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An investigation of arsenic(V)-catechol complexes

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There is not, at this time, a simple method for the simultaneous determination of As(III) and As(V) at trace levels. The development of such a method is needed, as the toxicities of these two species differ so greatly.

As(III) and As(V) are polarographically reducible in the presence of excess catechol, but the wave produced by As(V) is dependent on time, pH and catechol concentration as well as As(V) concentration. In order to understand this behavior, determination of formation constants for any complex species present were needed to identify which species is electroactive. The literature to date on the subject of As(V) - catechol compounds has shown that there is not a thorough understanding of what species are present and what their stabilities are.

By potentiometrically measuring the amount of protons liberated in the reaction between H_3AsO_4 and catechol it was found that $\beta_1 \simeq 0.01$ $\beta_2 \simeq 0.02$, $\beta_3 = 7.5 \pm 1$. It appears that all the complexes are moderately acidic and have $pK_a < 1$. While the tris complex is by far the predominant species, by comparing distribution curves of the complexes as a function of catechol concentration and the limiting current produced polarographically as a function of catechol concentration it was found that the 1:1 complex is the reducible species. Together with rate information about the reactions involved, the time-concentration behavior of the reduction wave was explained.

AN INVESTIGATION OF ARSENIC(V)-CATECHOL COMPLEXES

by

RONALD P. HAAK

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TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

It is well known that various oxidation states of arsenic are more toxic than others. As(V) is only about one-tenth as toxic as As(III) (1). Arsine gas is extremely toxic in concentrations as low as $0.3mg/m^3$ (2). In addition to its natural occurence, arsenic (usually As(III)) has been used extensively as a herbicide and has therefore been found in increasing concentrations in natural water systems. It would be much more advantageous when determining the amount of arsenic present, to be able to distinguish between these oxidation states.

The methods used for arsenic analysis are quite varied. A standard method now employed utilizes a red colored complex resulting from a reaction between arsine and silver diethyldithiocarbamate. This analysis has a working range of 1-20µg of arsenic (about 1ppm) (4). Atomic absorption (5) and emission spectroscopy (4) have given low detection limits but also require the generation of arsine gas and do not distinguish between the oxidation states. Isotope dilution (6) and a colorimetric method (7) can be used to determine the distribution between As(V) and As(III) but these methods tend to be slow and insensitive. A complete review of methods used for arsenic determinations has been compiled by Talmi and Feldman (8).

Historically, electrochemical techniques have often been able to combine low limits of detection and the ability to distinguish

between the various oxidation states of a metal. There has been an ongoing attempt since the mid 1950's to develope potentiometric and voltammetric methods to be used for arsenic analysis.

Fabrication of an arsenate selective electrode has been attempted and met with limited success (9). Whereas nernstian response was found over a reasonable arsenate concentration range (10^{-2}-10^{-4}M), this range was too high to be applicable to trace analysis.

Ridgeway et al. (10,11) have utilized differential pulse polarography to study the reduction of various alkyl and aromatic arsinic and arsonic acids. They found all the waves are irreversible, using cyclic voltammetry, but give linear response for i_p vs. concentrations and detection limits of about 0.1-1ppm, depending upon the organic group present. They note that studies are needed to elucidate the electrode reaction mechanism. The half wave potentials were found to be pH dependent and they speculate that it is the protonated form of the acid that actually undergoes the initial charge transfer. They also found that the limiting current is not entirely diffusion controlled.

Anodic stripping voltammetry (ASV) has been used by Matson et al. (12) to determine total arsenic and could conceivably be used to distinguish between As(V) and As(III). The procedure reported consisted of an initial reduction step of As(V) to As(III) using 1% Cu_2Cl_2 in 37% HCl solution. $AsCl_3$ vapor was generated from this solution and was collected in deionized water, which was analyzed for arsenic by ASV. This method appears to be accurate to the nanogram level and shows excellent selectivity. It was speculated

that by first running the analysis in the absence of Cu_2Cl_2, to allow for the detection of the As(III) alone and then reducing the As(V) to As(III) and repeating the measurement, the concentrations of both species might be measured.

Polarography has been the one method where the simultaneous determination of both As(V) and As(III) is possible. Meites (13) found that both species produced reduction waves in 12M HCl, but the wave associated with As(V) is not well defined. Bard and White (14) studied the polarographic waves resulting from the reduction of As(V) and As(III) in the presence of pyrogallol. Arsenate solutions show a three step wave corresponding to the reduction steps As(V)→As(III)→As(0)→As(-III). From the first wave they calculated a diffusion coefficient for the As(V)-pyrogallol species of 1.7×10^{-7} cm/s which suggested a bulky, slow moving complex. Polarograms arising from the reduction of As(III) in the absence and presence of pyrogallol showed little difference, which suggested to Bard that As(III) is not complexed by pyrogallol. Comparing $E_{\frac{1}{2}}$ values for the different steps of the As(V) and As(III) reduction waves indicated the As(V) pyrogallol complex proceeds to uncomplexed As(III).

The determination of As(III) at the parts per billion level was demonstrated by Myers and Osteryoung (15) utilizing differential pulse polarography. In a 1M HCl electrolyte, response is linear from 0.3µg/l up to 60mg/l. Above 60 mg/l, it was found, As(0) is apparently adsorbed and when the concentration is up to 600mg/l the current becomes independent of As(III) concentration. By using methylene blue, analysis of solutions with the As(III) concentration between 60 and

600mg/l is possible.

Roe (16) observed that As(V) in the presence of catechol as well as pyrogallol produces a reduction wave. These waves are time dependent. The current increases to a maximum and subsequently decays to a minimum. Holding the As(V) concentration and drop time constant it was found the maximum and final current and the rate of the rise and fall of the current are functions of pH and catechol concentration.

While it has been demonstrated by the forementioned researchers that As(III) can be determined at trace levels by voltammetric techniques there has yet to be a system where As(V) can be determined at these low levels simultaneously with As(III). The arsenate-catechol system showed promise as a polargraphic technique, demonstrated by Bard and White (14), for such an analysis. In order to rationalize the data obtained thus far, a thorough understanding of the arsenate catechol system is needed. From the identification and determination of formation constants for any complexes present the species which is responsible for the reduction wave could be identified and conditions adjusted to maximize its concentration.

Weinland and Heinzler (17) first prepared an arsenate-catechol complex in 1919 by adding catechol to a boiling aqueous solution of arsenic acid. Upon standing over a period of days, colorless crystals separated out which were assigned the "structure" $H_3(O\text{-}As\text{-}(OC_6H_4O)_3)\cdot 4H_2O$. They found in all cases the compound behaves as a monobasic acid. There then arose a controversy as to the structure of the solid salt and the complex in solution. Reihley, Sapper and Kall (19)

studied the compound and assigned structure I in Figure 1. They based this decision on the fact that only four molecules of water could be removed from the pentahydrate and the compound behaves as a monobasic acid. Rosenheim and Plato (18) proposed structure II, Figure 1, and were able to resolve the anion into optically active forms, compatable with their structure. Jones and Craddock (20) commented that structure I could also be optically active if the monodentate catechol and the coordinated water molecule occupied cis positions.

Jones et al. (20-24) went on to do several studies mainly concerned with their observations that upon dissolution of the levo form of the complex ion the complex loses its optical activity in acidic solution. Using the method of Mann and Watson (25) for resolution of the anion and conversion to the barium salt, Jones et al. made a series of kinetic measurements on the hydrolysis of the complex using the loss in optical activity (20,21), the resulting change in pH of the solution (20), and the change in conductance of the solution (22). They found that the complex is apparently stable in basic solutions (they typically used 10^{-2}M solutions) but as the pH was lowered the rate of hydrolysis becomes measurable at about pH=3. They found that the rate of hydrolysis is apparently first order in complex concentration and first order in hydrogen ion concentration. From titration curves obtained from the titration of solutions in which the complex acid had been dissolved they determined the pK_a of the complex to be in the range of 2.75-2.2. These values bear a suspicious resemblence to pK_1 for arsenic acid, which is 2.22. An important point to note here is that

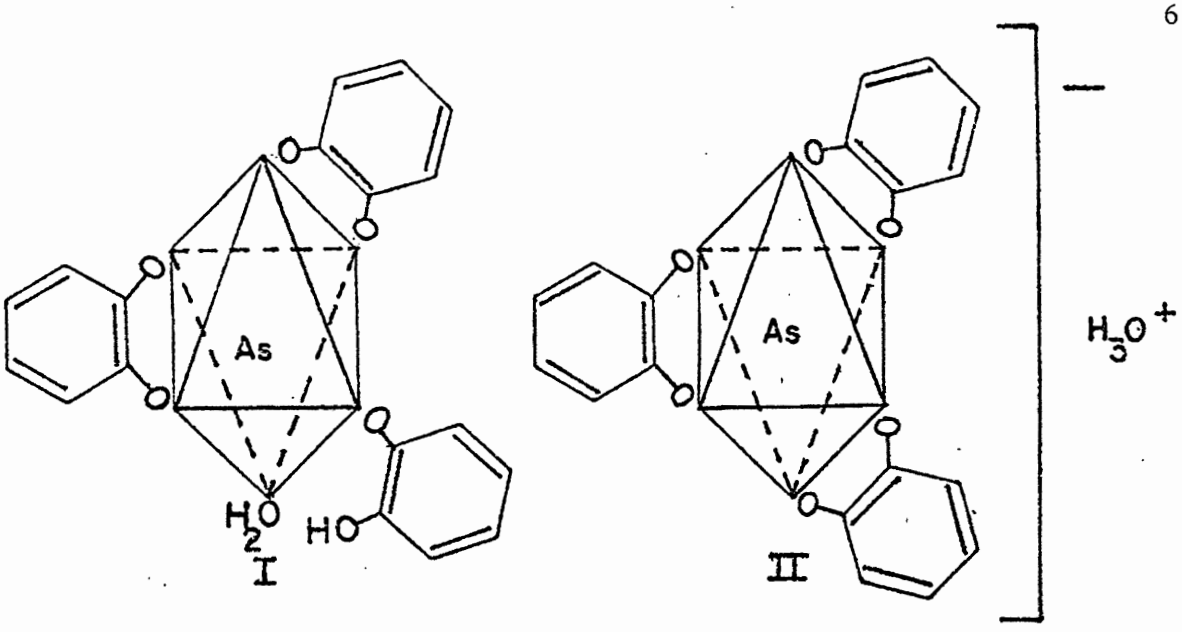


Figure 1. Proposed structure for the 1:3 As(V) catechol complex.

because of the pK_a value assigned to the complex, a complete dissociation reaction is not in agreement with the experimental data. Since arsenic acid has a lower pK_1 the pH would fall, not rise as was observed. The equilibria proposed by Jones et al. is:

(1) $((RO_2)_2As(ORO)H_2O)^- + H_3O = H_2O + ((RO_2)As(OROH)(H_2O))$

(2) $((RO_2)_2As(OROH)H_2O) = (RO_2)_2AsOH + R(OH)_2$

An overall equilibrium constant for the combination of the two reactions was calculated to be K_0=0.960 (22), and the rate constant for the hydrolysis reaction (21) was determined as $k=5.71\times10^{-3}$/Ms.

A disturbing inconsistancy between this reaction mechanism and the experimental data which was not explained was that the rate of loss of optical activity of solutions containing dissolved complex was reported to increase when excess catechol was present (20).

Following the above publications there appeared a number of studies pertaining only to the structure of the 1:3 As(V) to catechol complex. Mason and Mason (26) noted that the absorbance spectra of solutions prepared from the solid complex are essentially the same as the spectrum of a catechol solution and the molar absorptivity of the catechol is one third that of the complex. From analysis of the absorbance spectra and circular dichroism by means of a coupled dipole model, they concluded that structure II, Figure I, is correct. As a sidelight they mentioned that an NMR spectrum of the dissolved complex in D_2O showed a closely spaced doublet for the aromatic protons, inconsistent with the structure chosen. They rationalized that while there might possibly be an exchange between the two structures, this would not be consistent with the relatively slow rate of racemization of the complex acid noted by Jones et al. By comparing the circular dichroism and absorbance spectra of the complex acid and complex anion they also concluded that the complex anion is not appreciably protonated at pH 1.0

Ito (27) used x-ray diffraction and circular dichroism to come to the same conculsion as to the structure of the solid complex. Utilizing a three dimensional Fourier method coupled with x-ray diffraction he was able to determine that the crystalline complex also has a tris chelate structure. His circular dichroism differed slightly from that presented by Mason and Mason (26) but still indicates that a tris structure is correct.

Wieber and Mallon (28) synthesized a number of organo-arsenate molecules in which arsenate is hexacoordinated and contains no water

molecules in the coordinate sphere. This fact was determined from NMR spectra. Mann (29) has compiled a number of different organo-arsenic compounds, among which are examples of bridged arsenites via a catechol molecule.

A group of papers (30-32) was published where the arsenate catechol system was utilized for a solvent extraction procedure. Rais et al. (30,31) found that cesium could be extracted efficiently into nitrobenzene from an acidic media in the presence of the 1:3 arsenate-catechol complex. Writing the general reaction

$$(3)\quad H_3AsO_4 + nH_2L = H^+ + AsO_{3-n}L_n^- + (n+1)H_2O$$

where n=1-3 and the complex formed may or may not be protonated. They utilized the fact that the titration curves of solutions of 0.005M As(V) changes as catechol (0-0.2M) is added to calculate a formation constant β_3'=1400 for the 1:3 species. It appears they were not consistent in the As(V) species for which they wrote the reaction, and the species they used to calculate the formation constant. All their data points to $H_2AsO_4^-$ as opposed to H_3AsO_4 being used in their calculation. This would correspond to a β_3=10±2 based on H_3AsO_4 being the species used in the calculation. These titrations were done in 1M NaCl solutions.

They assumed that the uncomplexed catechol concentration was essentially equal to the added catechol concentration. The authors commented that although there is a possibility of three complexes being present their experimental data was apparently reliable only in the region where the 1:3 complex is formed. The point was also brought out that as the concentration of the As(V) is increased, the formation con-

stant appears to decrease (β_3'=680 when C_{As}=0.1M). From the titration curves the acid dissociation constant, K_{a3}, of the complex was estimated to be between 0.04-0.1.

A number of years later Rais and Krtil (32) estimated from solvent extraction data, that β_3^*=0.6 where β^* is written in terms of a protonated complex and H_3AsO_4. Noting the range of K_{a3} puts β_3 between 6 and 15.

Essentially the same titration experiment done by Rais et al. (31) was recently reported by Votava and Bartusek (33). Titrating 0.037M KH_2AsO_4 solutions which had various catechol concentrations (between 0.16 and 0.80M) with base they calculated from the shift in the second inflection point that β_2=0.041, β_3=0.054. They also assumed that the uncomplexed catechol concentration was essentially equal to the concentration added.

