a 10-ml. buret and the potential determined at 1 to 2 minute intervals until a fairly stable (± 0.5 mv.) reading was obtained.

A solution of 27 mg. of Q and 64.0 mg. of H_2QMIDA dissolved in 50 ml. of 0.1 M sodium acetate-acetic acid buffer, pH 5.00, and diluted to 500 ml. with deionized water, was obtained using the procedure above and the freshly prepared 5×10^{-4} M solution. Then, "unknown" amounts of the aluminum were added to exactly 50 ml. of the Q-H_2QMIDA solution and the potential determined after 5 minutes standing. Samples were all in the 0.2 to 1.0 equivalents (of aluminum per total equivalents of ligand) range, the range of optimum stability.

Later work involved use of the above procedure to obtain calibration curves with a pretreatment of the platinum electrode being used in an attempt to increase reproducibility. The treatment consisted of 3 sets of

alternate anodic and cathodic polarizations of the electrode in 0.1 N perchloric acid. Another platinum electrode was used to complete the circuit and 1.5 volts was applied to the cell. The current was passed for about 15 seconds and the treatment was always stopped with the platinum electrode being conditioned cathodic.

B. Results and Discussion

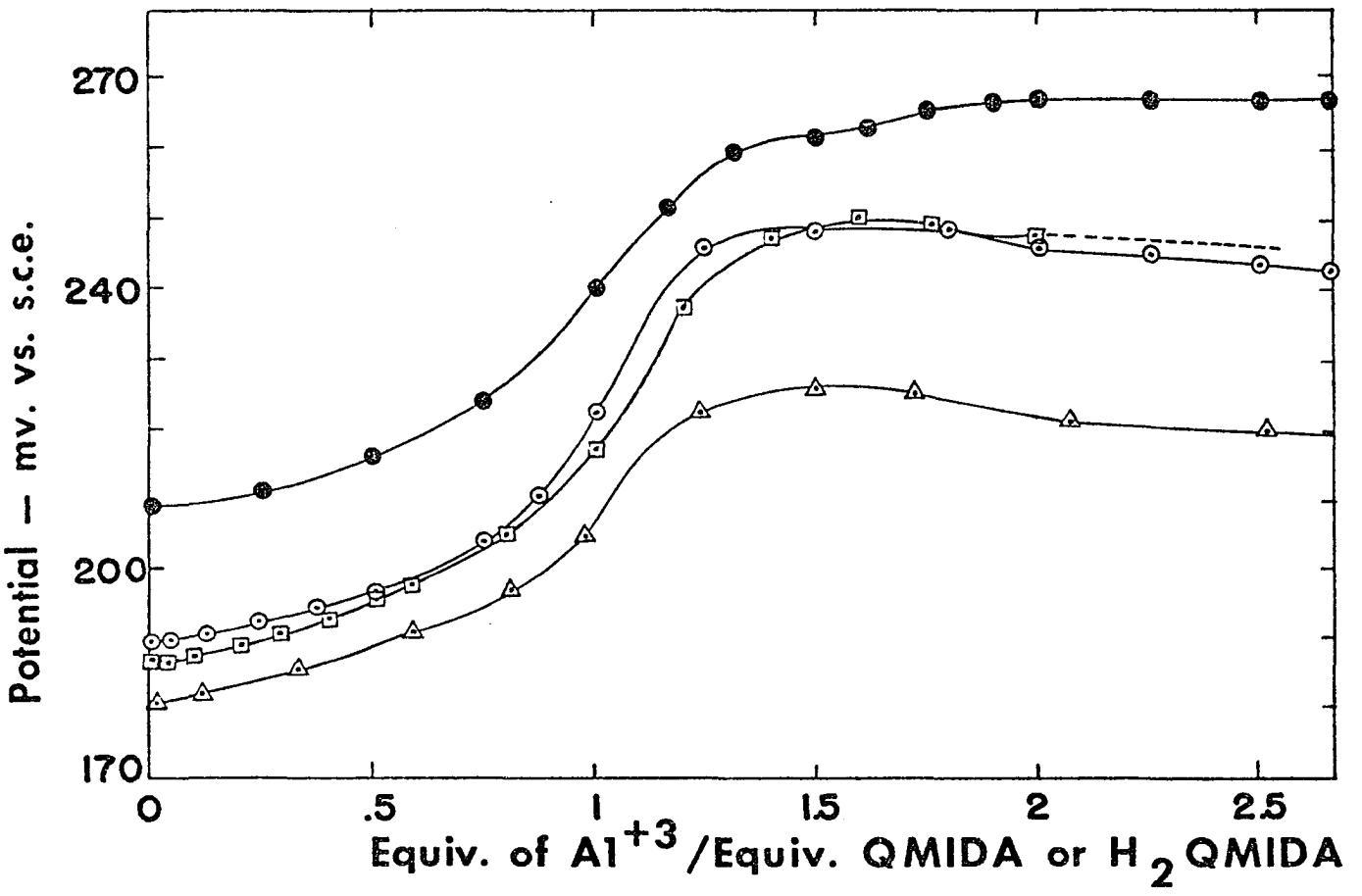
1. Potential of the QMIDA-H_2QMIDA couple as a function of the concentration of aluminum

Of the three metals that produced a consistent and significant shift in the potential of the QMIDA-H_2QMIDA couple in Section VI, aluminum was investigated in detail because it produced the largest potential shift, approximately 65 mv. in the work described in Section VI. Also, aluminum has only one valence state and oxidation-reduction reactions which would complicate work with iron are absent. The first step in the study was to determine the concentration range over which the QMIDA-H_2QMIDA system would respond to aluminum. The procedure described in Section VII A. 1. was followed.

Curves of the potential in mv. vs. equivalents of aluminum added over the concentration range of 5×10^{-2} M to 5×10^{-5} M QMIDA-H_2QMIDA are shown in Figure 14. The solutions were continuously deaerated and kept at constant temperature during these experiments. Sodium hydroxide was added during these titrations to maintain the pH at exactly 5.00 after each addition of aluminum. In this way the acid produced by the union of alumin-

Figure 14. Potential of the QMIDA-H_2QMIDA couple in sodium acetate-acetic acid buffer of pH 5.00 as a function of aluminum added

△ 5×10^{-2} M QMIDA and H_2QMIDA
○ 5×10^{-3} M QMIDA and H_2QMIDA
□ 5×10^{-4} M QMIDA and H_2QMIDA
● 5×10^{-5} M QMIDA and H_2QMIDA


270
240
200
170
Potential — mv. vs. s.c.e.
0
.5
1
1.5
2
2.5
Equiv. of Al^{+3} /Equiv. QMIDA or H_2 QMIDA

um and H_2QMIDA was neutralized. Because of the acid present in the solutions of aluminum and the relatively high buffer capacity of the 0.1 M sodium acetate-acetic acid at pH 5.00 compared to the concentrations of the ligand, attempts to add standard base and determine the number of acidic hydrogen atoms displaced when union occurred were not successful. Use of buffer of lower concentrations made pH adjustment more difficult and potential readings more erratic.

As will be seen by examination of Figure 14 the behavior of the system toward aluminum is the same at all four concentrations of ligand. A slow increase in potential occurs as the first aluminum is added. At about one equivalent the slope is a maximum. The rate of increase then falls and a maximum reading is obtained at about 1.5 equivalents of aluminum. Beyond the 1.5 equivalents point the potential decreases. An explanation of the shapes of the curves is given in Section VII C.

Briefly, the aluminum first unites preferentially with the H_2QMIDA species, causing a slow initial increase in potential and more rapid increase as a mole ratio of 1:1 is reached. The Nernst equation for this system is,

$$E = E^{\circ}_{QMIDA,\ H_2QMIDA} + \frac{0.0591}{2}\log\frac{[QMIDA][H^+]^2}{[H_2QMIDA]}$$

which at constant pH can be simplified to

$$E = E^{\circ\prime}_{QMIDA,\ H_2QMIDA;\ pH\ 5} + \frac{0.0591}{2}\log\frac{[QMIDA]}{[H_2QMIDA]}$$

As H_2QMIDA unites with aluminum the denominator of the fraction in the logarithm term decreases, causing the potential of the system to shift in

the positive direction. Some excess aluminum is necessary to cause the union of aluminum and H_2QMIDA to proceed. As the concentration of free H_2QMIDA is depleted the union of aluminum and QMIDA begins. At a ratio of 1.5 moles of aluminum to 1 mole of total ligand the potential reaches a maximum, Figure 14. Beyond this point the union of aluminum and QMIDA proceeds faster and the potential decreases. This effect is caused by the decomposition of the QMIDA after union with aluminum.

