LEAD ZINC AND COPPER CHELATES OF PYRIDYLAZO RESORCINOL IN WATER

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Master of Science

LEAD, ZINC, AND COPPER (II) COMPLEXES OF 4-(2-PYRIDYLAZO)-RESORCINOL IN AQUEOUS SOLUTION: THEIR IDENTIFICATION, STABILITY AND SPECTROPHOTOMETRIC TITRATION.

by

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ABSTRACT

A new analytical method was developed for the quantitative analysis of mixtures of copper, lead, and zinc in aqueous solution in trace levels (10^{-5} - 10^{-6} M). The method consists in the use of a chelating agent 4-(2-pyridylazo)-resorcinol (abbreviated PAR) as titrant in a spectrophotometric determination.

Each one of the systems:

Copper-PAR
Zinc-PAR
Lead-PAR

was studied separately. The composition and stability of the chelates in solution were studied spectrophotometrically. The different species were identified by the Continuous Variation method and the Mole-Ratio method. The stability constants were evaluated by an analysis of pH-absorbance curves obtained from solutions containing different metal:ligand ratios, over a range of pH values.

RESUME

On a mis au point une méthode analytique pour doser les traces (10^{-5} - 10^{-6} M) de métaux dans une solution aqueuse contenant un mélange de cuivre, plomb (II), et zinc. On dose le mélange métallique par une solution étalon de 4-(2-pyridylazo)-résorcinol (PAR). On détecte le point final par mesure spectrophotométrique.

Les systèmes suivants ont été étudiés séparéments:

Cuivre-PAR
Zinc-PAR
Plomb-PAR

Les complexes formés et leur stabilités ont été étudiés par mesures spectrophotométriques. On a identifié les espèces chimiques de chacun des systèmes par la méthode des variations continues et par la méthode des rapports molaires. Les constantes d'équilibres ont été évaluées à partir des courbes d'absorbances-pH obtenues pour divers rapports métal: ligand à différents pH.

ACKNOWLEDGEMENTS

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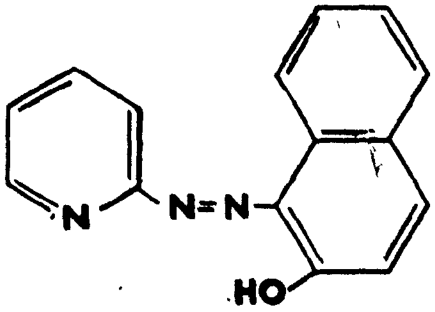
I INTRODUCTION

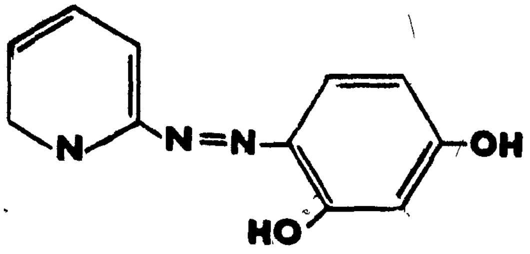
Chelating agents have been widely used as titrants in spectrophotometric determinations of metal traces; the titrant was in a non-aqueous medium (1) or an aqueous solution as with EDTA (2, 3).

The study of the 2-pyridylazo reagents showed that some of these compounds are among the most sensitive ones reported so far for the spectrophotometric determination of certain metals. In 1955 Cheng and Bray (4) introduced 1-(2-pyridylazo)-2-naphthol (abbreviated PAN), as a metallochromic indicator in EDTA titrations. Metal-PAN complexes have low solubility in water, and as a result organic and mixed solvents are required. Because of this and the fact that certain metal-PAN complexes react slowly with EDTA, the use of this reagent in direct EDTA titrations is limited. In addition to its use as a complexometric indicator, PAN was also used as a spectrophotometric reagent. However, since most of the PAN chelates are insoluble in water, this application is generally associated with solvent-extraction methods. Water-soluble pyridylazo derivatives are prepared by adding sulfonic acid substituents to the pyridylazo substrate, or by replacing the naphthol group of PAN with resorcinol, orcinol, or chromotropic acid. Spectophotometric and complexometric determinations can then be carried out in aqueous solution with these water-soluble derivatives.

In 1957 the use of 4-(2-pyridylazo)-resorcinol (abbreviated PAR) was recommended by Wehber (5) because its solubility and that of its metal chelates in water are higher than the solubility of PAN and its metal derivatives in water. Furthermore, in the spectrophotometric titrations the use of PAR gave sharper end points.



PAN



PAR

Pyridylazo compounds have high molar absorptivities making their spectrophotometric detection highly sensitive. However, due to the similarities in the spectra of the different metal chelates, the selectivity is low, which makes mixtures of metals difficult to analyse directly. Several techniques have been developed to make the determination of a metal in a mixture of metals possible, namely (4) :

I).- pH control

II).- selective masking or demasking of metals or group of metals.

III).- back-washing of an organic extract with a solution of an acid or complexing agent.

IV).- selection of solvent.

V).- selection of wavelength for photometric determination.

VI).- utilization of different rates of complexation.

VII).- change of oxidation state of the metal.

VIII).- utilization of exchange reactions of the Cu(II)-EDTA-PAN system.

IX).- extraction of the metal into an organic phase.

In the present study, the titration of metal ions using PAR as a titrant was studied at different hydrogen-ion concentrations. PAR forms with metal ions water-soluble intensely colored (commonly red or red-orange) complexes, most of which have an absorptivity larger than 10^4 at the maximum of absorption. Ions giving a color reaction with PAR are shown in Table I (4). The reactivity of PAR with metals is greater than that of PAN with the same metals. It is reported to be the most sensitive reagent for cobalt. and the most sensitive water-soluble reagent for uranium (5).

PAR has been used so far as a spectrophotometric reagent to determine the concentration of single metals after a previous separation from interfering ions (6,7). Iwamoto (8) has used a spectrophotometric titration for the determination of copper with PAR. A copper solution in an

	A							8			B							
	1	2	3	4	5	6	7				1	2	3	4	5	6	7	8
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	A
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac															

Lanthanide series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide series	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf					

Table I. Elements reacting with PAR.

acetate-buffered medium was titrated against standard PAR solution. A sharp inflection in the titration curve was obtained. The method does not require a calibration curve and it can be applied to other metals.

In this work the determination of the concentration of copper, lead and zinc alone in solution, and in the presence of each other was studied. In the method proposed here, selectivity was improved by pH control: hydrogen ions compete with the metal ion for combination with PAR. Consoquently the higher the stability of a metal complex, the lower the pH at which it can be determined.

II STATEMENT OF THE PROBLEM AND PLAN OF RESEARCH

The purpose of the present investigation was to examine the possibility of using a water-soluble matallochromic indicator as a volumetric reagent for the spectrophotometric titration of cations in aqueous media. The procedure used has been described previously by Grey and Cave (9).

The dye 4-(2-pyridylazo)-resorcinol was selected and used as titrant for the determination of copper, lead, and zinc alone and in the presence of each other. In the study of a metal-dye system the identification of the different participating species as a function of pH, the calculation of the stability constants for the reaction involved, and the optimum conditions for the titrations needed to be investigated.

Spectrophotometric data were used in order to achieve the proposed goal. In a first step the species present at the different pH values were postulated from the analysis of the pH-absorbance curves. Once a given species was proposed its existence was proved by the Continuous Variation method and the Mole-Ratio method. The speed at which the different species came to equilibrium was studied and the stability constant of the reactions taking place was determined.

It was also proposed to predict the titration graphs of the different metals from the pertinent equilibrium data as well as the optimum conditions for the determination of the mixture of metals.

III GENERAL APPROACH TO THE PROBLEM

III-1-1 IDENTIFICATION OF THE SPECIES

1.1 Introduction.

It was one of the aims of the present research to explain and predict the titrations curves for the spectrophotometric determination of certain metals contained in an aqueous solution. In order to achieve this goal, it was necessary to identify the different species present at all pH values, as well as to determine the equilibrium constant relating the species one to each other. Thus, a detailed study of the reaction of three metals, namely copper, zinc and lead, with 4-(2-pyridylazo)-resorcinol (PAR), was undertaken at several pH values. The reactions were studied by spectrophotometric techniques e.g. the Continuous Variation Method, the Mole-Ratio Method and by the analysis of pH-absorbance curves.

1.2 The Method of Continuous Variations.

In the method of Continuous Variations developed by Job (10), the sum of the concentrations of the reactants($C_T = C_M + C_L$) is kept constant, while their ratio (C_M/C_L) is varied. A series of solutions is thus prepared. The absorbances of the solutions are read at a few chosen wavelengths. The graph of the absorbance vs composition of the solution is called a Job plot at the chosen wavelengths. These graphs exhibit two straight line portions intersecting at a point corresponding to the composition of the product obtained from the reaction. If more than one product are present, the plot deviates from the simple ratios.

In the present work, the total amount of reactants, C_T, was approximately 10^{-5} M. For higher H^+ activities (pH = 5), C_T was twice the amount at low H^+ activities (pH = 8). This was necessary because of the low absorbance of the solution at low pH. The plots were made at 400, 500, 510, 520 nm wavelengths. At pH greater than 8, the wavelengths selected were such that the absorbance due to the ligand PAR could be neglected.

1.3 The Mole-Ratio Method (11).

This graphical method of analysis gives the molar ratio in which two reactants combine to form a compound. In this method, the concentration of one of the reactants is kept constant while the concentration of the second reactant is gradually increased by stepwise additions. Any unique property of the concentration of one of the reactants or of the compound produced will increase until the stoichiometric ratio is reached, after which it remains constant.

For the reaction:

$$mM + nN \underset{K_f}{\rightleftharpoons} M_mN_n$$

the method allows the determination of the ratio m/n. When M is kept constant and N gradually increased, we have that the maximum concentration of product M_mN_n after any addition C_N of N is given by:

$$[M_mN_n] = C = \frac{C_N}{n}$$

from which:

$$\frac{dC}{dC_N} = 1/\text{[illegible]} \quad \text{........(1)}$$

when the property measured is the absorption of light by the compound formed M_mN_n , we have for a cell of unit lightpath:

$$A = aC$$

where A is the absorbance, 'a' the absorptivity of M_mN_n and C is the concentration of absorbing species. Therefore:

$$\frac{dA}{dC} = a \quad \text{........(2)}$$

if we multiply both sides of equation (2) by equation (1), we obtain:

$$\left(\frac{dA}{dC}\right)\left(\frac{dC}{dC_N}\right) = (a)(1/n)$$

or:

$$\frac{dA}{dC_N} = a/n \quad \text{........(3)}$$

consequently, a graph of the measured absorbance versus the concentration of added N should be a straight line having a slope equal to a/n . The knowledge of the absorptivity allows the evaluation of n, the number of atoms of N in the molecule M_mN_n produced. Similarly, holding N constant while adding M, allows one to evaluate the other coefficient m.

When K_f is not too large (≈200 or below) so that the species at equilibrium are all present in measurable concentrations it can be readily evaluated. We can write:

$$K_f = \frac{[M_mN_n]}{[M]^m\,[N]^n} = \frac{C}{[M]^m\,[N]^n}$$

and $$\log K_f = \log C - m \log [M] - n \log [N] \qquad .....(4)$$

Also since $A = aC$ provided M and N do not absorb at the chosen wavelength

$$\log A = \log C + \log a \qquad .....(5)$$

substitution of (5) in (4) gives after rearrangement:

$$\log A = \log K_f + \log a + m \log [M] + n \log [N] \qquad .....(6)$$

if one of the reactants, say M is kept constant, three terms on the right part of equation (6) are constant. Then a plot of log A vs log $[N]$ will be a straight line with slope equal to n. However, $[N]$ is not known but in the limiting condition as $[N]$ added is equal to zero, equation (6) applies i.e.

$$\lim_{N \to 0} \left(\frac{d \log A}{d \log N} \right)_{M\ cte} = n \qquad .....(7)$$

the limiting slope gives the value of n. Similarly, if N is kept constant, we can calculate m .

In the present work, series of solutions containing a known fixed amount of metal (1×10^{-5} M) (copper, lead or zinc) and varying amounts of 4-(2-pyridylazo)-resorcinol were prepared. The ligand was added to cover a ligand to metal ratio varying from 0.1 to 4 and sometimes from 0.1 to 6 . The absorbance of the complex formed was read at 500 and 520 nm. At those wavelengths the complex absorbs strongly and the reactants contribute very little to the absorbance at pH values below 11. The analysis of the data obtained permitted an evaluation of the equilibrium constant K_f .

III-1-2 DETERMINATION OF EQUILIBRIUM CONSTANTS.

2.1 Introduction.

The equilibrium constants were determined mostly by a numerical analysis of the pH-absorbance curves. In some cases the Mole-Ratio method described previously was used and the values obtained compared with the ones evaluated from the pH-absorbance graphs.

2.2 pH-absorbance curves.

It has been demonstrated by Sommer and co-workers (12) that spectrophotometric procedures based on linear extrapolation can be used to study the complex equilibrium of systems based on compounds of the type of PAR. The method involves a detailed algebraic study of the equilibria of the reagents.

First the chelate reaction and the species formed over a particular pH range are postulated, then a series of linear algebraic transformations are derived using the equilibria data from the reagent. Experimental values of absorbance and pH are introduced into these equations, which then provide values of the equilibrium constants. Typically these transformations are straight lines and false assumptions are readily detected by the presence of curvature or random scatter when experimental values are substituted into the transformations.

Given that the method is based on extrapolation it is very sensitive to the choice of points used for calculations. If the points used correspond to one end of the part of the pH-absorbance curve used for the analysis, the assumption that one species is of negligible concentration compared with the others becomes less valid.

III-2 EXPERIMENTAL

2-1 Apparatus for Spectrophotometric Titrations.

2-1a Beckman Model D.U.Spectrophotometer.

The apparatus used to make the titrations has been previously described (9); it consists of a Beckman Model D.U. spectrophotometer which can accomodate a rectangular 65-ml glass cell. The cell compartment was flanked by two rectangular copper tanks through which constant temperature water could be circulated. A 1 in. x 1/8 in. disc of silicone elastomer was countersunk in the removable lid of the cell compartment and provided the entrance for the microburet to the cell.

A calibrated 1-ml Koch microburet with a 60-ml reservoir adapted with a platinum-rhodium hypodermic needle (2 in. long and 28 standard gauge bore) was used for the delivery of titrant to the cell (a glass cell of 65-ml capacity, 54 mm long by 30 mm wide, by 55 mm deep. The path length of the cell was 5 cm.). The hypodermic needle was inserted through the silicone disc in the lid of the cell housing so that the tip of the needle was below the surface of the solution for titration. The solution was stirred during titrations by the use of a magnetic stirrer placed under the cell compartment. A Teflon-coated micro-stirring bar was inserted in the 65-ml cell.

2-1b Beckman Model D.B. Spectrophotometer.

A double beam spectrophotometer Beckman Model D.B. using 1-cm and 4-cm cells was also used. It was coupled to a Sargent Model SRLG recorder capable of recording absorbance directly. Constant-temperature water from a water bath could be circulated in the cell compartment.

2-1c Unicam SP-500 Manual Spectrophotometer.

A Unicam SP-500 manual spectrophotometer was used with 1-cm or 10-cm cells. Constant-temperature water from a water bath could be circulated in the cell compartment.

With the first two spectrophotometers mentioned, the end points obtained for the titrations were precise; for exact absorbance readings and for the measurements of the molar absorptivities reported, the Unicam SP-500 was used exclusively.

2.2 Thermostat.

Sargent-Welch thermostatic water bath (Cat.No. S-84880) was used for external circulation of water. It controls the temperature to 0.1°C.

2.3 Beckman Zeromatic 11. pH meter.

The pH meter used for pH adjustment was provided with a glass electrode (Beckman No 40495) responding until pH 14.

2.4 Glassware.

Red low-actinic glass 50-ml volumetric flasks were used for the zinc-PAR chelate , because this compound is light sensitive.

Due to the fact that the concentration of the metal chelates was very low, special care had to be taken in the cleaning of glassware material. The glassware was washed normally (laboratory detergent), rinsed several times with distilled water, and then filled with a saturated solution of E.D.T.A. in water. This solution was left in the glassware for at least 20 minutes, after which the glassware was washed several times with distilled water, and then filled with deionised water and left overnight, after that it was emptied and dried in an oven at 110°C.

2.5 Reagents.

2.5.1 Ethanol.

Absolute ethyl alcohol, U.S.P. (The Consolidated Co.) was used without further purification.

2.5.2 Standard Metal Solutions.

Accurate metal solutions were required to evaluate the precision and accuracy of the method studied. The standard metal solutions were prepared from a weighed amount of a reagent-grade metal into a 100-ml beaker, the metal was dissolved in 1:1 nitric acid, quantitatively transfered to a 1-liter volumetric flask with deionised water, and made up to the mark. These stock standard solutions (10^{-2}M) were kept in glass flasks sealed with Teflon tape. Dilute solutions (10^{-4} M) were prepared fresh every day. The stock solutions were standardized against standard E.D.T.A. solution.

2.5.3 Water.

Ion-exchanged water was used exclusively in this work. Distilled water was passed through a Barnstead ultrapure (mixed bed) column (Cat. No D8902).

2.5.4 Sodium Hydroxide, Fisher electrolytic pellets.

When large amounts of this reagent-grade sodium hydroxide were used to adjust the pH, a blank solution of PAR with the sodium hydroxide in some cases showed impurities. Therefore the reagent was purified before use by an ion-exchange column AGA-542 (13). After regenerating the ion-exchange column with 1 N sodium hydroxide solution, the column was washed with distilled deionized water until no hydroxyl or chloride ions were coming out of the column. Then a 0.1 N sodium chloride solution was passed through the column to produce a pure, approximately 0.1 N sodium hydroxide solution.

The reagents and buffers used in the present work are given in Tables II and III.

TABLE II

REAGENTS

Reagent	Source	Form for use	use
Tris(hydroxymethyl) Aminomethane, certified primary standard	Fisher	0.1 M in water	Buffer preparation
Sodium Borate Analytical Reagent	Fisher	0.025 M in water	Buffer preparation
Ammonium Chloride Analytical Reagent	McArthur Chemical Co. Ltd.	crystals	Buffer preparation
Ammonium Hydroxide Analytical Reagent	Anachemia	28.0-30.0 %	Buffer preparation
Potassium Phosphate Analytical Reagent	Fisher	0.05 M in water	Buffer preparation
E.D.T.A.* Analytical Reagent	American Chemicals	0.05 M in water	Titrant for metals; standardized against Zn metal, with Eriochrome black T as indicator.
Zinc Metal 99.9 % pure	Analar	1.02×10^{-2} M	Standard metal soln.

TABLE II (continued)

REAGENTS

Reagent	Source	Form for use	Use
Copper Metal 99.93 % pure	General Chemical Division	1.0×10^{-2} M in water	Standard metal solution
Lead Metal 99.9 % pure	Fisher	1.0×10^{-2} M in water	Standard metal solution
Nitric Acid Analytical Reagent	Anachemia	71 %	

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* Disodium ethylenediaminotetracetate dihydrate.

TABLE III
BUFFER SOLUTIONS (14,15)

pH	x	u*
50 ml 0.1 M tris (hydroxymethyl)aminomethane + x ml 0.01 M HCl diluted to 100 ml.		
7	46.6	0.047
8	29.2	0.029
9	5.7	0.006
50 ml 0.025 M sodium borate + x ml 0.1 M HCl diluted to 100 ml		
8	20.5	0.025
9	4.6	0.025
50 ml 0.025 M sodium borate + x ml 0.1 M NaOH diluted to 100 ml		
10	18.3	0.043
50 ml 0.05 M KH_2PO_4 + x ml 0.1 M NaOH diluted to 100 ml		
8	46.1	
13 g NH_4OH diluted to 500 ml		
10	42	

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* ionic strength

2.5.5 4-(2-pyridylazo)-resorcinol.

4-(2-pyridylazo)-resorcinol is abbreviated to PAR throughout this work; and PAR also indicates a stoichiometric amount of the reagent. The several species actually present in an aqueous solution will for convenience be abbreviated to H_3P^+ , H_2P , HP^- , and $P^=$. The PAR used was Eastman Kodak Analysed Reagent grade, further purified by two recrystallizations from ethanol.

The synthesis of PAR involves the diazotization of 2-amino pyridine in ethanol using isopentyl nitrite treatment with sodium ethoxide, and coupling with resorcinol (16).

The purified PAR was a bright-orange coloured solid; m.p. 184°C (lit. (4) m.p. 182°C). Analysis calcd. for $C_{11}H_9N_3O_2$: C, 61.33 % ; H, 4.18 %; N, 19.51 % ; O, 14.87 % . Analysis found: C, 61.03 % ; H, 4.59 %; N, 19.7 % ; O, 15.23 %. PAR can be obtained as both the mono and disodium salts. The disodium derivative dihydrate is slightly hygroscopic. PAR was found to be heat-sensitive, and decomposed slowly to a black powder. It is readily soluble in aqueous alkaline solutions and in water to the extent of 5 mg/100 ml of solution at 10 °C (4) to give a bright yellow solution; in alkaline solutions with a pH of 12 or higher the solution is orange. It is soluble in alcohol and insoluble in ether. The absorbance of an aqueous solution of PAR has been found to decrease with time (4). This problem is avoided by using PAR as an ethanolic stock solution which proved to be stable for months.

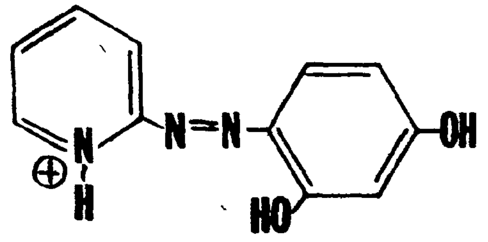
Four species of PAR exist in solution, which have the following absorbance peaks:

(I)	H_3P^+	max	395 nm
(II)	H_2P	max	383 nm
(III)	HP^-	max	415 nm
(IV)	$P^=$	max	485 nm

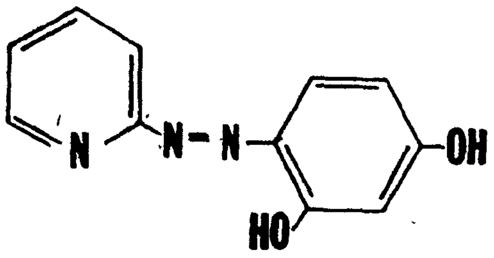
Hnilickova and Sommer (17) made a study of the dye and in addition to the species already reported they found two more chromophoric species of PAR:

(V)	H_4P^{2+}	max	390 nm
(VI)	H_5P^{3+}	max	433 nm

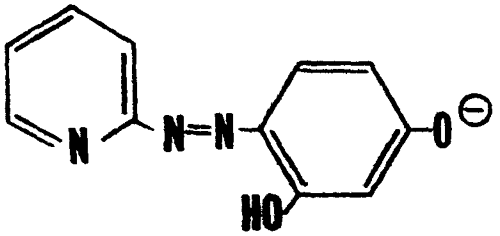
These species were found in 90 % and in 50 % sulphuric acid. They propose that the two extra protons are attached to the hydroxyl group and to the azo group.



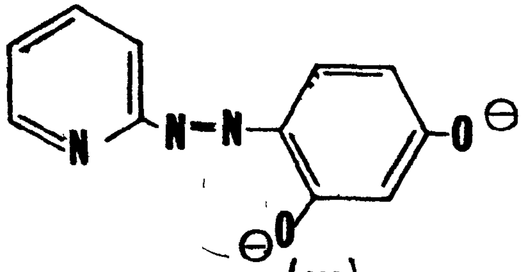
(I)



(II)



(III)



(IV)

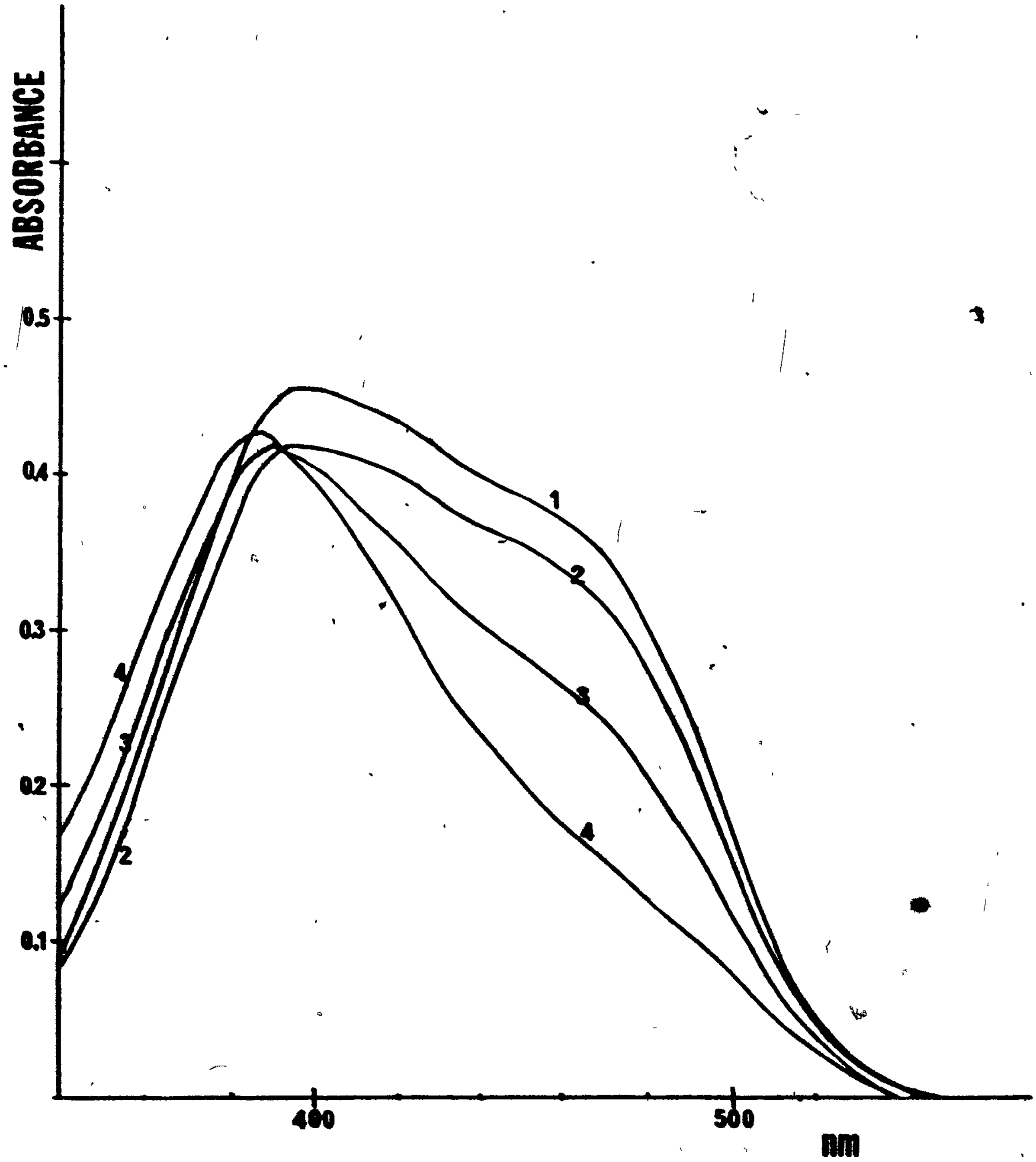
The spectra of PAR as a function of pH are shown in Fig 1. Three isosbestic points are observed, the first at 396 nm at pH 2, 3 and 4 is attributed to the equilibrium between the species H_3P^+ and H_2P. The second at 380 nm for pH 5, 6, and 7 is attributed to the equilibrium between H_2P and HP^-. The third at 444 nm for pH 11, 12 and 13 is attributed to the equilibrium between the species HP^- and $P^=$.