Votava and Bartusek also pointed out that redox reactions of the type

$$H_3AsO_4 + H_2L = H_3AsO_3 + L + H_2O$$

$$H_2AsO_4^- + H_2L = H_3AsO_3 + L + OH^-$$

are possible, but that oxidation products of catechol would discolor the solution (L=quinone) which was not observed, also the reaction of catechol with $H_2AsO_4^-$ does not involve consumption of a proton.

Summarizing the information about the system to date, it is obvious that As(V) forms a weak complex with catechol. The formation constants determined by the two groups (31,33) mentioned differ by two orders of magnitude. Using this information it seems that Jones et al.

(21-24) were apparently observing a simple dissociation of the 1:3 complex and, although it is not clear from the publications, they probably titrated essentially arsenic acid solutions which were the basis for the pK_a values reported. Roe (16) observed that the current produced from the reduction of As(V) in the presence of a large excess of catechol rises to a maximum and decays. The maximum current found by extrapolation was the same at all pH's studied (pH=0-3). The final current and rate of decay between the initial and final current is a function of pH and catechol concentration. At pH=0 the current was essentially a factor of ten greater than the current at pH=2.

The object of this study was to determine the formation constants of any complex present and from these values, along with rate measurements associated with the dissociation of the 1:3 complex, identify the species which is polarographically reducible and explain its time concentration behavior.

MATERIALS AND APPARATUS

pH Meter and Accessories:

All pH measurements were made with a Chemtrix plon Meter Type 50, utilizing the expanded scale for all pH-stat titrations. The electrodes used were a Corning, rugged pH glass electrode and a double junction reference electrode consisting of a saturated calomel electrode inserted into a glass sleeve containing 1M NaCl and in contact with the solution by means of a porous vycor plug. The meter was initially calibrated with standard buffers.

Catechol:

Baker grade pyrocatechol was used without further purification. The crystals were pure white except for small amounts of black crystals, presumibibly oxidized catechol, which could be removed prior to weighing.

Arsenic Acid Solutions:

Arsenic acid solutions were typically prepared by boiling Baker analyzed As_2O_5 in distilled water until the solution cleared. This solution was filtered and standardized by potentiometric titration.

Acids and Bases:

All acids and bases were prepared and standardized in the normal way. Sodium hydroxide and perchloric acid were from Mallinckrodt and were analytical grade.

Sodium Perchlorate:

The sodium perchlorate used for ionic strength adjustment was prepared by titrating solutions of NaOH with $HClO_4$.

Preparation of Tris(1,2-dioxybenzenato)Arsenic(V) Pentahydrate:

The procedure of Mann and Watson (25) was used for the preparation of the solid 1:3 complex, $HAs(O_2C_6H_4)_3 \cdot 5H_2O$. 200g of catechol were dissolved into a boiling solution of 80g H_3AsO_4 in 200ml H_2O. This solution was stored under a nitrogen atmosphere to avoid oxidation of the contents. After three days large colorless crystals had developed. After a total of ten days the crystals were seperated from the solution and washed with cold H_2O. Because it had been noted that the complex undergoes decomposition easily upon heating the crystals were vacuum dried. NMR spectra showed that there was about six water molecules present for every molecule of complex.

Polarography:

All polarographic measurements were made with a Sargent Model XV polarograph. Potentials were calibrated with a digital voltmeter. Currents were calibrated utilizing a test resistor in the polarograph. An H-cell was used for the reaction vessel. The reference electrode was a saturated NaCl, Hg/Hg_2Cl_2 system and was connected to the sample reservoir with a 1M $NaNO_3$ in 4% agar salt bridge. Solutions were deoxygenated by bubbling argon through for five minutes. The same capillary and drop time were used for all current measurements. At E_{de} vs SCE(NaCl)=-0.4v, m=8.17mg/drop, t=5.5sec/drop.

NMR Spectroscopy:

All NMR spectra were run on a Varian EM390 NMR spectrometer equipped with a varible temperature controller. Samples were dissolved in "spec" grade D_2O.

Raman Spectroscopy:

Raman spectra were recorded in a 90^{o} geometry with a Jarrell-Ash 25-300 spectrophotometer equipped with an ITT FW 130 130(S - 20) photomultiplier and photon-counting electronics. A Coherent Radiation MG52 Ar-Kr ion laser was used for sample illumination. The exciting wavelength was 514.5nm the scan speed 1.2cm/s and the resolution was $8cm^{-1}$. Scans were made between $520\text{-}880cm^{-1}$.

EXPERIMENTAL RESULTS

Potentiometric Titrations:

As mentioned in the introduction, potentiometric titrations have been used previously (31,33) for formation constant determination. Because of the descrepency between these results and to bring out some additional information, it appeared worthwhile to take another look at this experiment.

One experiment consisted of titrations of solutions of arsenic acid solutions (0.113M) containing various amounts of catechol. These solutions were allowed to sit for a day before titrating them with NaOH. The titration curves obtained are shown in Figure 2. These curves were not analyzed quantitatively for the amount of As(V) uncomplexed in a given solution, but will be used to provide general information on the acidic characteristics of the complexes.

Since Jones et al. work (20-24) can be interpeted as a slow dissociation of the 1:3 complex, it would be expected that titration curves of solutions prepared from the solid 1:3 complex would vary with time. Figure 3 shows two such titration curves. Curve I was obtained by rapidly titrating immediately after the solid complex had dissolved. Curve II was obtained from a similar sample which was titrated more than twelve hours after the complex was dissolved.

From the pK_a values of arsenic acid and catechol (arsenic acid, pK_1=2.22, pK_2=7.00, pK_3=11.5; catechol, pK_1=9.3, pK_2=12) the pH's which

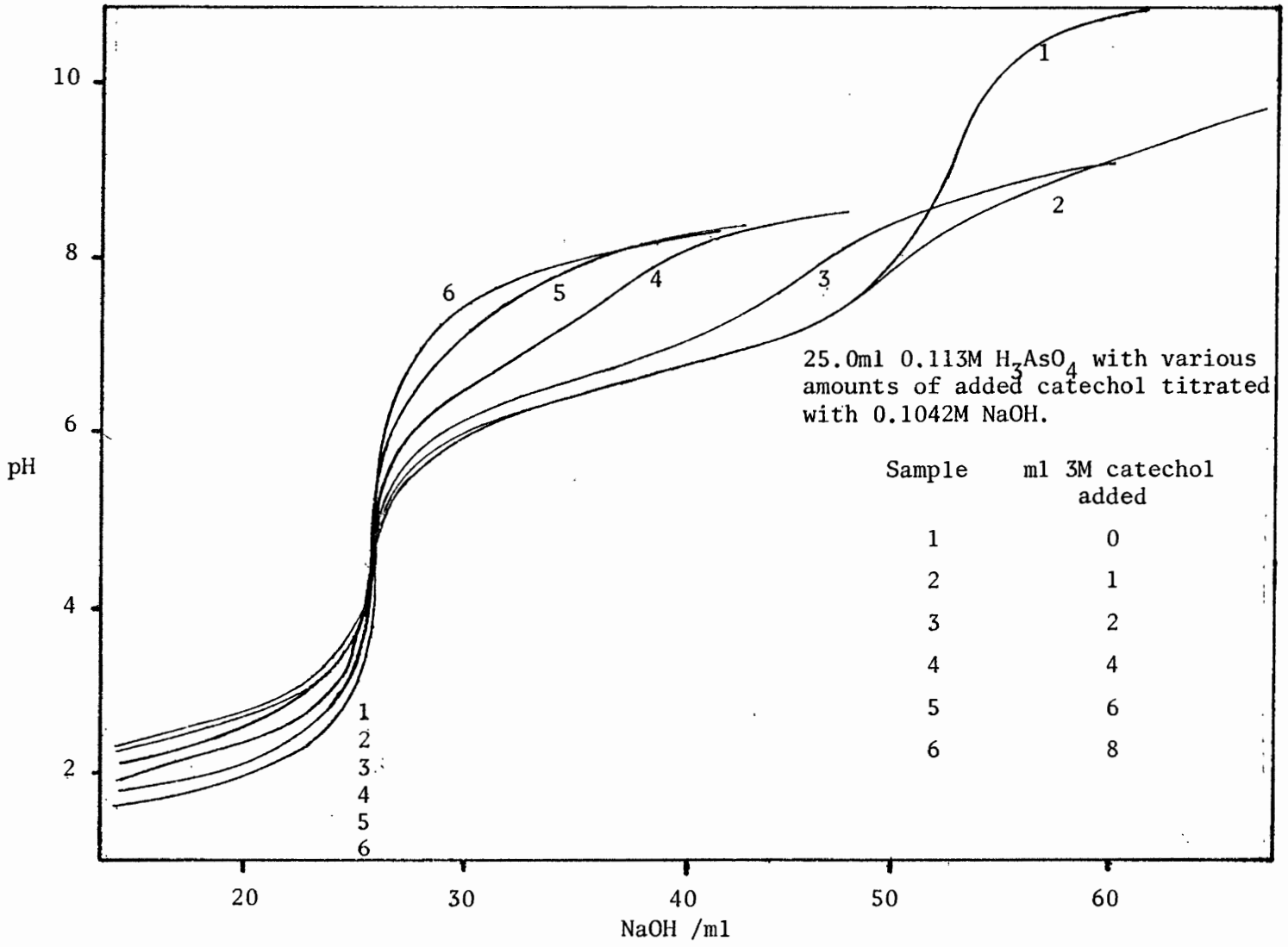


Figure 2. Titration curves of arsenic acid-catechol mixtures.

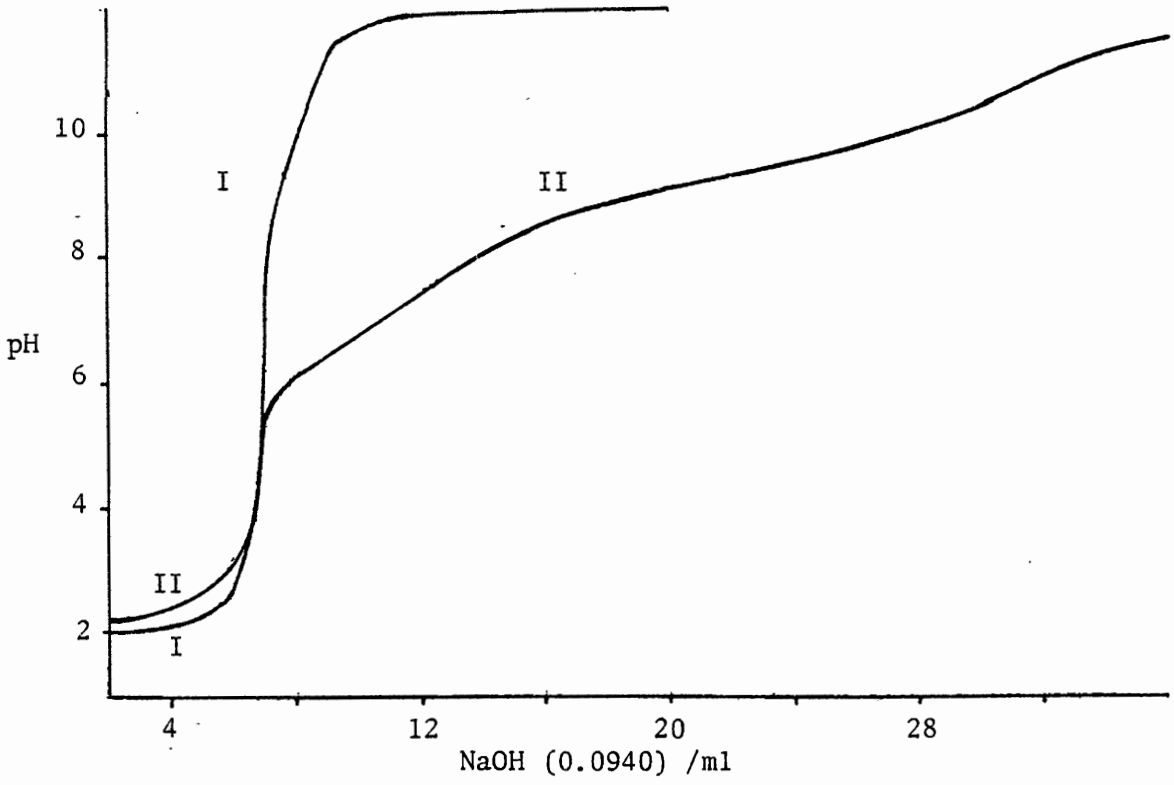


Figure 3. Titration curves of solutions prepared from the 1:3 complex. 0.29g complex in 25ml H_2O, curve I obtained from immediate titration, curve II from the solution which sat for twelve hours.

should correspond to the inflection points when titrating a mixture containing both should be about pH=4.6 and 9.3 for arsenic acid and pH=10.6 for catechol. The inflection points of curve II, Figure 3 correspond to these. This shows that all of the 1:3 complex has dissociated, and that there is 0.64mmoles As(V) and 1.8mmoles of catechol, essentially the 1:3 ratio expected.

Measurements of the Liberation of Protons in the Reaction Between H_3AsO_4 and Catechol:

By measuring the number of protons liberated in the reaction between H_3AsO_4 and catechol, it should be possible to calculate formation constants and estimate acid dissociation constants for any complexes present. The procedure for this measurement is as follows. An As(V) solution was prepared, typically with a concentration between 0.04-0.01M, and the pH adjusted to a selected value in the range 1-3. The pH of catechol solutions (0.1-2M) was then adjusted to be within 0.002 pH units of that of the As(V) solution. All solutions had an ionic strength I=1M using $NaClO_4$ and $HClO_4$. 10.0ml of the catechol solution was added to 20.0ml of the As(V) solutions, the resulting mixture sealed and allowed to equilibrate for at least twenty hours. The pH of these solutions was then checked and readjusted if necessary using NaOH, to the original pH of the As(V) solution, once again to within 0.002 pH units. The solutions were again sealed and sat for a number of hours at which time the pH was again checked and adjusted if necessary. This procedure was repeated until there was no longer any perceptible pH change. Care was taken to choose appropriate concentrations of NaOH so that there resulted only about a 1% dilution of the original solution. Much effort was made to insure that pH readings were correct. There were three blanks used in each run which were simply the As(V) solution used in the experiment with no catechol added. The pH meter was recalibrated after each sample. If any drift had occurred the sample pH would be rechecked and adjusted if necessary. This rather tedious prodedure was necessary as there were drift problems associated with leaving the electrodes immersed in the catechol

solution.

A slight variation in the procedure was used for one run, at pH=1.71, where solid catechol instead of a solution was added to the As(V) solution. By a very nonrigorous determination of the partial molar volume (10.0ml H_2O+1g catechol equals 10.7ml solution) corrections for the actual volume were made and were quite small for the case where the catechol concentration is between 0.05-0.2M. This procedure was utilized because of its simplicity and was found to yield results consistent with the other runs.