At the lowest concentration of QMIDA-H_2QMIDA, 5×10^{-5} M, relatively more aluminum must be added to cause complete union of the H_2QMIDA and there the maximum potential did not occur until about 2 moles of aluminum was added. Potential readings increased slowly for about 4 minutes after additions of aluminum in the 0.25 to 1.50 mole range. This was probably an indication that union of the aluminum was slower at this low concentration (5×10^{-5} M) and was taking longer to reach equilibrium. Accordingly, then, if the aluminum-H_2QMIDA compound is not as readily formed, the weaker aluminum-QMIDA compound is even less readily formed and the decrease in the potential of the system, caused by the subsequent disproportionation of the Al-QMIDA, is slower after the maximum is reached. No appreciable decrease in potential is observed until about 4 moles of aluminum have been added. Conversely then, in the most concentrated solution of ligand, 5×10^{-2} M, the potential reached a maximum smoothly at 1.5 moles and then decreased immediately with no need for a large excess of aluminum.

The curves of the potential vs. aluminum are shown in Figure 14. Although all four curves were of similar shape, they varied in initial

potentials (no aluminum added) from 180 to 209 mv. vs. s.c.e. The displacement of the curves toward higher potential as the concentration of ligand was decreased cannot be explained by the usual Nernst theory. This displacement is probably caused by the high irreversibility (i.e. low exchange current density) of the QMIDA-H_2QMIDA at the lower concentrations. The amount of change in the potentials from the initial to the maximum potential of each curve also varied. The overall range of the potentials obtained was 46, 61, 63 and 58 mv. respectively for each curve passing from the highest concentration of ligand, 5×10^{-2} M, to the lowest, 5×10^{-5} M. The preferred concentration for the QMIDA-H_2QMIDA is around 1×10^{-3} M where both optimum reproducibility (of initial potentials) and optimum potential shift (the largest change in potential per given amount of aluminum) are obtained.

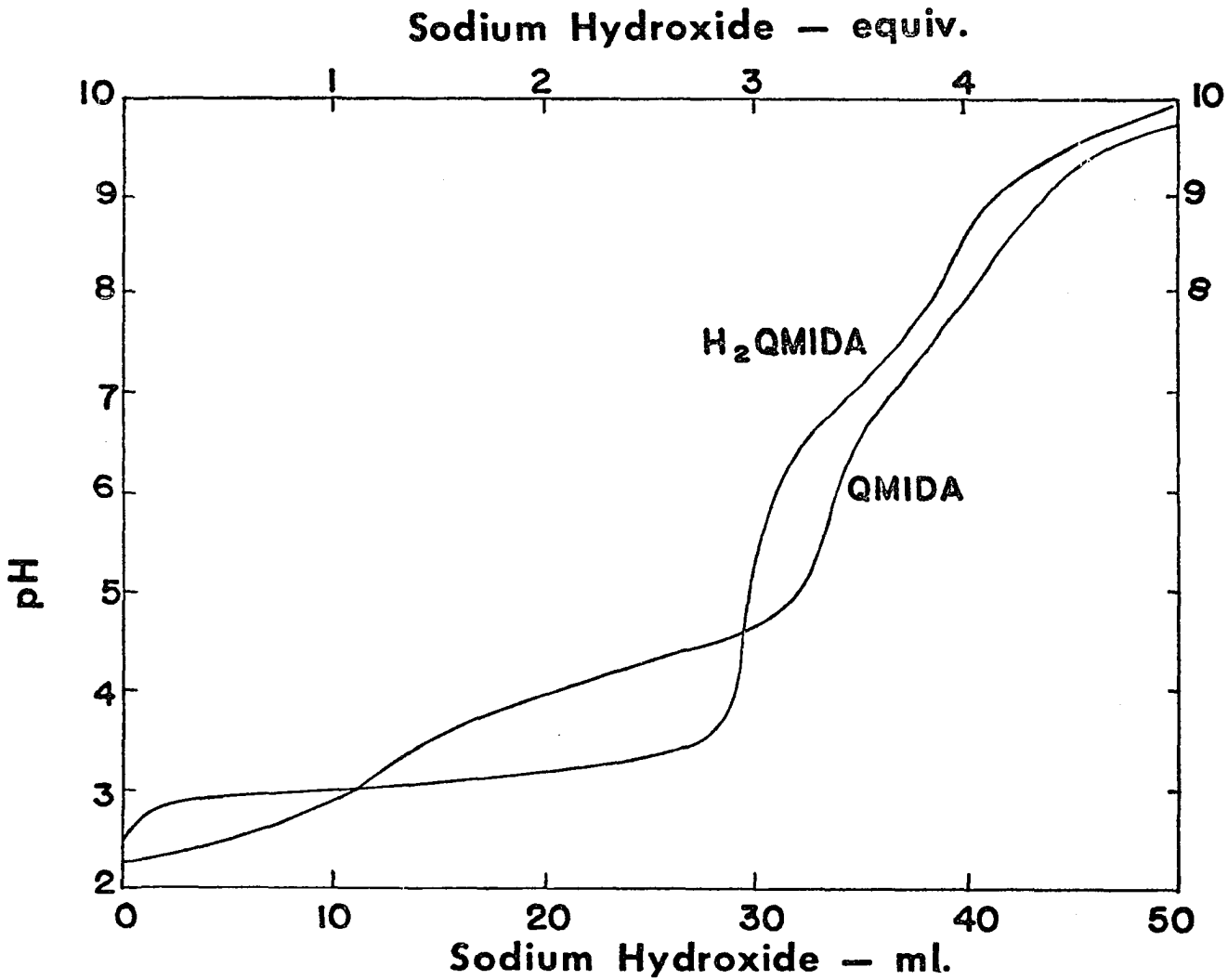
2. Potentiometric titration with sodium hydroxide of QMIDA and of H_2QMIDA in the presence of aluminum

In the two sections below the results of the neutralization titrations of QMIDA and H_2QMIDA in the presence of aluminum are given. The procedure followed was given in Section VII A. 2. H_2QMIDA was found to unite with one atom of aluminum and form a stable compound. QMIDA was found to unite with one atom of aluminum and thereafter to disproportionate to H_2QMIDA and a mixture of other products. The curves obtained from these titrations are shown in Figure 15.

a. QMIDA The curve obtained in the titration of QMIDA with sodium hydroxide is shown in Figure 9, that of QMIDA in the presence of aluminum in Figure 5. The two curves are essentially the same to the

Figure 15. Titration of QMIDA and of H_2QMIDA with alkali in the presence of equimolar aluminum

0.2588 g. of QMIDA
0.2608 g. of H_2QMIDA
0.1022 N Sodium hydroxide


Sodium Hydroxide — equiv.
1
2
3
4
10
9
8
7
6
5
4
3
2
pH
H_2QMIDA
QMIDA
0
10
20
30
40
50
Sodium Hydroxide — ml.

point at which 0.7 equivalents of sodium hydroxide have been added. The effect of the aluminum is small, because of the low solubility (5 g./l.) of QMIDA, unitl the first replaceable hydrogen atom (from the carboxylic acid) is removed, producing $H(QMIDA)^-$. Beyond this point the curves are radically different, the aluminum is now able to unite with the QMIDA.

(7.1) $H(QMIDA)^- + Al^{+3} + OH^- \longrightarrow Al(QMIDA)^+ + H_2O$

making the second replaceable hydrogen atom (from the zwitter ion) appear to be a much stronger acid (pK value about 3.5).

Theoretically, a small break at one equivalent and a large break at two equivalents with no further release of hydrogen ion past the two equivalents point would be expected. The first small break is observed but there is no break at two equivalents in the titration, in fact the large break comes at about 3.3 equivalents, which indicates that an extra 1.3 equivalents of hydrogen ion are released after union occurs. This can not be accounted for by a simple union with aluminum.

The pH was stable before any base was added. The mixture was turbid and light amber in color because of undissolved QMIDA. As the titration proceeded the solution became clear at the point where one equivalent of sodium hydroxide had been added. By the time two equivalents were added the solution had darkened somewhat and was a clear orange. At about three equivalents turbidity resembling aluminum hydroxide appeared. This increased as the titration continued. The precipitation was accompanied by a slow decrease in pH on standing. Finally near the end of the titration (about 4.5 equivalents) the turbidity disappeared leaving a

clear, dark amber solution.

In repeating the titration with a 2:1 molar ratio of aluminum to QMIDA, the early part of the curve was shifted downward an additional 0.15 pH units. The break at one equivalent is just barely discernible and no other break is observed, even with a total of 5 equivalents of base being added. As above, precipitation started at about three equivalents, pH 4.1.