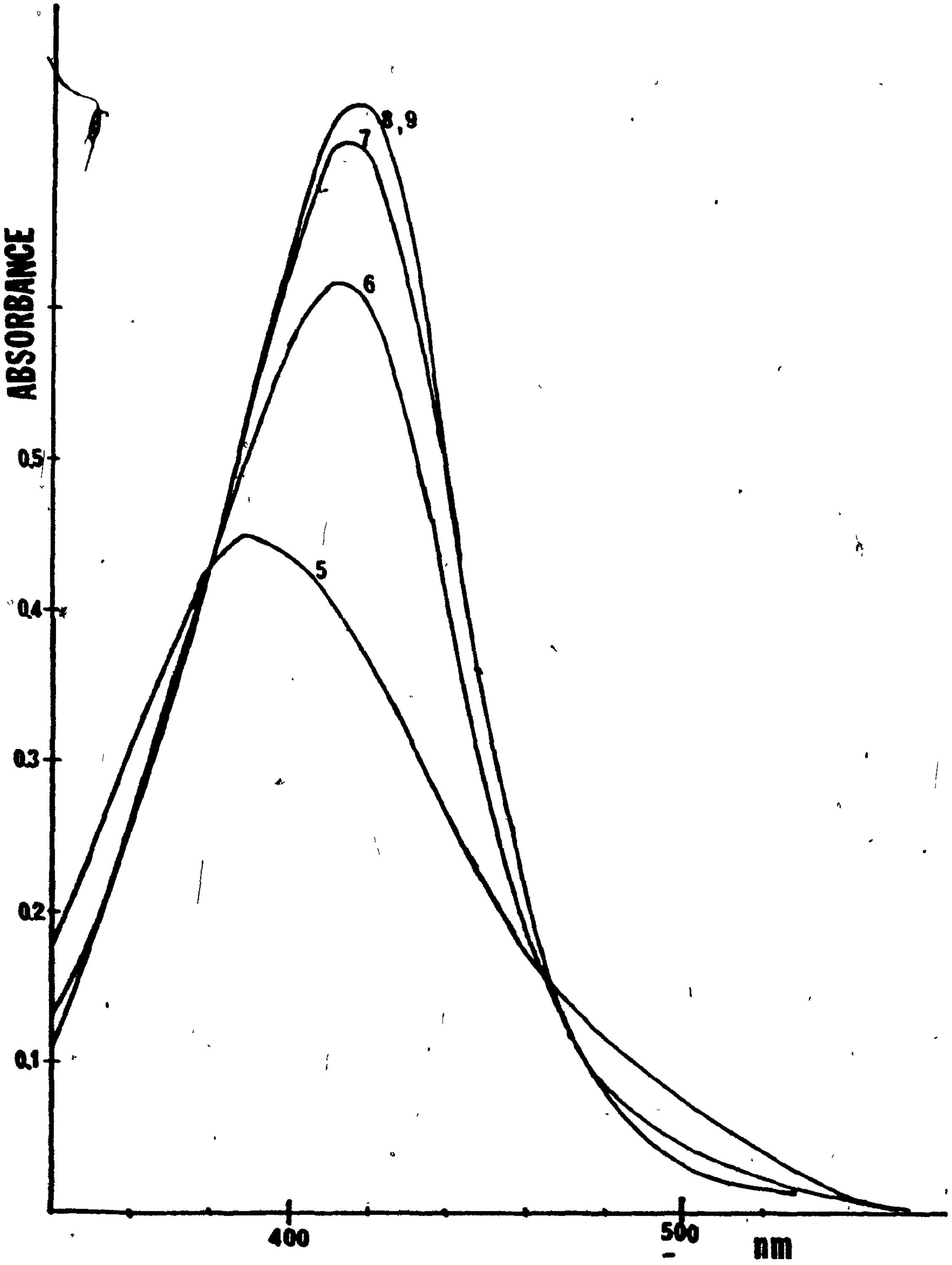
The acid dissociation constants of PAR are given in Table IV. Strong intramolecular hydrogen bonding between the ortho hydroxyl group and the azo group, and the inductive effects of the azo group give basis to the assumption that the dissociation constant for the proton in the para position will be higher than for the proton in the ortho position.

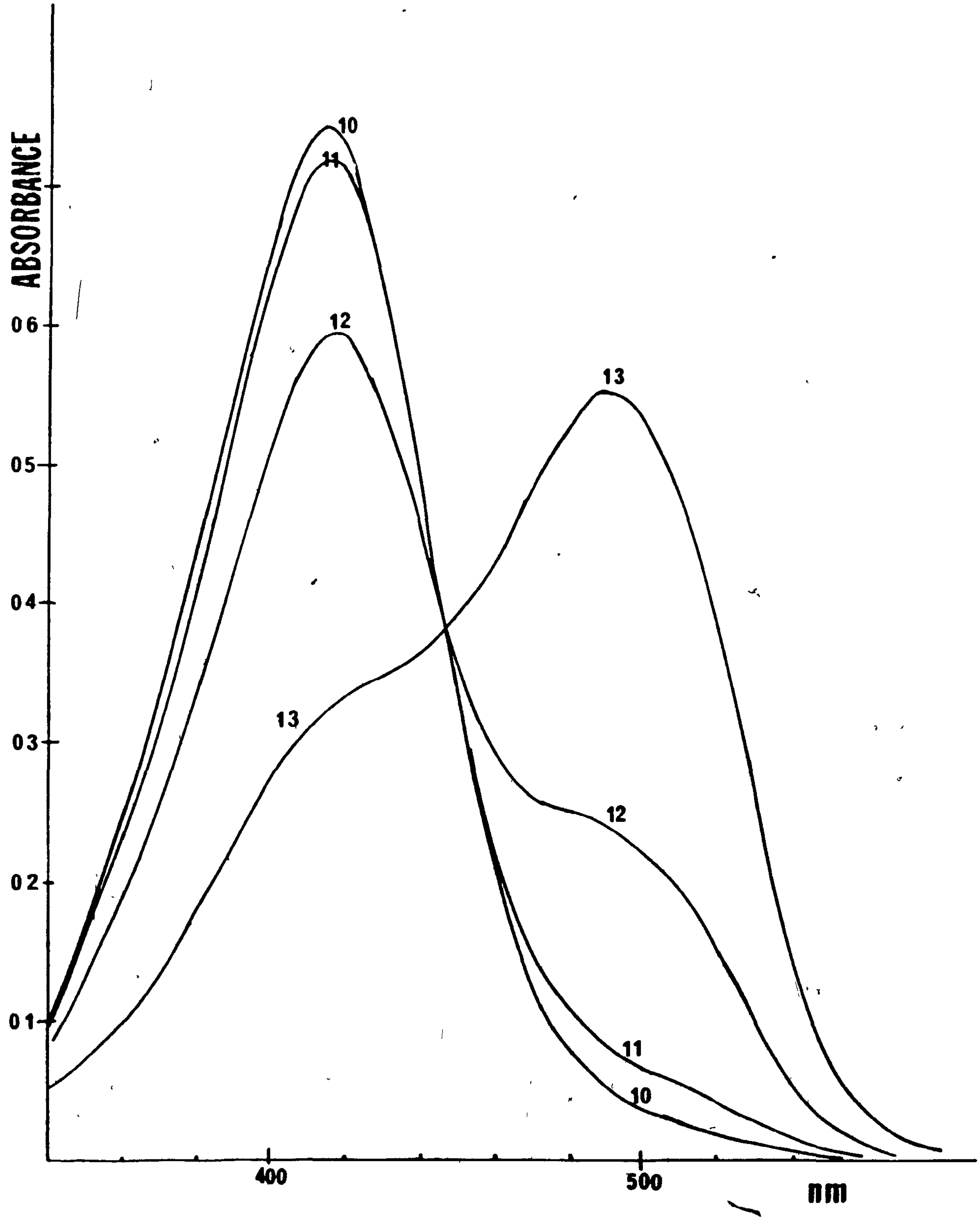
TABLE IV. THE ACID DISSOCIATION CONSTANTS OF PAR IN WATER

pKa_1	pKa_2	pKa_3	Method used	References
2.69	5.5	12.31*	Potentiometry * Photometry	18 , 19
3.1	5.6	11.9	Photometry	17 , 20
	5.83	12.5	Potentiometry	21

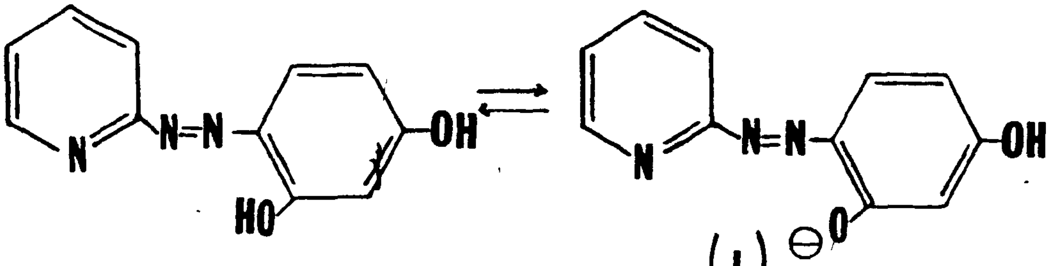
FIGURE I. ABSORBANCE CURVES OF PAR IN AQUEOUS SOLUTION. $C = 2.0 \times 10^{-5}$ M 1-cm CELL. The number with each curve is the pH of the solution.


ABSORBANCE
0.5
0.4
0.3
0.2
0.1
400
500
nm
1
2
3
4
4
3
2
4


ABSORBANCE
0.5
0.4
0.3
0.2
0.1
400
500
nm
8,9
7
6
5


ABSORBANCE
0 6
0 5
0 4
0 3
0 2
0 1
400
500
nm
10
11
12
13
13
12
11
10

In addition, comparison with the dissociation constant of the ortho hydroxyl group of PAN (pKa = 12.3) confirms this view. Consequently the dissociation constant (pKa = 12.4) for PAR is assigned to the ortho group and the other dissociation constant (pKa = 6.9) corresponds to the para hydrogen. Some authors do not agree with this assumption and different articles have appeared discussing this point (22, 23) Chalmers (23) argues that the species HP^- corresponds to (I) according to the following dissociation step:



(I)

The reason he gives for this assumption is that the intramolecular bonding through the ortho proton would increase the pKa to a small extent as compared with the inductive effect of the para hydroxyl group; without hydrogen bonding the ortho hydroxyl group will be as acidic as the para group.

The distribution diagram for the different species of PAR as a function of pH is shown in Fig 2. The formation curves were calculated from the pKa values reported by Hnilickova (17).

FIGURE 3. DISTRIBUTION DIAGRAM FOR THE DIFFERENT SPECIES OF PAR AS A FUNCTION OF pH.

Calculated by means of the values (17): $pK_1 = 2.66$ $pK_2 = 5.48$, $pK_3 = 12.31$. Where $[PAR]_T$ denotes the stoichiometric concentration of the reagent.

$$\alpha_1 = \frac{[H_3P^+]}{[PAR]_T}$$

$$\alpha_2 = \frac{[H_2P]}{[PAR]_T}$$

$$\alpha_3 = \frac{[HP^-]}{[PAR]_T}$$

$$\alpha_4 = \frac{[P^=]}{[PAR]_T}$$

FIGURE 2. DISTRIBUTION DIAGRAM FOR THE DIFFERENT SPECIES OF PAR AS A FUNCTION OF pH.

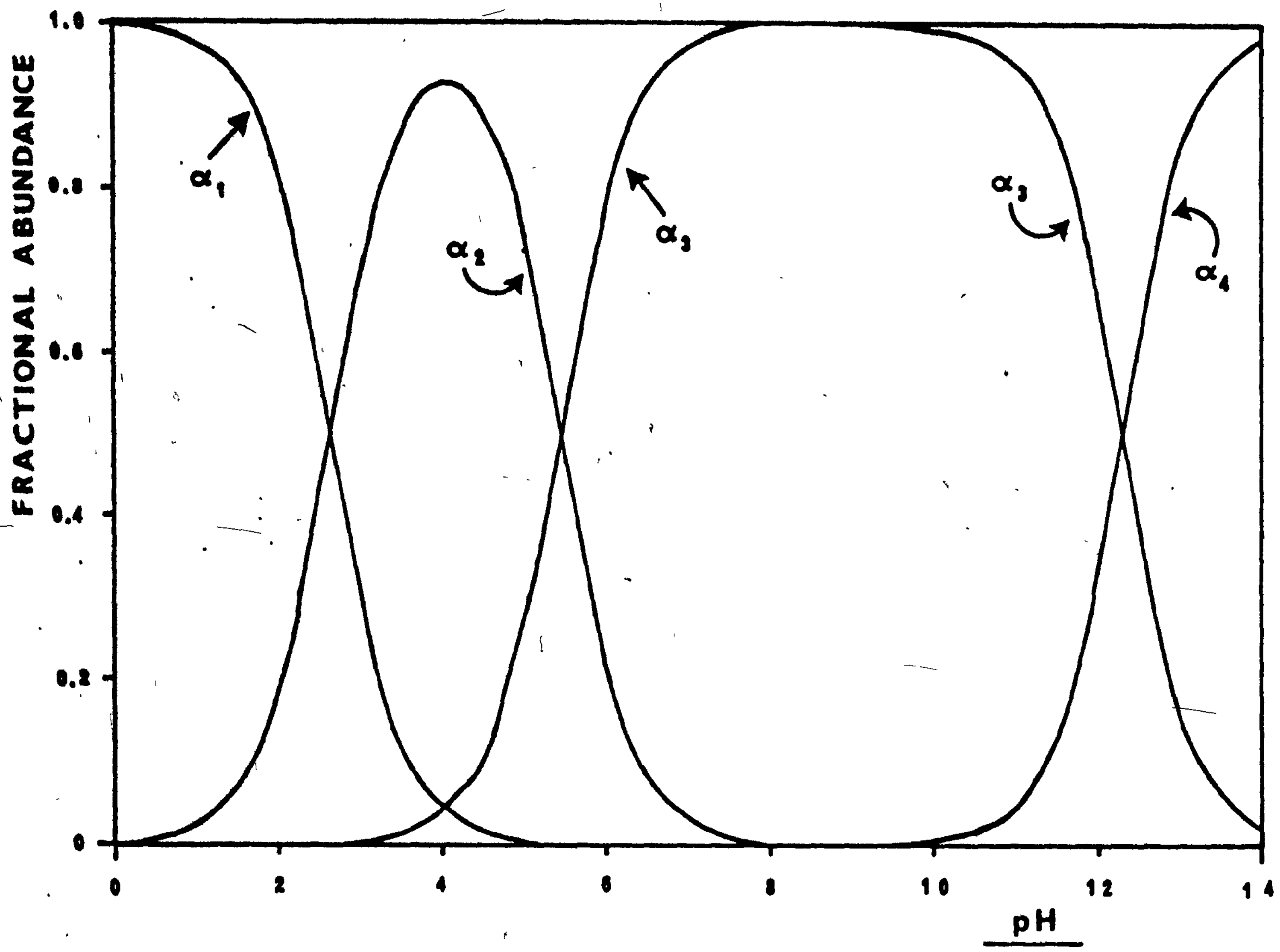
Calculated by means of the values (17): $pK_1 = 2.66$ $pK_2 = 5.48$, $pK_3 = 12.31$. Where $[PAR]_T$ denotes the stoichiometric concentration of the reagent.

$$\alpha_1 = \frac{[H_3P^+]}{[PAR]_T}$$

$$\alpha_2 = \frac{[H_2P]}{[PAR]_T}$$

$$\alpha_3 = \frac{[HP^-]}{[PAR]_T}$$

$$\alpha_4 = \frac{[P^=]}{[PAR]_T}$$


FRACTIONAL ABUNDANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pH
α_1
α_2
α_3
α_3
α_4

The apparent molar absorptivities (a*) of PAR at different pH values are given in Table V. These values were used every time a correction for absorbance due to free PAR in solution was needed.

The absorptivities of each species of PAR was necessary for the evaluation of the equilibrium constants and they were obtained by using the available mass-balance equations and from the simultaneous solution of as many Beer's law equations as were necessary. The absorptivities values obtained for each species are given in Table VI.

2.5.6 Metal-PAR Complexes.

PAR may act as a tridentate ligand, complexing with the metal ion through the ortho hydroxyl group, the azo nitrogen nearest to the phenolic ring, and the heterocyclic nitrogen atom, giving two stable five-membered chelate rings (19). In most cases PAR forms complexes with a metal-ligand ratio of 1:1 and 1:2 but other types have been reported, e.g. ThP_4 and GaP_5 (5). The structures of the 1:1 and 1:2 PAR-chelates are shown in the formulas A and B ; B generally exists at low hydrogen ion concentration, therefore it is represented in ionized form.

$$a^* = \frac{A}{[PAR]_T}$$

where: A = total absorbance

$[PAR]_T$ = stoichiometric PAR added.

TABLE V

APPARENT MOLAR ABSORPTIVITIES (a*) OF PAR AT DIFFERENT pH VALUES. $C = 1.0 \times 10^{-5}$ M.

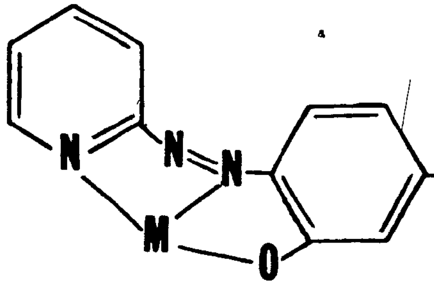
nm	400	500	520
pH	$a^* \times 1.0 \times 10^5$	$a^* \times 1.0 \times 10^5$	$a^* \times 1.0 \times 10^5$
1	0.21	0.055	0.017
2	0.21	0.054	0.017
3	0.197	0.046	0.016
4	0.192	0.037	0.017
5	0.22	0.032	0.016
6	0.30	0.014	0.007
7	0.344	0.01	0.005
8	0.35	0.01	0.005
9	0.354	0.01	0.005
10	0.338	0.012	0.006
11	0.334	0.026	0.012
12	0.275	0.083	0.044

TABLE VI

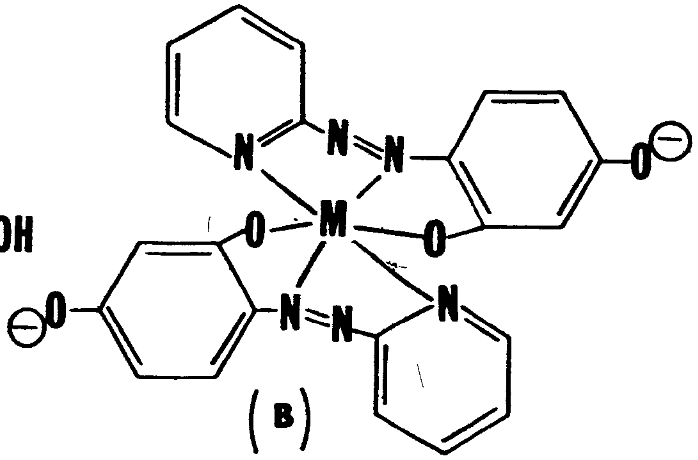
MOLAR ABSORPTIVITIES OF PAR SPECIES.

nm	400	500
Species	a**	a**
H_3P^+	2.1×10^4	5.87×10^3
H_2P	1.9×10^4	3.5×10^3
HP^-	3.5×10^4	1.0×10^3
$P^=$	1.3×10^4	2.2×10^4

** molar absorptivity in litres $mole^{-1}$ cm^{-1} .

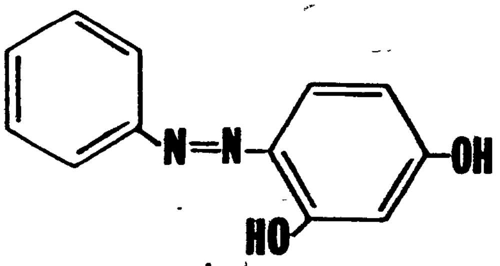


(A)

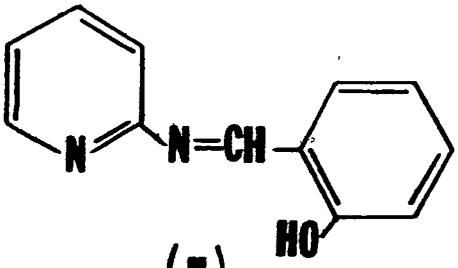


(B)

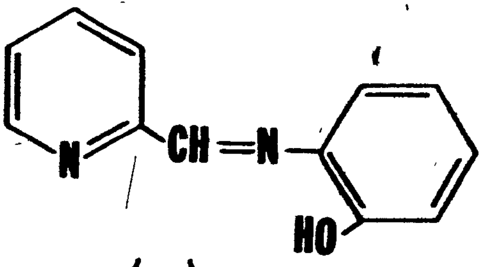
In order to study the role of the bonding group in the chelate formation, Geary, Nickless and Pollard (19) measured the stability constant of some metal chelates using complexes of: benzeneazo-resorcinol (I), salicylidene 2-amino-pyridine (II), and 2-pyridilidene-o-aminophenol (III).



(I)



(II)



(III)

The results showed that with (I) there is no significant shift in λmax on chelation (λmax 385 nm for the ligand and 360 for the copper chelate, at pH 6.35 where a potentiometric reaction indicates the formation of a 1:2 copper chelate.). With (II) the shift is just 15 nm for the copper chelate, and can not be compared with the shift of 100 nm for copper-PAR chelate at pH 8.5. The ligand (III) is highly reactive and the chelates formed are very similar to the metal-PAR chelates (at pH 4.88 the main peak of the ligand was shifted from 350nm to 452 nm.). These results demonstrate that in PAR the chromophoric reaction is due to coordination by the pyridine nitrogen, the azo nitrogen farthest from the heterocycle, and the o-hydroxyl group.

The formation of the chelate affects the acid dissociation constant of the para hydroxyl group (22) by increasing the acidity of this group. The acid-strengthening effect of the metal ion is transmitted primarily through the bonding oxygen atom rather than through the azo group; this was concluded by analysing the chelate's model, where it was observed that in the 1: 2 chelate the azo group does not lie in the plane of the resorcinol ring.

2.6 Procedures

2.6.1 Procedure for the titrations.

Three basic methods were followed in the titrations of the different metals with PAR:

1) 2 ml of buffer (pH values 7, 8 , 9, and 10) were added to a 1 ml aliquot of standard metal solution (1.0×10^{-4} M) directly in the titration cell. The final volume was brought to 50.0 ml with deionized water. The titration vessel was then inserted into the sample chamber of the Beckman D.U. spectrophotometer. The needle of the titrant buret was inserted through the rubber septum into the sample to be titrated. Standard PAR solution, the titrant, was added through the platinum needle, and the absorbance of the solution recorded. An alternative to this method was used at pH below 3, since there was no suitable buffer for the mixture of metals. Furthermore, close control of pH in that range proved to be unnecessary since the concentration of H^+ ions is very large ($\geq 10^{-3}$) as compared to the amount of H^+ obtained from the reaction. The pH was adjusted to the required value with nitric acid and the solution was brought to a final volume of 100 ml with a few ml of water. A 50-ml aliquot of that solution was pipetted to the titration cell and the titration was carried out as described above. In this procedure volume corrections for dilution were negligible.

2) A 5.0 ml aliquot of standard metal solution (1.0×10^{-4} M) was pipetted into each of a series of

volumetric flasks all containing approximately 30 ml of water and 5 ml of buffer of the appropriate pH. Different volumes of a standard PAR solution (1.0 x 10^{-3} M) were added from a microburet to each of the flasks. The solutions were diluted to the mark with deionized water and the spectrum recorded against a water blank from 340 to 600 nm.

3) A 5-ml aliquot of a standard metal solution (1.0 x 10^{-4} M) was pipetted in a 250 ml beaker, containing approximately 40 ml of water. Sodium hydroxide or nitric acid was added to the solution until the pH was at the desired value. The volume was then adjusted to 50.0 ml with deionized water. The pH was measured with a pH-meter whose electrodes were kept in the sample solution during the titration to allow continuous reading of the pH and readjustment to a constant value by the addition of sodium hydroxide or nitric acid as required; the titrant PAR was added from a microburet, the nitric acid or sodium hydroxide was added from a graduate micropipet. The volumes added were recorded for absorbance corrections. At high pH, an inert (N_2) atmosphere was kept in the system to prevent pH changes from the atmospheric CO_2. A small aliquot of that solution was carefully taken with a Pasteur pipet into a previously cleaned and dried 1-cm spectrophotometric

cell. The spectrum was recorded between 340 to 600 nm or the absorbance measured against a water blank at the required wavelengths with a Beckman D.B. spectrophotometer. The small aliquot in the cell was then returned to the titration beaker ; more PAR was added and the pH was readjusted to its constant value, an aliquot was taken to the sample cell previously used and returned carefully to the main solution at least three times before running the spectra. This insured that the small amount of solution sample that was left from the previous filling was removed and brought into the bulk of the solution. This was repeated for each point on the titration graph. For the final absorbance readings, volume corrections considering the addition of titrant as well as acid or base were taked into account.