From the polarography data (16) reported, it was apparent that at least two species of complex are present so that the simultaneous presence of 1:1, 1:2, and 1:3 As(V):catechol complexes must be considered. In the pH range 1-3 the two uncomplexed forms of As(V) are H_3AsO_4 and $H_2AsO_4^-$. From a mass balance equation for As(V) considering all the possible equilibria the following equation can be derived (see Appendix).

$$(1)\quad C_{As}(H^+)/(H_3AsO_4) = (H_2L)\{\beta_1+\beta_1(H^+)/K_{a1}\} + (H_2L)^2\{\beta_2+\beta_2(H^+)/K_{a2} + (H_2L)^3\{\beta_3+\beta_3(H^+)/K_{a3}\} + (H^+) + K_1$$

n = 1-3

β_n = overall formation constant of any complex present

K_{an} = acid dissociation constant of any complex present

K_1 = first acid dissociation constant of arsenic acid = 0.0088 in 1M $NaClO_4$

C_{As} = total concentration of As(V) present

Methods for calculation of uncomplexed H_3AsO_4 and catechol (H_2L) concentrations are presented in the Appendix. From equation (1) it can be

seen that if the uncomplexed catechol concentration, (H_2L), is approximately equal to the concentration added, C_{H_2L}, and if it is assumed that for each proton liberated one H_3AsO_4 is complexed the calculation is quite straightforeward. Using a minumum of two runs at different pH's, the results could be fit to a third order polynomial. Comparing the coefficients obtained would yield both β's and K_a's and the intercept of each curve should agree with the sum $(H^+) + K_1$ as seen in equation (1). Unfortunately in order to get a resolvable pH change the As(V) concentration must be relatively high and therefore $C_{H_2L} \neq (H_2L)$. In a situation such as this, when more than one complex must be assumed, an iterative technique is used for calculation of the uncomplexed ligand. It was found that it was not possible to simply do a third order polynomial fit on the experimental data. The regression method appears to be very sensitive to precisions of experimental data. In almost every case some negative coefficients were obtained, corresponding to negative formation constants.

It appeared that in order to evaluate the formation constants another procedure must be used. The method decided upon consists of guessing initial values of β to allow the uncomplexed catechol concentration to be calculated, then using equation (1) to calculate the uncomplexed H_3AsO_4 concentration, which is known experimentally from the number moles of protons liberated, and comparing the experimental and calculated values. By choosing β's so there appeared to be no systematic deviation between the calculated and experimental H_3AsO_4 concentration it was found that β_3=6.5-9, $\beta_2 \simeq 0.02$ and $\beta_1 \simeq 0.01$. It was also found that there was no systematic increase in these values as the pH

decreased, which is predicted from equation (1) if $pK_a > pH$. (In essence the second term inside the parenthesis in equation (1) has been omitted for these estimations.) This means that apparently at least the predominant 1:3 complex has a $pK_a < 1$. Between runs there was a systematic deviation which is probably associated with the uncertainty of knowing the absolute pH which is very important in the calculation.

In order to compare the results between runs and get an estimate of how well the β's are known, equation (1) was rearranged slightly to yield a linear expression.

$$(2) \quad Y = \{C_{As}(H^+)/(H_3AsO_4) - K_1\text{-}(H^+)\text{-}\beta_1(H_2L)\}/(H_2L)^2 = \beta_2 + \beta_3(H_2L)$$

Figure 4 shows the results of a plot of the experimental data gathered at three pH's. Figure 5 shows the results from two of those pH's and obviously gives a much better fit. These curves do show that the estimations of β's made previously were very nearly correct, although β_1 and β_2 must be regarded as only estimates as they are so small and there was much experimental error (as seen at the beginning of the curves in Figures 4 and 5) in the area where these complexes are present.

Using the values $\beta_1=0.01$, $\beta_2=0.02$ and $\beta_3=7.5$ it is possible to calculate the fraction of each species at a given pH and catechol concentration. Table I and Table II contain a short summary of these values at pH 1 and 2. Figures 19 and 20 in the Appendix show the entire distribution curves arising from these values at pH 1 and 2.

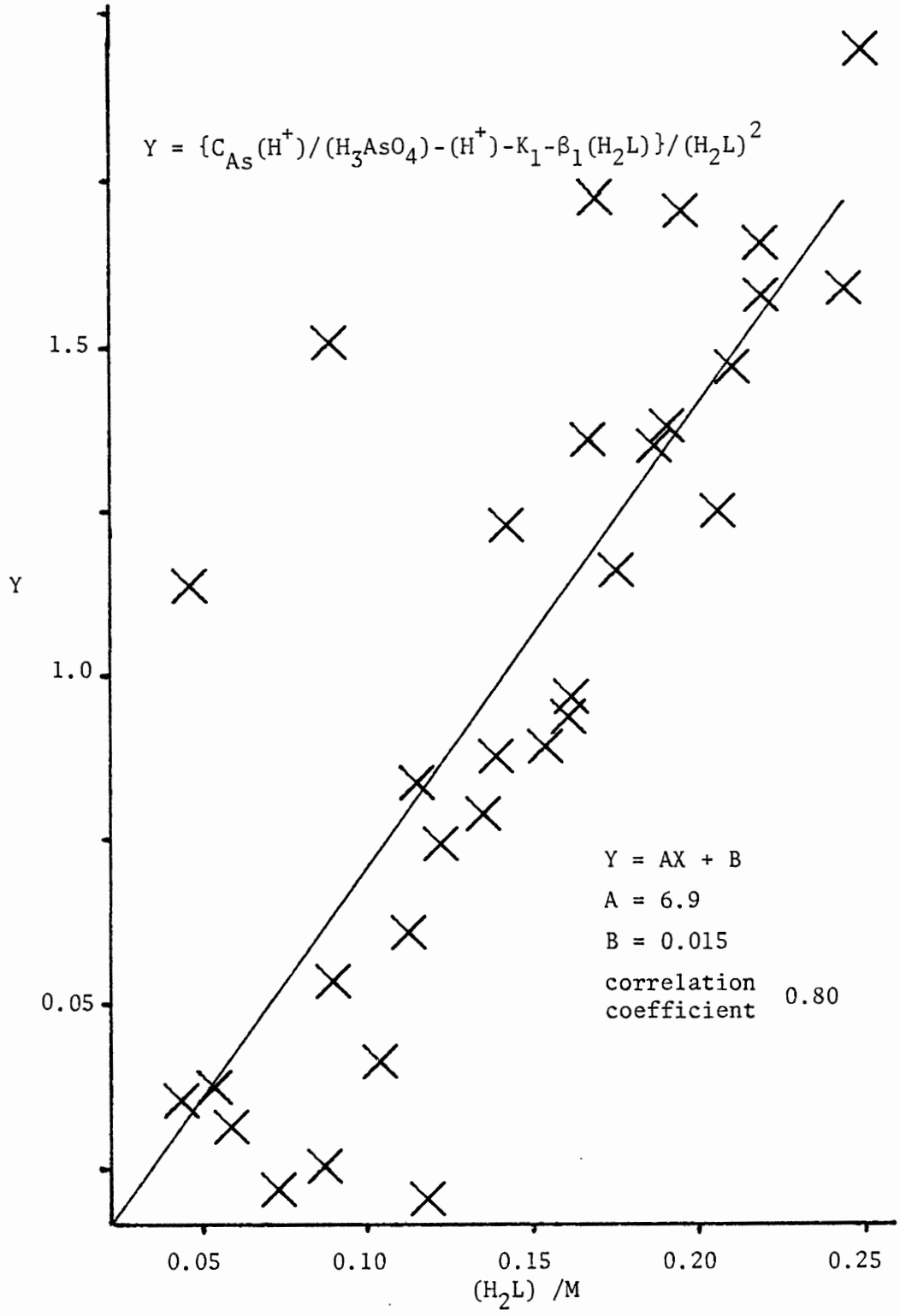


Figure 4. Evaluation of formation constants assuming β_1. Data collected at pH=1.62, 1.68 and 1.71.

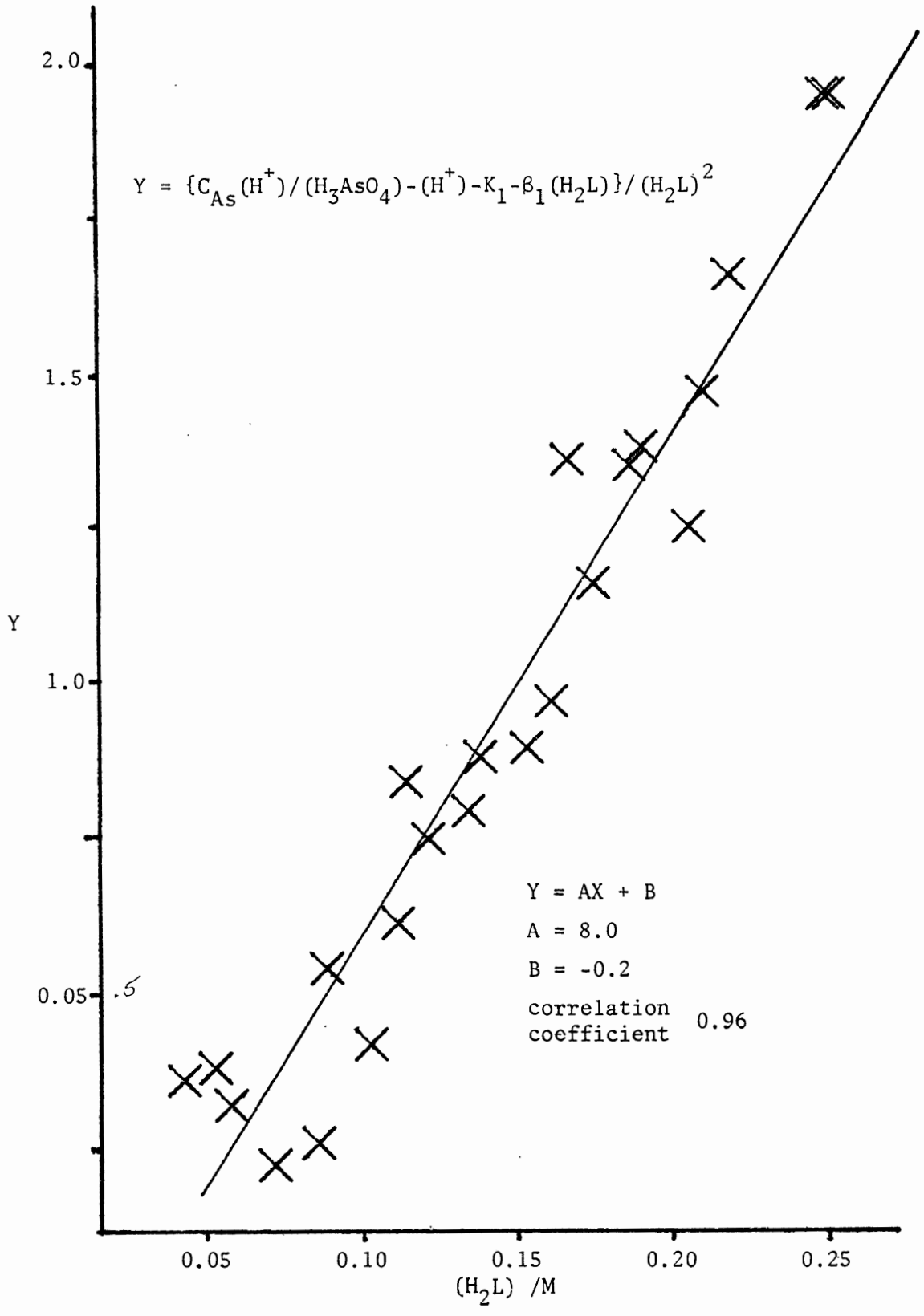


Figure 5. Evaluation of formation constants assuming β_1. Data collected at pH=1.68 and 1.71.

TABLE I

DISTRIBUTION OF ALL SPECIES AS A FUNCTION OF CATECHOL CONCENTRATIONS AT pH = 1

pH = 1	percent of each species					
(H_2L)	(H_3AsO_4)	$(H_2AsO_4^-)$	$(As(OH)_4L^-)$	$(As(OH)_2L_2^-)$	(AsL_3^-)	total complexed
0.10	85	7.5	0.8	0.2	6.4	7.5
0.15	73	6.5	1.1	0.3	19	20
0.20	58	5.1	1.2	0.5	35	37
0.25	43	3.8	1.1	0.5	51	53
0.30	31	2.8	0.9	0.6	64	66
0.35	23	2.0	0.8	0.6	73	75
0.40	17	1.5	0.7	0.5	80	82

TABLE II

DISTRIBUTION OF ALL SPECIES AS A FUNCTION OF CATECHOL CONCENTRATIONS AT pH = 2

pH = 2	percent of each species					
(H_2L)	(H_3AsO_4)	$(H_2AsO_4^-)$	$(As(OH)_4L^-)$	$(As(OH)_2L_2^-)$	(AsL_3^-)	total complexed
0.05	49	43	2.5	0.2	4.6	7.3
0.10	36	32	3.6	0.7	27	32
0.15	22	19	3.2	1.0	55	59
0.20	12	11	2.4	1.0	73	77
0.25	7.2	6.3	1.8	0.9	84	87
0.30	4.4	3.8	1.3	0.8	89	92
0.35	2.9	2.5	1.0	0.7	93	95

Temperature Study of the NMR Spectra of the 1:3 Complex:

The object of this study was to carry the experiments of Mason and Mason (26) one step further by investigating any possible changes in the NMR of the 1:3 complex with changing temperature.

By preparing an approximately 1M solution from solid 1:3 complex the value for β_3 insures that almost all the As(V) will remain complexed. This solution sat four days before the temperature study was done. Figures 6,7 and 8 show the NMR spectra for catechol done at room temperature (25°C) and the 1:3 complex at room temperature and 10°C.

Integration of the peaks in the catechol spectrum indicate a very small amount of H_2O contamination. Integration of the 1:3 complex spectrum indicates that there were about equal amounts of water protons and aromatic protons ie. six waters for each complex ion.

Looking at the types of aromatic protons present in these three spectra yields some interesting observations. The catechol spectrum shows that there are two types of aromatic protons, which is also the case for the 1:3 complex at room temperature. When the temperature was lowered to 10°C though it is seen that there is now only one type of aromatic proton present in the spectrum of the 1:3 complex.