The observations described above, involving a marked deviation from the expected behavior (there are only 2 replaceable hydrogen atoms) of QMIDA with aluminum, can be explained by assuming that QMIDA disproportionates in the presence of aluminum. This is discussed in Section VII C.

b. H_2QMIDA The H_2QMIDA was titrated in the same manner as the QMIDA above, following the procedure in Section VII A. 2. The curve is shown in Figure 15. In comparison with the titration curve of pure H_2QMIDA (5, pp. 28, 61), a decrease in pH similar to the one described in Section a. is observed up to the point where one equivalent of sodium hydroxide had been added. There is no break until three equivalents were added and then a small inflection is observed at four equivalents indicating the removal of the last acidic hydrogen, that of the phenolic group meta to the IDA substituent. After removing the first acidic hydrogen atom the aluminum unites with the $H_3(H_2QMIDA)^-$ species releasing two more acidic hydrogen atoms

$$(7.2)\quad H_3(H_2QMIDA)^- + Al^{+3} + 2OH^- \longrightarrow AlH(H_2QMIDA) + 2H_2O$$

which must be titrated with the base before an end-point is observed.

The last phenolic hydrogen atom is also more acidic, pK_4~7, and is subsequently titrated with the fourth equivalent of base.

A picture of the H_2QMIDA molecule with the attached aluminum ion present is given in Figure 16. This interpretation is in accord with the behavior of H_2QMIDA with certain metals (5, p. 61). At the beginning of the titration solid H_2QMIDA was present and the pH decreased slowly after each addition of base. The solution did not become clear until almost three equivalents of base were added. At the clear-point a small inflection occurred and the large increase in pH began. Because the pH was still below 4 at the clear-point, all of the solid present up to this point was probably free H_2QMIDA. The neutral aluminum-H_2QMIDA species is apparently polar enough to be soluble, the two open coordination sites on the aluminum ion probably enhancing the solubility. Beyond the clear-point the solution was colorless to about pH 9; a faint amber color then appeared. The stability of the H_2QMIDA species, as indicated by lack of darkening, in basic solution when united with aluminum is in marked contrast to the behavior of H_2QMIDA observed earlier (5), and of that observed for other substituted hydroquinones. After the titration, when air was allowed to diffuse into the quiescent solution, a darker layer indicative of decomposition formed on the surface of the solution and slowly spread downward over a period of several hours.

3. Potentiometric titration of aluminum with QMIDA and H_2QMIDA

a. Titration with equimolar QMIDA-H_2QMIDA An equimolar solution of QMIDA-H_2QMIDA was added to a solution of aluminum and the poten-

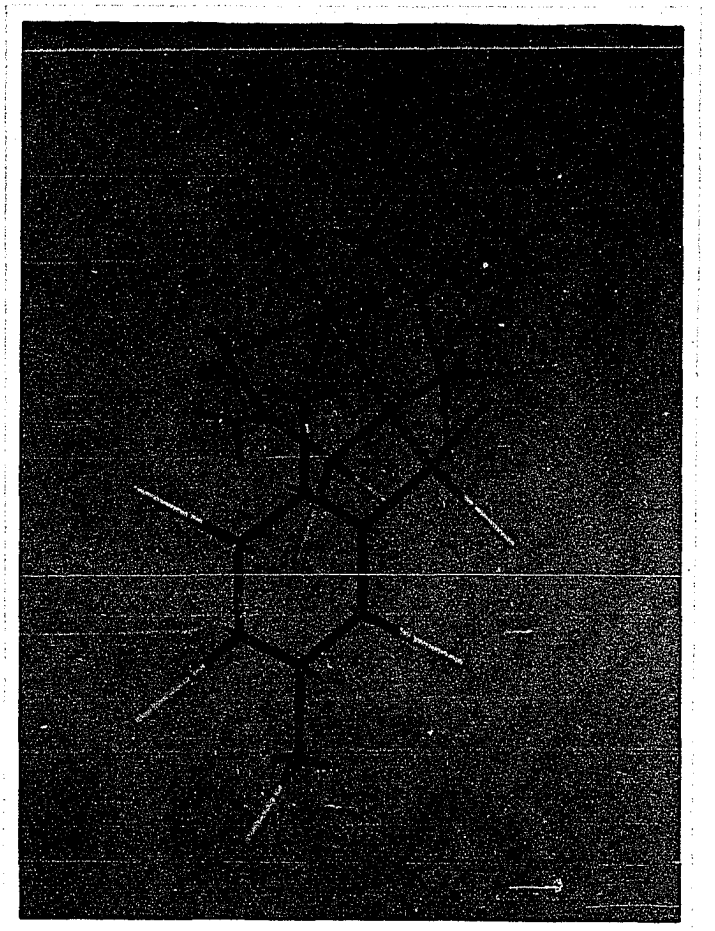


Figure 16. A model of the H_2QMIDA-aluminum compound

Black-carbon

White-hydrogen

Blue-nitrogen

Red-oxygen

Green-aluminum

tial measured following the procedure given in Section VII A. 3. a. The curve for the titration, Figure 17, resembled a normal titration curve but proved to be of no utility for the determination of aluminum.

After each addition of titrant between 0.0 and 1.0 equivalents per equivalent of aluminum, the potential drifted downward on standing. Beyond this point the potential was stable. This stability of the potential on standing is a result of all the aluminum being coordinated and therefore, no further disproportionation of QMIDA, the cause presumably of the drift, occurs, see Section VII C.

The rather rapid potential shift in the 4-ml. region gives the curve the resemblance of a typical titration curve. This would tend to make the method seem attractive for titrimetric analysis of aluminum, but the persistent drift in the potential through the entire region and the non-stoichiometric nature of the reaction makes the method of no use for the determination of aluminum.

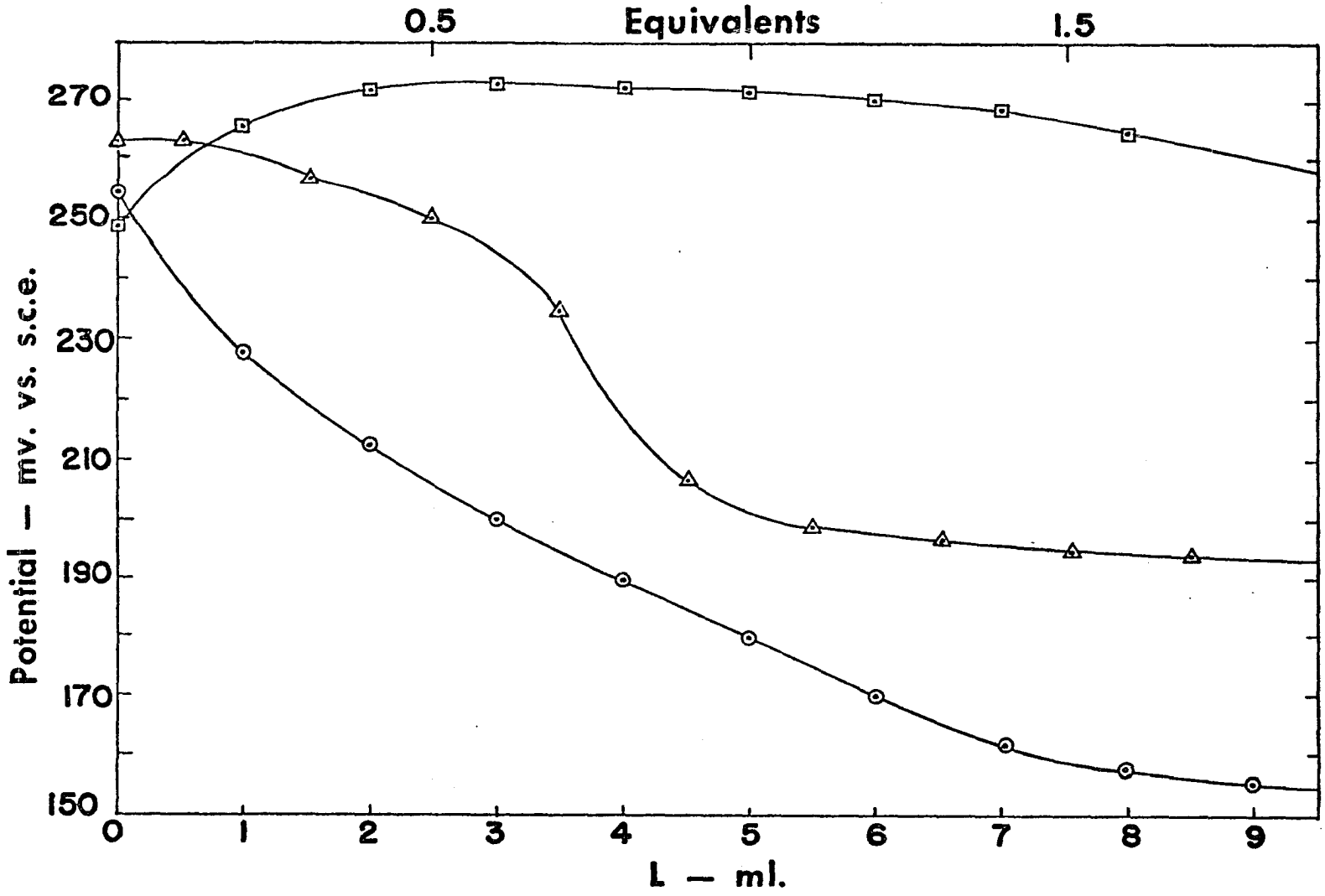
b. Titration with QMIDA and H_2QMIDA individually Two titrations of a solution of aluminum were made, one with QMIDA and the second with H_2QMIDA. The procedure used was quite similar to the preceding titration using the equimolar solution and is given in Section VII A. 3. b. In the titration using QMIDA the potential increased up to 0.5 equivalents added and thereafter decreased slowly. The titration using H_2QMIDA was more striking. A curve of negative slope was obtained, the initial potential being 255 mv. At two equivalents the potential had dropped to 154 mv. The curves are given in Figure 17.