2.6.2 Procedure for Time Behaviour Study.

For the time behaviour study, the solutions were prepared according to the method described in section III-2.6.1b. The absorbances of the solutions were read at 400, 500, and 520 nm as a function of time for a period as long as necessary to ascertain the behaviour of the solution with time . In certain cases solutions were followed for periods as long as 6 weeks.

2.6.3 Procedure for Identification of Species.

For the identification of the species by the Continuous

Variation method, a continuous variation plot was made from a series of up to 14 solutions. The solutions were prepared by accurately measuring the volumes of the reactants, PAR and the appropriate metal such that the sum of ligand and metal stoichiometric concentration was kept constant and of the order of 2.0 x 10^{-5} M. The standard solutions of the reactants were delivered from a 2-ml and 1-ml Koch microburet into 50 ml volumetric flasks containing some water and the appropiate buffer. The solutions were brought to the mark with deionized water and the absorbance of these solutions was read at 400, 500, 520 nm in the Unicam S.P. 500 Spectrophotometer.

2.6.4 Procedure for Determination of Equilibrium Constants.

A series of solutions with different ratios metal: ligand was prepared at different pH values, covering a pH range from 1 to 12. The method is the same as the procedure described above, in section III-2.6.1c . Each solution was prepared by the addition to an accurately measured amount of water (35-40 ml) of: 5-ml of metal solution (1.0 x 10^{-4} M), an appropiate amount of sodium nitrate to adjust the ionic strength to 0.1 and measured amounts of sodium hydroxide or nitric acid to adjust the pH to the required value. The solutions were brought to a final volume of 50 ml. Different amounts of ligand were added (0.5-2.5 ml, 1.0 x 10^{-3} M). The solution was kept all the time in the pH-meter to allow readjustment of pH if neccesary. The absorbances of the solutions were read at 400, 500, 510 and 520 nm in the Unicam S.P. 500 spectrophotometer. A volume correction was made for the amount of ligand, acid or base added.

III-3 RESULTS AND TREATMENT OF DATA

3.1 Time Behaviour.

In order to determine the time required for the establishment of equilibrium, an absorbance versus time study at different pH values was made on each system. The results are shown in Table VII.

TABLE VII

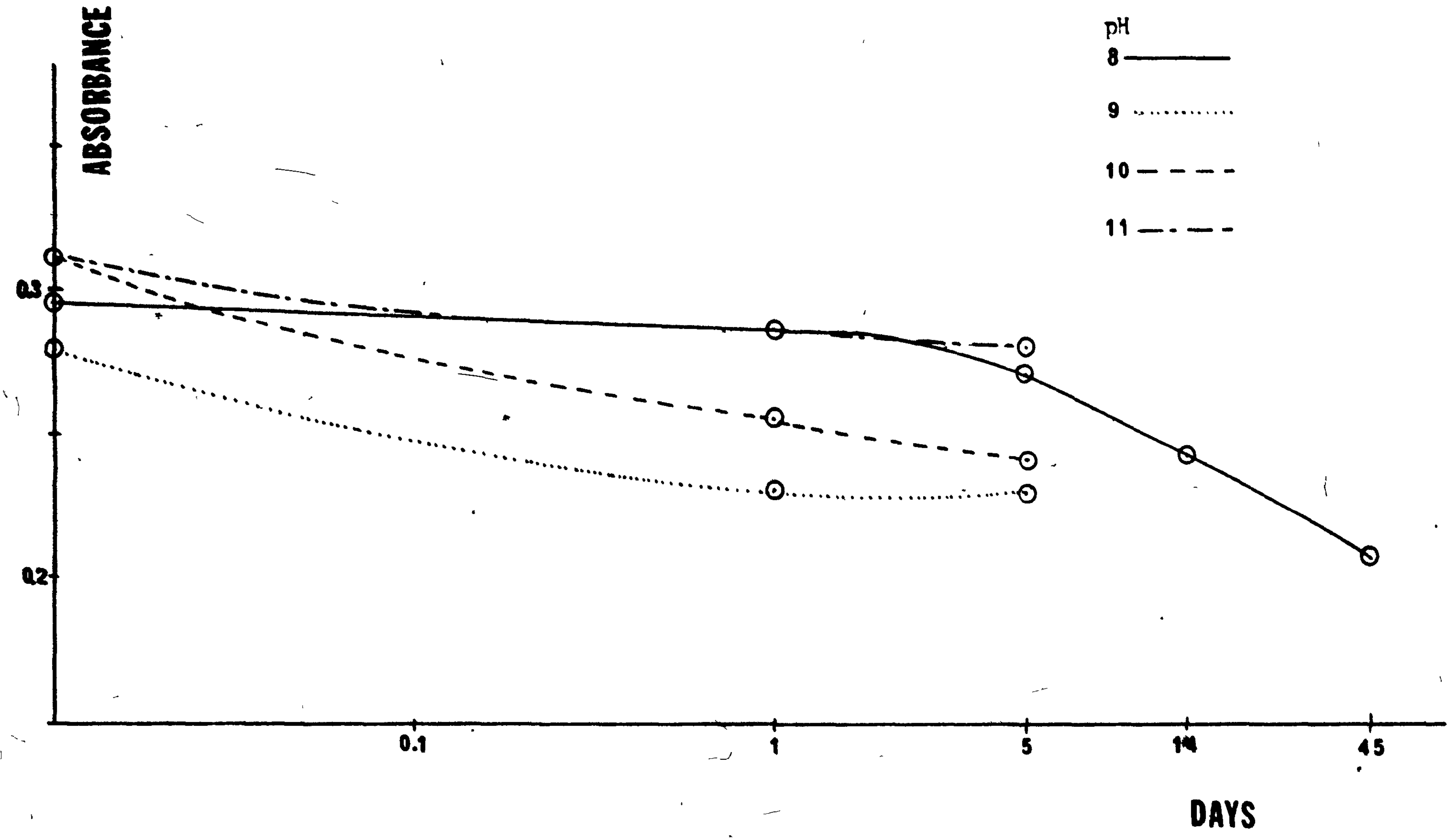
TIME NECESSARY FOR THE METAL-PAR SYSTEMS TO COME TO EQUILIBRIUM, AND BEHAVIOUR WITH TIME AT ROOM TEMPERATURE.

System	pH	M:L Ratio	time to reach equilibrium	Behaviour with time
Cu-PAR	1.5-4.0	1:1	immediate	stable
		1:3	immediate	indefinitely
	5-7	1:1	immediate	stable for 48 hrs.
	5-7	1:3	immediate	absorbance decreases after 17 hrs.

Zn-PAR	4	1: 1	immediate	stable indefinitely.
	5, 6	1: 1	immediate	absorbance decreases after 18 hrs.
	5, 6	M< L	precipitate forms.	precipitation increases with time.
	7-10	M< L	5 minutes	stable indefinitely.
Pb-PAR	4, 5	1: 1 1: 3	immediate	stable indefinitely.
	6, 7	1: 3	immediate	absorbance decreases after 24 hrs.
	8-11	1: 1	no equilibrium was reached*	absorbance still decreasing after 6 weeks.
	12	1: 1 1: 3	immediate	stable indefinitely.

* The decrease in absorbance with time at pH 8 is small for the first 24 hrs., compared with the decrease at pH values 9, 10 and 11. The decrease of absorbance with time is shown in Fig. 3 .

FIGURE 3. ABSORBANCE VS TIME GRAPHS FOR
Pb-PAR SYSTEM FOR pH RANGE 8-11.
C=1.0 x 10^{-5} M. 1-cm CELL. λ=500 nm.


ABSORBANCE
0.3
0.2
pH
8
9
10
11
0.1
1
5
14
45
DAYS

3.2 Effect of Light on the Stability of the Compound.

Standard solutions were prepared with concentrations ca. 1.0 x 10^{-5} M. The metal-PAR peak absorbance was measured in the presence and in the absence of daylight as a function of time. No differences were observed in the case of copper and lead chelates. For zinc an appreciable decrease in absorbance was observed in the solutions exposed to the daylight, as is shown in Fig 4.

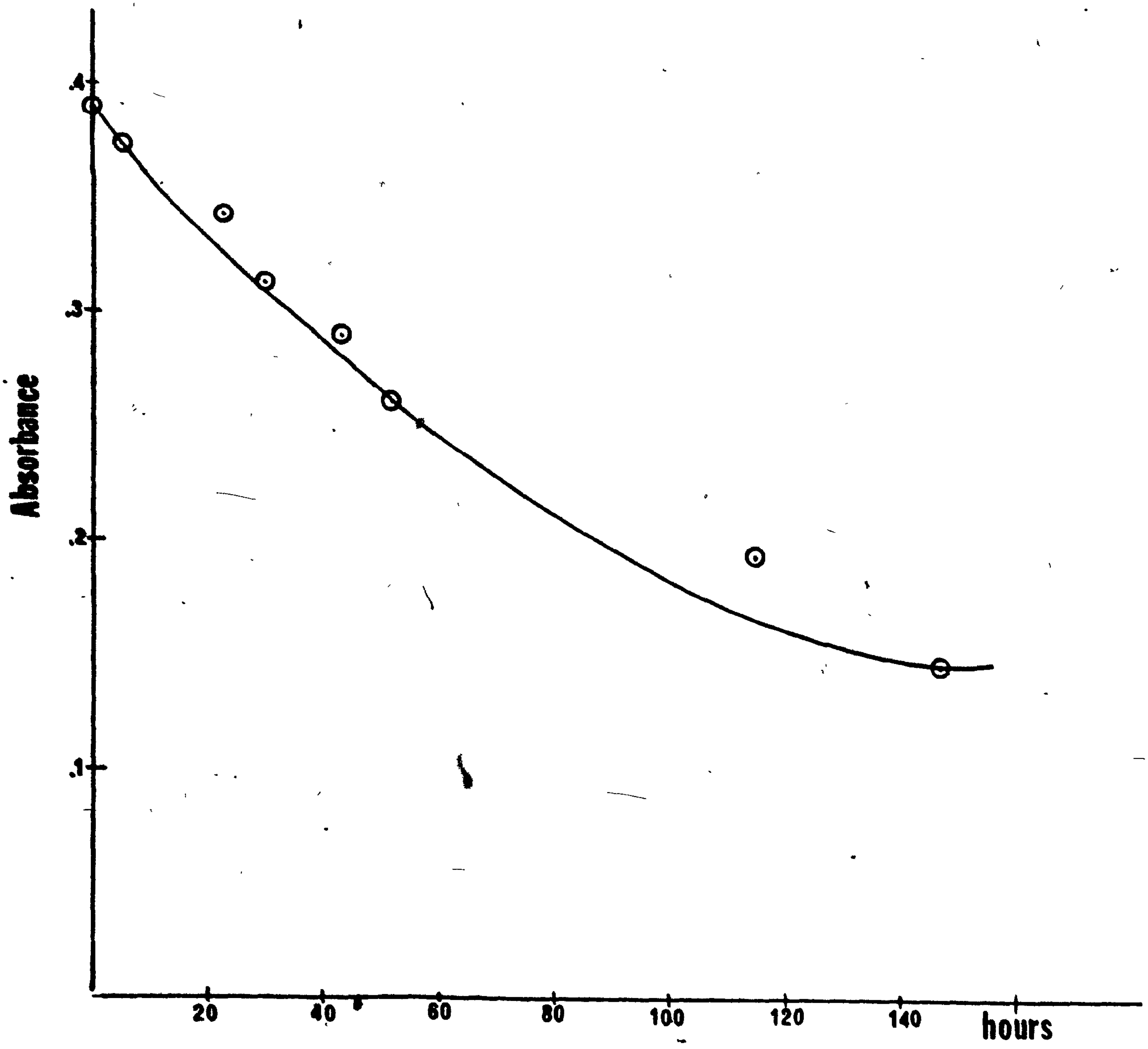
3.3 Buffers.

As will be shown in the absorbance vs pH curves (Figs. 6, 10, 15) the composition of the metal system in water is very much dependent on the hydrogen ion concentration. Furthermore, at certain pH values, precipitation occurred and at others the amount of complex formed was too small to be practically useful in a titration. Therefore the pH has to be adjusted within narrow limits; this was achieved by the use of buffer solutions. Several buffers were used in the determination of the mixture of metals and their effect was studied.

The borate ion complexes with zinc and a titration of zinc using a borate buffer took 24 hours to reach equilibrium but gave an accurate end point.

The use of buffer phosphate was not possible because the phosphate ion complexes with lead more strongly than PAR

FIGURE 4. EFFECT OF LIGHT ON ZINC-PAR CHELATE. pH=8, C = 1.5 x 10^{-6} M. Cell 4-cm. λ 500 nm.


Absorbance
.4
.3
.2
.1
20
40
60
80
100
120
140
hours

and the pink color of the lead-PAR chelate disappears in the presence of phosphate.

In ammonia solutions, copper behaves differently than in sodium hydroxide solutions. A determination of copper with PAR using ammonia buffer gave a lower end point than expected.

3.4 Identification of Species.

3.4.1 System Copper-PAR.

At pH values greater than 1.5, a water-soluble copper-PAR chelate was formed. The color of the solution was intensified as the pH of the solution increased. The composition of the chelate was studied spectrophotometrically by an analysis of the pH-absorbance curves for solutions containing various ratios of metal ion and ligand ; the method of Continuous Variation and the Mole-Ratio method were used to complete the information.

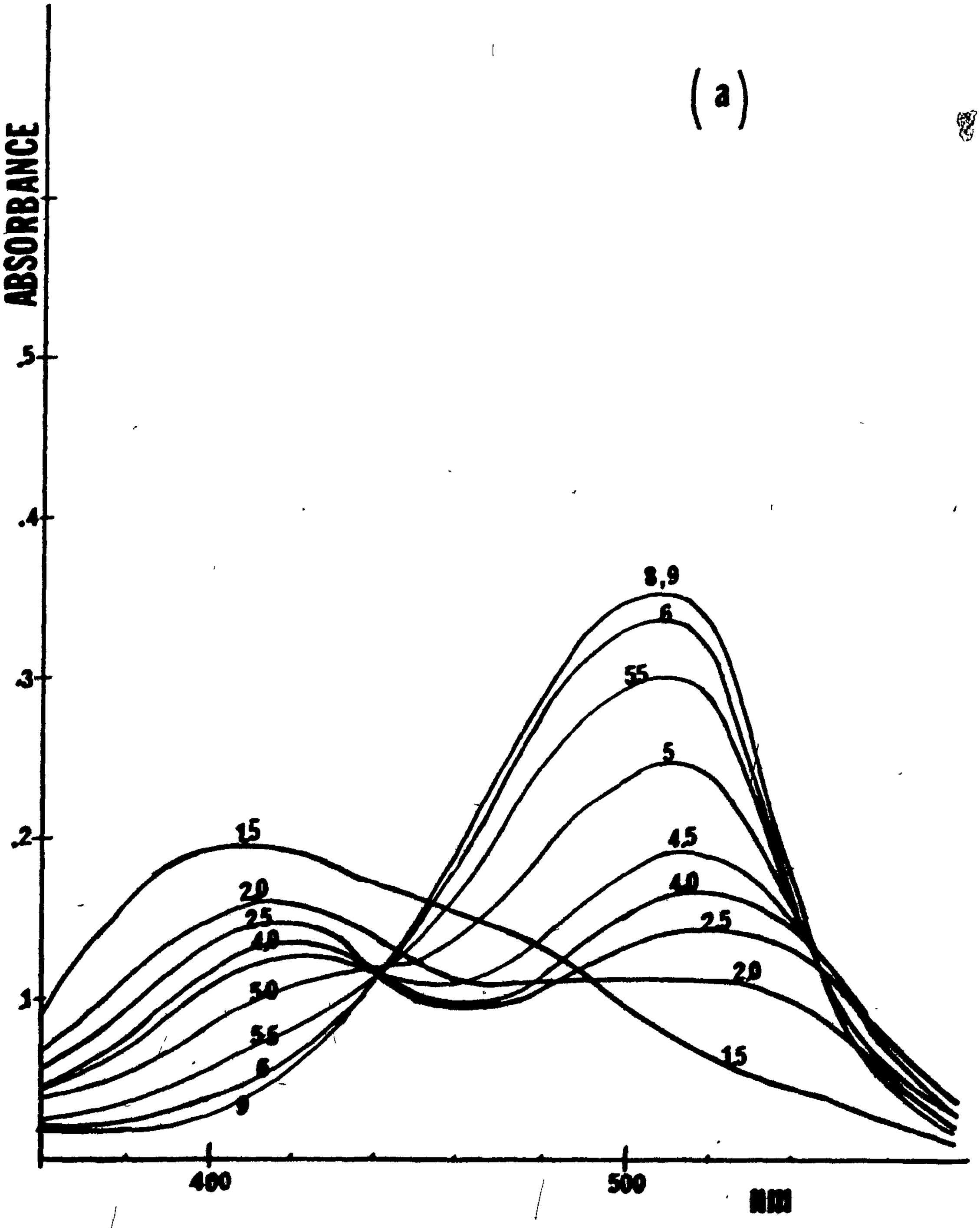
The absorption curves for solutions containing an equimolar amount of the reagents are shown in Fig 5a. Below pH 4, there is no true isosbestic point observed. The succesive curves cross at wavelengths that change continuously from 490 nm to 440 nm. At pH above 4 an isosbestic point is present at 442 nm. When the ligand was present in a 2: 1 ratio, and the pH was above 9 (Fig 5b) an isosbestic point was observed at 450 nm in the spectra.

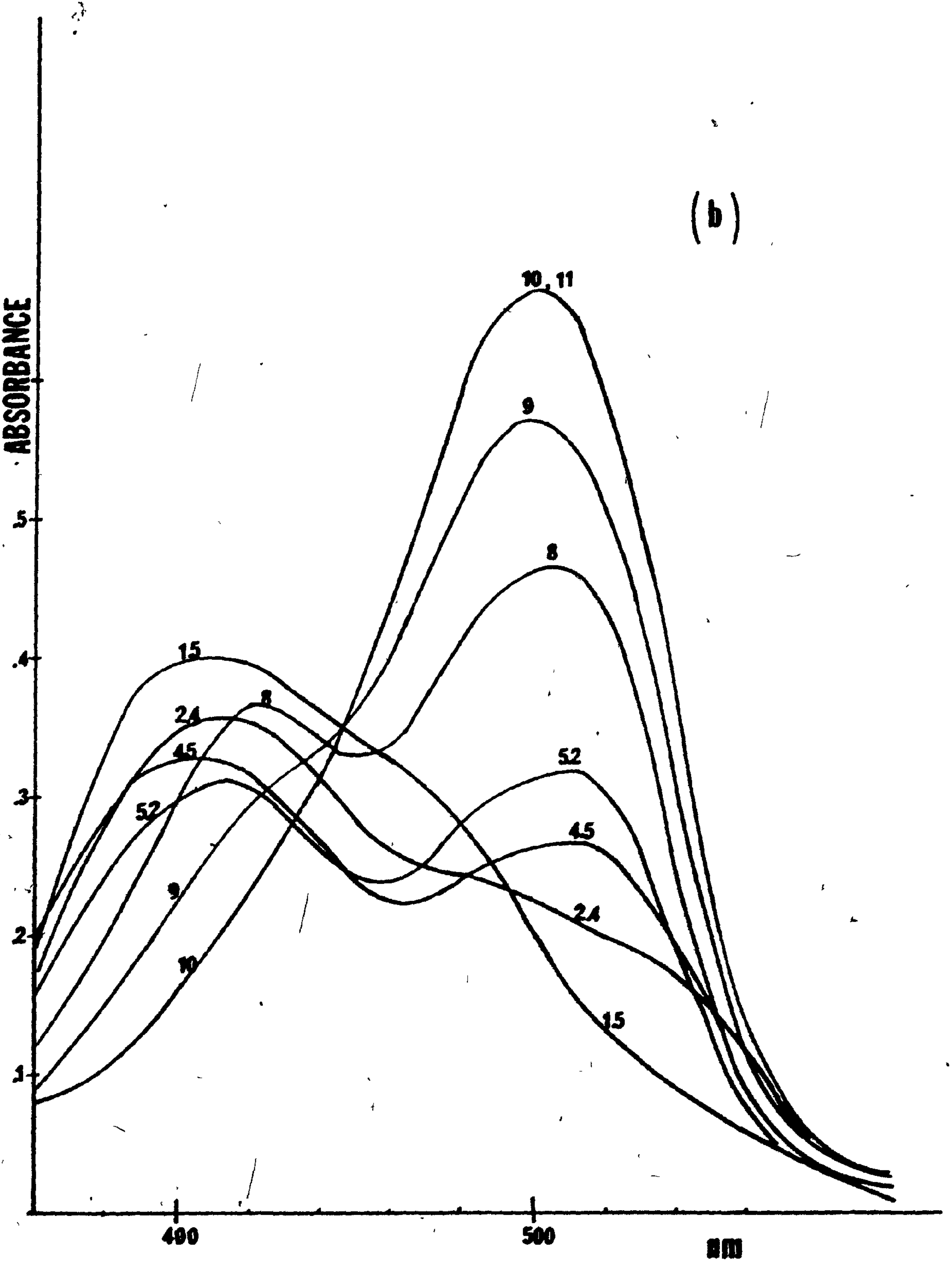
FIGURE 5 . ABSORBANCE CURVES OF Cu-PAR IN AQUEOUS SOLUTION. Cu = 1.0×10^{-5} M . 1-cm cell.

a) Ratio Cu: PAR 1: 1

b) Ratio Cu: PAR 1: 2

The number with each curve is the pH value of the solution.


(a)
ABSORBANCE
.5
.4
.3
.2
.1
400
500
nm
8,9
6
55
5
45
40
25
20
15
20
25
40
50
55
6
9
15


(b)
ABSORBANCE
.5
.4
.3
.2
.1
490
500
nm
10, 11
9
8
1.5
8
2.4
4.5
5.2
5.2
4.5
9
10
2.4
1.5

The spectra of the mixtures at different pH values as well as the shape of the absorbance vs pH curves suggest the series of reactions shown in Fig 6. The chemical model was ascertained by comparing the pH-absorbance curves to the curves that could best be predicted from the Continuous Variation method, the Mole-Ratio method and the absorptivities measurements obtained independently.

The solutions used in order to obtain the pH-absorbance curves (Fig 6) were prepared according to the procedure described in section III-2.3.3 . The composition of each of the solutions prepared is given on Table VIII. The absorbance values of these solutions were read against water as the spectrophotometric blank at 400, 500, 510, and 520 nm. The results are given in Appendix I.

An analysis of the pH-absorbance curves showed the presence of different species as the pH changed. In acidic pH, PAR is present principally as H_3P^+ and H_2P (c.F. Fig 2). In the system Cu-PAR the following reactions seem possible at high H^+ concentrations:

$$Cu^{++} + H_3P^+ = CuHP^+ + 2\,H^+ \qquad (I)$$

$$Cu^{++} + H_2P = CuHP^+ + H^+ \qquad (II)$$

In the above scheme of reactions only a 1:1 metal complex was postulated. The existence of the 1:1 Cu-complex

TABLE VIII

COMPOSITION OF SOLUTIONS USED FOR THE EVALUATION OF THE EQUILIBRIUM CONSTANTS.

Solution Number	Stoichiometric Molarity of Copper	Stoichiometric Molarity of PAR
1	1.0×10^{-5}	0.5×10^{-5}
2	1.0×10^{-5}	1.0×10^{-5}
3	1.0×10^{-5}	1.5×10^{-5}
4	1.0×10^{-5}	2.0×10^{-5}
5	1.0×10^{-5}	3.0×10^{-5}
6	1.0×10^{-5}	4.0×10^{-5}
7	1.0×10^{-5}	5.0×10^{-5}
8	1.0×10^{-5}	6.0×10^{-5}

FIGURE 6. pH-absorbance CURVES FOR Cu-PAR SYSTEM. Cu = 1.0×10^{-5} M. Cell 1-cm. λ = 500 nm.