Raman Spectra of As(V) Catechol Solutions:

Raman spectra were taken of several solutions having different As(V) to catechol ratios. The solutions were prepared in 1M $HClO_4$ for all but the solution which contained only catechol, which was in 0.1M $HClO_4$. A summary of the peak locations and intensities which could be attributed to catechol or complex formation is given in Table III. Figures 9 and 10 show the spectra of a solution of catechol with-

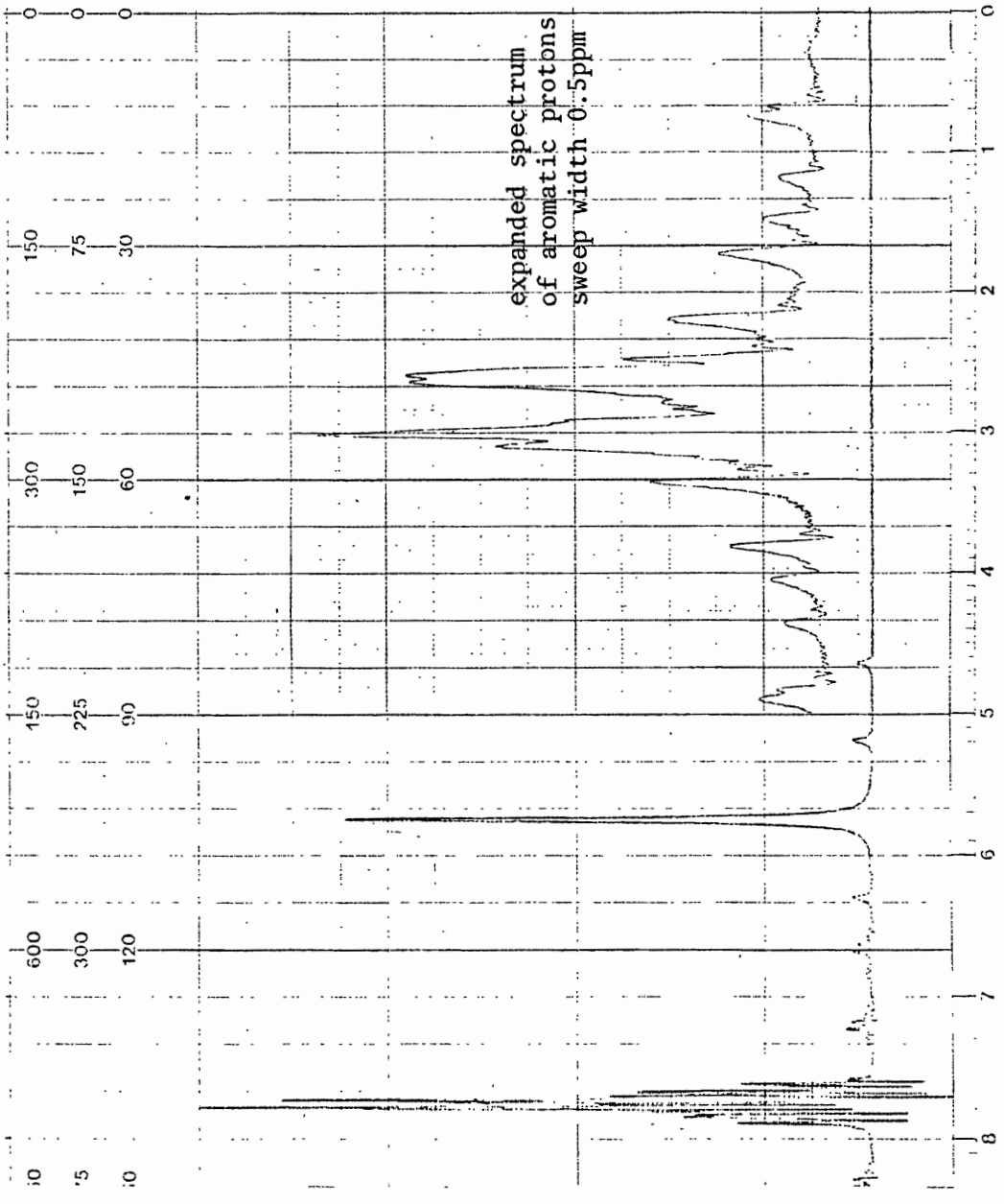


Figure 6. NMR spectrum of catechol in D_2O (≃2M) at 25°C

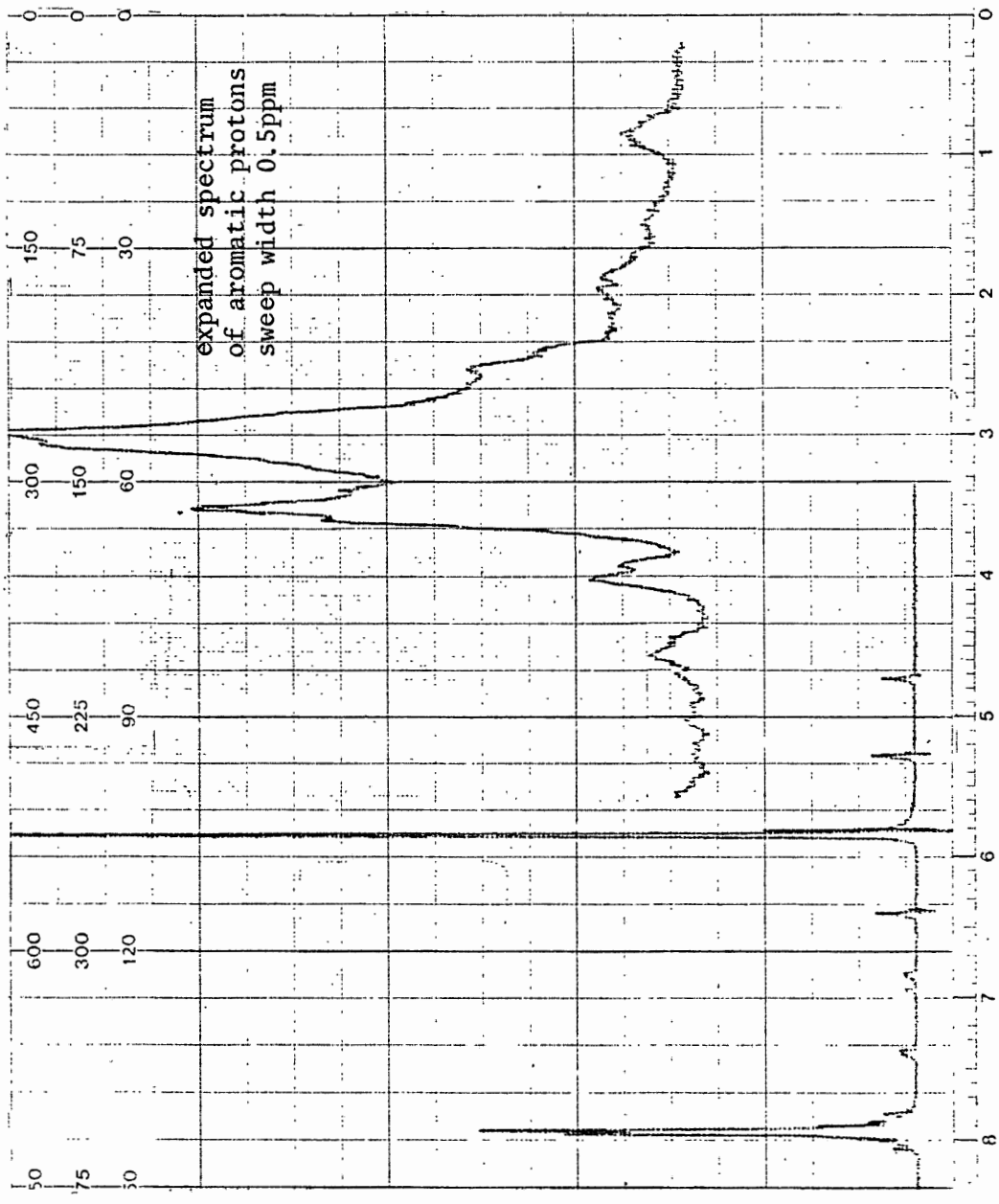


Figure 7. NMR spectrum of 1:3 complex in D_2O (≈1M) at 25°C

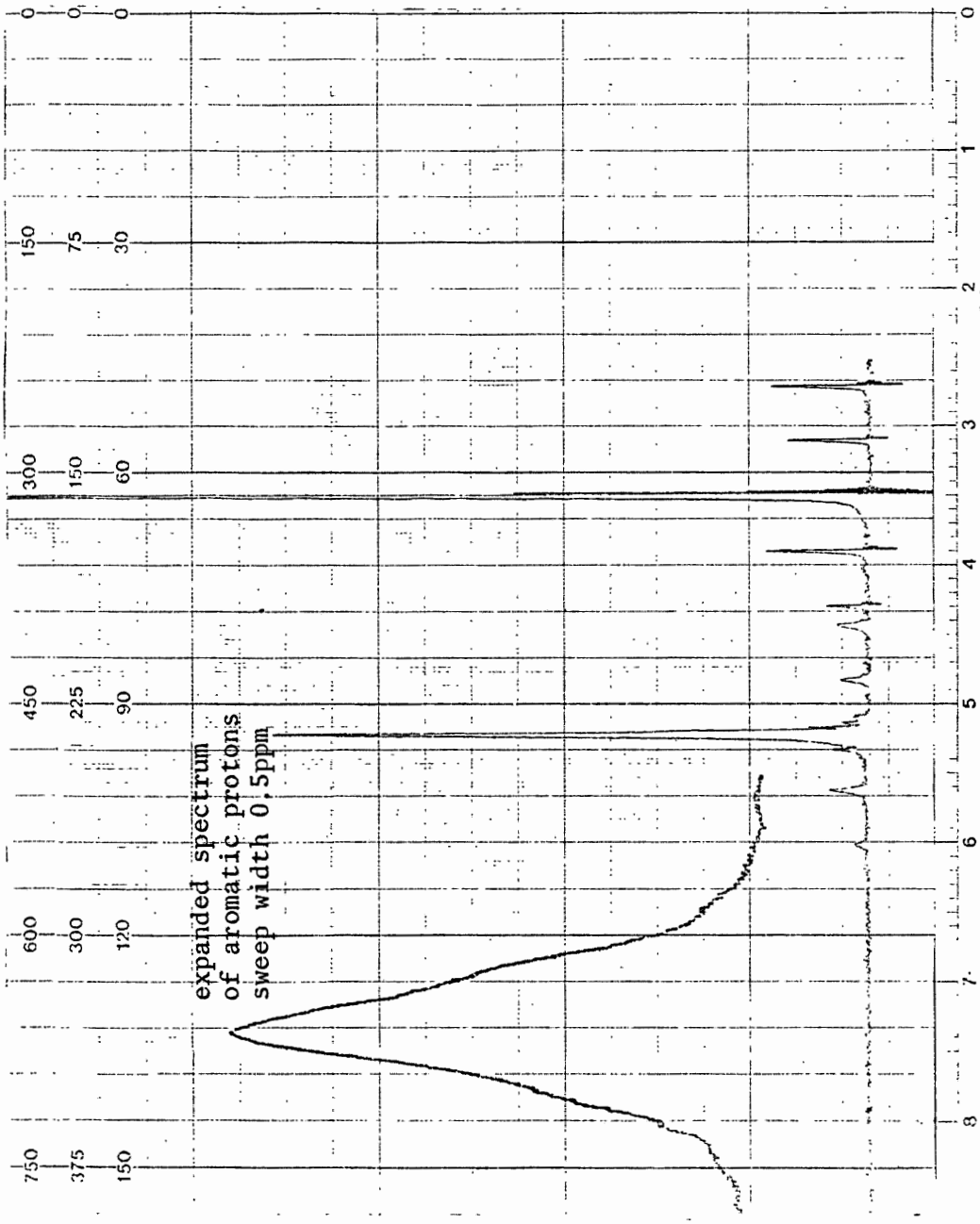


Figure 8. NMR spectrum of 1:3 complex in D_2O (≈1M) at 10^oC

out and with arsenate, respectively.

No attempt was made to rigorously interpet the spectra obtained or predict what pattern of peaks would be expected from the types and amounts of complexes that might be present under the given conditions. Since there appeared a need for spectral information this experiment was undertaken to determine the feasibility of using Raman spectroscopy for elucidation of the structure of any complex present as well as another method to estimate formation constants.

It was found that the best conditions for observing the development of peaks due to complex formation is >0.2M catechol and 0.1M As(V). Mixtures which were only 0.01M in As(V) showed very little difference from those with catechol alone. The magnitude of the absorptions due to apparent complex fromation as a function of catechol concentration appears to be in at least qualitative agreement with the pH measurements. Since peak intensity is directly proportional to the concentration of the absorbing species, the spectrum of the 0.5M catechol solution can be compared with that of the solution containing 0.1M As(V) and 0.7M catechol. Comparing the spectra at 1275, 1032 and 580cm^{-1} and assuming these absorption peaks are characteristic of uncomplexed catechol, it appears that the concentration of uncomplexed catechol in the solution containing As(V) is about 0.5M. Noting the predominance of the 1:3 species and estimating that pH≈0.2 yields $\beta_3 \approx 10$, very close to the value obtained potentiometrically.