Figure 17. Potentiometric titration of 5.00 ml. of 5.0×10^{-3} M aluminum with QMIDA and H_2QMIDA in 0.1 M sodium acetate-acetic acid buffer at pH 5.00

□ L = 5.0×10^{-3} M QMIDA

○ L = 5.0×10^{-3} M H_2QMIDA

△ L = 5.0×10^{-3} M QMIDA and H_2QMIDA


0.5
Equivalents
1.5
270
250
230
210
190
170
150
Potential — mv. vs. s.c.e.
0
1
2
3
4
5
6
7
8
9
L — ml.

The titration of the aluminum using QMIDA gave a potential with a continuous upward drift after the first 1 ml. (0.2 equivalent of QMIDA per equivalent of aluminum) of titrant was added. The magnitude of the drift decreased as more titrant was added and a stable potential was obtained when 0.8 equivalents had been added. Past 0.8 equivalents the potential decreased after additions of titrant, the rate of the drift increasing as the end of the titration was approached. Analysis of the complete curve, however, revealed no useful information except to confirm the earlier indications that the QMIDA disproportionates in the presence of aluminum and that the maximum potential occurs at the point at which the ratio of Al:QMIDA is approximately 2:1.

In the early portion of the second titration, using H_2QMIDA, there was a slight decrease in the measured potential for 2-4 minutes after addition of titrant after which fairly stable readings were obtained. After 1.0 equivalents of titrant had been added a slow but persistent downward drift was observed. The slope of the curve is approximately that calculated from the Nernst equation from about 1 to 7 ml., having a decrease of approximately 60 mv./pAl.

4. Irreversibility of QMIDA and H_2QMIDA

Unfortunately, the drift observed of the QMIDA-H_2QMIDA system along with the earlier unsuccessful attempts at oxidation of H_2QMIDA at a platinum electrode (Section III B. 2.) all tend to indicate that the couple is highly irreversible (i.e. the electrode reaction is characterized by very low exchange current density). Even though oxidation of

platinum tended to catalytically enhance the oxidation of H_2QMIDA it has been shown by many workers that the potential response of such irreversible systems is very irreproducible and interpretation of the data is difficult and unreliable. Meites and Thomas (25, p. 30) state: "Direct potentiometry with such irreversible systems is out of the question, for the measured potential cannot be related unambiguously to the composition of the solution". Kolthoff agrees, noting (20, pp. 65, 70) that "irreversibility is especially noticeable when the corresponding ion concentrations become very small" and cautions that "theoretical consideration can be applied only in cases where the electrode reaction is strictly reversible." In fact, Cassidy et al. (33) has reported that in his work with substituted hydroquinones and low molecular weight hydroquinone polymers that there was some sort of irreversible poisoning of the platinum electrodes with some of these systems. He reports: "It was found that the use of new bright platinum wire electrodes was required to give reproducible potentials. Used platinum electrodes were unsatisfactory, in spite of efforts to clean them. There seemed to be no criterion of a 'good' electrode other than its behavior in an actual titration." Furthermore, he later admits that: "Unlike ordinary titrations, when several platinum electrodes would usually agree within one or two millivolts, the electrode agreement in polymer titrations was usually only within ten millivolts for three new electrodes. This is, however, better than previously achieved." Such critical studies of quinone-hydroquinone systems, reveal that many of these systems are highly irreversible and unsatisfactory for direct potentiometric applications. Decisions regard-

ing the application of any quinone-hydroquinone systems to direct potentiometry must then be based on experimental results and not strictly on theoretical considerations.

5. Ultraviolet absorption spectra of the QMIDA-H_2QMIDA system during titration with aluminum

The ultraviolet spectra of pure QMIDA and H_2QMIDA were obtained with and without aluminum present. Then an equimolar solution of QMIDA and H_2QMIDA was titrated with aluminum and the ultraviolet spectrum of the solution obtained at several points during the titration. The procedure used is given in Section VII A. 4. Analysis of the spectra revealed that aluminum unites first with H_2QMIDA and then with QMIDA and that the QMIDA then undergoes disproportionation.

Rather dilute solutions of QMIDA-H_2QMIDA and aluminum were used so that direct ultraviolet spectra could be obtained without dilution. In Section 1. it was noted that at these low concentrations a relatively larger excess of aluminum was necessary to force the reaction to completion. This effect was also reflected in the ultraviolet spectra.

To obtain a proper comparison, spectra of fresh solutions of QMIDA and H_2QMIDA were obtained and then excess aluminum added and the spectra obtained. These spectra are shown in Figure 18 and the data from the titration summarized and given in Table 6.

The absorbance of fresh 8.35×10^{-5} M solution of QMIDA was 1.37 at the wavelength of maximum absorption, 246 nm., with end absorption occurring at about 210 nm. On the addition of excess aluminum the band at

Figure 18. Ultraviolet absorption spectra of QMIDA and H_2QMIDA in the presence of excess aluminum at pH 5