(I) M : L = 1 : 0.5

(II) M : L = 1 : 1.0

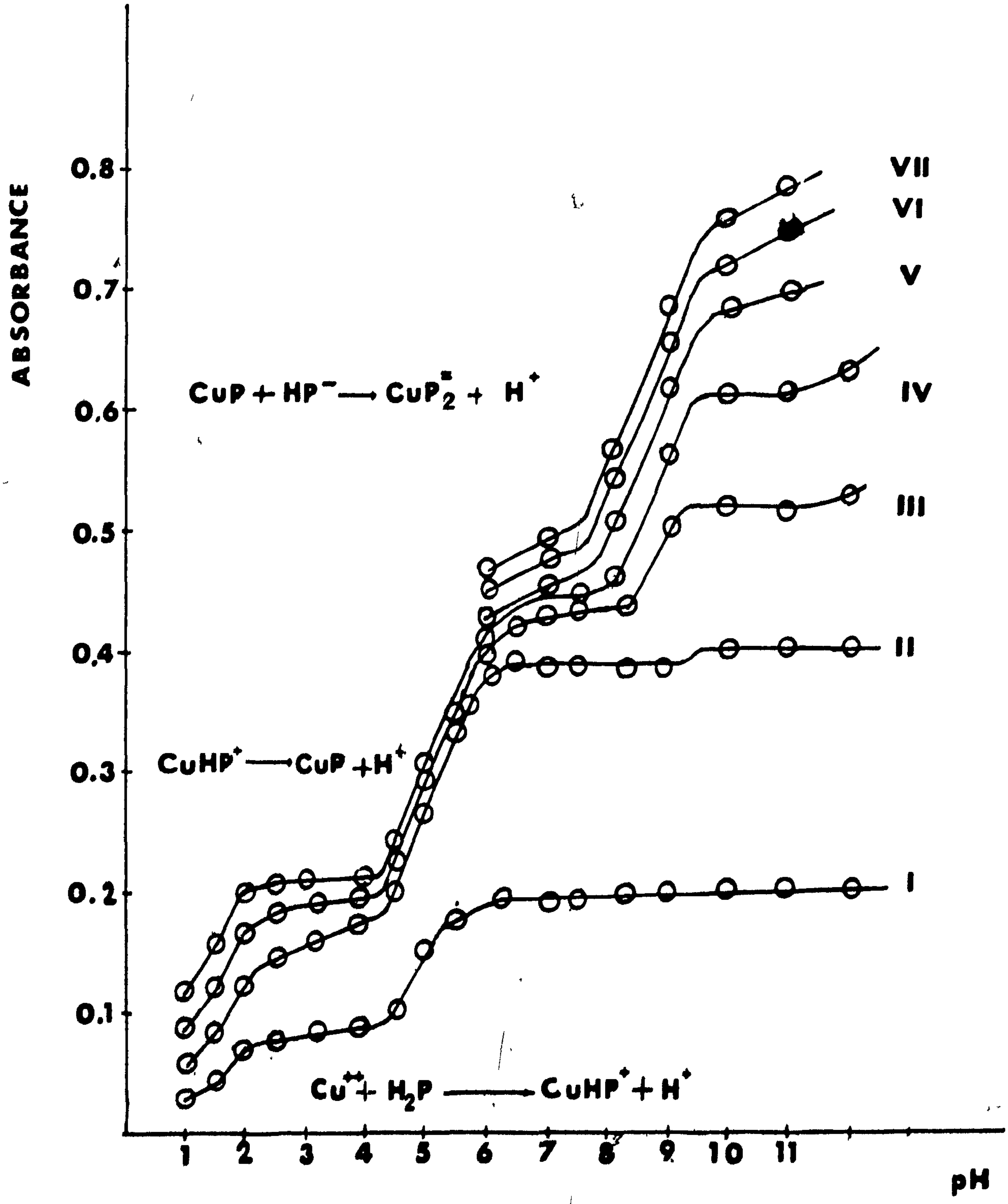
(III) M : L = 1 : 1.5

(IV) M : L = 1 : 2.0

(V) M : L = 1 : 3.0

(VI) M : L = 1 : 4.0

(VII) M : L = 1 : 5.0


ABSORBANCE
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
7
8
9
10
11
pH
VII
VI
V
IV
III
II
I
$CuP + HP^{-} \longrightarrow CuP_2^{=} + H^{+}$
$CuHP^{+} \longrightarrow CuP + H^{+}$
$Cu^{++} + H_2P \longrightarrow CuHP^{+} + H^{+}$

as the only significant species present was proved by the method of Continuous Variation at pH 2.1 and by the Mole-Ratio method at pH values between 2 and 8.

The Job plot at pH 2.1 is shown in Fig 7a. The solutions were prepared according to the procedure described in section III-2.3.3 . The composition of the solutions and the absorbance results are given in Appendix I. The results obtained with the Mole-Ratio method are shown in Fig 8 . The graphs were obtained according to the procedure described in section III-2.3.1 , with 50-ml volumes of solution having a metal concentration 1.0×10^{-5} M, and the concentration of titrant PAR 1.0×10^{-3} M.

To prove the suggested scheme of reactions I and II (page 51), the pH-absorbance curves were analysed graphically to evaluate K by a function $f\left\{[H^+], C_L, C_m, A\right\}$, where C_L and C_m are the stoichiometric concentrations of ligand and metal respectively, A is the absorbance, and $[H^+]$ is the hydrogen ion concentration. The molar absorptivity of the complex was obtained by extrapolation of the flat part of curves III and IV of the pH-absorbance graphs, after correcting them for free PAR under the assumption of a 1:1 complex. The value obtained was $a_{CuHP} = 1.69 \times 10^4$ 1-m^{-1} cm^{-1} . As the pH increases in the range 5-6 the absorbance rises steeply due to the formation of CuP.

FIGURE 7. JOB PLOTS FOR Cu-PAR SYSTEM.

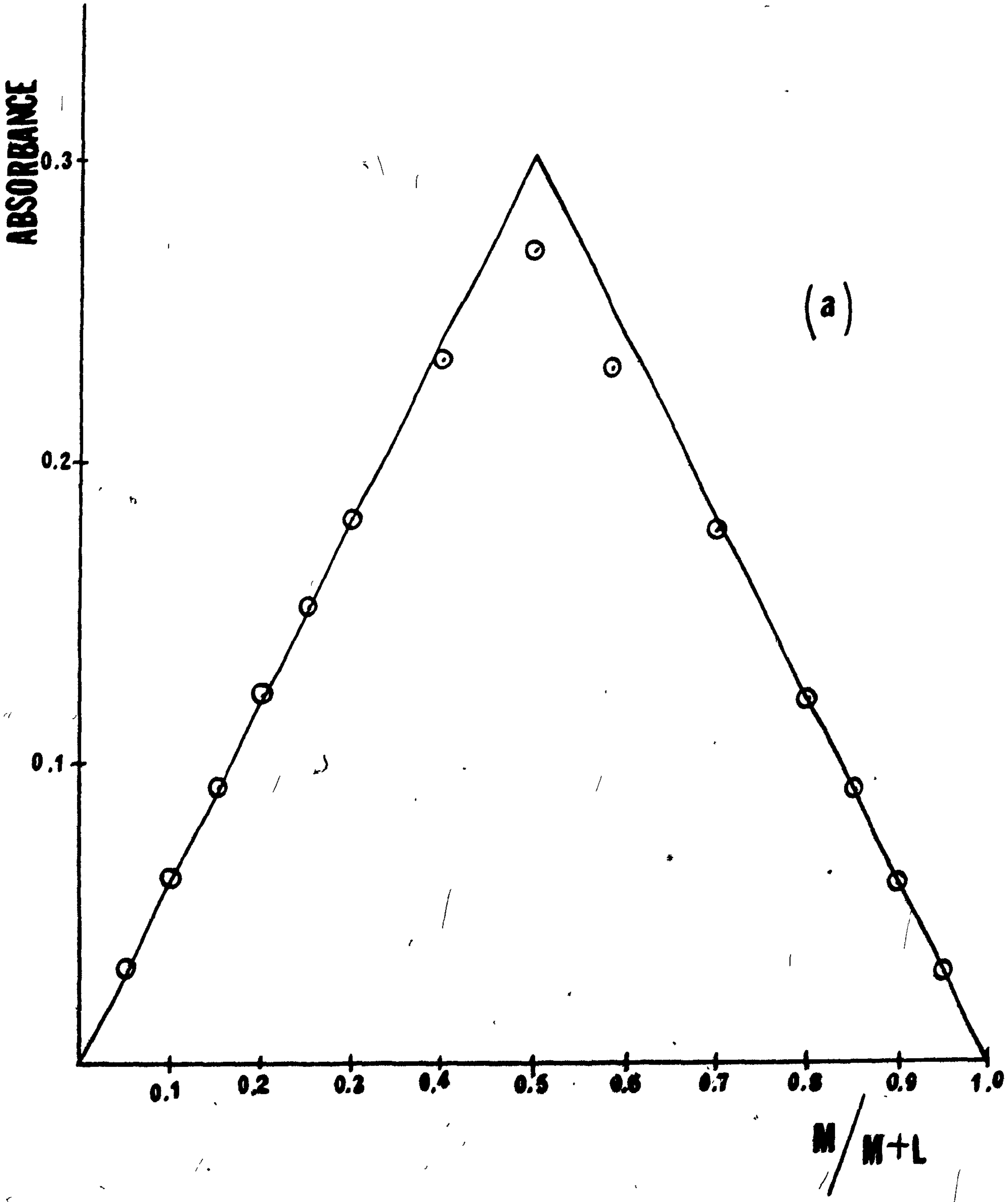
Cell 1-cm. o- 500 nm, ◊- 520 nm.

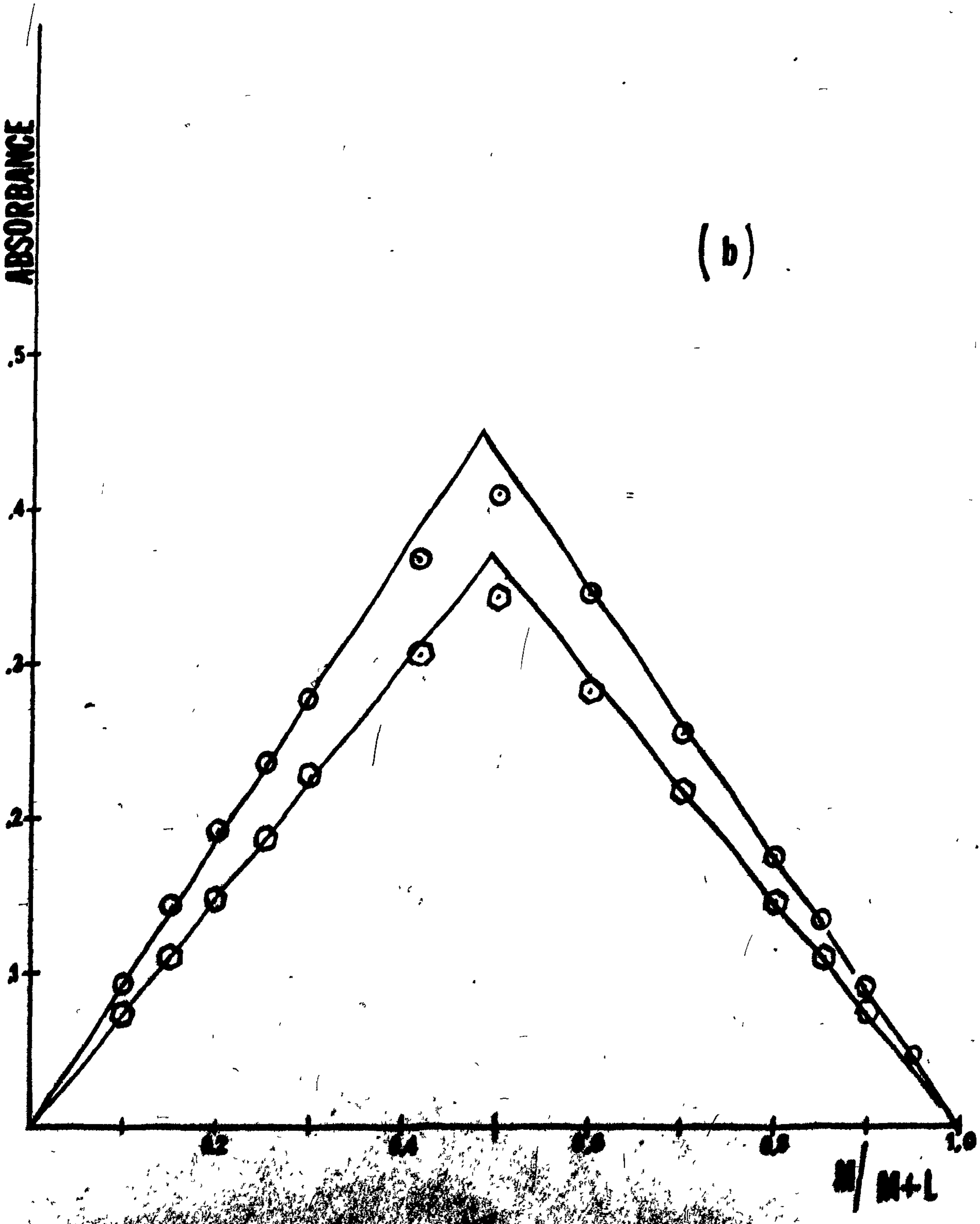
a) pH 2.1 , $C_T = 4.0 \times 10^{-5}$ M.
b) pH 8.0 , $C_T = 2.0 \times 10^{-5}$ M.
c) pH 10.0, $C_T = 2.0 \times 10^{-5}$ M.

M denotes stoichiometric concentration of copper.

L denotes stoichiometric concentration of PAR.

$C_T = M + L$.


ABSORBANCE
0.3
0.2
0.1
(a)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
M/M+L


ABSORBANCE
(b)
.5
.4
.3
.2
.1
0.2
0.4
0.6
0.8
1.0
M/ M+L

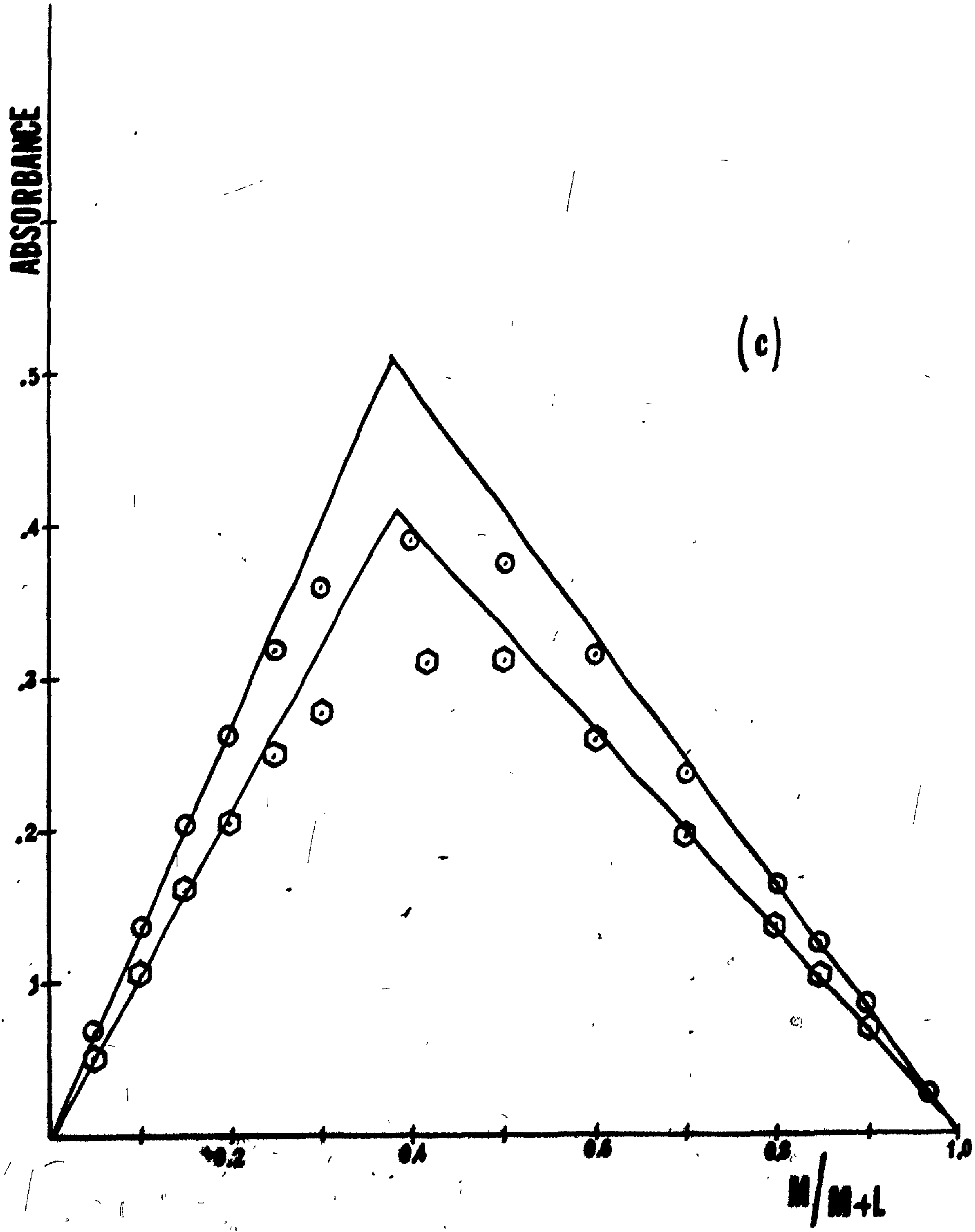
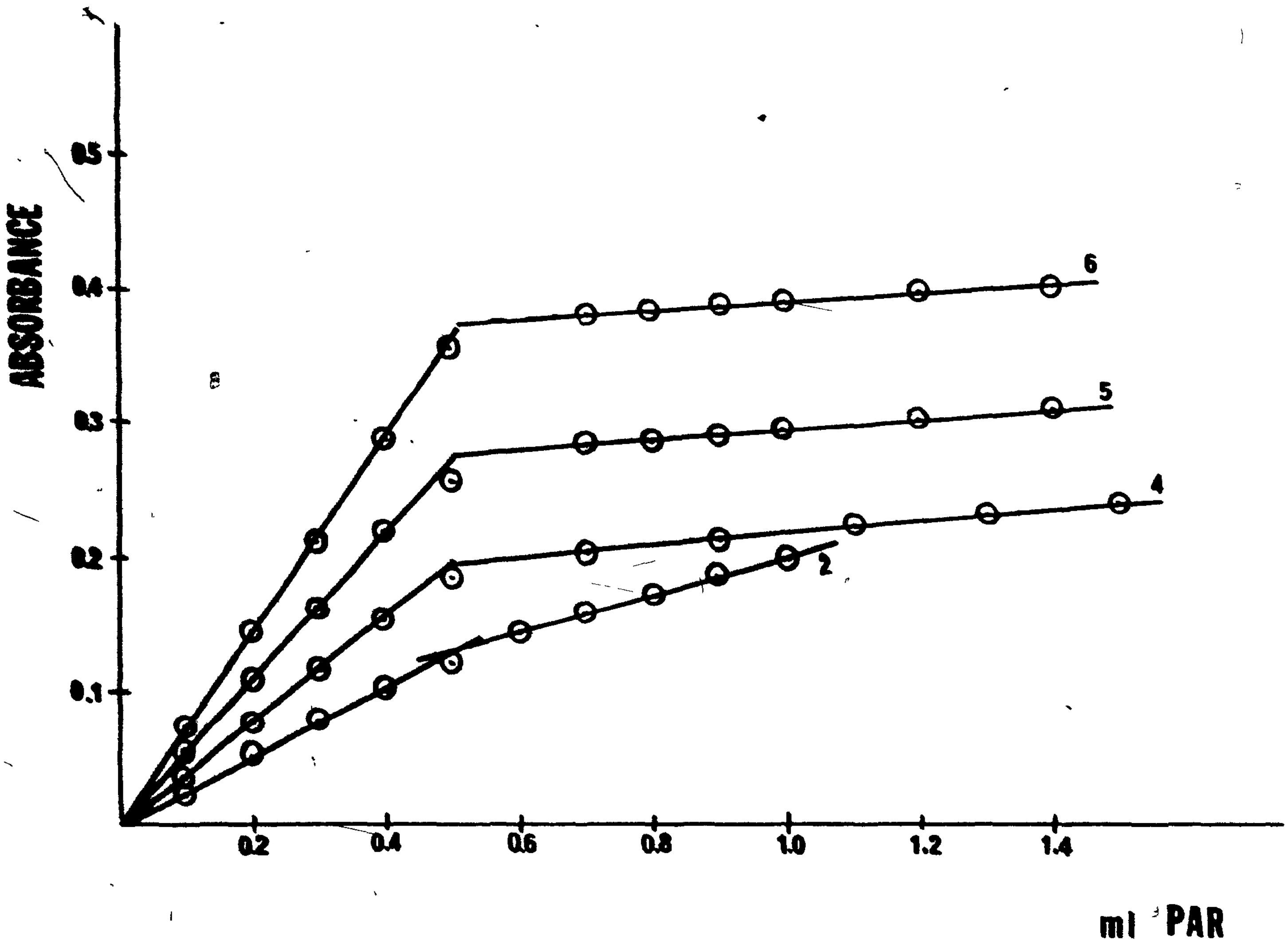

ABSORBANCE
.5
.4
.3
.2
.1
(c)
0.2
0.4
0.6
0.8
1.0
M/M+L

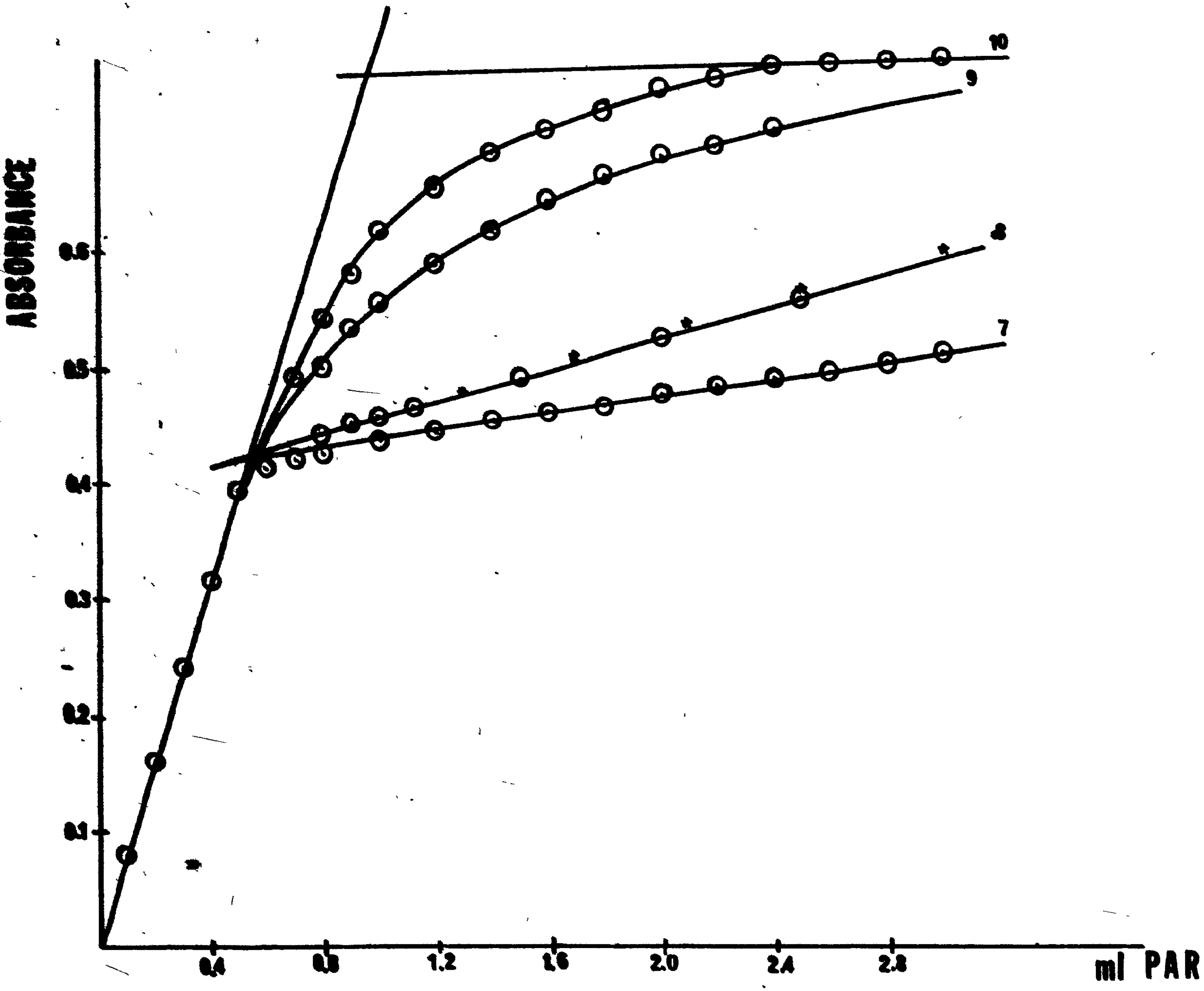
FIGURE 8. TITRATION GRAPHS FOR COPPER AT DIFFERENT pH values . Cu = 1.0 x 10^{-5} M. PAR = 1.0 x 10^{-3} M. λ= 500 nm. 1-cm cell.

Volume of solution = 50 ml.

The number with each titration graph is the pH value for that solution.

* CALCULATED GRAPH AT pH 8.


ABSORBANCE
0.1
0.2
0.3
0.4
0.5
0.2
0.4
0.6
0.8
1.0
1.2
1.4
ml PAR
6
5
4
2


ABSORBANCE
0.1
0.2
0.3
0.4
0.5
0.6
0.4
0.8
1.2
1.6
2.0
2.4
2.8
ml PAR
10
9
8
7

The equations used are:

For reaction (I), on page 51:

$$K_I = \frac{[CuHP^+]\,[H^+]^2}{[Cu^{++}]\,[H_3P^+]}$$

$$C_m = [Cu^{++}] + [CuHP^+]$$

$$C_L = [H_3P^+] + [H_2P] + [CuHP^+]$$

$$K_{a1} = \frac{[H_2P]\,[H^+]}{[H_3P^+]}$$

$$A = a_{CuHP}[CuHP^+] + a_{H_3P}[H_3P^+] + a_{H_2P}[H_2P]$$

$$K_I = \frac{\left\{C_L a_{H_3P} + C_L a_{H_2P} K_{a1} / [H^+] - A - AK_{a1} / [H^+]\right\}[H^+]^2}{[M^{++}]\left[A - a_{CuHP}C_L\right]} \quad (1)$$

For equilibrium (II) on page 51,

$$K_2 = \frac{[CuHP^+]\,[H^+]}{[Cu^{++}]\,[H_2P]}$$

$$K_2 = \frac{\left\{C_L\,(a_{H_2P} + a_{H_3P}[H^+] / K_{a1}) - A(1 - [H^+] / K_{a1})\right\}[H^+]}{[M^{++}]\left[a_{CuHP}C_L - A\right]} \quad (2)$$

The values found for K_1 and K_2 were constant for all the solutions, within experimental error. These results show that both reactions were taking place. The dispersion of K calculated from equations (1) and (2) were the same. The K values evaluated by the use of formulas (1) and (2) are summarized in Table IX.