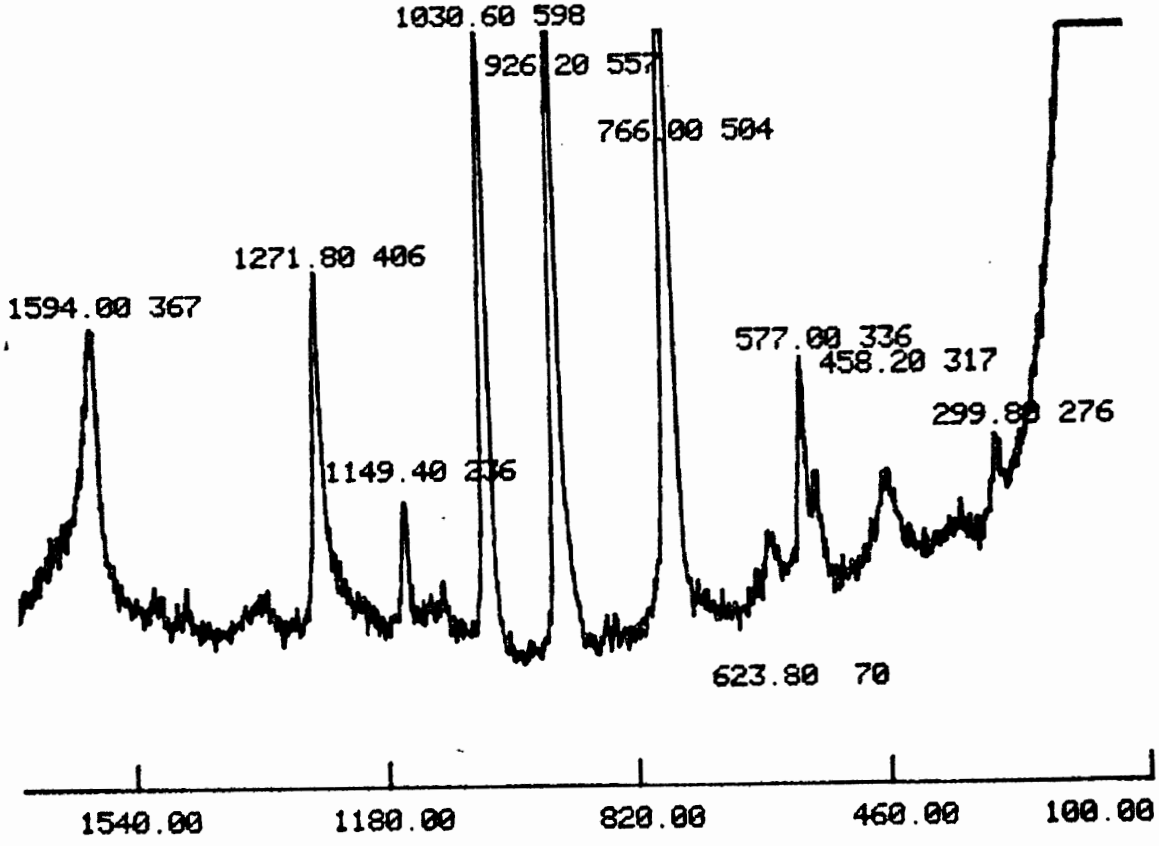


Figure 9. Raman spectrum of 0.5M catechol in 0.1M $HClO_4$

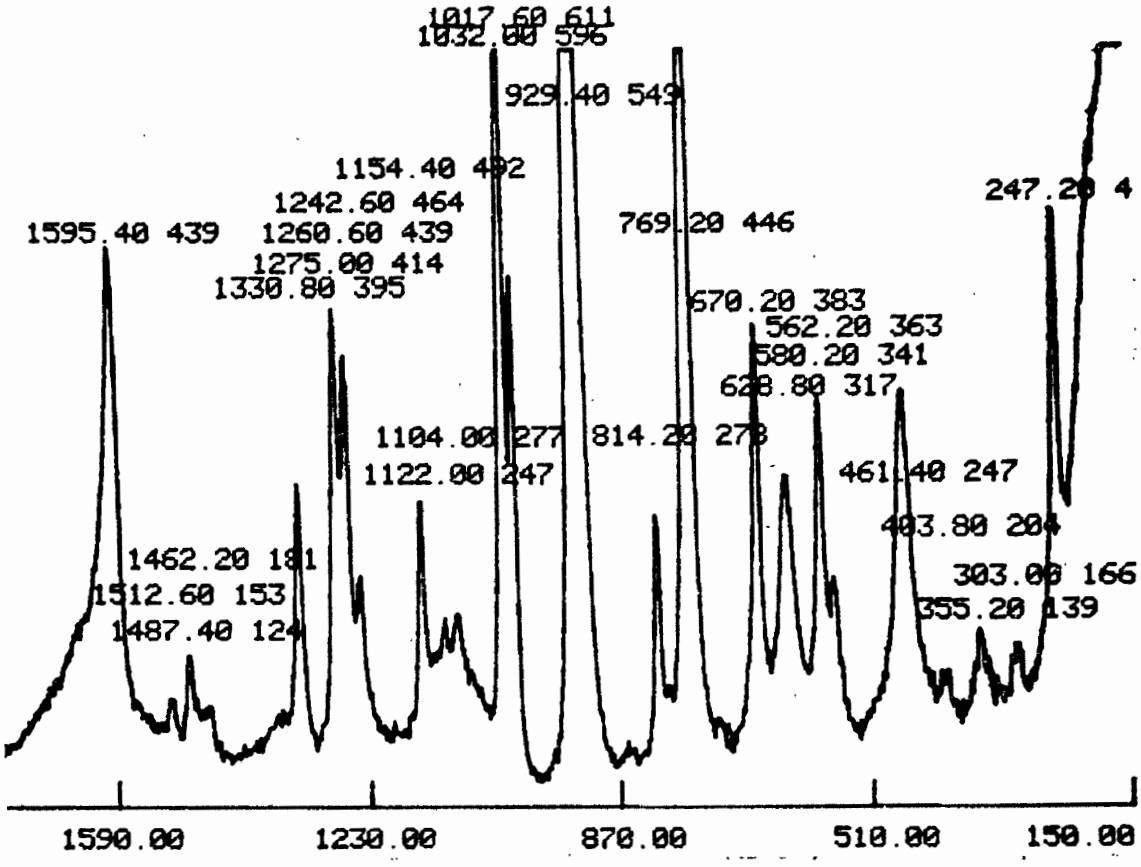


Figure 10. Raman spectrum of solution containing 0.1M As(V), 0.7M catechol and 1M $HClO_4$.

TABLE III

SUMMARY OF RAMAN PEAKS DUE TO COMPLEX FORMATIONS OR FREE CATECHOL

As(V):Catechol (M)						Catechol	
0.1:0.7		0.1:0.2		0.1:0.1		0.5	
cm^{-1}	relative intensity	cm^{-1}	relative intensity	cm^{-1}	relative intensity	cm^{-1}	relative intensity
1595	(439)	1594	(222)	1595	(147)	1594	(367)
1513	(153)						
1487	(124)						
1462	(181)						
1331	(395)	X					
1275	(414)	1275	(167)	1275	(95)	1272	(406)
1261	(439)	X					
1243	(464)	X					
1154	(492)	X				1149	(236)
1122	(247)	X					
1104	(277)	X					
1032	(596)	1032	(310)	1032	(186)	1031	(598)
1018	(611)						
860							
814	(278)	X					
769	(446)	766	(579)	766	(308)	766	(504)
670	(383)	X					
580	(341)	580	(146)	578	(127)	577	(336)
562	(363)	X					
404	(204)						
355	(139)	X					
303	(166)	X				300	(206)
247	(400)	X					

X - peak present but small and poorly resolved

Polarography of As(V)-Catechol Complexes:

The object of this experiment was to observe the magnitude of the limiting current, arising from the reduction of some As(V)-catechol species, as a function of pH and catechol concentration. Correlating this information with distribution curves for the system, as in Figures 19 and 20, should show which species is electroactive under these conditions. Polarograms were run on solutions used in the experiment described previously (pg.17 to 24). This insured constant pH conditions. Figures 11 and 12 show two polarograms typical of those obtained. The leading edge (around -0.2v) of the initial wave changes appearance at different catechol concentrations. The general shape of the wave, though, was the same for all solutions studied, prepared in this manner. A plot of the limiting current of the first wave (about E_{de} vs. SCE(NaCl)=-0.4v) vs. catechol concentration is found in Figure 13.

In order to understand whether the limiting current is diffusion, adsorption or kinetically controlled, the effect of mercury height on current was investigated. Figure 14 shows the results of plotting i vs. $h^{\frac{1}{2}}$ for the solutions listed. Noting that no dependence of the limiting current on mercury height is indicitive of a kinetic process it might be inferred that a decrease in slope of the lines shows increasing kinetic control. It can then be observed from comparison of the conditions under which each plot was made, that decreasing the pH increases the kinetic effect, particularily as the pH gets below 1.5. Also, when the catechol concentration is high (above 0.3M) the kinetic effect is decreased.

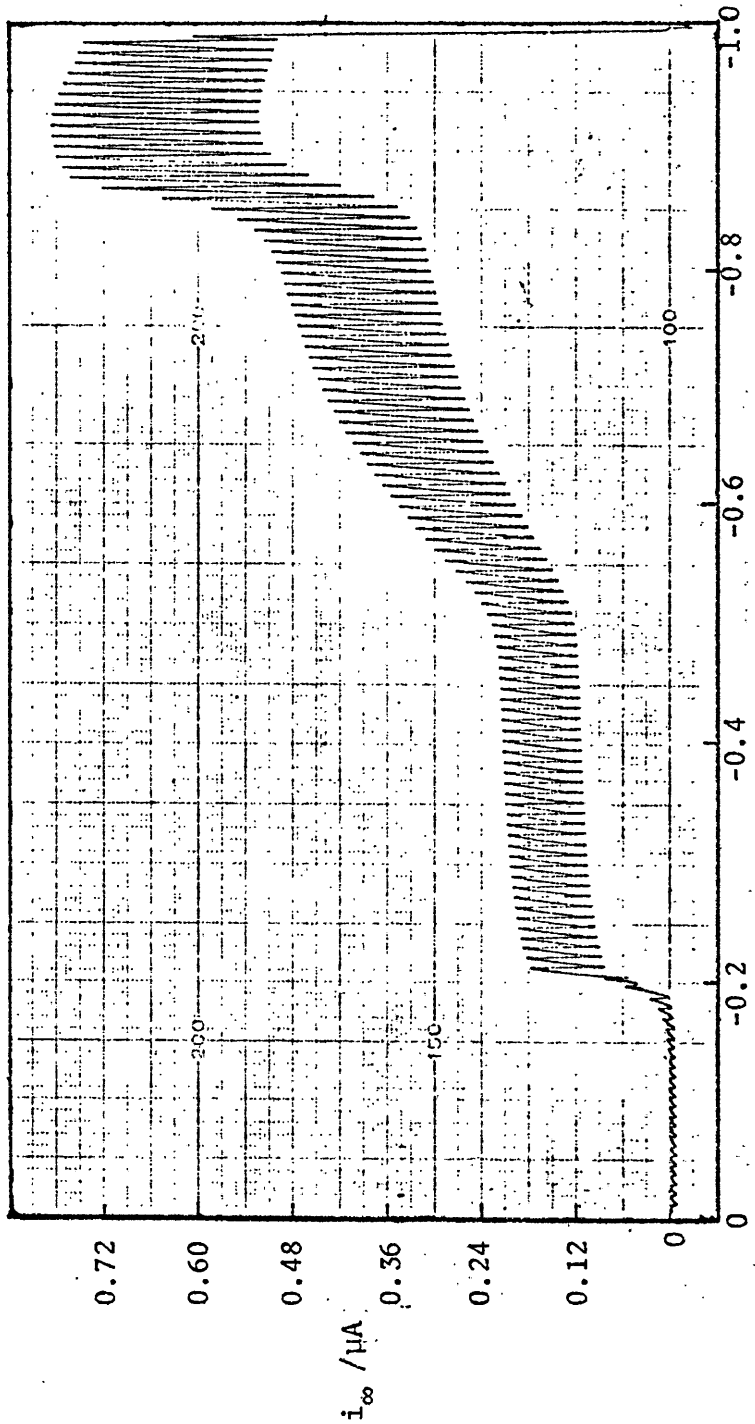


Figure 11. Polarogram of As(V) catechol solution. 30ml 1M $NaClO_4$, 3mmoles catechol, 0.2mmoles As(V) pH=2.10. i_∞, the current when equilibrium is attained.

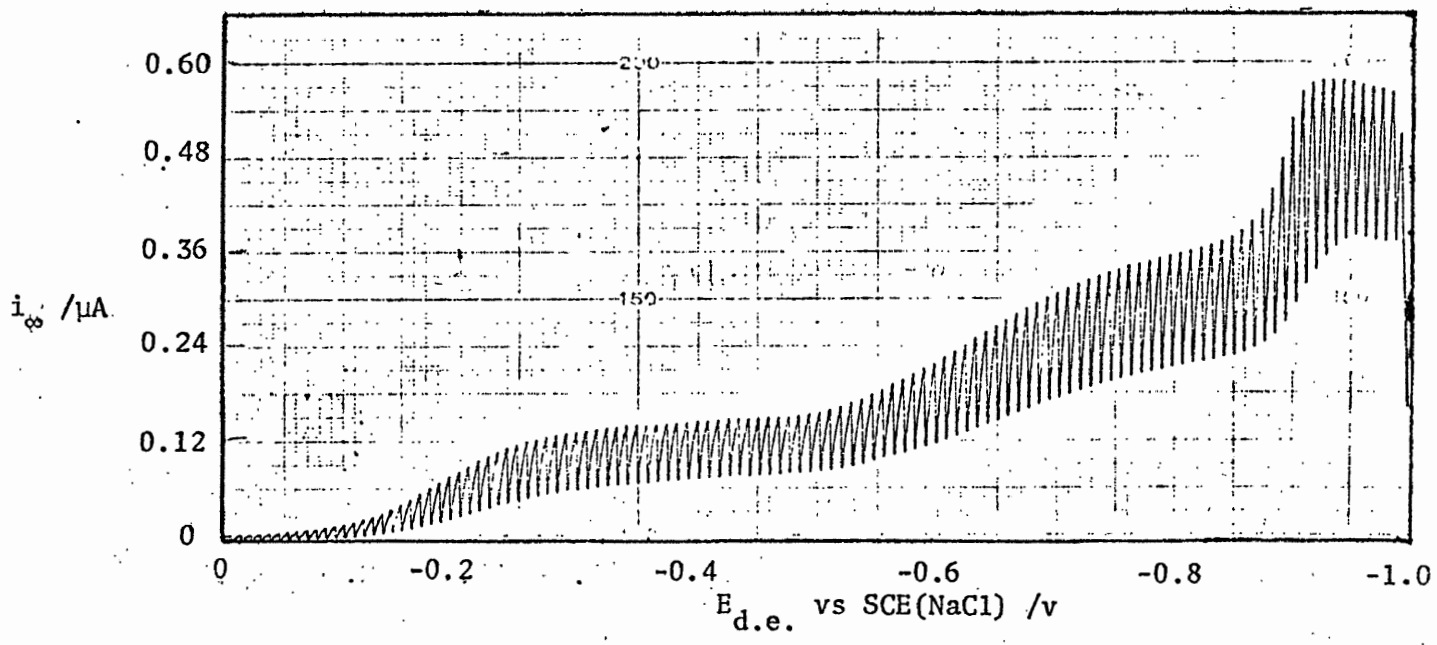


Figure 12. Polarogram of As(V) catechol solution. 30ml 1M $NaClO_4$, 9mmoles catechol, 0.2mmoles As(V), pH=2.10.