A. 5.0×10^{-3} M H_2QMIDA with excess aluminum

B. 7.9×10^{-5} M QMIDA

C. 7.9×10^{-5} M QMIDA after excess aluminum was added (now having 4.1×10^{-5} M H_2QMIDA present)

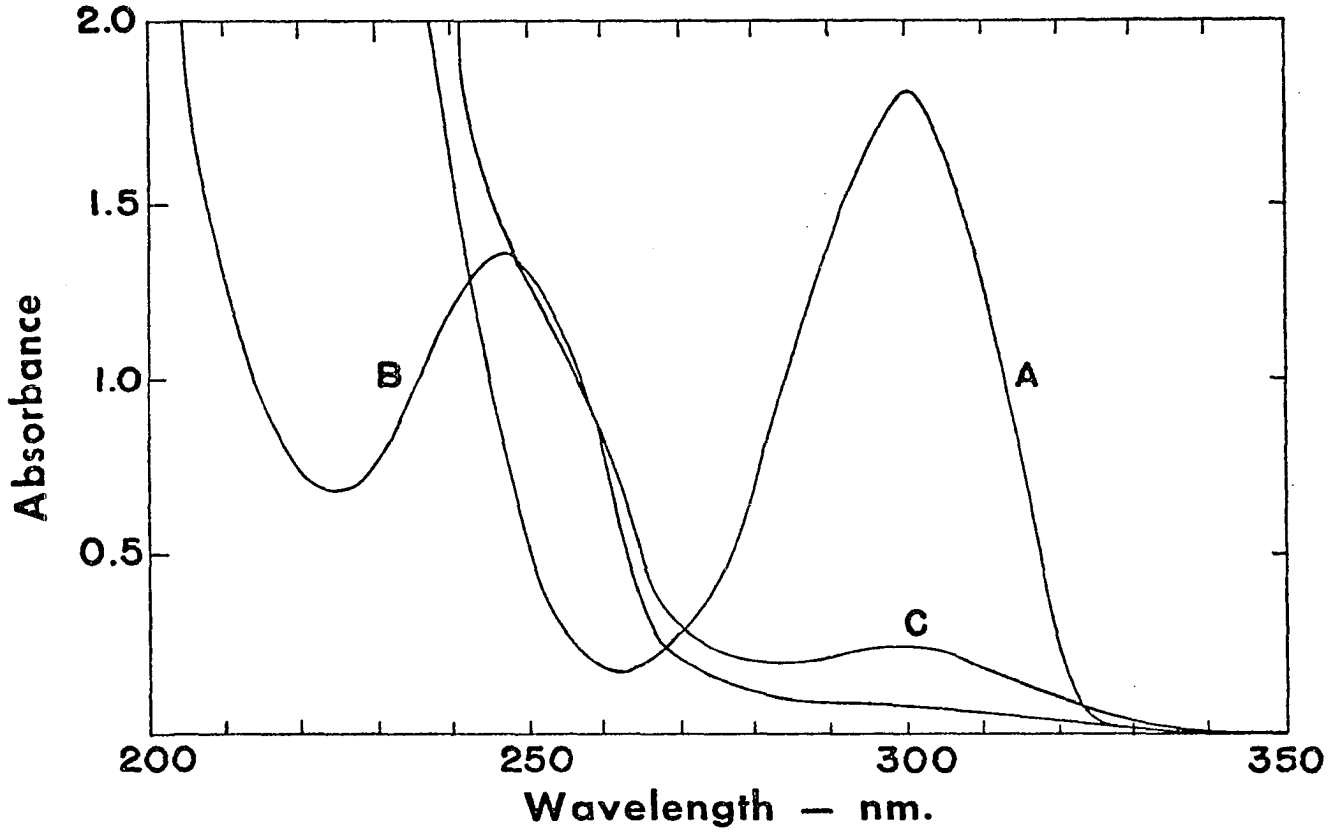

2.0
1.5
1.0
0.5
Absorbance
B
A
C
200
250
300
350
Wavelength — nm.

Table 6. Changes in the ultraviolet absorption spectra of QMIDA and H_2QMIDA as a function of aluminum present

Material	Pure		pH 5	Excess Al	
	λmax (nm.)	A		λmax (nm.)	A
QMIDA	246	1.37		<240 298	--- 0.24
H_2QMIDA	297	1.86		300	1.82

Titration with Aluminum

Ml. of Al added	Eq. Al/eq. of each ligand	QMIDA λmax	QMIDA A	H_2QMIDA λmax	H_2QMIDA A
0.00	0.0	246	0.82	297	0.22
0.50	0.25	246	0.82	298	0.22
1.00	0.50	246	0.82	299	0.22
2.00	1.00	246	0.83	300	0.22
3.00	1.50	245	0.80	300	0.22
4.00	2.00	244	0.74	300	0.23
6.00	3.00	230[a]	0.65	300	0.24
8.00	4.00	---[b]	---	300	0.25

[a]Value approximate, band was a shoulder on the end absorption.

[b]Only end absorption remaining.

246 nm. disappeared completely and an H_2QMIDA band (see below) that was somewhat broader than normal, but at the usual wavelength, appeared, see Figure 18. The broadening of the H_2QMIDA absorption was noted in decomposition studies in earlier work (5, pp. 51-59) and has been reported by Moser and Cassidy (27) to be a result of polymerization. Addition of excess aluminum to the solution of QMIDA caused the end absorption to shift from 210 to 240 nm. Further dilution of the solution moved the end absorption to shorter wavelengths but yielded no absorption peaks. This end absorption is attributed in part to the decomposition products of the QMIDA having no aromatic character and in part to the normal end absorption produced by the H_2QMIDA species that was generated by the disproportionation of the Al-QMIDA species, see Section VII C.

The absorbance of a fresh 5.12×10^{-4} M solution of H_2QMIDA was 1.86 at the wavelength of maximum absorption, 297 nm., with end absorption occurring at about 230 nm. On the addition of excess aluminum the absorption band shifted from 297 to 300 nm. with no significant change in intensity, and the end absorption occurred at 237 nm. This is an indication that the Al-H_2QMIDA compound is stable and that there is no major change in the electronic structure of the hydroquinone ring when the aluminum is coordinated.

In the titration of the QMIDA-H_2QMIDA system with aluminum the ultraviolet absorption was first determined with no added aluminum. The wavelengths of maximum absorption of this spectrum were the same as those of the two respective components above and the experimental absorbances agreed with those calculated using the respective molar ab-

sorptivities determined in Section V B. 2. and earlier work (5, p. 42). Each 2 ml. of the aluminum solution was equimolar to the amount of each ligand present. Thus, 4 ml. was required to give an equimolar ratio of ligand to aluminum. As the first mole of aluminum was added the only change that occurred was the shift of the wavelength of maximum absorption for the H_2QMIDA species to 300 mm. This indicated that the aluminum had selectively united with the H_2QMIDA species and that no union had yet occurred between QMIDA and aluminum. During the addition of the second mole of aluminum the only change in the H_2QMIDA portion of the spectrum was a slight increase in absorbance between the 1.5 to 2.0 mole point, due to the disproportionation of Al-QMIDA. The QMIDA band, however, shifted to a slightly shorter wavelength and decreased. As was determined above, this signified that union of the aluminum by the QMIDA was starting to occur. If the coordination of the aluminum by QMIDA were producing a stable compound a bathochromic shift in the absorption band of the QMIDA would be expected. The decrease in the absorption of QMIDA along with the hypsochromic shift in the wavelength of maximum absorption is actually due to a combination of the disappearance of QMIDA and production of new compounds (cf. VII C.) that absorb at shorter wavelengths.

If the chelation were quantitative, all of the ligand should be coordinated at this point. The small change in the spectrum of QMIDA at 2 moles of aluminum added is an indication that only small amounts of the QMIDA had been combined with aluminum, because the disproportion of the QMIDA does not occur until after union has occurred. The addition of the

third mole of aluminum caused a larger decrease in absorbance and shift in wavelength of maximum absorption of QMIDA. Comparison of the ultraviolet spectrum with that of the QMIDA in the presence of a large excess of aluminum revealed that at this low concentration even the present 100 per cent excess of aluminum was not enough to cause attachment of all of the QMIDA to aluminum. A repetition of the ultraviolet scan five minutes later indicated that either the union or subsequent disproportionation reaction was slow because the disappearance of the QMIDA band continued to occur. The slow step is most likely the union of aluminum and QMIDA. There is no evidence of any detectable concentration of a QMIDA-aluminum compound accumulating before disproportionation occurs (e.g. another absorption band of QMIDA in the ultraviolet at longer wavelength).

After the addition of a fourth mole of aluminum, the absorption band of QMIDA disappeared completely leaving only the H_2QMIDA band. Apparently then, the small increase in the height of the absorption band of H_2QMIDA was a result of the disproportionation of QMIDA. A more detailed treatment of the stoichiometry of the disproportionation is given in Section VII C.

6. Potential of the Quinone-H_2QMIDA system as a function of the concentration of aluminum

In the subsequent work after the study of the QMIDA-H_2QMIDA system with various concentrations of aluminum (cf. Section VII B. 1. and Figure 14) it became apparent that the decrease in the potential readings after more than 1.5 equivalents of aluminum was added was caused by the dispro-

portionation of the Al-QMIDA compound. Such disproportionation produces a decrease in the concentration of the oxidized form of the couple and the measured potential decreases accordingly. Quinone (Q) was added to a solution of H_2QMIDA in place of QMIDA. The decrease in potential observed with the QMIDA present then disappeared and a stable reading was obtained.

From the average zero milliliter reading in Figure 14, the formal potential of the QMIDA-H_2QMIDA couple at pH 5.00 was found to be about 175 mv. vs. s.c.e. The potential of the quinone-hydroquinone (Q-H_2Q) couple under identical conditions is 158 mv. (19, p. 1725). Because of this rather small increase in the formal potential of the system after iminodiacetic acid was introduced into the molecules it was felt that it might be possible to substitute quinone for QMIDA in the couple with H_2QMIDA. A significant mixed potential in the presence of aluminum might then be obtained because of the stability of Q in the presence of aluminum and the known reversibility of the Q-H_2Q system with platinum electrodes.

The titration curve for the addition of aluminum to the Q-H_2QMIDA system was almost identical in shape to those of the QMIDA-H_2QMIDA system (Figure 14) up to one equivalent of aluminum added. Potential shift in both systems is caused by the union of H_2QMIDA with aluminum in this region (cf. Section B. 1.). The curve of Q-H_2QMIDA was, however, displaced downward about 15 mv. compared to the corresponding curve of the QMIDA-H_2QMIDA (5×10^{-4} M). This shift can be attributed, at least qualitatively, to the fact that the formal potential of the Q-H_2Q couple is lower than that of the QMIDA-H_2QMIDA couple and, thus, the overall mixed po-

tential measured would be lower.