In the upper part of the pH-absorbance curve at pH values between 4 and 6 a different equilibrium predominates; it corresponds to the following reaction:

$$CuHP^{+} = CuP + H^{+} \qquad \text{(III)}$$

This reaction is described by the following equations:

$$K_3 = \frac{[CuP][H^{+}]}{[CuHP^{+}]}$$

$$Cm = [CuP] + [CuHP^{+}]$$

$$C_L = [CuP] + [CuHP^{+}]$$

$$A = a_{CuHP}[CuHP^{+}] + a_{CuP}[CuP]$$

$$K_3 = \frac{[A - a_{CuHP}\,C_L][H^{+}]}{[a_{CuP}\,C_L - A]}$$

this equation can be re-written as:

$$\frac{A}{C_L} = a_{CuP} - \left\{ \frac{\left[\frac{A}{C_L} - a_{CuHP}\right][H^{+}]}{K_3} \right\}$$

TABLE IX

VALUES OF K_1 AND K_2 FOR Cu-PAR SYSTEM.

pH	C_L	A	log K_1	log K_2
1.5	0.5×10^{-5}	0.043	1.63	4.26
2.0	"	0.069	1.71	4.37
2.5	"	0.074	1.13	3.79
3.2	"	0.082	0.93	3.58
1.5	1.0×10^{-5}	0.083	1.62	4.28
2.0	"	0.123	1.65	4.15
2.5	"	0.145	1.53	3.93
3.0	"	0.155	1.36	4.02
3.3	"	0.16	1.41	4.07
3.6	"	0.165	0.80	4.46
1.5	1.5×10^{-5}	0.12	1.60	4.19
2.0	"	0.165	1.62	4.03
2.5	"	0.18	1.33	3.99
3.2	"	0.188	1.53	4.20
1.5	2.0×10^{-5}	0.155	1.57	4.15
2.0	"	0.20	1.59	3.92
2.5	"	0.208	1.23	3.90
		Average:	1.43	4.08
		Standard error of mean :	0.06	0.05

A plot of A/C_L vs $(A/C_L - a_{CuHP})\ H^+$ should be a straight line with a slope $-1/K_3$ and an intercept equal to a_{CuP}. When deviations from the straight line were observed the equation could no longer apply and thus the range of pH where it is valid could be established. This range is a function of the M: L ratio as shown in Fig 6.

The value of a_{CuHP} calculated previously for the equilibium (II) existing in the curve below pH 4. a_{CuP} was calculated using two points (A_1 , A_2) from the pH-absorbance curve, by means of the following equation:

$$a_{CuP} = \frac{\left[A_1 A_2 [H^+]_1 - [H^+]_2 + a_{CuHP} \left(A_1 [H^+]_2 \quad A_2 [H^+]_1 \right)\right]}{\left[C_L \left(A_1 [H^+]_1 - A_2 [H^+]_2 \right) + a_{CuHP} C_L^{\ 2} \left([H^+]_2 - [H^+]_1 \right]\right.} \qquad (5)$$

When excess of ligand was present the different PAR species were included in the mass balance equation. In those cases the final equation used for the evaluation of K_3 was:

$$K_3 = \frac{\left[C_m a_{CuHP} - A + a_{H_2P} X + XY\right] \left[H^+ \right]}{\left[A - a_{CuP} C_m - a_{H_2P} X - XY\right]} \qquad (6)$$

where:

$$X = \frac{C_L - C_m}{1 \quad K_{a2}/\left[H^+\right]} \qquad Y = \frac{a_{HP} K_{a1}}{\left[H^+\right]} \qquad K_{a2} = \frac{\left[HP^-\right]\left[H^+\right]}{\left[H_2P\right]},$$

The value obtained for a_{CuP} by use of equation (5) was 3.9×10^4 l-m^{-1} cm^{-1} at 500 nm; it agrees with the value (3.9×10^4) obtained by extrapolation of the flat part of curves (I) and (II) of the pH-absorbance graphs, (Fig 6), at the same wavelength.

Using the absorptivity of CuP evaluated from equations (3) and (5), it is possible to calculate K_3. The results are in Table X.

TABLE X

CALCULATED VALUES OF K_3 FOR REACTION:

$$CuHP^+ = CuP + H^+ \qquad \text{(III)}$$

pH	A	C_L	$-\log K_3$
4.8	0.12	0.5×10^{-5}	5.17
5.1	0.137	0.5×10^{-5}	5.17
5.0	0.27	1.0×10^{-5}	5.10
5.5	0.333	1.0×10^{-5}	5.11
4.5	0.224	1.5×10^{-5}	5.17
5.0	0.291	1.5×10^{-5}	5.03
5.5	0.345	1.5×10^{-5}	5.03
4.5	0.241	2.0×10^{-5}	4.97
5.0	0.304	2.0×10^{-5}	5.01
		Average:	5.08
		Standard error of mean:	0.03

The value of K_3 calculated from equations (3) and (6) corresponds to the K_3 obtained by the half titration method.

Above pH 6, for a metal-ligand ratio of 1:1 or less, the reaction is not pH dependent as can be seen in Fig. 6, curves I and II. Starting at pH 6 copper starts to be present in solution as $CuOH^+$ (Fig. 9) ; at pH 8, 90 % of the copper not bonded to PAR is present as $CuOH^+$. This can react with PAR as follows:

$$CuOH^+ + HP^- = CuP + H_2O \qquad (IV)$$

In addition, after CuP has been formed the absorbance is a function of the PAR content indicating that the reaction must involve the presence of free PAR. Moreover, the results of a Job plot at pH 8 (ratio 1:1) and 10 (ratio 1:2), and the increasing absorbance on the titration graphs after the break corresponding to a 1:1 metal-PAR chelate from pH 7 to 10 seem to indicate that the reaction taking place was:

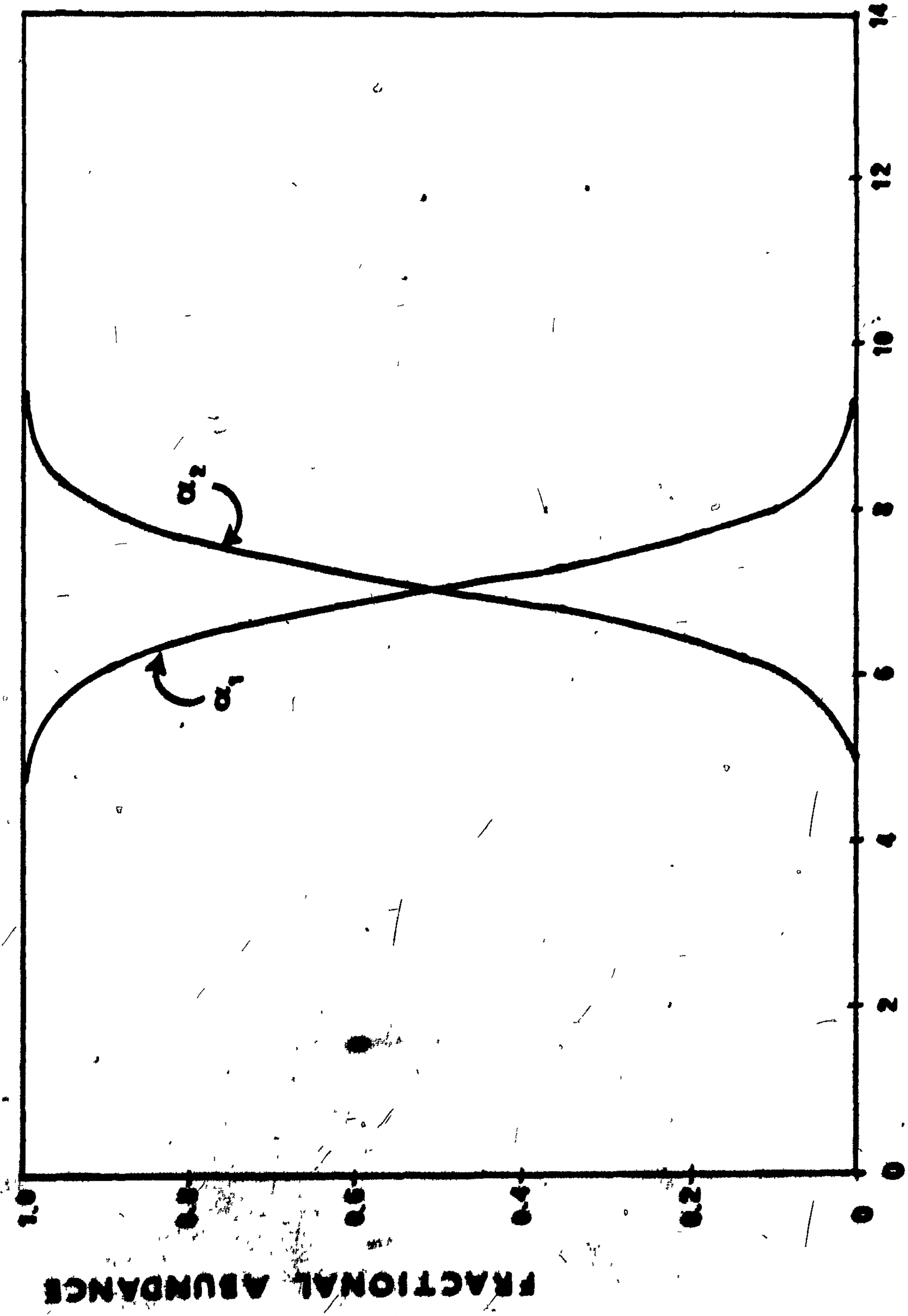
$$CuP + HP^- = CuP_2^= + H^+ \qquad (V)$$

Job plots are shown in Figs 7b and 7c; the solutions were prepared as described in section III-2.3.3 . The composition of the solutions and the absorbance measured are given in Appendix II. A Job plot at pH 8 indicates a 1:1.1

FIGURE 9. DISTRIBUTION DIAGRAM FOR THE DIFFERENT SPECIES OF COPPER AS A FUNCTION OF pH. (24)

$$\alpha_1 = \frac{[Cu^{++}]}{[Cu]_T}$$

$$\alpha_2 = \frac{[CuOH^{+}]}{[Cu]_T}$$


pH
0
2
4
6
8
10
12
14
FRACTIONAL ABUNDANCE
1.0
0.8
0.6
0.4
0.2
0
α_1
α_2

metal-ligand ratio. The shift of the maximum towards a 1: 2 ratio indicates the presence of a small amount of the 1: 2 chelate ; at pH 10 the maximum of a Job plot is at 1: 1.8 (M: L) ratio which shows that the chelate was mostly as CuP_2

The titrations graphs from pH 7 to 10 were obtained according to the procedure described in section III-2.3.1 with solutions containing a known metal concentration of 1.0×10^{-5} M . The concentration of titrant PAR was 1.0×10^{-3} M. The graphs obtained at 500 nm. are shown in Fig 8 .

At pH 7 a sharp break was obtained for the CuP chelate, but after the end point the absorbance kept on increasing after each new addition of PAR, the apparent absorptivity of PAR under these conditions(pH 7, 500 nm.) did not account for this increase. The slope after the break corresponding to the formation of CuP chelate became more pronounced as the pH increased, at pH 9 curvature started to appear and became very obvious at pH 10. At this pH, when the amount of ligand added was in great excess (1: 1.5 ratio) the absorbance became constant and an extrapolation of the two straight line portions of the curve gave a break corresponding to a 1: 2 molar ratio. This seems to indicate that if the titration at pH 7 were carried far enough (1: 20 approximatly) a constant absorbance would finally be obtained and by extrapolation of both lines the end point for the CuP_2 chelate could be estimated.

To evaluate the equilibrium constant of reactions IV and V,(page 68), a series of equations were derived assuming the existence of $CuP_2^=$ species at pH values above 6.

$$K_4 = \frac{[CuP]}{[CuOH^+][HP^-]}$$

$$K_5 = \frac{[CuP_2^=][H^+]}{[CuP][HP^-]}$$

$$C_m = [CuOH^+] - [CuP] - [CuP_2^=]$$

$$C_L = [CuP] + 2[CuP_2^=][HP^-]$$

$$A = a_{CuP}[CuP] + a_{CuP_2^=}[CuP_2^=]$$

If we use the absorbance readings from curves where PAR concentration is smaller than or equal to the metal concentration, we can neglect the presence of $CuP_2^=$. Under this assumption the value of K_4 is given by equation (7), and the value obtained is 5.7×10^8.

$$K_4 = \frac{(C_m a_{HP} - A)/(a_{HP} - a_{CuP})}{\left(\frac{A - a_{CuP} C_m}{a_{HP} - a_{CuP}}\right)^2} \qquad C_m = C_L \quad (7)$$

When the concentration of ligand is larger than that of the metal, $CuP_2^=$ starts to form and K_5 is given through the use of equation (8).

$$CuP_2 = \frac{\left[A - a_{CuP}\, C_m\right]}{\left[a_{CuP_2} - a_{CuP}\right]}$$

$$K_5 = \frac{\left[\dfrac{A - a_{CuP}\, C_m}{a_{CuP_2} - a_{CuP}}\right] \left[H^+\right]}{\left[\dfrac{C_L a_{CuP_2} - C_L a_{CuP} - C_m\, a_{CuP_2} \quad 2C_m a_{CuP} - A}{a_{CuP_2} - a_{CuP}}\right] \left[\dfrac{C_m a_{CuP_2} - A}{a_{CuP_2} - a_{CuP}}\right]} \qquad .....(8)$$

At pH values between 6 and 7 the presence of $CuHP^+$ was taken into consideration in the derivation. CuP was evaluated from equation (9) and by the use of the appropriate mass balance equations, the concentration of CuP and HP^- were evaluated and therefore K_5 .

$$(CuP) = \frac{\left[A - a_{CuP_2}\, C_m\right]}{\left[a_{CuP} - a_{CuP_2} - \dfrac{a_{CuHP}\, H^+}{K_3} - \dfrac{a_{CuP_2}\, H^+}{K_3}\right]} \qquad (9)$$

The molar absorptivity of $CuP_2^=$ was obtained by extrapolation of the flat part of the titration graph at pH

10 (Fig. 8). A value 7.6×10^{-4} $1\text{-}m^{-1}cm^{-1}$ was found.

The values obtained for K_5 by the use of equation (8) and (9) are summarized in Table XII. Values of K_5 obtained from the titration graphs are given in Table XI.

TABLE XI

VALUES OF K_5 OBTAINED FROM THE TITRATION GRAPHS.

$$CuP + HP^{-} = CuP_2^{=} + H^{+}$$

pH	$-\log K_5$
7.0	2.97
8.0	3.7
9.0	3.7
10.0	4.44

As regards the variations in the calculated values for K_5 at pH below ca. 7.5, more involved measurements would be required to explain them. At pH 8 to 9.5, reaction (V) predominates; the K values obtained are constant and pH dependent as it is seen in Fig. 6 curves III and IV. The value obtained for pK_5 is 3.7 .

Above pH 10 the reaction once more becomes pH independent, and it is suggested that the reaction is:

$$CuP + P^{=} = CuP_2^{=} \qquad \text{(VI)}$$

TABLE XII

VALUES OF K_5 OBTAINED BY THE USE OF EQUATIONS (7) AND (8)

$$CuP + HP^- = CuP_2^= + H^+$$

pH	A	C_L	$-\log K_5$
8.1	0.505	3.0×10^{-5}	3.67
8.1	0.542	4.0×10^{-5}	3.67
8.1	0.567	5.0×10^{-5}	3.68
8.3	0.437	1.5×10^{-5}	3.8
8.3	0.477	2.0×10^{-5}	3.76
9.0	0.503	1.5×10^{-5}	3.73
9.0	0.615	3.0×10^{-5}	3.95
9.0	0.563	2.0×10^{-5}	3.82
9.0	0.653	4.0×10^{-5}	3.90
9.0	0.681	5.0×10^{-5}	3.94
10.0	0.532	1.5×10^{-5}	4.36
10.0	0.613	2.0×10^{-5}	4.45
10.0	0.682	3.0×10^{-5}	4.50

TABLE XIII

SUMMARIZED VALUES OF EQUILIBRIUM CONSTANTS EVALUATED IN THE Cu-PAR SYSTEM.

pH Range	pK	Equilibrium
1.5 - 3.0	-1.43	$K_1 = \frac{[CuHP^{+}][H^{+}]^{2}}{[Cu^{++}][H_3P^{+}]}$
1.5 - 4.0	-4.08	$K_2 = \frac{[CuHP^{+}][H^{+}]}{[Cu^{+}][H_2P]}$
4.0 - 6.0	5.08	$K_3 = \frac{[CuP][H^{+}]}{[CuHP^{+}]}$
7.0 - 9.5	-8.76	$K_4 = \frac{[CuP]}{[CuOH^{+}][HP^{-}]}$
7.0 - 9.5	3.7	$K_5 = \frac{[CuP_2^{=}][H^{+}]}{[CuP][HP^{=}]}$
10	-8.6	$K_6 = \frac{[CuP_2^{=}]}{[CuP][P^{=}]}$

From the equilibrium constant evaluated for reaction (V) at pH 10 and the equilibrium constant K_{a3} of PAR ($pK_{a3} = 12.31$) the value of pK_6 was determined ($pK_6 = -8.6$).

The equilibrium constants evaluated in the copper system are summarized in Table XIII.

A titration graph was predicted at pH 8 taking into consideration CuP and $CuP_2^=$ as the only Cu-PAR species present at that pH. The graph was built using K_4 and K_5 and the proper mass-balance equations. The graph obtained is shown in Fig. 8. The difference between the predicted and observed graphs is negligible as can be seen in the figure.

Corsini (35) has critically reviewed the work published on the system Cu-PAR. He reports a value of K_2 and K_3 in good agreement with the present work, as seen in Table XIV.

TABLE XIV

REPORTED VALUES OF Cu-PAR SYSTEM IN THE LITERATURE AS COMPARED WITH THIS WORK.

	This work	Corsini (35)
log K_2	4.08	4.1
log K_3	-5.08	-5.5

3.4.2 System Lead-PAR.

The reaction between PAR and lead(II) is readily observed at pH values greater than 3 when the plumbous ion is in stoichiometric excess (Fig. 10, curve V). The use of PAR as an analytical reagent for the photometric determination of lead has been investigated previously by Pollard et all (16, 18, 19), and by Kristiansen and Langmyhr (25). Pollard reports the formation of a 1:1 and a 1:2 (M:L) complex, whereas Kristiansen reports only a 1:1 (M:L) complex. To solve the disagreement about the nature of the lead species, Dagnall et al (26) made a complete study of the system by the use of the Continuous Variation method and the Mole-Ratio method. They made the study at pH 10 and they observed the formation of only a 1:1 (M:L) complex. In the present investigation, use of the Continuous Variation method showed that a single ratio of 1:1 (M:L) was observed for the Pb-PAR species between pH 4 and 9. Therefore, only a 1:1 complex will be assumed in the reaction scheme at all pH values studied.

In order to understand the titration graphs and predict them at different pH values, pH-absorbance curves were obtained for solutions containing various amounts of metal ion and ligand PAR mixed in different ratios. A graphical and numerical analysis of the curves obtained was made according to the procedure described in section III-2.2 . The molar absorptivities and the equilibrium constants of the complexes could be evaluated from the data.

The appearance of the pH-absorbance curves (Fig. 10) for different M:L ratios and the fact that the ratio of Pb/PAR in the complex is reported to be 1:1, suggest that the following reactions were taking place:

$$Pb^{++} + H_2P = PbHP^{+} + H^{+} \qquad (VII)$$

$$PbHP^{+} = PbP + H^{+} \qquad (VIII)$$

The decrease in absorbance at pH 12 may indicate the presence of a new species.

The spectra for solutions containing an equimolar amount of the reagent are shown in Fig. 11. In these curves, an isosbestic point is observed at 455 nm for solutions with pH between 5.6 and 8.2. At pH = 12, there is a displacement of the wavelength of maximum absorption (520 to 510 nm). The absorbance also decreases. These facts support the hypothesis that a new species was forming at this pH.

The solutions used to record the pH-absorbance curves shown in Fig. 10 were prepared according to the procedure described in section III-2.3.4. The composition of each of the solutions prepared is given in Table VIII (page 52). The absorbance values of these solutions were read against water as the reagent blank at 400, 500, 510, and 520 nm. The results are given in Appendix II. The behaviour of the

FIGURE 10 . pH-absorbance CURVES FOR Pb-PAR* SYSTEM. Pb = 1.0×10^{-5} M , 1-cm cell, λ= 500 nm. The number with each curve is the pH value of the solution.

(I) M:L = 1:0.5
(II) M:L = 1:1.0
(III) M:L = 1:1.5
(IV) M:L = 1:2.0
(V) M:L = 1:100

* The arrows indicate corrected values for free PAR assuming the formation of a 1:1 Pb:PAR chelate.

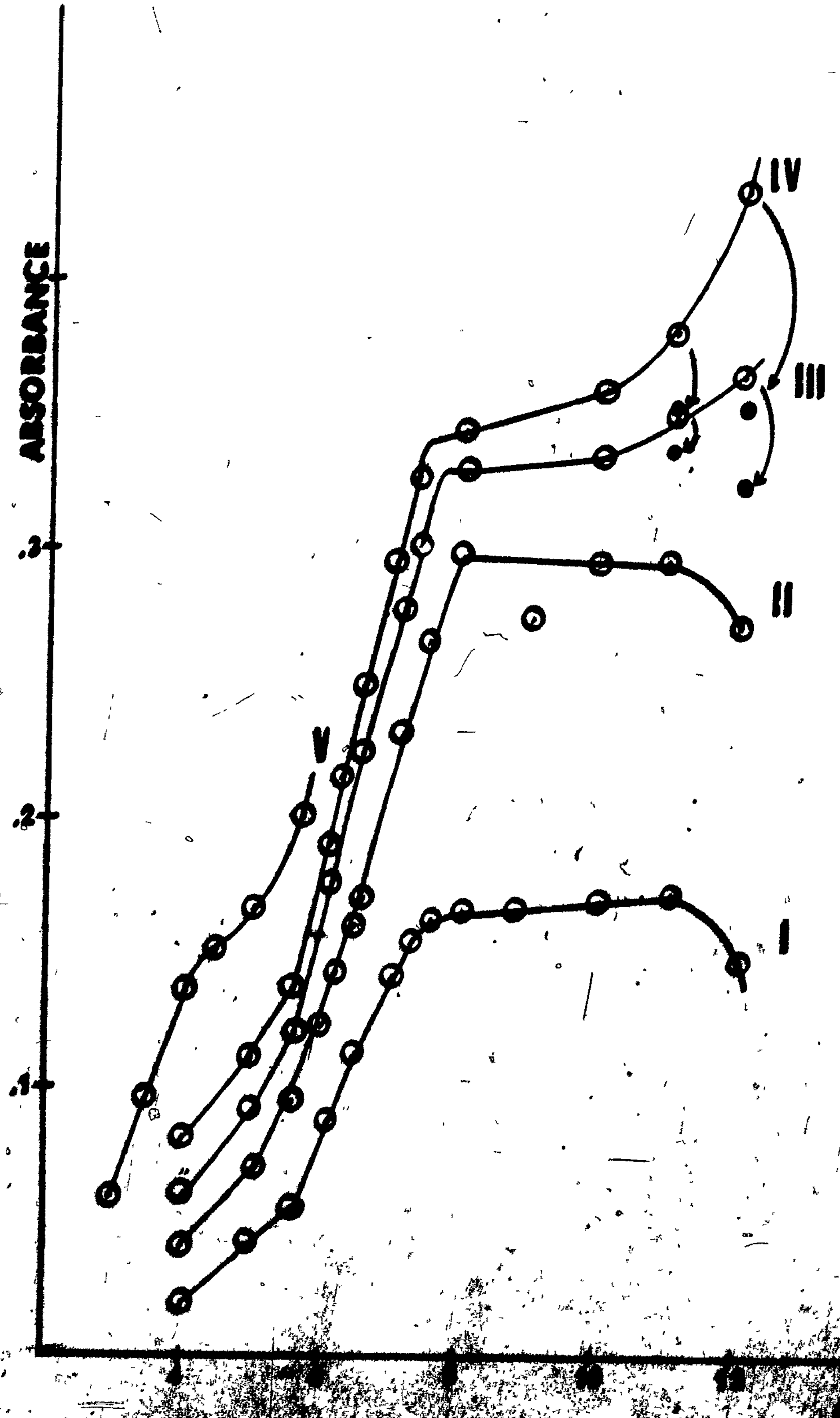

ABSORBANCE
.3
.2
.1
IV
III
II
I
V

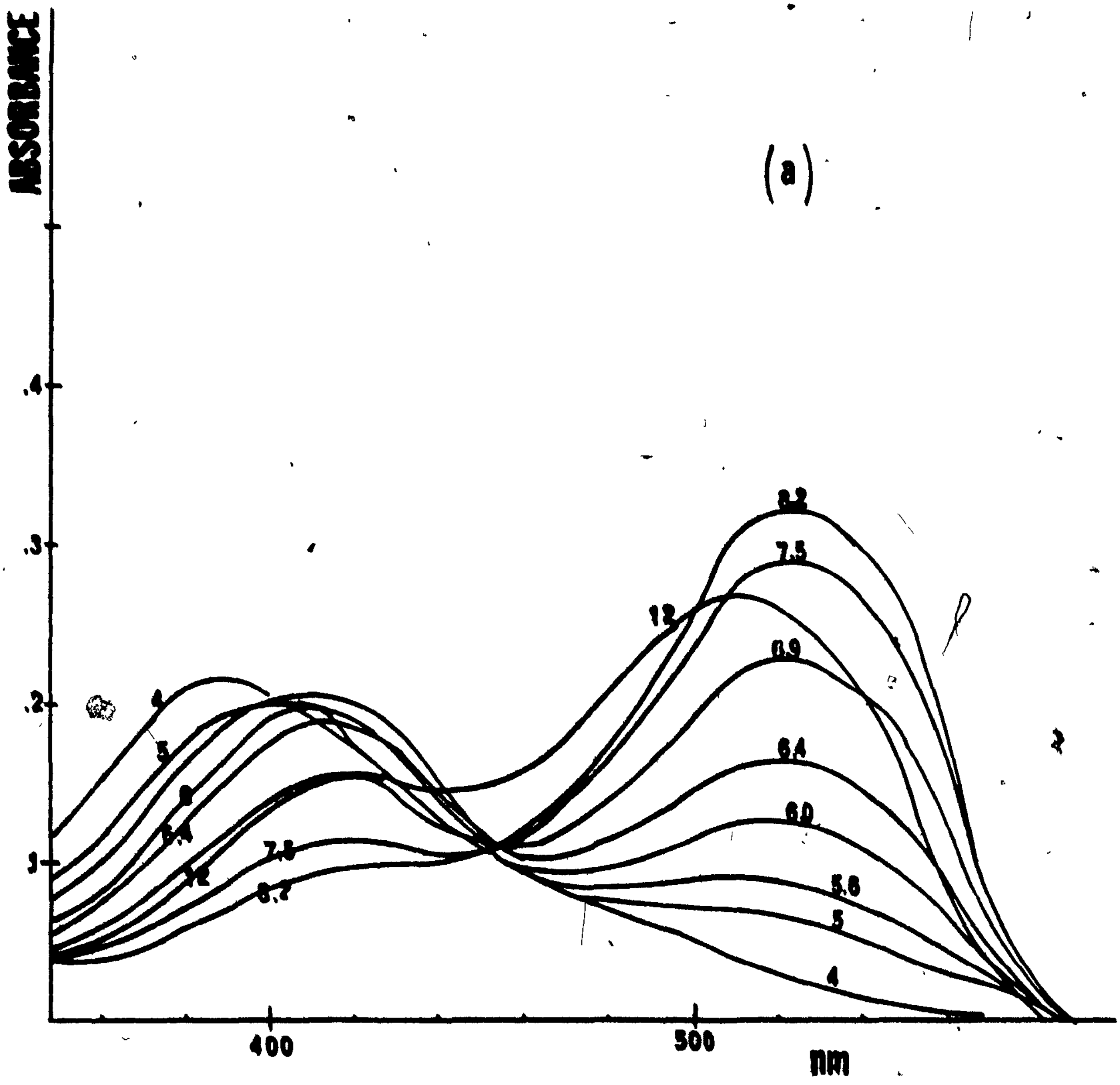
FIGURE 11 . ABSORBANCE CURVES OF Pb-PAR IN AQUEOUS SOLUTION. Pb =1.0 x 10^{-5} M.