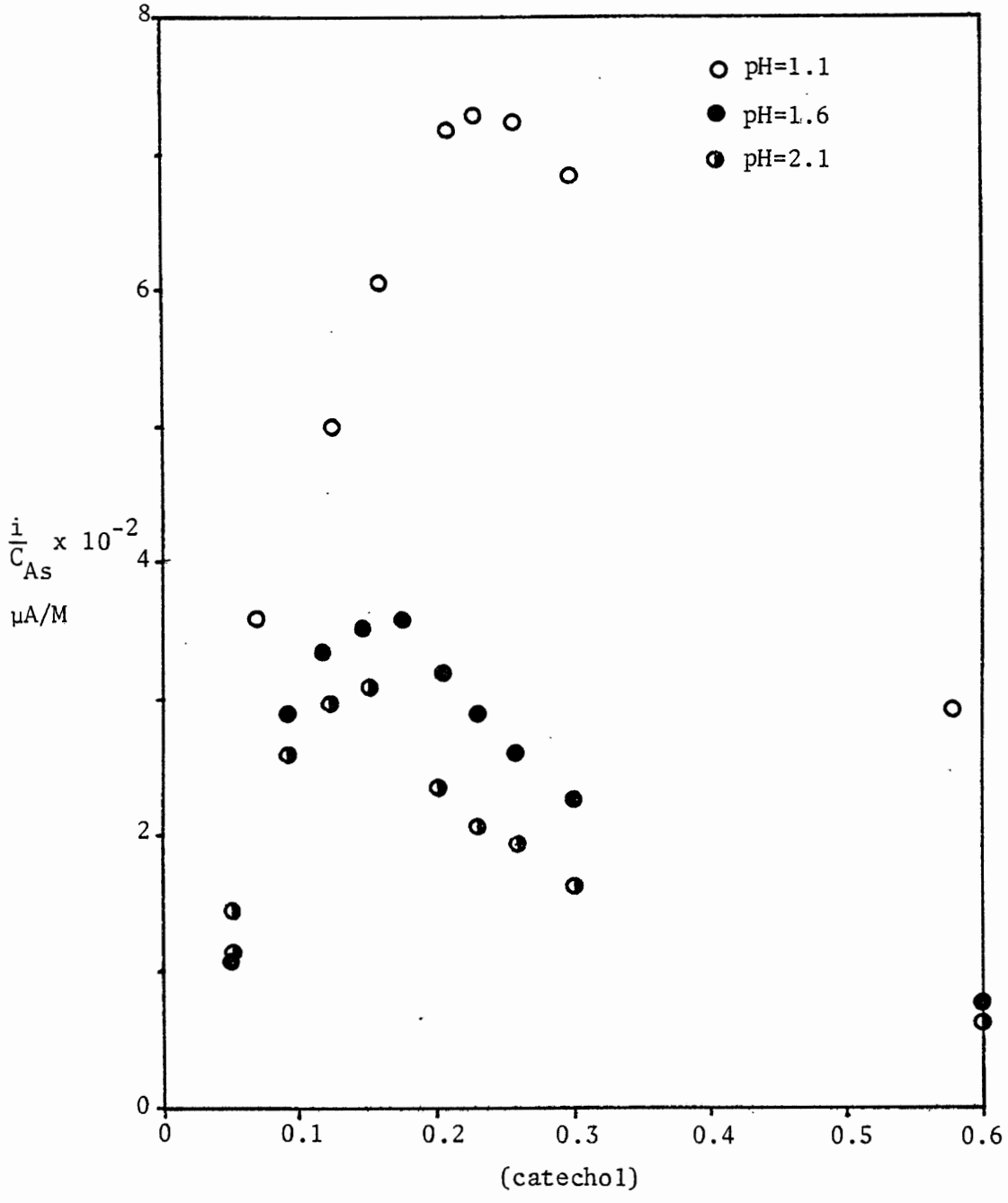
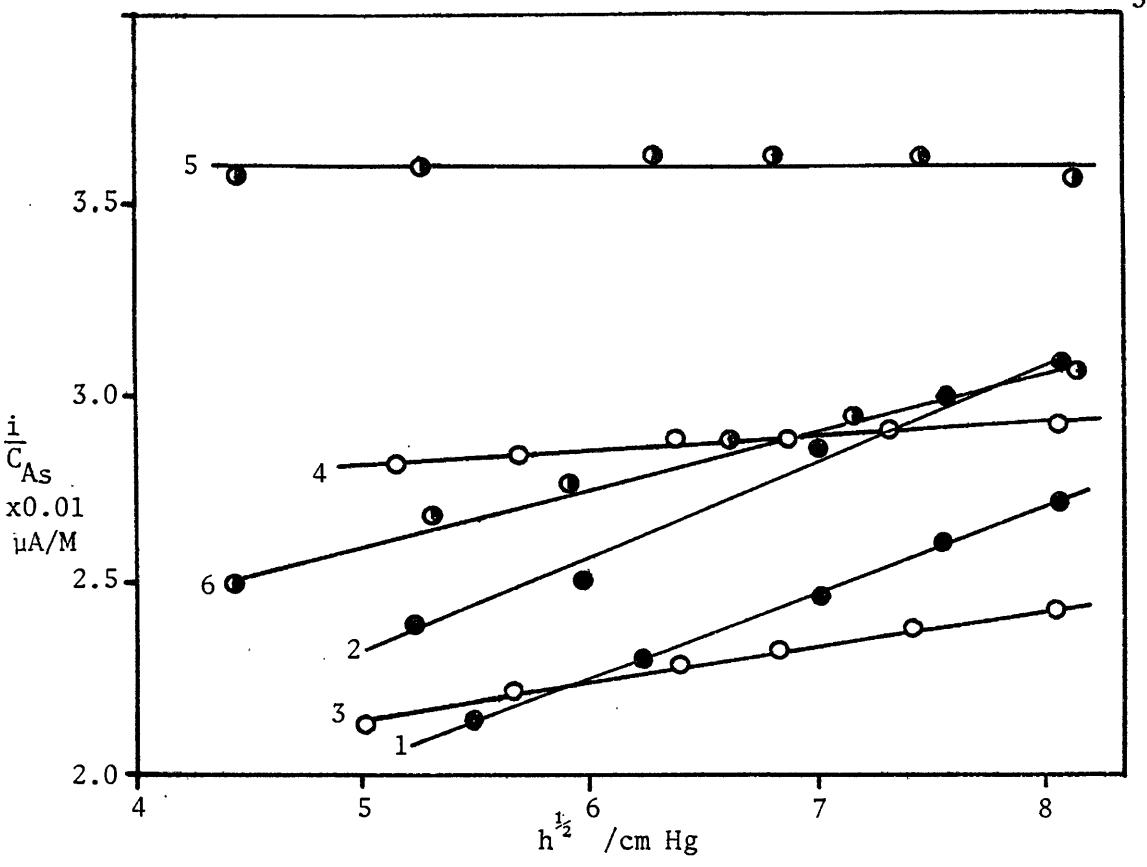


Figure 13. Dependence of the limiting current on pH and catechol concentration.



#	As(V) (mmoles)	catechol (mmoles)	pH	intercept	slope	correlation coefficient
1	0.20	6.0	2.10	0.93	0.221	1.000
2	0.20	3.0	2.10	1.00	0.261	0.994
3	0.60	10.0	1.62	1.62	0.101	0.996
4	0.60	3.0	1.62	2.63	0.036	0.988
5	1.00	3.0	1.10	3.57	0.005	0.232
6	1.00	20.0	1.10	1.84	0.153	0.993

Figure 14. Effect of mercury height on current.

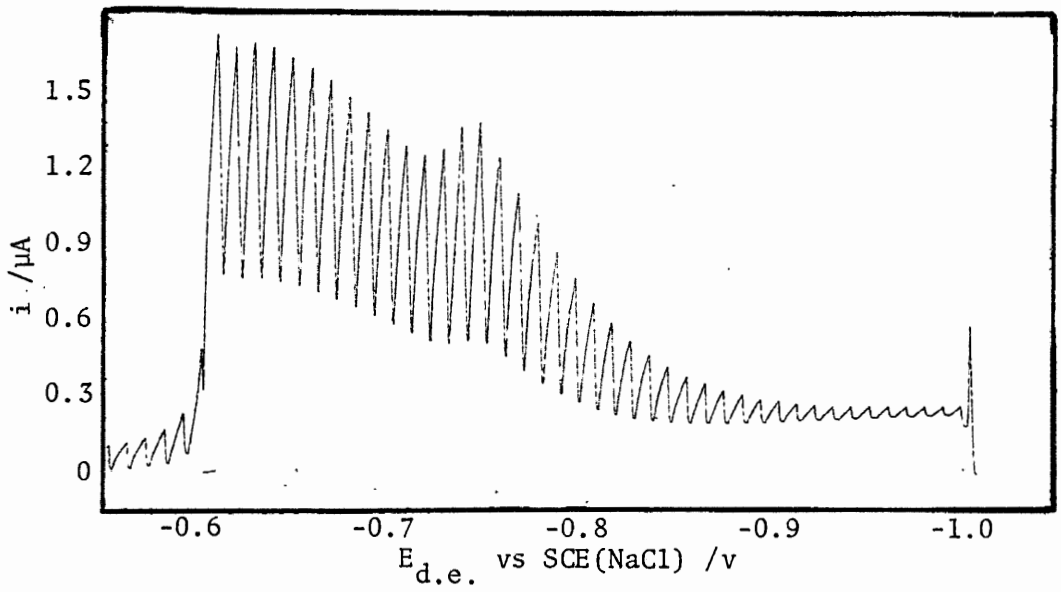


Figure 15. Polarogram of solution containing 0.012g 1:3 complex 0.25ml 1M $HClO_4$ and 25ml 1M $NaClO_4$. Scan (0 to -1v) began three minutes after dissolution and took a total of ten minutes.

It was found that upon dissolution of solid 1:3 complex in 1M $NaClO_4$ a reduction wave was obtainable, Figure 15. This wave was initially at a maximum and decayed with time disappearing completely when a 10^{-3}M solution with respect to complex was used. The rate of decay appeared to be a function of pH and the magnitude a function of pH and catechol concentration as well as initial complex concentration. It was also found that a similar wave could be obtained by injecting 70μl of a solution containing 1M catechol and 0.05M As(V) into 25ml $NaClO_4$. This indicated the wave was not due to an impurity (such as oxidation reduction product) in the solid crystals. This wave was never obtained when a large excess of catechol was present.

To gather information as to the kinetic behavior of this wave the following precedure was used: 25ml of 1M $NaClO_4$ was deoxygenated, 0.010g of solid 1:3 complex dissolved into it and current measurements

were recorded at a previously fixed potential. In the cases where the effect of catechol was examined a small amount (25-275µl) of deoxygenated, pH-adjusted catechol was added to the cell after the solid complex had dissolved. In the case where excess As(V) was examined, the arsenate was present when the solid complex was dissolved. The pH of the set of measurements where excess As(V) was present was not the same as the pH in the other runs.

By assuming that the limiting current measurements are directly proportional to the concentration of the 1:3 complex and that the rate of decay is first order in its concentration a plot of $-\ln(i-i_r)$ vs. t/sec. was made. A summary of the results obtained is found in Table IV, where k is a pseudo first order rate constant for the decay of the polarographic wave and i_o is the current obtained by extrapolation to t=0.

It was found that the decay is first order in reducible species and, at least roughly, appears to be first order in hydrogen ion concentration. Added As(V) seems to have no effect on k or i_o. The presence of excess catechol seems to have no effect on the rate of decay but does suppress the wave, that is decrease i_o. Phenol was found to have the same effect on the wave. Increasing the hydrogen ion concentration increases i_o, which may infer that it is a protonated species which undergoes charge transfer.

Measurements of i vs. mercury height were made to try to determine if the limiting current is diffusion controlled. 0.500g of solid complex was added to 50ml 1M $NaClO_4$ pH=2.45 (1M $HClO_4$). Ten minutes after the preparation of this solution a polarographic scan was taken. Be-

TABLE IV

SUMMARY OF THE KINETIC BEHAVIOR OF THE POLAROGRAPHIC WAVE OBTAINED FROM SOLUTIONS PREPARED FROM THE SOLID 1:3 COMPLEX

Effect Of Added Catechol

molarity of added catechol	$k(x10^4)$ /$(s\mu A)^{-1}$	i_0 /μA	correlation coefficient
0	5.8	5.5	.9996
0	6.8	5.8	.9987
0	7.0	5.9	.9971
$1x10^{-3}$	6.1	4.5	.9997
$2x10^{-3}$	5.6	4.0	.9995
$4x10^{-3}$	6.2	3.2	.9990
$11x10^{-3}$	6.8	1.8	.9997

Effect Of Added As(V)

molarity of added As(V)	$k(x10^3)$ /$(s\mu A)^{-1}$	i_0 /μA	correlation coefficient
0	1.1	7.8	.9999
0.02	1.1	7.9	.9996
0.05	1.1	7.8	.9999

Effect Of pH

pH	k /$(s\mu A)^{-1}$	i_0 /μA	T /°C
2.2	$7.0x10^{-5}$	0.92	20
1.1	$4.9x10^{-4}$	5.2	19
0.2	$4.0x10^{-3}$	11.5	18

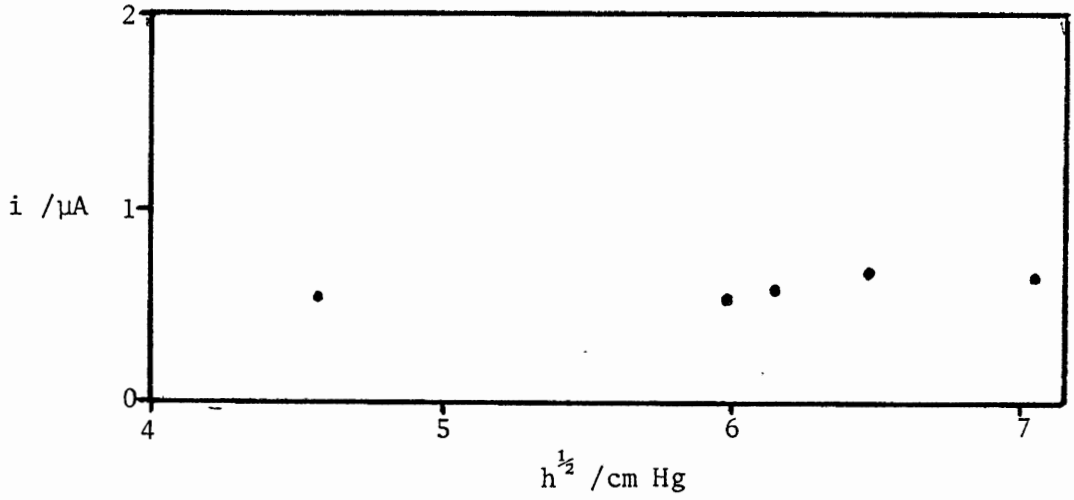


Figure 16. Effect of mercury height on the polarogram of a solution prepared from the 1:3 complex.

cause of the error involved in such measurements where the current is time dependent precise results were not possible but the results of plotting i vs. $h^{\frac{1}{2}}$ in Figure 16 indicate that the wave is not simply diffusion controlled.

DISCUSSION

In order to understand which complex gives rise to the polarographic wave, formation constants were necessary to determine the distribution of any species present. Calculation of these formation constants required an assumption of what complexes are present followed by an iteration procedure.