Beyond the first equivalent point the Q-H_2QMIDA potential did not increase as quickly as that of the QMIDA-H_2QMIDA. The potential leveled out at about 1.5 equivalents and only a slight increase, 2 mv., was observed with further additions of aluminum. The significant fact was that no decrease occurred in the potential beyond 1.5 equivalents. This behavior confirms the theory that the measured potential shift is caused predominantly by attachment of the H_2QMIDA to aluminum in the presence of the oxidized form of the couple, QMIDA (or Q). As more aluminum is added, union of QMIDA and aluminum occurs and then disproportionation occurs, causing the potential to decrease. When QMIDA is replaced by Q, however, the excess aluminum has no effect and the potential remains constant.

Unfortunately, several other factors discourage hope that a direct potentiometric determination of aluminum using the Q-H_2QMIDA system can be developed. The main problem is the drift in the potential. A significant potential drift has been observed in all of the work with the Q-H_2QMIDA system. This drift did not occur beyond 1.5 equivalents of aluminum added but was as large as 20 mv. during a 10 minute pause after one equivalent has been added. The drift was greatest around the one equivalent region, which corresponds to the most vertical portion of the curve. Both positive and negative drift were observed, with the positive being larger. Although the rate of drift decreased with time, it is often as high as 1 mv. per minute, 10 minutes after the last addition of aluminum. A consistent drift in the positive direction might be attributed to slow formation of the Al-H_2QMIDA compound, but the presence

of negative drift in other titrations makes this explanation improbable. The most likely explanation is the irreversibility of the oxidation of H_2QMIDA on platinum as was discussed in Section VII B. 3. b. The drift only occurs over the part of the titration in which union of aluminum and H_2QMIDA controls the potential of the couple. This irreversibility together with the fact that a mixed potential of the two systems (Q-H_2Q and QMIDA-H_2QMIDA) is being measured results in consistently unstable readings.

The two other limitations of the Q-H_2QMIDA system are the smaller potential range observed and the insolubility of quinone. For the QMIDA-H_2QMIDA system of equal concentration the total range of potential change measured as aluminum was added was 63 mv. The total range of the Q-H_2QMIDA couple was only 30-40 mv. which makes the effects of drift relatively large. The last limitation, although not critical, is the low solubility of Q at pH 5.

The results of the "unknown" samples determined with the calibration curve prepared as described in the corresponding section of Experimental Work were poor. The "unknown" amounts of aluminum were between 0.2 to 1.0 moles per mole of ligand. The relative error in the values obtained was ± 20 per cent for the lower samples (0.2 to 0.6 moles) and somewhat better in the 0.6 to 1.0 mole range.

Pretreatment of the platinum electrode did not improve the results obtained. The instability and drift of the Q-H_2QMIDA potentials were greater than before treatment. After the last cathodic polarization the electrode repeatedly indicated a potential of about 250 mv. vs. s.c.e.

after standing in the solution for 3 minutes. The earlier work without electrode pretreatment had always given starting potentials near 170 mv. The potentials measured with the treated electrode consistently drifted downward until the 1.5 mole point in the titration where stable readings were obtained. At this point the H_2QMIDA is completely coordinated and the potential being measured is due to the reversible Q-H_2Q couple.

Except for the high drift in the readings the system behaved as it did without pretreatment of the electrode. The net effect of the pre-polarizations of the electrode was to displace the curve upward, but not change the shape or range. The increase in potential cannot be readily explained but probably resulted from the effects of traces of more reversible systems on the "sensitized" surface of the platinum. In fact, the enhanced sensitivity of the electrode was evident in the variation of the potential as related to stirring speed. The increase in the drift of the potential over the range where the H_2QMIDA species was producing the potential change is further proof of the high irreversibility of H_2QMIDA as discussed in Section VII B. 3. b.

C. The Nature of the Reaction of Aluminum with QMIDA and H_2QMIDA

From the data and results presented in Section B. it became evident that the QMIDA-H_2QMIDA system was too irreversible to be useful for the direct potentiometric determination of aluminum. It was also clear that the reactions of aluminum with QMIDA and with H_2QMIDA were quite different. In this section the data obtained will be combined with related work

from the literature, to further elucidate the chemistry of the reaction of aluminum with QMIDA and H_2QMIDA.

In the following section the order of events occurring as aluminum is added to a solution of QMIDA and H_2QMIDA is briefly described.

1. Order of reaction

When aluminum is slowly added to an equimolar solution of QMIDA-H_2QMIDA at pH 5 (preferably of concentration about 1×10^{-3} M), combination first occurs only with H_2QMIDA. This reaction is accompanied by a shift of the reduction potential in the positive direction, Section B. 1., by a change in the ultraviolet spectrum, Section B. 4., and by a change in the shape of titration curve of H_2QMIDA with sodium hydroxide, Section B. 1. Titration of H_2QMIDA with sodium hydroxide in the presence of aluminum involves the neutralization of three hydrogen atoms. The compound formed is thus a one to one compound, Al-H_2QMIDA, carrying no charge, Section B. 2. The formation of this compound reduces the concentration of H_2QMIDA causing the reduction potential to shift in the positive direction.

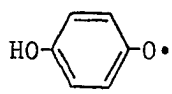
After one equivalent of aluminum has been added to the equimolar mixture of QMIDA and H_2QMIDA formation of a slightly-dissociated compound of QMIDA begins. This reaction is accompanied by the disappearance of the absorption band at 246 nm., Section B. 4., by a change in the neutralization titration curve, an additional 1.4 moles of hydrogen ions being neutralized that are not released by mere chelation, Section B. 2., and by a shift in the reduction potential in the negative direction (beyond

1.5 equivalents of added aluminum), Section B. 1.

2. Disproportionation of QMIDA

The disappearance of QMIDA was a direct result of the formation of the aluminum compound. Although QMIDA decomposes slowly when alone in aqueous solution Section V B. 8., the composition is greatly accelerated by the aluminum. The aluminum then either causes the decomposition of QMIDA as union occurs by attacking the ortho carbonyl group, or stabilizes some subsequent reactive intermediate formed by the QMIDA molecule.

It is widely accepted that quinone systems react through a variety of radical mechanisms. Many of these radical systems have been studied and the radicals with finite lifetimes identified using ESR. Waters (46) has reported that semiquinone radicals such as



usually disproportionate to a mixture of quinone and hydroquinone. If aluminum in some way facilitated the formation of an analogous radical the appearance of H_2QMIDA after aluminum was added to QMIDA, Section B. 4., could be easily explained.

Under similar conditions (neutral aqueous solution, but no aluminum) several workers have reported the oxidation of quinone to hydroxyquinones (6; 14; 16; 31; 48). These hydroxyquinones are not stable and undergo change by a variety of reactions, one of the more common being ring-opening (13; 36).