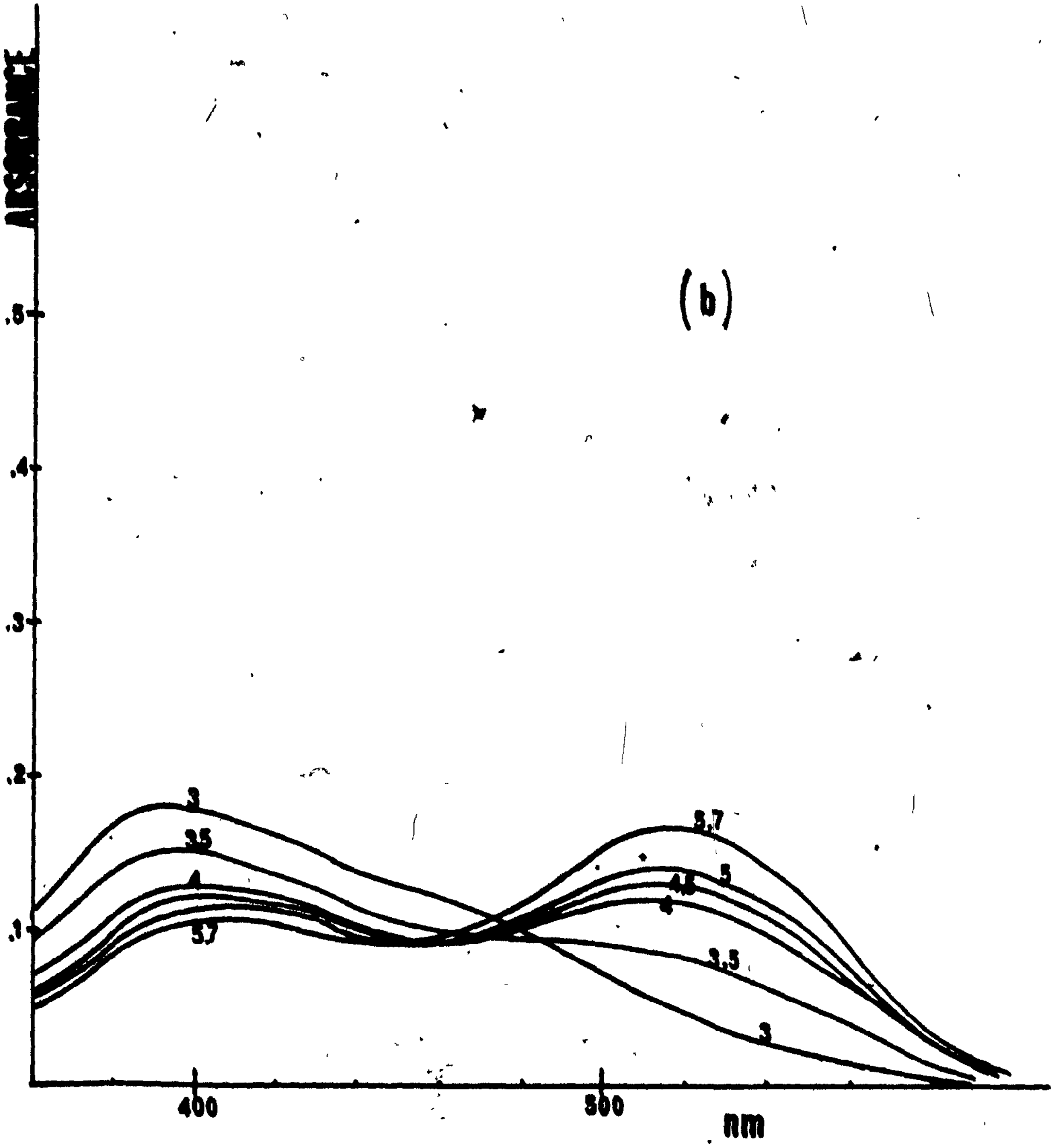
1-cm cell.

a) Ratio Pb: PAR 1: 1

b) Ratio Pb: PAR 1: 100

The number with each curve is the pH value of the solution.


ABSORBANCE
(a)
.4
.3
.2
.1
400
500
nm
8.2
7.5
12
6.9
6.4
6.0
5.6
5
4
4
5
6
6.4
7.2
7.8
8.2


ABSORBANCE
(b)
.5
.4
.3
.2
.1
400
500
nm
3
3.5
4
5.7
5.7
5
4.5
4
3.5
3

system with time was studied and showed that at pH 8, 9, 10 and 11 the absorbance of the solutions was decreasing with time (Fig. 3). No constant absorbance values were reached. In addition to the proposed scheme of reactions, it seems that several other reactions could also take place in this system of reagents.

The analysis of the pH-absorbance curves shown in Fig. 10 was made as described in section III-2.2 . Thus the molar absorptivities and the equilibrium constants could be evaluated. At pH below 5, the significant reaction taking place was VII, (page 79). In order to have a measurable amount of chelate $PbHP^+$, a large excess of metal ion ($C_m = 1.0 \times 10^{-3}M$) over the ligand was used ($C_L = 1.0 \times 10^{-5}$ M). This was possible due to the low pH of the solutions. The absorbance was read at different pH values and the curve is shown in Fig. 10, curve V. The value of the molar absorptivity of $PbHP^+$ was calculated by using two absorbance points on the pH-absorbance curve, in the formula:

$$a_{PbHP} = \frac{X_1\left[H^+\right]_1 A_2 - X_2\left[H^+\right]_2 A_1}{C_L X_1\left[H^+\right]_1 - X_2\left[H^+\right]_2} \qquad (10)$$

$$\text{where } X = A_n\left[1 - \frac{\left[H^+\right]_n}{K_{a1}}\right] - C_L\left[a_{H_2P} - \frac{a_{H_3P}\left[H^+\right]_n}{K_{a1}}\right]$$

the value calculated was $a_{PbHP} = 1.48 \times 10^{4}$ l-m^{-1}-cm^{-1} at $\lambda = 500$ nm.

The value of K_I could then be evaluated from the following set of equations:

$$K_I = \frac{[PbHP^+][H^+]}{[Pb^{++}][H_2P]}$$

$$C_m = [Pb^{++}] + [PbHP^+] \approx [Pb^{++}]$$

$$C_L = [PbHP^+] + [H_2P] + [H_3P^+]$$

$$A = a_{PbHP^+}[PbHP^+] + a_{H_2P}[H_2P] + a_{H_3P^+}[H_3P^+]$$

$$K_{a1} = \frac{[H_2P][H^+]}{[H_3P^+]}$$

$$K_I = \frac{\left[A\left(1 + \frac{[H^+]}{K_{a1}}\right) - C_L\left(a_{H_2P} + \frac{a_{H_3P}[H^+]}{K_{a1}}\right)\right][H^+]}{C_m(a_{PbHP}\, C_L - A)} \qquad (11)$$

Using the value calculated for the molar absorptivity and the data of curve V (Fig 10) below pH 4.5, the value of K_I was found to be 0.5 .

Assuming that reaction VIII in the suggested scheme was taking place in the rising part of the pH-absorbance curve (pH values 5.5 to 7.5), the following formula can be derived (see page 66) from the proper mass-balance and Beer's law equations.

$$K_2 = \frac{\left[C_m a_{PbHP} - A + a_{H_2P} X - XY\right]\left[H^+\right]}{A - a_{PbP} C_m - a_{H_2P} X + XY}$$

where:

$$X = \frac{C_L - C_m}{1 - K_{a2} / \left[H^+\right]}$$

$$Y = \frac{a_{HP} K_{a2}}{\left[H^+\right]}$$

$$K_{a2} = \frac{\left[HP^-\right]\left[H^+\right]}{\left[H_2P\right]}$$

The large deviations observed in the K_2 evaluated are due to the propagation of errors produced by the different terms in the above equation and also, possibly, to the fact that the assumption made,(reaction VIII only takes place in this pH range)is not completely justified.

In order to understand the behaviour of the system as the pH is increased gradually from acid medium, the distribution diagram (α-distribution) for the lead (II) ion was constructed (Appendix 3). It is shown in Fig 12. The following set of reactions seems reasonable when Pb(II) and PAR are present in a solution whose pH is gradually increased:

$$Pb^{++} + H_2P = PbHP^+ + H^+ \qquad (VII)$$

$$PbHP^+ = PbP + H^+ \qquad (VIII)$$

$$Pb^{++} + HP^- = PbP + H^+ \qquad (IX)$$

$$PbOH^+ + HP^- = PbP + H_2O \qquad (X)$$

$$PbOH^+ + H_2P = PbP + H_2O + H^+ \qquad (XI)$$

Consideration of the α-distribution diagram of PAR (Fig. 2) and of lead (Fig. 12) with the pH leads to the conclusion that the reactions that can reasonably be taking place at pH 5 are the reactions VII, VIII, and IX. Using the molar absorptivity calculated previously for $PbHP^+$ and the value of K_I as found above, and the molar absorptivity of the species PbP obtained through the Mole-Ratio method data at pH 8, the equilibrium constant for reactions VIII and IX can be evaluated through the following equations:

$$C_m = [PbHP^+] + [PbP] + [Pb^{++}]$$

$$C_L = [PbHP^+] + [PbP] + [H_2P] + [HP^-]$$

$$K_I = \frac{[PbHP^+][H^+]}{[Pb^{++}][H_2P]}$$

$$K_{a2} = \frac{[HP^-][H^+]}{[H_2P]}$$

$$A = a_{PbP}[PbP] + a_{PbHP}[PbHP^+] + a_{HP}[HP^-] + a_{H_2P}[H_2P]$$

Solving these equations, we obtain:

$$a(HP^-)^2 + b(HP^-) + c = 0 \qquad (12)$$

where: $a = \frac{X}{K_{a2}/K_I}(a_{PbHP} - a_{PbP})$

$$b = \frac{a_{PbHP}}{K_{a2}/K_I}(C_m - C_L) - \frac{a_{PbP}}{K_{a2}/K_I}(C_m - C_L) - a_{PbP}\frac{C_L - C_m}{1 - K_{a2}/[H^+]} - \frac{a_{HP}K_{a2}}{[H^+]}$$

$$c = a_{PbP}C_L - A$$

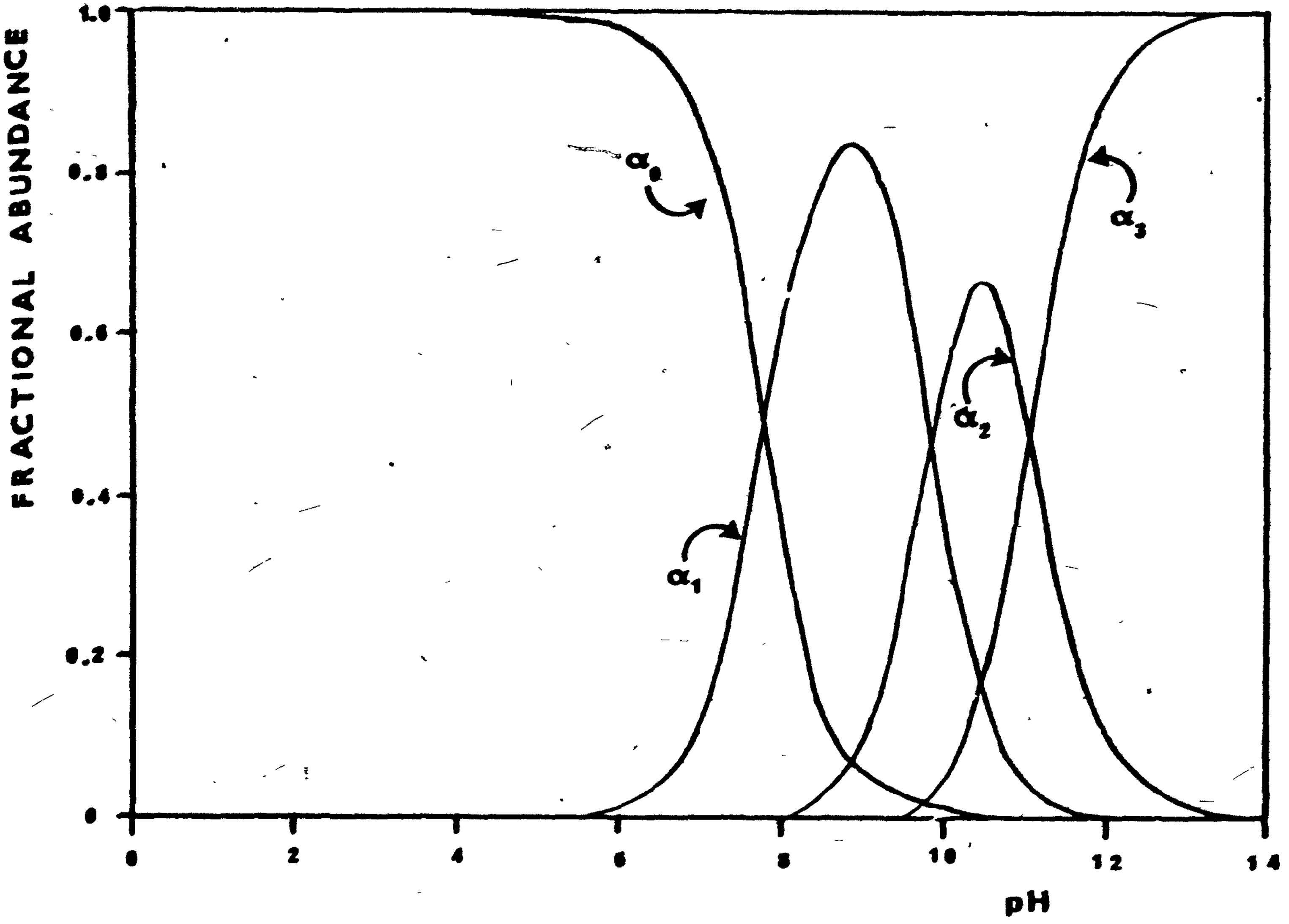
Applying these equations to curves I to IV at pH 5 , we obtain the following values for K_2 and K_3.

$K_2 = 2.5 \times 10^{-6}$. $K_3 = 0.4$

FIGURE 12. DISTRIBUTION DIAGRAM FOR THE DIFFERENT SPECIES OF LEAD AS A FUNCTION OF pH. (27-32)

$$\alpha_0 = \frac{[Pb^{++}]}{[Pb]_T} \qquad \alpha_2 = \frac{[Pb(OH)_2]}{[Pb]_T}$$

$$\alpha_1 = \frac{[PbOH^{+}]}{[Pb]_T} \qquad \alpha_3 = \frac{[Pb(OH)_3^{-}]}{[Pb]_T}$$


FRACTIONAL ABUNDANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pH
α_0
α_1
α_2
α_3

Above a pH 8, the equilibrium could not be reached, possibly due to a slow reaction between $PbOH^+$ and $HP^=$.

When the chelate is formed by small additions of the ligand to the lead solution, as in the Continuous Variation method, the absorbance at the equivalent point is smaller than that obtained by quickly mixing the stoichiometric amounts of the reagents. A titration graph at pH 8 is shown in Fig. 13b. The break is sharp and the end point is accurate. The absorbance is stable at least for a period of one hour following the titration (Fig. 3). An apparent K was evaluated from the titration graph, with a value of 0.76×10^6; this value gives the order of magnitude of K for the reaction taking place at that pH (8). This value of K can not be considered an equilibrium value since the absorbance of the solutions at this pH and higher were decreasing continually. It may be that the decrease in absorbance was due to other reactions taking place. Garrett et al (33) reported that glass is attacked by the solutions of lead and alkali.

Titrations at pH values 5, 6, and 7 are shown in Figs. 13a and 13b, comparison of these titrations shows that pH 8 is the best choice for the determination of Pb(II) with PAR.

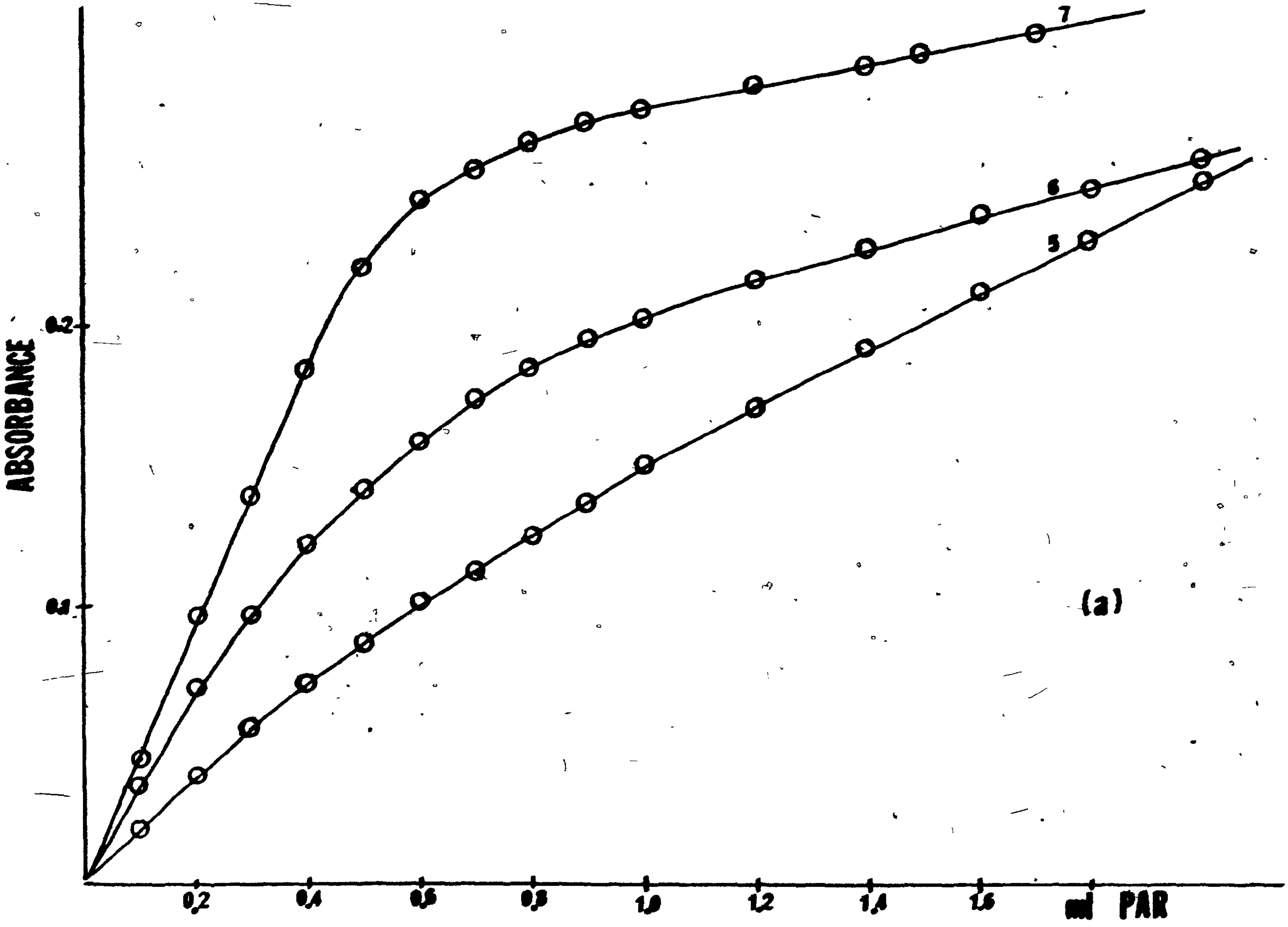
The decrease in absorbance at pH 12 and above could be due to the formation of a new lead complex or to the destruction of the species existing at lower pH. At very high

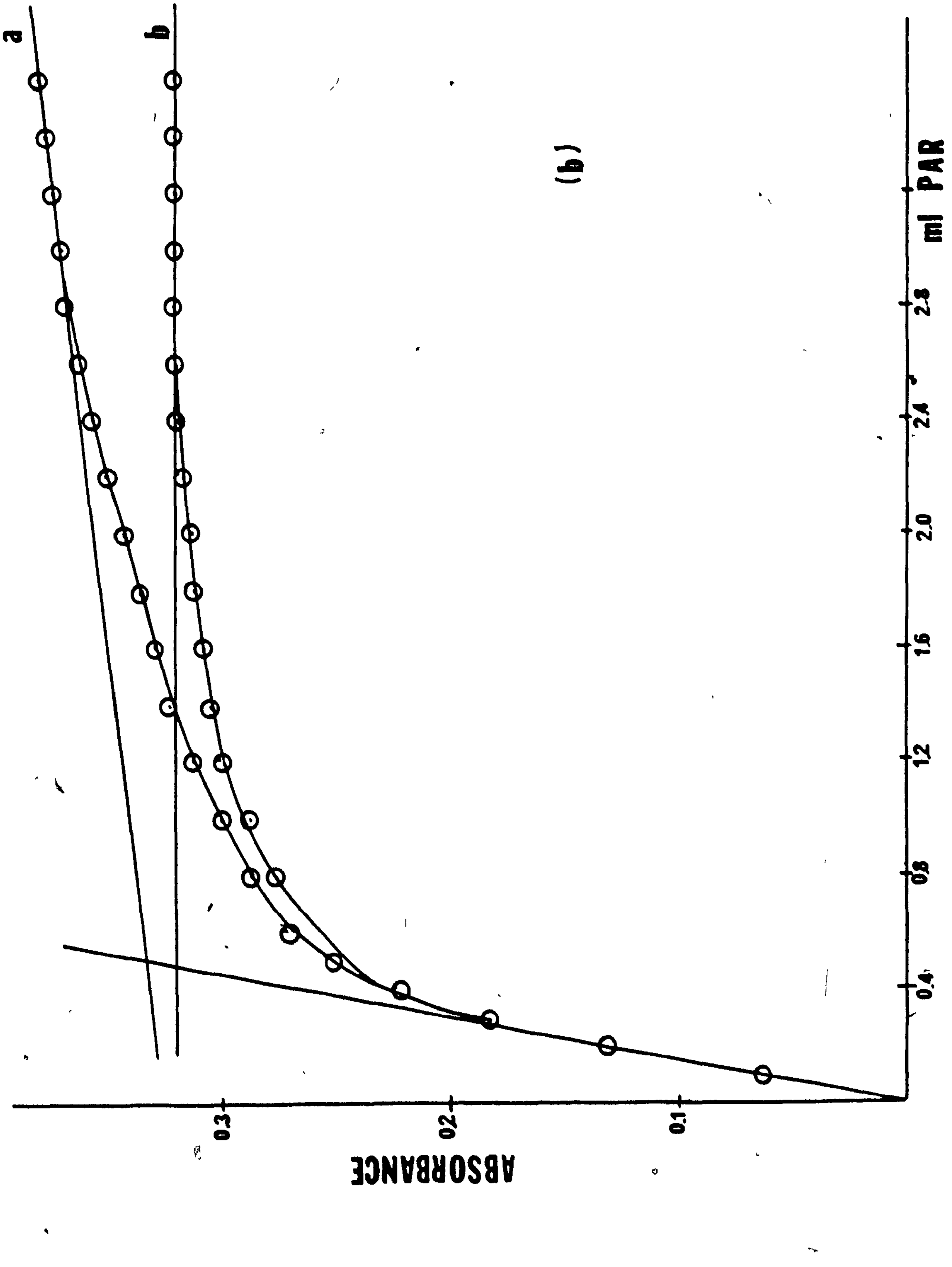
FIGURE 13 . TITRATION GRAPHS FOR LEAD AT DIFFERENT pH VALUES . Pb = 1.0 x 10^{-5} M. PAR = 1.0 x 10^{-3} M . = 500 nm.

a) pH values 5, 6, and 7.

b) (a) without correction for free PAR, pH 8.

   (b) corrected for free PAR, pH 8 .