Potentiometric titrations were interpreted in terms of the types of complexes that might be present. Figure 2 shows that the first endpoint never shifts when solutions of arsenic acid containing catechol are titrated, though there is a gradual shift in the second endpoint. Only those complexes which either liberate a proton upon formation or have a pK_a comparable to pK_1 for arsenic acid need be considered noting that there is no shift in the first inflection point. Since the pH of the solution was lowered as increasing amounts of catechol were added the complexes must be more acidic than H_3AsO_4. These titration curves were not used for measurement of complexed As(V) for two main reasons. First, since complex formation is pH dependent (except where there is essentially 100% $H_2AsO_4^-$), and second because of the overlap between the titration curve of catechol with that of $H_2AsO_4^-$.

The titrations of solutions prepared from solid 1:3 complex (Figure 3) show that the 1:3 complex is a moderately strong acid ($pK<1$), monoprotic, undergoes a slow dissociation, and because it dissociates completely in dilute solution, it is a weak complex. All these observations agree with the types of species assumed in the introduction.

The one method that can be used to determine the amount of As(V) complexed when a given concentration of catechol is added to a solution of arsenic acid is to measure the concentration of protons liberated. Rather than use the change in pH to determine the amount of protons liberated any change in solution pH was followed by an addition of NaOH to return the solution to its original pH. This introduces dilution errors (<1%) but keeps data in terms of concentrations instead of activities. Using this method, at room temperature and ionic strength of 1M, formation constants were calculated to be: $\beta_1 \simeq 0.01$, $\beta_2 \simeq 0.02$ and $\beta_3 = 7.5 \pm 1$, where β_1 and β_2 should be regarded as estimates since they are so small and depended upon data in the region subject to much experimental error. It will be shown later that the distribution curves resulting from these values are very much in agreement with the polarographic data. Also from these measurements it was found that no complex is appreciably protonated as low as pH=1, so that $pK_a < 1$.

There were many experimental problems associated with the measurements described in the preceding paragraph. It was not possible to know by independent means the uncomplexed catechol concentration. This meant that an iteration procedure had to be used, based upon estimates of the formation constants. The greater the As(V) concentration the more critical this correction, particularily when one considers that this term must be squared and cubed. The lower pH region (1-2) is the most advantageous place to make the measurements, since in that region H_3AsO_4 is less dissociated, and knowledge of the absolute pH is not nearly as critical (being off 0.1pH unit at pH=3 would result in a 26% difference in the amount of H_3AsO_4 believed present, at pH=1.5 only a

5% error would result). Unfortunately as the pH is decreased, higher As(V) concentrations are needed to produce enough of a pH change to get adequate resolution on the pH meter. The experiments were done using the best compromise between these points.

A summary of formation constants reported by other researchers and those calculated in this work is given in Table V. Rais et al. (31), as was stated in the introduction, were inconsistant in their notation. The value given in paranthesis is this author's interpretation of their experimental results. Noting the agreement of this value with the value of β_3 estimated from solvent extraction (32) it appears that there was merely a notation error. The formation constant values from Votava and Bartusek (33) differ by some two orders of magnitude. The reason for this disagreement is their omission of a correction for uncomplexed catechol. When dealing with solutions as concentrated as 0.04M As(V) this correction becomes very important. Rias et al. (31) also made no correction for uncomplexed catechol in their calculation but used a much more dilute solution of arsenic acid (0.005M). Rias noted that as the concentration of As(V) was increased, the formation constant seemed to decrease, which was only due to the failure to correct for the uncomplexed catechol concentration. From the experimental data of Votava and Bartusek (33), formation constants were estimated, and are in much better agreement with the other tabulated values in Table V.

In light of the results up to this point it is of interest to go back and take a look at the experiments done by Jones et al. (20-24). It is fairly clear that the pK_a value they reported was obtained from

TABLE V

COMPARISON OF EQUILIBRIUM CONSTANTS

Reference	β_1	pK_{a1}	β_2	pK_{a2}	β_3	pK_{a3}	Method
(31)					$1.4(10^4)$	1-1.4	Potentiometric titration
(31)					(10±2)		
(32)					10±5	1-1.4	Solvent extraction
(33)			0.05	<1	0.07	<1	Potentiometric titration
(33)					(2.5)		
This work	≃0.01	<1	≃0.02	<1	7.5±1	<1	Potentiometric

Values in parenthesis were estimated from the experimental data reported.

titration of a solution in which the 1:3 complex had dissociated. The hydrolysis mechanism proposed was based on the increase in the solution pH as the complex dissociated. If they had observed that the complex is more acidic than arsenic acid they would have probably proposed that a complete dissociation was taking place. The rate of this dissociation, $k=0.006 s^{-1}M^{-1}$, is essentially the same as the rate of the disappearance of the polarographic wave obtained from solutions prepared from 1:3 complex, $k=0.004 s^{-1}M^{-1}$. The presence of this wave is confusing as it is not found with any solutions prepared from combining seperate solutions of As(V) and catechol. The way its disappearance parallels the dissociation of the 1:3 complex seems to imply that the 1:3 complex can undergo charge transfer. One possibility is that the 1:3 complex can be adsorbed on the mercury and reduced. In the presence of excess catechol though, the catechol is preferentially adsorbed, perhaps because it is a neutral species and the bulky 1:3 complex for steric reasons cannot

approach in the correct orientation to undergo reduction . This would explain why catechol and phenol have a suppressive effect on the limiting current (Table V).

The NMR temperature study of the 1:3 complex appears to have shown that there is either a distinct equilibrium between structure I and II in Figure 1, or at least some type of partial bonding in a coordinate position between a water molecule (or hydronium ion) and catechol. Lowering the temperature only 15^{o}C gave a distinct shift, so that a singlet for the aromatic protons was formed. This infers that a tris chelate structure is indeed the most stable. Mason and Mason (26) observed that there was a singlet for the aromatic protons in the NMR spectra when the 1:3 complex was dissolved in dimethysulphoxide but a doublet when dissolved in D_2O and could not explain the results. It is apparent that in a non-aqueous media there would be no reason to expect that structure I would be present. Mason points out that an equilibrium between structure I and II is inconsistent with the slow rate of optical activity loss observed by Jones (20). This does not seem to be a valid argument as all experimental evidence indicates that there is an equilibrium between these structures and there is no evidence to the contrary.

The objective of this study was to identify the species that is polarographically reducible and explain the time-concentration dependency of the limiting current. As mentioned in the introduction, Roe (16) did a number of measurements with regard to the time, pH and catechol concentration dependency of the polarographic wave. It was found that varying only the catechol concentration at pH=1 the limiting

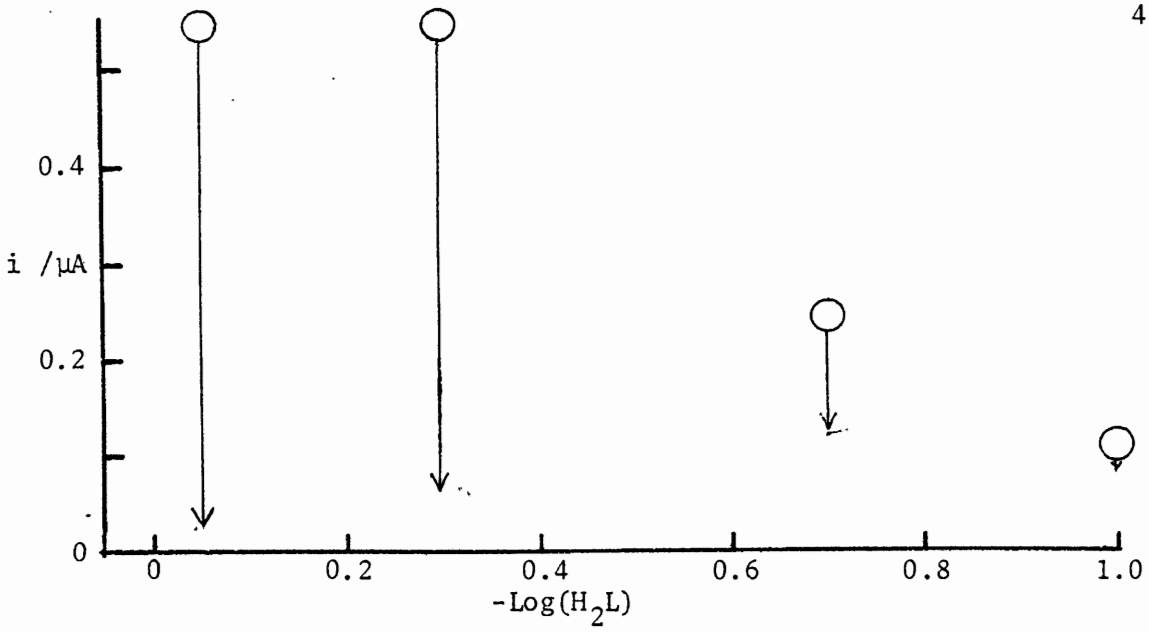


Figure 17. Current dependence on time and catechol concentration. 0.2mM As(V), 0.1M $HClO_4$, 0.9M $NaClO_4$ (16)

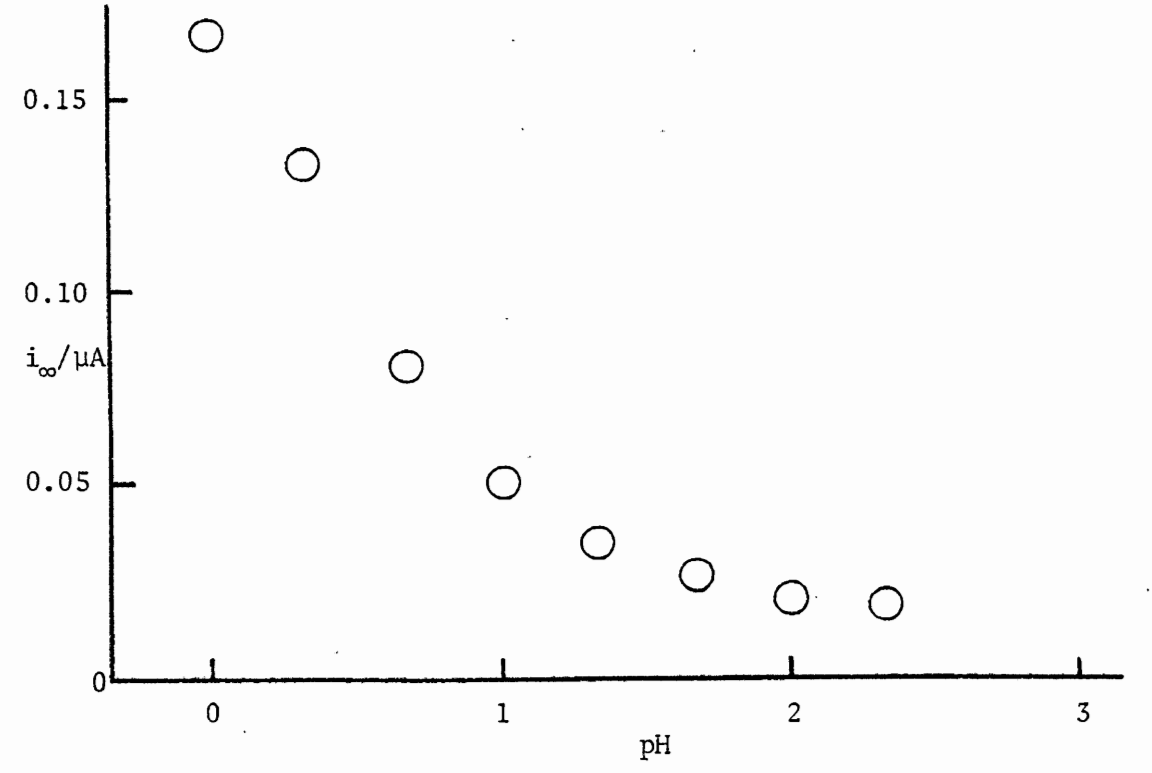


Figure 18. Dependence of limiting current on pH. 0.20mM As(V), 0.5M catechol, I=1M ($NaClO_4$). (16)

current was initially at some peak value, i_o, and decayed at different rates to some final value i_∞. The value of i_o did not change going from 0.5-1.0M catechol. This data is summarized if Figure 17. It was also found that in 0.5M catechol, i_∞ increased as the pH was varied from 2.3-0, although this effect seems to level off if the pH is above 2. The i_o associated with all the samples where 0.5M catechol was used was the same at all the pH's investigated. The polarographic measurements made in this experiment were of i_∞. Figure 18 shows this variation of i_∞ as a function of pH. Going from pH=2 to pH=0 there is a ten fold increase in i_∞. Figure 13 shows the variation in i_∞ as a function of both pH and catechol concentration. The current at pH=1 is about three times that at pH=2. At pH=1 the peak value of i_∞ is at a catechol concentration of 0.25M while at pH=2 the peak is at a catechol concentration of about 0.15M. It was also found that at pH=1 the limiting current is kinetically controlled whereas as pH=2 it is more diffusion controlled.

In order to tie the formation constant information together with the polarographic data it is first necessary to go to Table I and II. From these distribution figures it can be seen that at pH=1 the maximum amount of 1:1 complex occurs at about 0.2M catechol and at pH=2 this maximum occurs at a catechol concentration of 0.1M. These maxima are in very close agreement with the data from the preceding paragraph.

In all cases i_o relates to the total amount of As(V) complexed, the current decaying as the higher ordered complexes are formed. Assuming that when all the As(V) is complexed $i_o=i_{max}$ it is possible to tell how much As(V) is complexed from the fraction i_o/i_{max}. Table I predicts that about 40% of the As(V) will be complexed at a catechol

concentration of 0.2M, pH=1. From Figure 17 at the same catechol concentration i_o/i_{max}=0.45.

According to the formation constants the amount of 1:1 complex should decrease as the pH decreases (in the pH range where pH<4). This is not the case with the i_∞ as is seen in Figure 18. In attempting to explain the rise in the limiting current as the pH decreases one is forced to consider three possibilities. First a simple protonation reaction may be taking place. As the pH decreases the equilibria would shift in favor of the protonated form. If this were the case i_{max} would also increase, which is not the case. Another situation is the formation of the 1:1 complex from As(V) as the 1:1 complex concentration is depleted at the mercury surface. Roe (16) found that the initial rise to i_o is slower at higher pH's which would mean that as the pH decreased complex formation is faster. This, though, is inconsistant with the observation that the kinetic current is less at higher catechol concentrations. The last possibility is the formation of 1:1 complex from the dissociation of the 1:2 and 1:3 complex. Jones et al. (24) found that the rate of hydrolysis is first order dependent upon hydrogen ion concentration. The effect of catechol is also agreeable with this process.