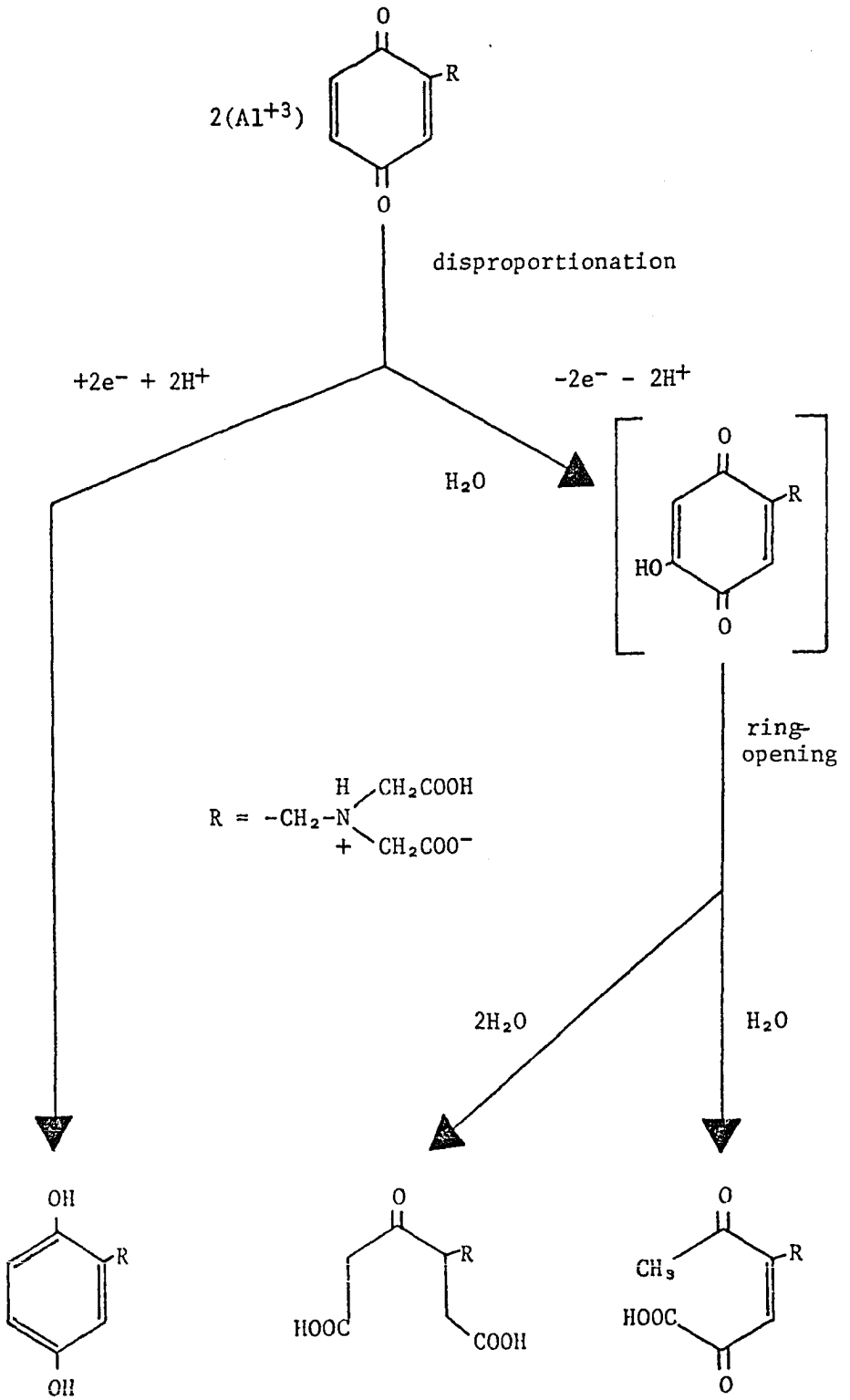
The combination of a disproportionation followed by ring-opening offers an explanation of the phenomena observed in the decomposition of the aluminum-QMIDA compound, Figures 19 and 20. Immediately after (or as) the aluminum-QMIDA compound is formed a disproportionation takes place. One molecule of QMIDA is oxidized to the hydroxyquinone, which being unstable undergoes ring-opening according to the mechanisms given by Schtschukina (36) and Flaig (13). The other molecule is reduced to H_2QMIDA. No net oxidation-reduction occurs in the overall process. Support for this proposal is provided by the results reported in Section B. In the following paragraphs the results and proposed mechanism are compared.

The reduction potential of the QMIDA-H_2QMIDA-aluminum system shifts in the negative direction beyond 1.5 equivalents of aluminum added, indicating that QMIDA is being removed, Section B. 1.

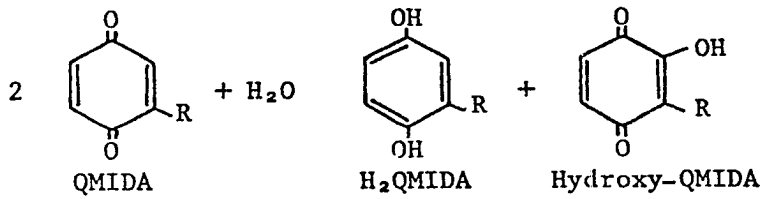
The titration of QMIDA in the presence of aluminum with sodium hydroxide, Section B. 2. a., with equimolar aluminum present, about 3.3 moles of hydrogen ions are produced per mole of QMIDA. The additional 1.3 moles can be explained as follows: 1) half of the QMIDA is reduced to H_2QMIDA which then unites (or remains united) with the aluminum. A precipitate, probably aluminum hydroxide (only half of the aluminum is tied up with the H_2QMIDA present, the other half can be pulled away from the weak compounds formed with the ketoacids present), was observed when about three moles of sodium hydroxide were added, but it redissolved later in the titration.

The H_2QMIDA loses 3 acidic hydrogen atoms upon union whereas the

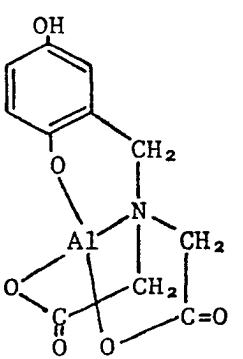
Figure 19. The disproportionation of QMIDA in the presence of aluminum


2(Al+3)
disproportionation
+2e- + 2H+
-2e- - 2H+
H2O
ring-opening
R = -CH2-N(H)(+)(CH2COOH)(CH2COO-)
2H2O
H2O
HO
HOOC
COOH
CH3
HOOC

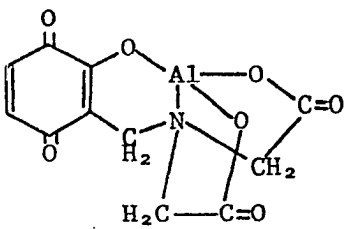
Disproportionation



Disproportionation in the presence of aluminum



Al-H_2QMIDA($-3H^+$)
Stable



Al-Hydroxy-QMIDA($-3H^+$)
Unstable. Undergoes
ring-opening

Figure 20. Disproportionation of QMIDA. Structural formulas of the aluminum derivatives of H_2QMIDA and QMIDA

QMIDA loses only 2, so there is a net increase of (1 hydrogen) x (½ mole of QMIDA) = 0.5 moles of hydrogen ion. 2) the other half of the QMIDA is oxidized to the hydroxyquinone which undergoes ring-opening and forms either an unsaturated ketoacid or a saturated ketoacid, Figures 19 and 20. The continued presence of aluminum would produce no change in the number of hydrogen atoms released when considering the iminodiacetic acid (-R) portions of these products. The carboxylic diacid would produce (2 x ½ mole of QMIDA) = 1 mole of additional acid if it were the sole product of the ring-opening. If the monocarboxylic acid were the sole product of the ring-opening there would, similarly, be ½ of a mole of acid produced. Therefore, the additional 0.8 moles of acid produced that was not a result of the H_2QMIDA formation was from a mixture of the mono and dicarboxylic acids in a ratio of approximately 2:3. The presence of greater amounts of aluminum increased the ratio of diacid but precipitation of aluminum hydroxide prevented attainment of more significant data. The darkening of the solutions after the titration indicated that further degradation of the products occurred as the titration indicated that further degradation of the products occurred as atmospheric oxygen diffused into the open beaker.

There was no data in Section B. 3. that could be applied toward further elucidation of the nature of the disappearance of the QMIDA.

The ultraviolet absorption spectra of QMIDA and aluminum, Section B. 4., proved to be the most enlightening of the data obtained. For after the aluminum had united with the H_2QMIDA the ultraviolet spectrum revealed that the QMIDA disappeared as more aluminum was added, but at the same

time more H_2QMIDA was produced, Figure 18. Calculations using the respective molar absorptivities of QMIDA and H_2QMIDA were employed to determine the amounts of QMIDA remaining and H_2QMIDA formed. It was found that at very low concentrations of aluminum and QMIDA, relatively less H_2QMIDA was formed than if excess aluminum was added to a higher concentration of QMIDA (here, the solution had to be diluted before the spectrum was obtained). At the higher concentrations which corresponded to the usual working ranges (1×10^{-3} M) of QMIDA, it was found that one-half of the QMIDA reverted to H_2QMIDA when aluminum was added. The reduction of QMIDA to H_2QMIDA was also observed in the earlier stability studies, Section V B. 8. In one study, although there was still a small amount of QMIDA present, measurement of the increase in absorbance at 297 mn., indicated that 75 per cent of the QMIDA had been reduced to H_2QMIDA after 3 days. It is, therefore, probable that the aluminum catalyses, somewhat drastically--to cause ring-opening, a type of normal decomposition for the QMIDA that usually is much slower (catalyzed by light and trace impurities) and less harmful to the ring system.

There was no evidence of any measurable amount of hydroxyquinone in the ultraviolet spectra although indications of it were found in earlier work, Section IV B. 1. The disappearance of all other bands in the ultraviolet spectrum, except for that of the H_2QMIDA (Figure 18), was a clear indication of loss of aromatic character of the remaining QMIDA, which could only be explained by ring-opening. The increased end absorption that accompanied the disappearance of QMIDA is consistent with this observation and was undoubtedly due to the saturated and unsaturated keto-

carboxylic acids formed in the ring-opening reaction. Such acids have strong ultraviolet absorption at wavelengths of less than 240 nm. (38, pp. 159-162).