ABSORBANCE
0.2
0.1
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
ml PAR
7
6
5
(a)


(b)
a
b
ABSORBANCE
0.1
0.2
0.3
ml PAR
0.4
0.8
1.2
1.6
2.0
2.4
2.8

pH, lead forms the following hydroxo complex: $Pb(OH)_3^-$. This negatively charged species may not react with the negatively charged PAR ions.

The values of the equilibrium constants evaluated for the lead-PAR system are given in Table XV.

TABLE XV

SUMMARIZED VALUES OF EQUILIBRIUM CONSTANTS EVALUATED IN THE Pb-PAR SYSTEM.

K	Equilibrium
0.5	$K_1 = \frac{[PbHP^+][H^+]}{[Pb^{++}][H_2P]}$
2.5×10^{-6}	$K_2 = \frac{[PbP][H^+]}{[PbHP^+]}$
0.4	$K_3 = \frac{[PbP][H^+]}{[Pb^{++}][HP^-]}$

3.4.3 System Zinc-PAR.

The formation of zinc-PAR chelate was observed at pH 4, but if metal is used in excess (100:1, M:L) the chelate is seen to form at pH 2.8: i.e. the red-orange color of the chelate is immediately observed.

The absorption spectra for solutions containing different M:L ratios, are shown in Fig. 14 . For a ratio M:L= 100:1 an isosbestic point was present at 430 nm for a pH greater than 4.8, and two maxima were observed at 400 nm and 490 nm. When the ratio was 1:2 there was a shift in λmax at 400 nm and the isosbestic point was observed at 440 nm, and above pH 6, the other λmax (490 nm) remained constant. The same kind of spectra were observed for a 1:1 (M:L) ratio as for the 1:2 . The shift at 400 nm corresponds to free PAR, and the absence of an isosbestic point below pH 6 indicates that more than two species were in equilibrium.

The pH-absorbance plots (Fig. 15) indicate the presence of at least three complexes in solution: one for solutions containing excess of metal ion at pH 4.8 (curve V), one between pH 4.8 and 8, and one above pH 8 .

In order to identify the complexes present in the system, the Method of Continuous Variation was used at pH 4, 5, and 8. The results are given in Table XVI.

The Job plots for the wavelengths of 500 and 520 nm, are

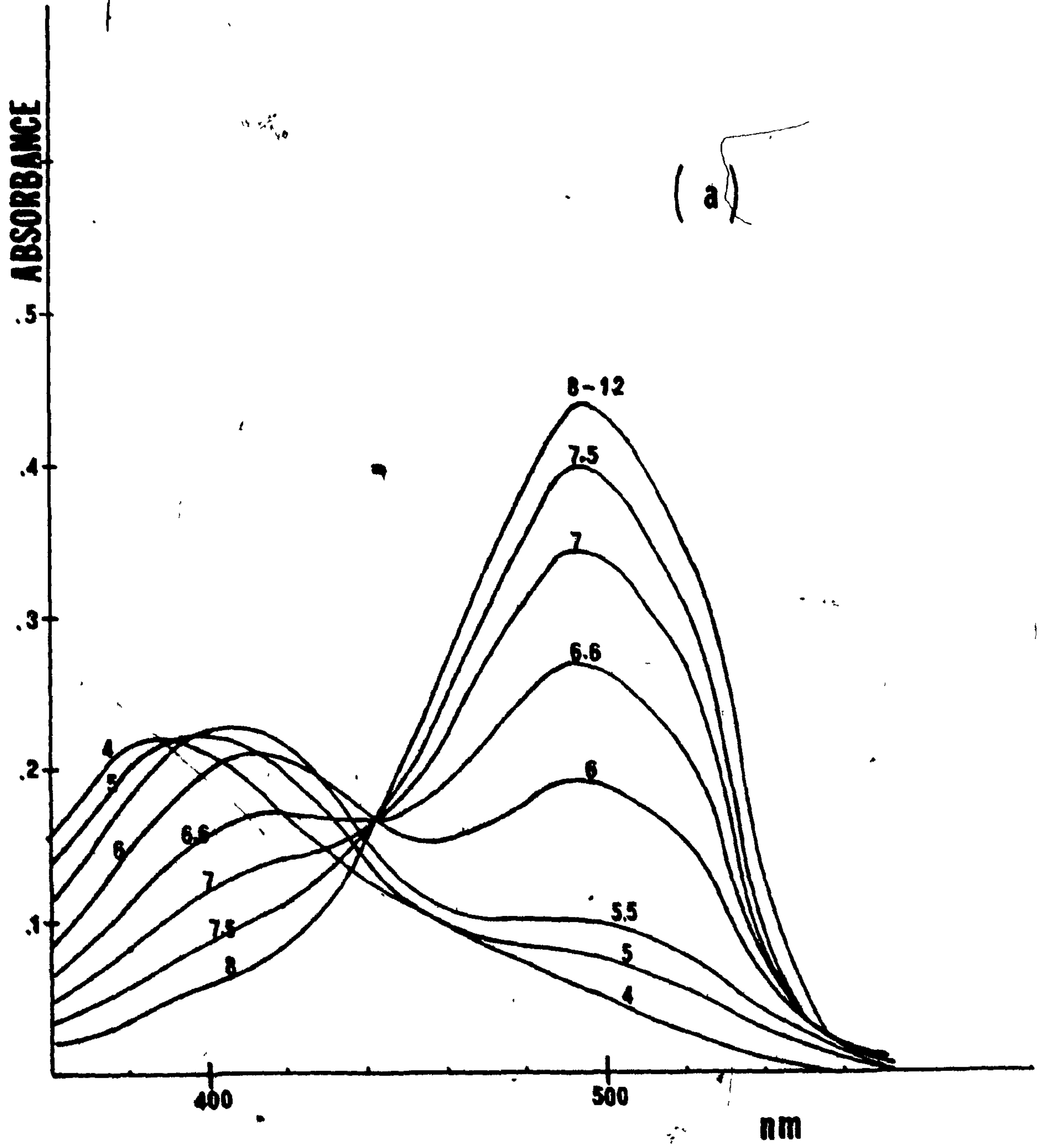
FIGURE 14. ABSORBANCE CURVES OF Zn-PAR IN AQUEOUS SOLUTION. Zn = 1.0×10^{-5} M. 1-cm cell.

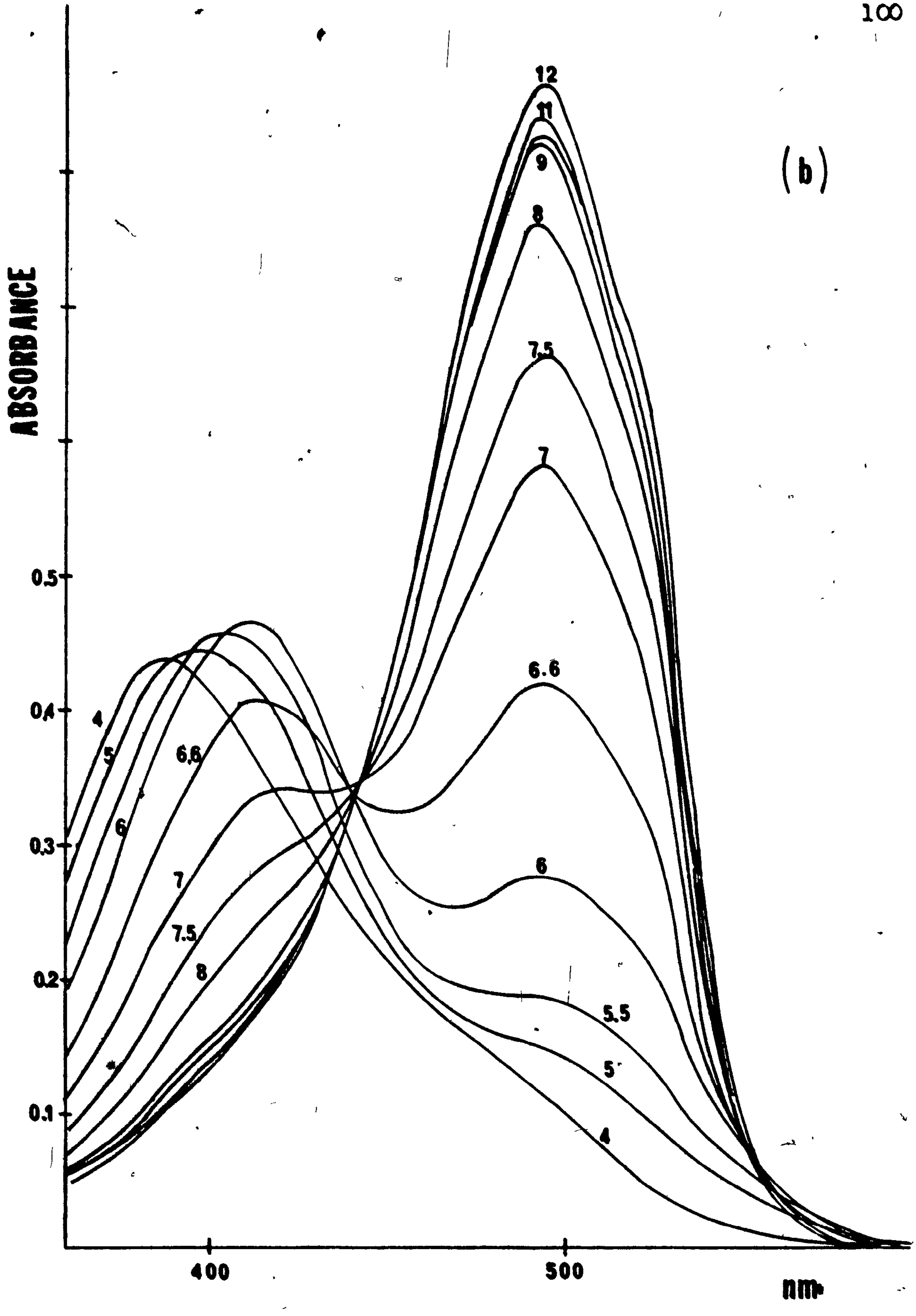
a) Ratio Zn: PAR 1: 1

b) Ratio Zn: PAR 1: 2

c) Ratio Zn: PAR 100: 1

The number with each curve is the pH value for that solution.


ABSORBANCE
(a)
.5
.4
.3
.2
.1
400
500
nm
8-12
7.5
7
6.6
6
5.5
5
4
4
5
6
6.6
7
7.5
8


(b)
ABSORBANCE
0.5
0.4
0.3
0.2
0.1
400
500
nm
12
11
9
8
7.5
7
6.6
6
5.5
5
4
4
5
6.6
6
7
7.5
8

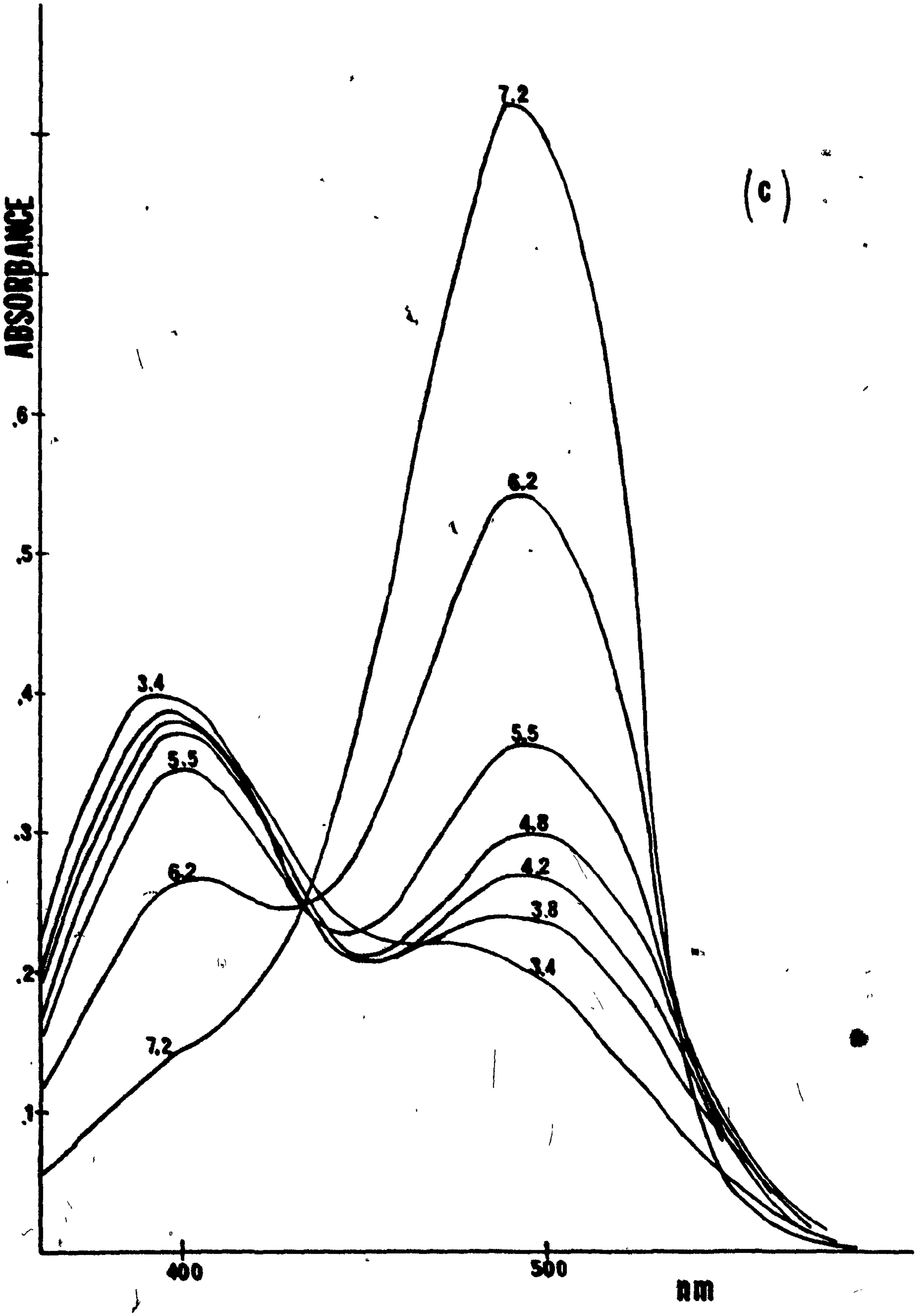

(c)
ABSORBANCE
.6
.5
.4
.3
.2
.1
400
500
nm
7.2
6.2
5.5
4.8
4.2
3.8
3.4
3.4
5.5
6.2
7.2

FIGURE 15. pH-absorbance CURVES FOR Zn-PAR SYSTEM. Zn $=1.0 \times 10^{-5}$ M. Cell 1-cm. $\lambda = 500$ nm.

(I) M: L = 1: 0.5
(II) M: L = 1: 1.0
(III) M: L = 1: 1.5
(IV) M: L = 1: 2.0
(V) M: L = 1: 2.5
(VI) M: L = 100: 1.0

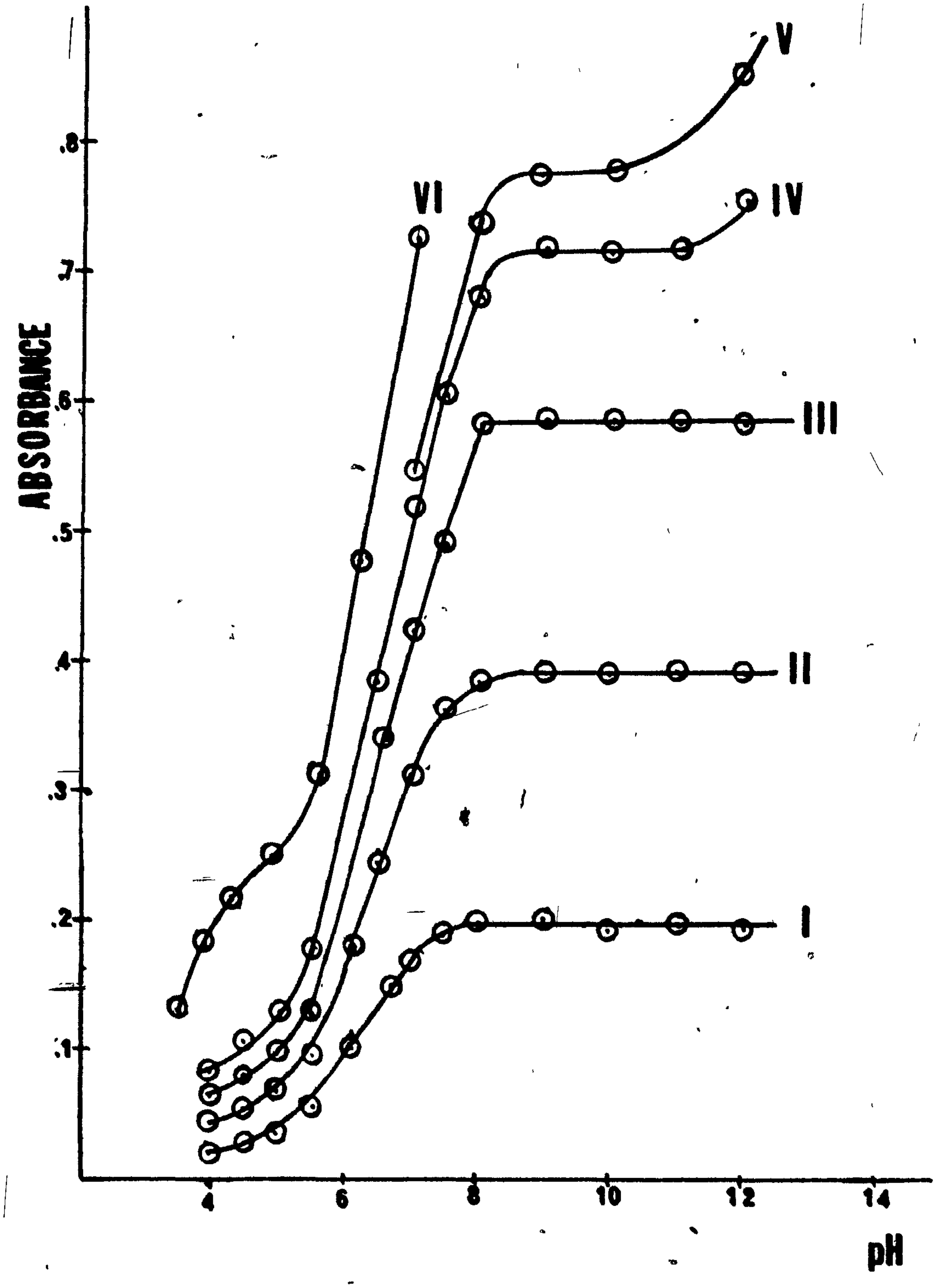

ABSORBANCE
.8
.7
.6
.5
.4
.3
.2
.1
4
6
8
10
12
14
pH
I
II
III
IV
V
VI

TABLE XVI

COMPOSITION OF Zn:PAR CHELATES AT DIFFERENT pH VALUES BY THE CONTINUOUS VARIATION METHOD.

pH	M: L
4	1: 1.5
5	1: 1.66
8	1: 1.9

shown in Fig 16 . The solutions were prepared according to the procedure described in section III-2.3.d . The composition of the solutions and the absorbance results are given in appendix I.

The spectra of the mixture at different pH values as well as the results obtained by the Continuous Variation Method and the shape of the pH-absorbance curves (Fig 15) suggest the following series of reactions:

$$Zn^{++} + H_2P = ZnHP^+ + H^+ \qquad (XII)$$

$$ZnHP^+ + H_2P = Zn(HP)_2 + H^+ \qquad (XIII)$$

$$ZnHP^+ = ZnP + H^+ \qquad (XIV)$$

$$Zn(HP)_2 = ZnP(HP)^- + H^+ \qquad (XV)$$

$$ZnP(HP)^- = ZnP_2^{=} + H^+ \qquad (XVI)$$

FIGURE 17. JOB PLOTS FOR Zn-PAR SYSTEM.

Cell 1-cm. ○ 500 nm. ⬡ 520 nm.

a) pH 4.0 , $C_T = 4.0 \times 10^{-5}$ M.

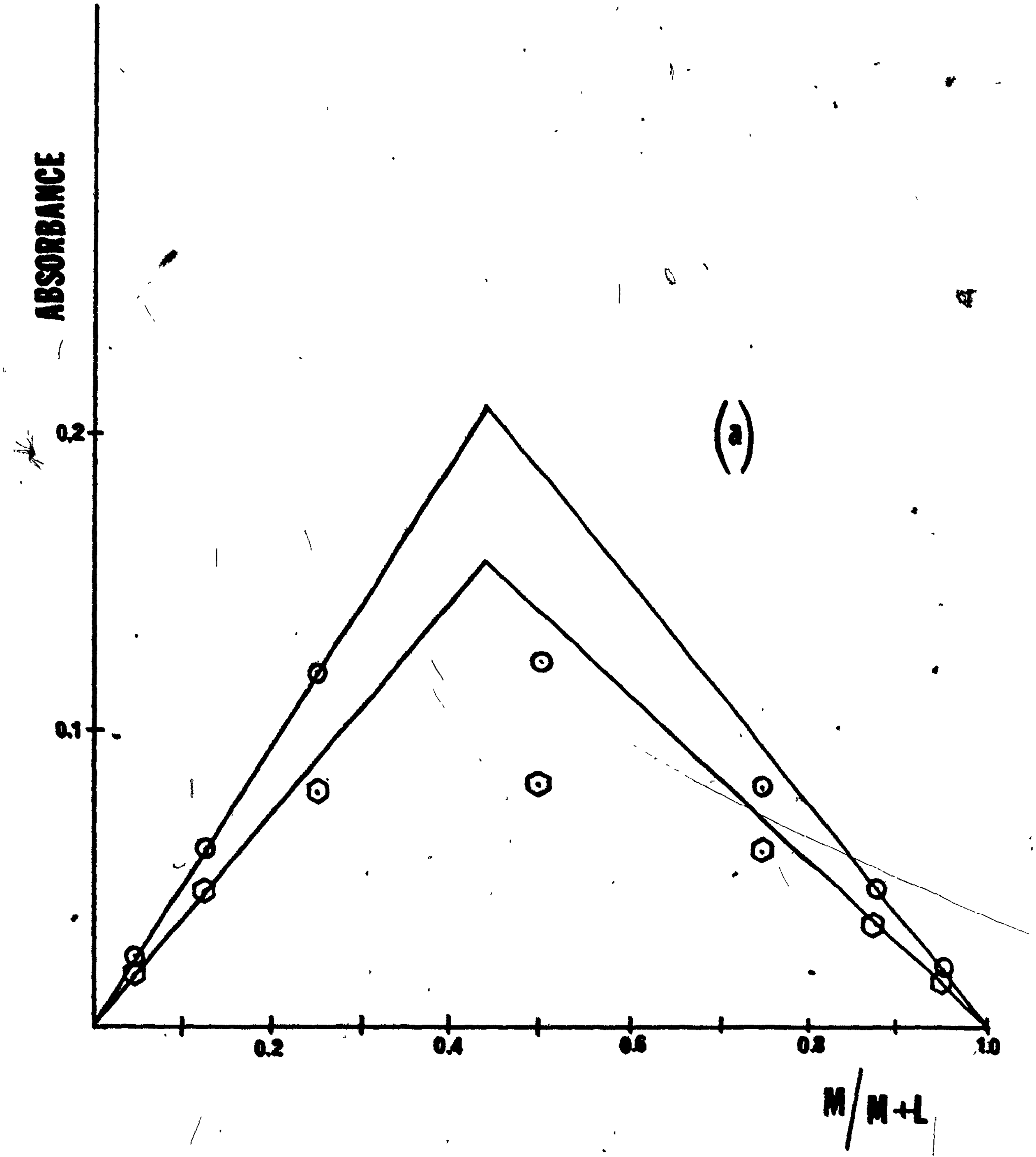
b) pH 5.0 , $C_T = 4.0 \times 10^{-5}$ M.

c) pH 8.0 , $C_T = 2.0 \times 10^{-5}$ M.