Assuming the protonated 1:1 species is the one which undergoes charge transfer the following equilibria to describe the formation of this species from the 1:3 species can be written:

$$4H_2O + AsL_3^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} As(OH)_4L^- + 2H_2L \qquad k_f = 6.0(10^{-3}) \qquad \frac{k_f}{k_b} = \frac{\beta_1}{\beta_3} = .0013$$

$$As(OH)_4L^- + H^+ \xrightarrow{\text{fast}} \underset{\text{reducible}}{HAs(OH)_4L}$$

The rate of the forward reaction is being assumed to be equal to the rate of hydrolysis Jones et al. observed (24).

Meites (34) gives an equation which enables the calculation of a kinetic current, i_k, given the pseudo-first order rate constants k_f' and k_b'.

$$i_k = 493nD^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{2}{3}}C(k_f'/k_b'^{\frac{1}{2}})$$

$$k_f' = k_f(H^+)$$

$$k_b' = k_b(H_2L)^2$$

All symbols have their usual meaning and C is the concentration of the 1:3 species. Since by changing the catechol concentrations the amount of 1:3 complex present would change, only pH effects will be investigated. Table VI shows how the relative kinetic current changes with respect to pH.

TABLE VI

KINETIC CURRENT DEPENDENCE ON pH

pH	$(k_f'/k_b'^{\frac{1}{2}})(10^4)$
3	1.8
2	5.6
1	18
0	56

The results of Table VI predict a three fold rise in i_k going from pH=2-1. Comparing this with the data in figure 13 shows good agreement. Figure 18 shows about a three fold rise in i_∞ going from pH=2-1 and a ten fold rise going from pH=2-0. This is exactly the

pattern predicted from the results in Table VI.

The correlation between the polarographic observation and formation constant and rate data is very convincing. The 1:1 complex is the reducible species in the presence of excess catechol. The 1:3 species, predominant under these conditions, is not able to undergo charge transfer by a diffusion controlled mechanism, if at all.

The system seems suitable for analytical application for the simultaneous determination of As(V) and As(III). One possible procedure is as follows. The sample is deoxygenated and acidified to pH=1; deoxygenated, concentrated catechol is added to a concentration of about 0.5M; this insures maximum i_o. Current readings are then taken for a couple of minutes at E_{de} vs. SCE=-0.4v. By finding the residual current at this potential later, a plot of $-\ln(i-i_r)$ vs. t is made, where i is the current at a given time t, and i_r is the residual current. By extrapolation to t=0, i_o will give a means of obtaining consistent results. This will yield the As(V) concentration. The solution is allowed to set for about 15 minutes, at which time a scan is made to give the residual for the As(V) current readings and to determine the amount of As(III) present. This method should easily be able to detect 0.5μM concentrations of As(V) and As(III).

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APPENDIX

Definition of Equilibria:

$$H_3AsO_4 + nH_2L \underset{\beta_n}{\rightleftharpoons} H^+ + AsL_n(OH)^-_{6-2n} + (n-1)H_2O;\ n=1,2,3.$$

OR:
$$H_3AsO_4 + nH_2L \rightleftharpoons H^+ + AsO_{3-n}L^-_n + (n+1)H_2O$$

$$HAsL_n(OH)_{6-2n} \underset{K_{an}}{\rightleftharpoons} H^+ + AsL_n(OH)^-_{6-2n}$$

$$H_3AsO_4 \underset{K_1}{\rightleftharpoons} H^+ + H_2AsO^-_4$$

Derivation of Catechol Arsenate Relationship:

Mass balance for As(V)

(1) $C_{As} = (H_3AsO_4) + (H_2AsO^-_4) + (AsL(OH)^-_4) + (HAsL(OH)_4) + (AsL_2(OH)^-_2) + (HAsL_2(OH)_2) + (AsL^-_3) + (HAsL_3)$

By substituting the appropriate equilibria expressions and rearranging

(2) $Y = C_{As}(H^+)/(H_3AsO_4) = (H_2L)\{\beta_1 + \beta_1(H^+)/K_{a1}\} + (H_2L)^2 \cdot \{\beta_2 + \beta_2(H^+)/K_{a2}\} + (H_2L)^3\{\beta_3 + \beta_3(H^+)/K_{a3}\} + (H+) + K_1$

If $K_{an} >> (H^+)$

(3) $Y = (H_2L)\beta_1 + (H_2L)^2\beta_2 + (H_2L)^3\beta_3 + K_1 + (H^+)$

Calculation of Base Correction:

$B_{corr} = (V_f - 30.0)(H^+)/V_f + B_{uncorr}$; B_{uncorr}, amount of base used to adjust the pH, V_f, final volume.

Calculation of (H_3AsO_4):

(5) $(H_3AsO_4)_I = \alpha_o C_{As} - B_{corr}$ α_o = fraction of As(V) as H_3AsO_4

If K_{an} >/> (H^+) an iterative procedure must be used after an initial estimation of the K_a values

(6) $(H_3AsO_4) = \alpha_o C_{As} - B_{corr} - (H_3AsO_4)_I\{\beta_1(H_2L)/K_{a1} + \beta_2(H_2L)^2/K_{a2} + \beta_3(H_2L)^3/K_{a3}\}$

This equation would iterate until there was less than a 0.5% change in (H_3AsO_4).

Calculation of Uncomplexed Catechol Concentration, (H_2L):

Mass balance equation for catechol;

(7) $C_{H_2L} = (H_2L) + (HAsL(OH)_4) + (AsL(OH)_4^-) + 2(HAsL_2(OH)_2) + 2(AsL_2(OH)_2^-) + 3(HAsL_3) + 3(AsL_3^-)$

Substituting the appropriate equilibria expressions and rearranging;

(8) $(H_2L) = C_{H_2L} - (H_3AsO_4)\{\beta_1(H_2L)/K_{a1} + \beta_1(H_2L)/(H^+) + 2\beta_2(H_2L)^2/K_{a2} + 2\beta_2(H_2L)^2/K_{a2} + 3\beta_3(H_2L)^3/K_{a3} + 3\beta_3(H_2L)^3/(H^+)\}$

Once again an iterative procedure is used, the initial guess for (H_2L) is based upon the assumption that there is predominately a 1:3 complex present.

(9) $(H_2L)_I = C_{H_2L} - 3B_{corr}/\alpha_o$

The iteration proceeds until there is less than a 1% change in the (H_2L) concentration.

Realizing that it was possible for the complexes to have K_a values in the range where they may be protonated to some extent, equation (6) was used in the calculations. Since (H_2L) is used in this equation, an estimation, using equation (9), was initially made.

The entire procedure was programmed onto a Tektronix 31 programmable calculator and essentially consisted of a triple iteration; iteration for (H_3AsO_4) and (H_2L), then since the calculation of (H_3AsO_4) depends on (H_2L) the entire procedure repeated until there was less than 0.5% change in either value. This program would also compare an experimentally determined (H_3AsO_4) value with one calculated using equation (2), which indicated what formation constants may need alteration. The calculations become simplified if $K_{an} << (H^+)$, in which case only an iteration for (H_2L) is needed.

Distribution Curve Calculation:

Calculation of the distribution values of all forms of arsenate in the presence of catechol was done using equation (2) assuming $C_{As}=1$, and the appropriate equilibrium expressions.

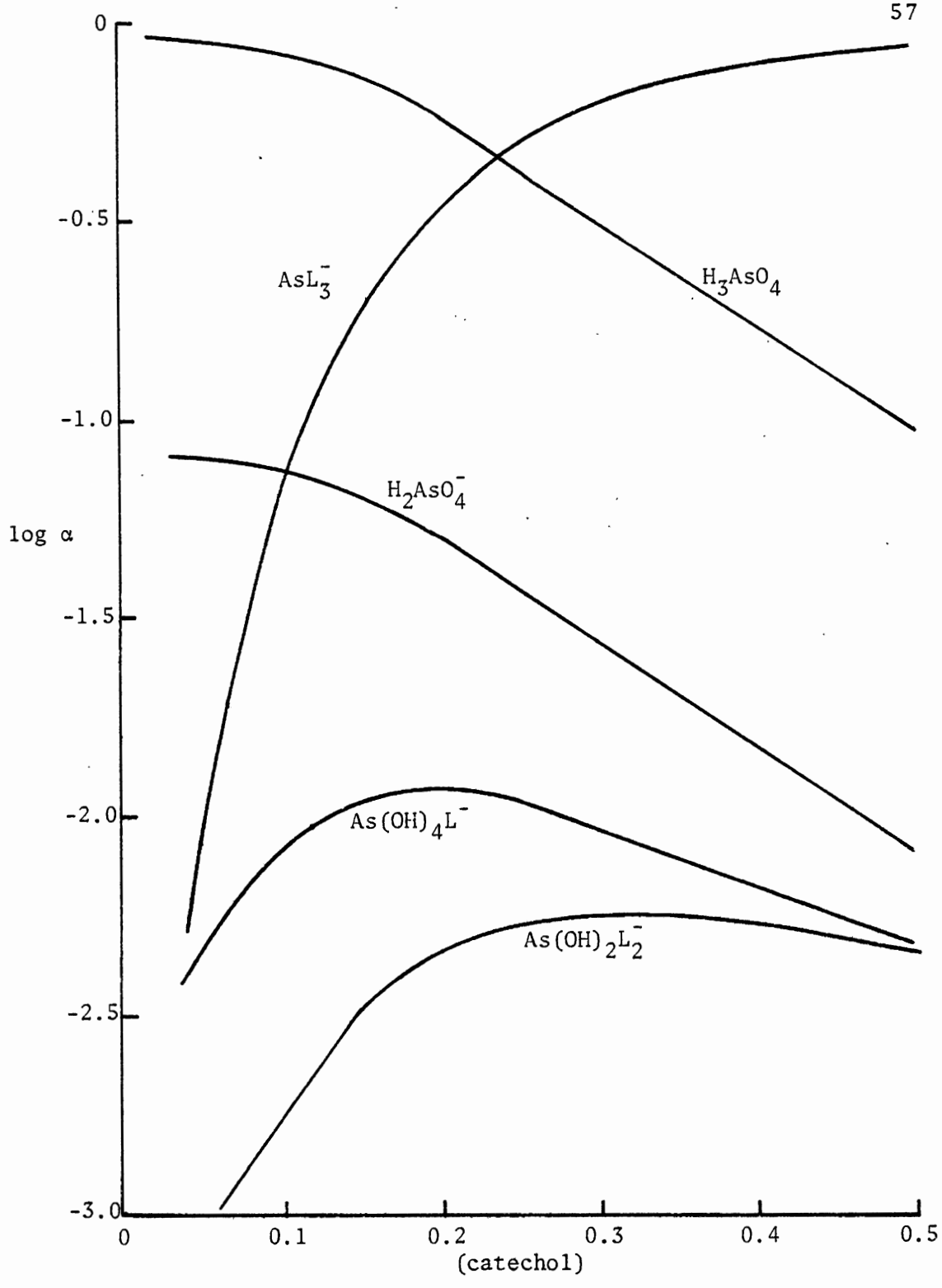

Figure 19. Distribution curves for As(V)-catechol system, pH=1.

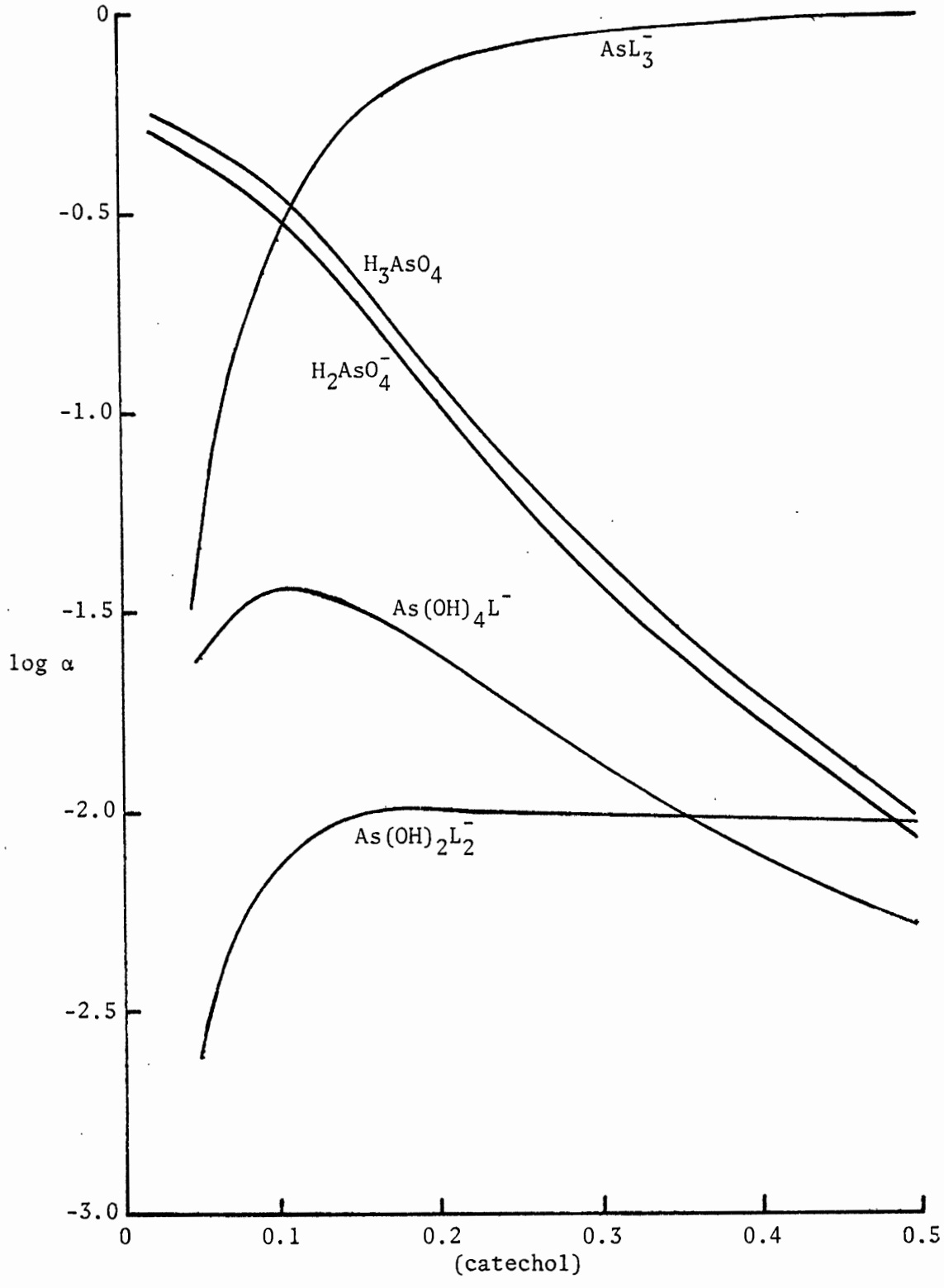

Figure 20. Distribution curves for As(V)-catechol system, pH=2.