The replacement of QMIDA with quinone (Q) was discussed in Section B. 5. and this section contains no data for the study of QMIDA other than to confirm the fact that the decomposition of QMIDA was the cause of the decreases in the potential of the QMIDA-H_2QMIDA in the earlier work.

The proposed disproportionation of QMIDA, Figures 19 and 20, is then consistent with the reported behavior of quinones as well as with the data obtained. However, it is probable that there are numerous other minor reactions occurring during the decomposition of QMIDA.

3. Additional related literature

A search of the literature revealed that since before the turn of the century workers have been quite active in the study of quinone-hydroquinone systems and the decomposition products of such systems as they relate to humic acid formation. Humic acid has been defined as "that portion of the soil organic matter which is soluble in base and insoluble in mineral acid and alcohol" (39). It is "an ubiquitous brown polymeric constituent of the organic matter of soil". The study of humic acids is so complex that to date no one agrees on even a general representative structure for them. However, because this subject deals with what we might call "spontaneous" reactions of quinones and hydroquinones in slightly acidic or basic solution, it was usefully applied to the decomposition of QMIDA. Two excellent, recent reviews on humic acids are available (40; 47). The

more recent works in the chemical literature dealing with reactions and decompositions of quinone systems are mainly of work done in wholly or partially nonaqueous solvents and thus of limited use here.

A number of workers have been engaged in studies of the polymerization products of quinones, H. G. Cassidy and W. Flaig having been the most active. Taylor and Battersby have edited a 350 page book dealing with the many forms of coupling reaction of phenols, quinones, and more complex naturally occurring compounds (8). Excellent summaries of the general chemical and physical behavior of quinones (42, pp. 899-913) and hydroquinones (32, pp. 483-492) are available.

The publications of two groups of workers dealing with similar compounds (6; 44) make it seem quite likely that there is formation of dimers between QMIDA molecules. Recently, it has also been reported that the slow but discernible drift in the quinhydrone electrode was caused by a nucleophilic attack by acetate ion on the quinone portion of the couple (7).

The overwhelming complexity of the decomposition mechanisms of quinones is evidenced by the large number of papers dealing with the subject, especially in the humic acid area. The great reactivity of quinones and the decomposition products of quinones led to the decision not to attempt isolation of the products of the disproportionation of QMIDA. The products would undoubtedly undergo further reactions during the isolation procedure and yield no data of practical value toward the study of the original oxidation-reduction system.

VIII. SUMMARY

An investigation has been made of an oxidation-reduction couple composed of compounds bearing a chelating group with the objective of making a reversible electrode responsive to metal ions.

The compounds studied are the analogs of quinone and hydroquinone: 1,4-quinone-2-methyleneiminodiacetic acid and 1,4-dihydroxyphenyl-2-methyleneiminodiacetic acid.

Earlier work (Contario, M.S. Thesis, Iowa State University, 1968) on 1,4-dihydroxyphenyl-2-methyleneiminodiacetic acid (H_2QMIDA) has been extended, particularly in respect to fluorescence when irradiated with ultraviolet light, union with calcium and magnesium, titration with standard oxidizing agents, and conversion to 1,4-quinone-2-methyleneiminodiacetic acid (QMIDA) by oxidation.

H_2QMIDA has been found to fluoresce in the ultraviolet with the wavelength of maximum fluorescence occurring at 352 nm. when an excitation wavelength of 292 nm. was used.

The fluorescence as affected by pH and by the presence of calcium and magnesium (other properties of the calcium and magnesium compounds are discussed in the M.S. work) has been investigated. The compound formed by calcium and H_2QMIDA proved to be eight times more fluorescent than the free acid or the magnesium compound.

Potentiometric titration of H_2QMIDA using eleven chemical oxidizing agents was attempted, in 1 N sulfuric acid and in acetate buffer of pH 5.5. Smooth oxidations resulting in conventional titration curves with

good end-points and interpretable stoichiometry have been obtained only with two oxidizing agents, potassium molybdicyanide and periodic acid. Four of the oxidizing agents used produced no oxidation under any conditions.

At low concentration a one-electron oxidation of H_2QMIDA to the semiquinone was obtained using the molybdicyanide. With higher concentrations of molybdicyanide and with periodic acid, a normal two-electron oxidation to QMIDA occurred.

The electrochemical oxidation of H_2QMIDA to QMIDA by controlled-anode potential on mercury, platinum, gold, and graphite electrodes has been attempted. No oxidation occurred; the QMIDA-H_2QMIDA system is apparently irreversible.

QMIDA has been prepared by the oxidation of H_2QMIDA with sodium periodate. Pure material can only be prepared by close attention to temperature, pH, manner of mixing reagents, and deaeration. Slow, spontaneous decomposition sets a limit on the maximum purity which can be obtained.

In the ultraviolet absorption spectrum of QMIDA only one band appears, at 246 nm. The molar absorptivity at this wavelength is 17,400.

The purity of QMIDA has been found to be 98.5 per cent by neutralization titration and 92.4 per cent by reduction titration; the major impurity is H_2QMIDA. From the titration data values were found for the acid dissociation constants: pK_1, 2.64; pK_2, 7.31. The formal potential of the QMIDA-H_2QMIDA couple has been found to be 0.68 volts vs. N.H.E. in 0.01 M sulfuric acid. The infrared and PMR resonance spectra of QMIDA have been obtained and found to be consistent with the proposed structure.

The solubility of QMIDA is 5.6 g. per 1. in deionized water and 6.3 g. per 1. in 0.1 M sulfuric acid.

Decomposition of QMIDA occurs on standing in aqueous solution; the rate of the decomposition is accelerated by light. Judging from the ultraviolet absorption spectrum, the decomposition product is probably H_2QMIDA.

Attempts to prepare the quinhydrone of QMIDA and H_2QMIDA in water, acetone and ethanol were not successful.

Potentiometric titrations of H_2QMIDA with potassium molybdicyanide and sodium periodate have been performed in the presence of various metal ions. The effects of thirteen metals on the formal potential of the QMIDA-H_2QMIDA potential were thus obtained. Three metal ions, aluminum, iron, and thorium, produced a significant shift of the formal potential, each in the positive direction.

A detailed investigation of the interaction of aluminum with QMIDA and H_2QMIDA has been made. The potential of the QMIDA-H_2QMIDA couple increases with increasing concentration of aluminum. The optimum concentration of the ligand is approximately 1×10^{-3} M. Aluminum first unites preferentially with H_2QMIDA and then with QMIDA as excess aluminum is added.

QMIDA and H_2QMIDA have been titrated with alkali in the presence of aluminum. Two acidic hydrogen atoms are displaced on the union of H_2QMIDA and aluminum. With QMIDA, the presence of the aluminum causes decomposition and the release of an additional 1.3 moles of hydrogen ions; these are not directly attributable to the union with aluminum. This discrep-

ancy arises from the disproportionation of QMIDA after union with aluminum.

Potentiometric titrations of aluminum with QMIDA, H_2QMIDA and an equimolar mixture of the two ligands have been carried out. The curves of each of the titrations are quite different but prove to be of no use in the determination of aluminum.

The ultraviolet absorption spectra of the QMIDA-H_2QMIDA system during titration with aluminum indicates that after union with aluminum, disporportionation of QMIDA occurs producing H_2QMIDA and hydroxy-QMIDA, the latter undergoing further change forming a mixture of saturated and unsaturated ketoacids. The decomposition of QMIDA results in a shift of the potential of the couple in the negative direction. A stable aluminum-QMIDA compound is not produced.

Because of the instability of QMIDA in the presence of aluminum, the QMIDA was replaced with quinone and the potential of the quinone-H_2QMIDA system measured as a function of the concentration of aluminum. There was little change in the behavior of the system except that the potential was stable with excess aluminum present. Determinations of the aluminum in "unknown" samples were carried out using a calibration curve prepared using known amounts of aluminum; the results were poor, owing largely to instability (drift) of the potential being measured. A pretreatment ("cathodic conditioning") of the platinum indicator electrode only increased the drift in potential.

The probable nature of the decomposition of QMIDA after union with aluminum has been deduced from various lines of evidence. Disproportionation to the corresponding hydroquinone (H_2QMIDA) and hydroxyquinone

(hydroxy-QMIDA) is probably the first step followed by further degradation of the hydroxyquinone by ring-opening and polymerization.

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