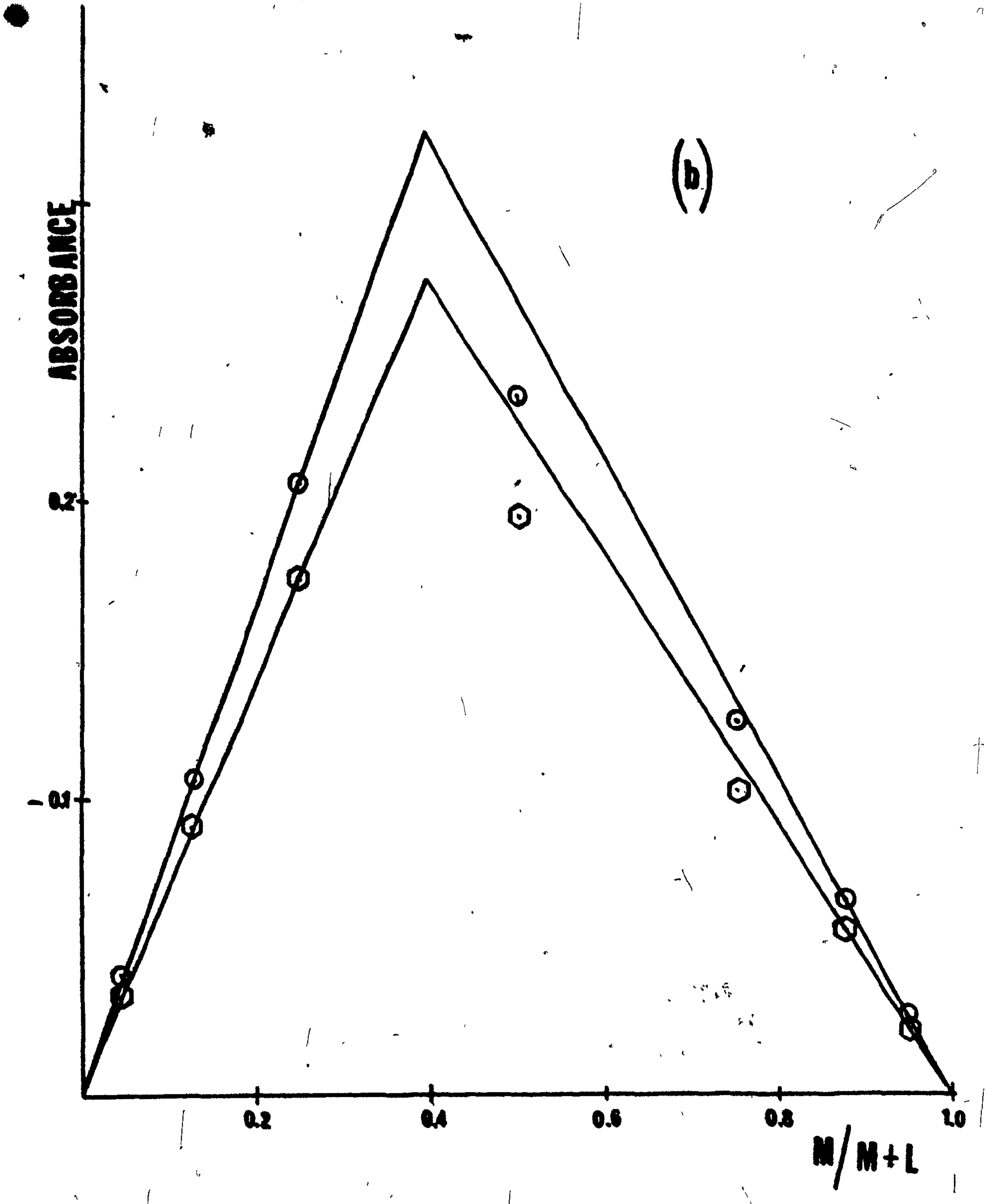
M denotes stoichiometric concentration of copper

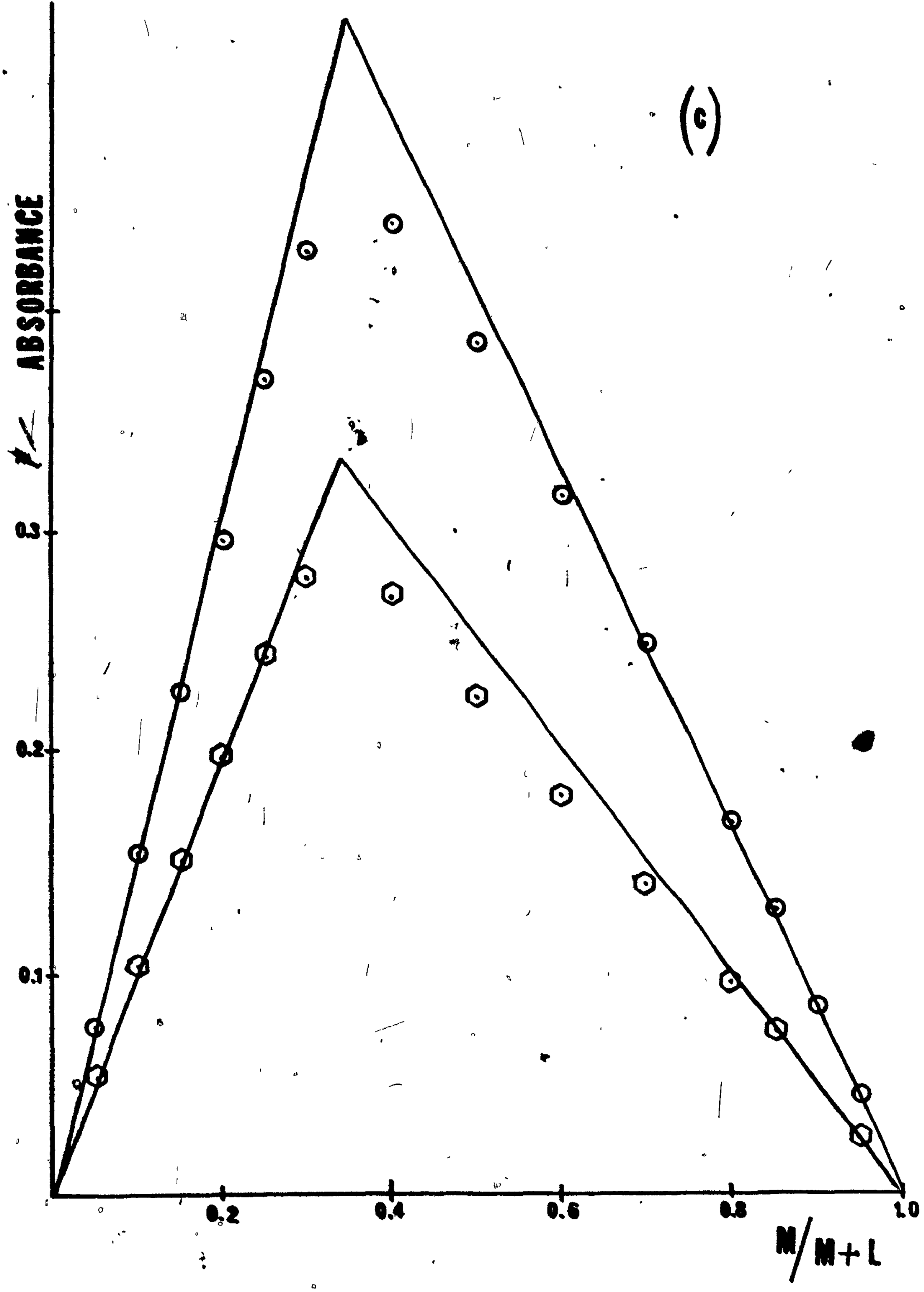
L denotes stoichiometric concentration of PAR

$C_T = M + L$


ABSORBANCE
0.2
0.1
(a)
0.2
0.4
0.6
0.8
1.0
M/M+L

6




(c)
ABSORBANCE
0.3
0.2
0.1
0.2
0.4
0.6
0.8
1.0
M/M+L

$$Zn^{++} + HP^{-} = ZnP + H^{+} \qquad (XVII)$$

$$ZnP + HP^{-} = ZnP_2^{=} + H^{+} \qquad (XVIII)$$

Above pH 8 hydrolysis of free zinc makes it necessary to take into consideration the different zinc-OH species (see Fig. 17) present. The reactions proposed at those pH values are not pH dependent, a conclusion that is evident from the pH-absorbance curves (Fig. 15) in that pH region:

$$Zn(OH)_2 + HP^{-} = ZnOHP^{-} + H_2O \qquad (XIX)$$

$$ZnOHP^{-} + HP^{-} = ZnP_2^{=} + H_2O \qquad (XX)$$

In the zinc system the simultaneous occurrence of several reactions makes it impossible to evaluate the equilibrium constant for each of the reactions involved. An attempt was made from the data for pH 8, to evaluate the K values; but the great number of zinc species coexisting makes the system highly complex.

Under the assumption that reactions XIX and XX are the only ones taking place at pH 8, a value of K* was calculated from the titration graphs at pH 8 and 9. This K* corresponds to the overall constant for reactions XIX and XX. The value obtained was 7.3×10^{14}.

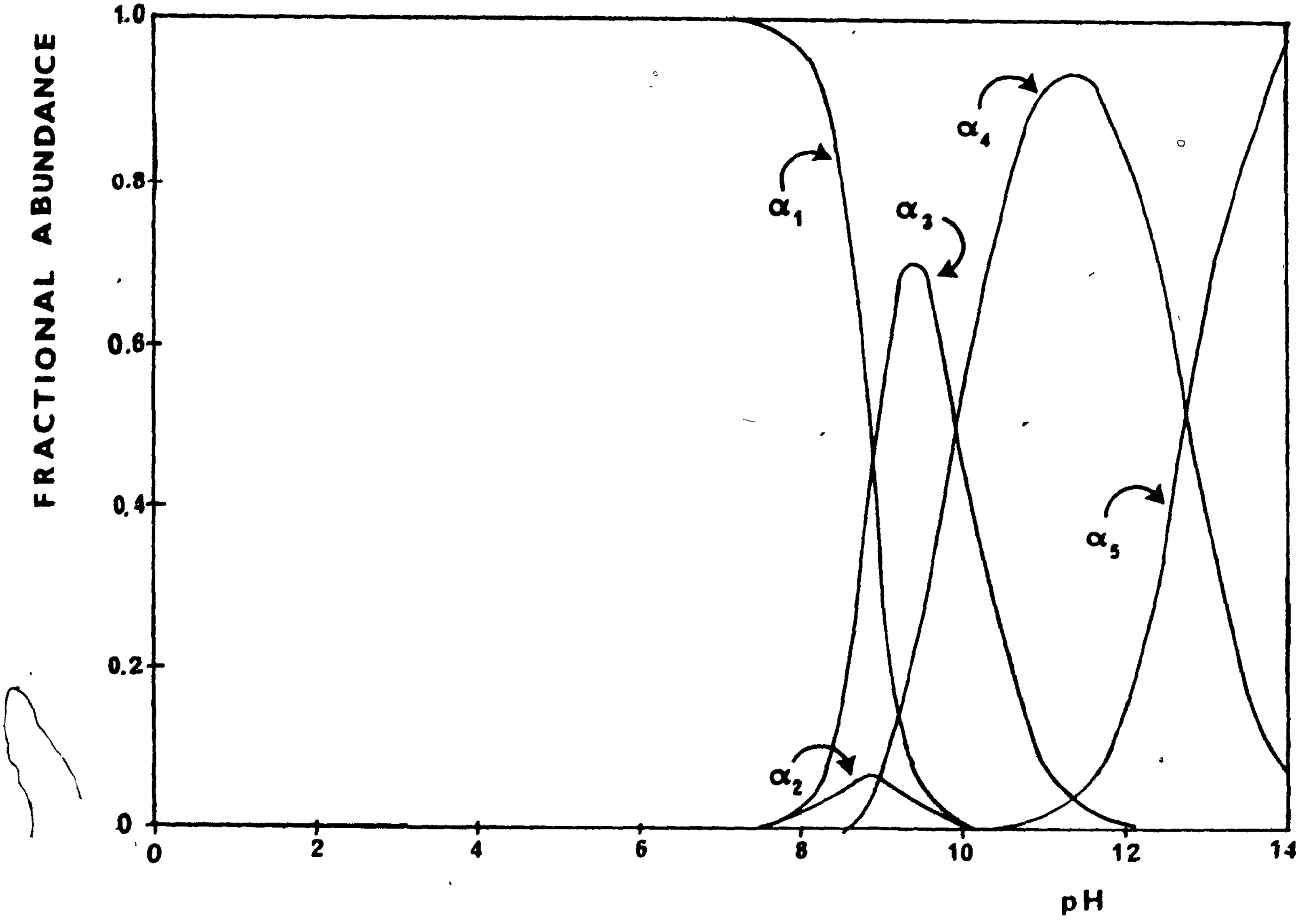
$$K^* = \frac{\left[ZnP_2^{=}\right]}{\left[Zn(OH)_2\right]\left[HP^{-}\right]^2}$$

FIGURE 17. DISTRIBUTION DIAGRAM FOR THE DIFFERENT SPECIES OF ZINC AS A FUNCTION OF pH (34)

$$\alpha_1 = \frac{[Zn^{++}]}{[Zn]_T} \qquad \alpha_4 = \frac{[Zn(OH)_3^-]}{[Zn]_T}$$

$$\alpha_2 = \frac{[ZnOH^+]}{[Zn]_T} \qquad \alpha_5 = \frac{[Zn(OH)_4^=]}{[Zn]_T}$$

$$\alpha_3 = \frac{[Zn(OH)_2]}{[Zn]_T}$$


FRACTIONAL ABUNDANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pH
α_1
α_2
α_3
α_4
α_5

The values of K found for reaction XIX and XX were: $K_8 = 2.3 \times 10^7$, and $K_9 = 4.35 \times 10^6$. These values were obtained by using the pH-absorbance graph data, and under the following assumptions:

1) when the concentration of ligand is smaller than that of the metal concentration, the main chelate formed is $ZnOHP^-$ and the amount of $ZnP_2^=$ is negligible.

2) when the concentration of ligand is twice or more than twice that of the metal concentration the main chelate species in solution is $ZnP_2^=$ and other non-hydroxo PAR species are negligible.

The equations used to obtain K_8 and K_9 were obtained by solving the appropiate mass-balance equations.

$$K_8 = \frac{\left[A - a_{HP}C_L\right]\left[a_{ZnOHP} - a_{HP}\right]}{\left[C_L a_{ZnOHP} - A\right]\left[C_m(a_{ZnOHP} - a_{HP}) - A + a_{HP}C_L\right]}$$

$$K_9 = \frac{\left[a_{HP}\ (C_L - C_m) - A + C_m a_{ZnOHP}\right]\left[a_{HP} - a_{ZnP_2} + a_{ZnP}\right]}{\left[a_{HP}\ (2C_m - C_L) - C_m a_{ZnP_2} + A\right]\left[A + a_{ZnP_2}(C_m - C_L) + a_{ZnP}(C_L - 2C_m)\right]}$$

The molar absorptivity of $ZnP_2^=$ was evaluated from the data obtained by Molar-Ratio method at pH 8, and 9. The value obtained was 7.7×10^4 $1\text{-}m^{-1}cm^{-1}$; for the molar absorptivity of $ZnOHP^-$, it was assumed to be of the order of half a_{ZnP_2} which proved to be correct in the copper system. Therefore the value used for a_{ZnP} was 4.0×10^4 $l\text{-}m^{-1}cm^{-1}$.

The values obtained for the equilibrium constants of reactions XIX and XX showed that one of the assumptions used for their evaluation is not correct. Given the order of magnitude of K_9 (4.35×10^6), the amount of $ZnP_2^=$ formed at low concentration of ligand is not negligible. Using the value obtained for K_9, a better value of K_8 can be calculated which takes into consideration the amount of $ZnP_2^=$ present in reaction XIX. The corrected value obtained for K_8 was 3.2×10^7.

From the values obtained for K_8 and K_9 and the proper mass-balance equations it is possible to predict a titration graph at pH values above 8. Using equation 13 the calculated absorbance at pH 8 was evaluated. The results obtained are compared with the observed results in Fig. 18b .

$$a(HP^-)^3 + b(HP^-)^2 + c(HP^-) + d = 0 \qquad (13)$$

$$a = -K_8K_9$$

$$b = -K_8K_9\,(C_L - 2C_m) - K_8$$

$$c = K_8\,(C_L - C_m) - 72.42$$

$$d = 72.42\,C_L$$

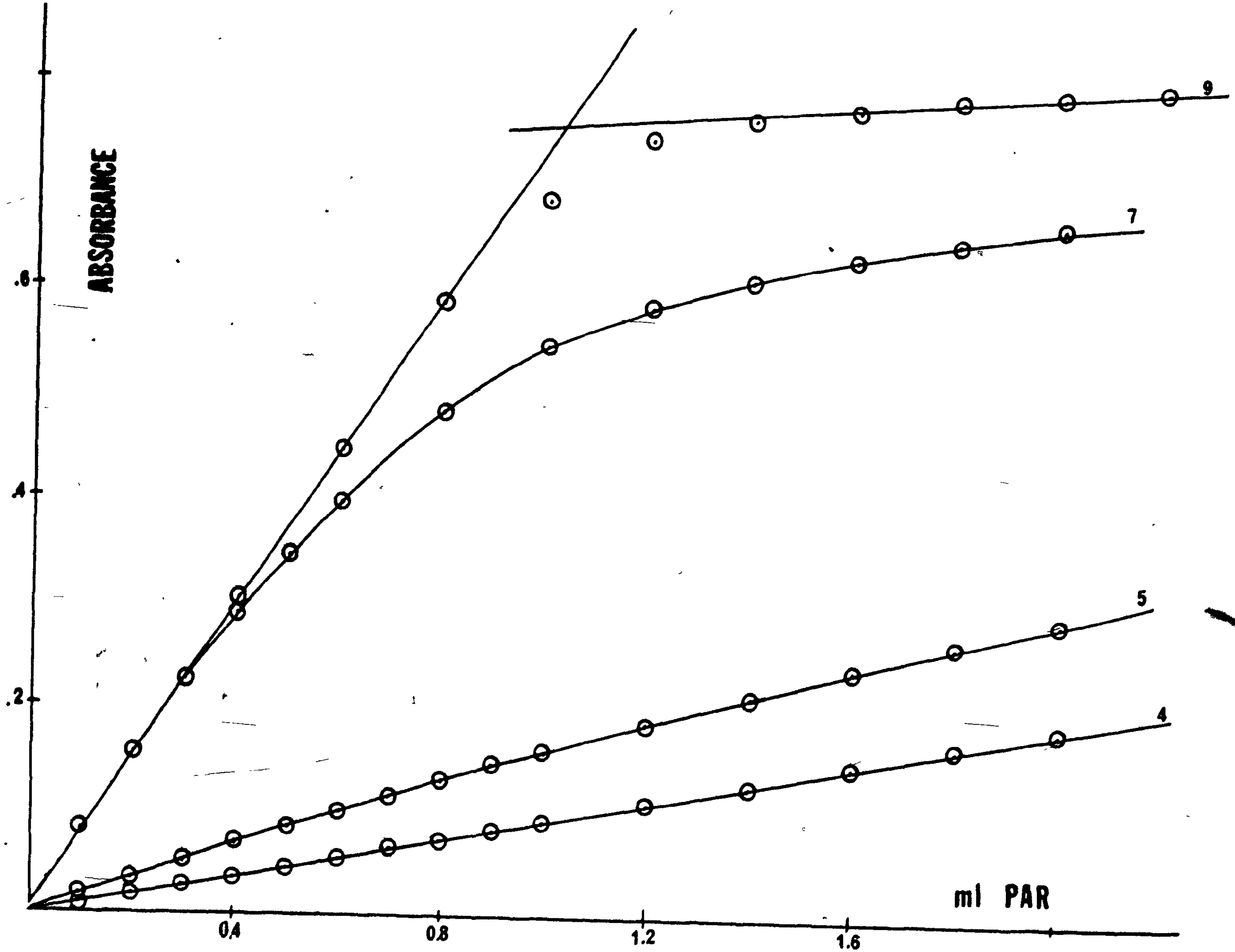
Titration curves for zinc at different pH values are shown in Fig. 18a . At pH 5 and 6 precipitation occurred when excess of PAR was present. At pH 5 this phenomenon was observed after the solution had been standing for some time (approximatly one hour). At pH 6 the precipitation was immediate; therefore at pH

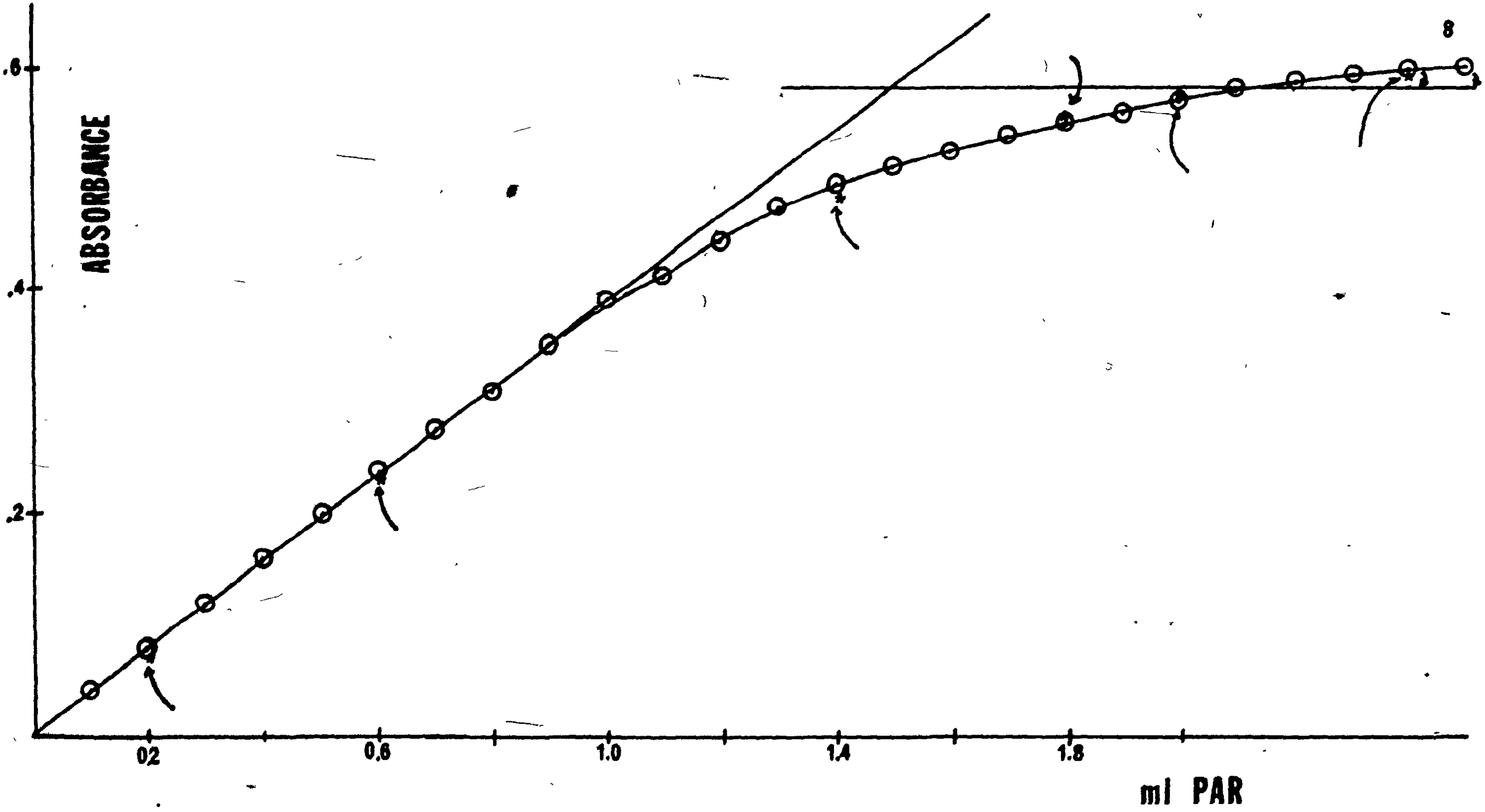
FIGURE 18. TITRATION GRAPHS FOR ZINC AT DIFFERENT pH VALUES. Zn = 1.0×10^{-5} M. PAR = 1.0×10^{-3} M. 1-cm cell. = 500 nm.

a) pH values 4, 5, 7, and 9 .

b) pH 8, Zn = 0.76×10^{-5} M. The arrows indicate calculated points by use of equation 13.

The number with each titration graph is the pH value for that solution.


ABSORBANCE
.2
.4
.6
ml PAR
0.4
0.8
1.2
1.6
9
7
5
4


ABSORBANCE
.6
.4
.2
02
0.6
1.0
1.4
1.8
ml PAR
8

6, it is not possible to do a titration. The formation of a precipitate suggests the existence of a new species in that pH range.

An analysis of the titration graphs at different pH values showed that the best pH for the determination of zinc is at a pH greater than 8, where a sharp break was observed at the end point. Moreover the higher absorptivity of the species present above that pH allows lower limits of detection.

The values of the equilibrium constants evaluated for the zinc-PAR system are given in Table XVII.

TABLE XVII

SUMMARIZED VALUES OF EQUILIBRIUM CONSTANTS EVALUATED IN THE Zn-PAR SYSTEM.

log K	Equilibrium
7.5	$K_8 = \frac{[ZnOHP^-]}{[Zn(OH)_2][HP^-]}$
6.64	$K_9 = \frac{[ZnP_2^=]}{[ZnOHP^-][HP^-]}$

3.5 Titration of Mixtures.

Once the study of each single metal-PAR system was completed, it was possible to make the determination of the mixture of metals. It was observed in the three systems that the species present at alkaline pH (above 8) have higher absorptivities than the ones present at lower pH values; this allowed the determination of lower concentrations of the metals.

In the case of the copper-PAR system, the presence of $CuP_2^{=}$ in significant amounts at pH 9 or higher, makes pH 8 the best choice for the determination of copper. The determination could also be made at pH 9 or 10, but the amount of ligand used at these pH values is larger in order to have a complete reaction, the determination is more time consuming, and the system more complex in presence of other metals. From pH 2 to 8, sharp breaks are observed and copper can also be titrated at any given pH in this range. From pH 4 to 7, there is an equilibrium between the two species present and small changes in pH cause a large change in absorbance. This makes the use of pH below 4 more suitable than from pH 4 to 7, because then the solutions need not be buffered. Even then, the higher absorptivity at pH=8 makes it the preferred choice.

It was observed in the lead system, that although the chelate starts to form at pH 3, sharp breaks were not obtained until lower hydrogen-ion concentration was present (pH above 8). The non-equilibrium of the system at some pH values made pH 8 the best choice, where the absorbance readings in a titration remained constant for the first 24 hours (see Fig. 3).

For the zinc system the best pH for the determination was above 8; at pH 4 and 5 even when formation of chelate was observed, it was not possible to obtain any break. At pH 6 the immediate formation of a precipitate does not allow any determination; besides, the high complexity of the system makes the evaluation of the stability constants impossible at pH lower than 7.

From the above discussion of the systems, it was concluded that the best pH for the determination of the mixture of metals was pH 8. A titration at that pH is shown in Fig. 19. Just two breaks are observed in the graph, which agree with those expected. The first break corresponds to the copper and zinc having been titrated together to form CuP and $ZnP_2^{=}$, and the second break to the lead having been titrated to form PbP. The relevant formation constants are: $K_{CuP} = 5.7 \times 10^8$ $K_{ZnOHP^-} = 3.16 \times 10^7$, $K_{ZnP_2} = 4.35 \times 10^6$, and $K_{PbP} = 0.7 \times 10^6$ (evaluated from the titration graph). Further the relevant absorptivities are 3.9×10^4 for CuP, 3.9×10^4 for $ZnOHP^-$, 7.6×10^4 for $ZnP_2^{=}$, and 3.4×10^4 for PbP. The increasing part of the curve after the last break corresponds to the formation of $CuP_2^{=}$ ($K_{CuP_2^{=}} = 8.2 \times 10^{-6}$, $a_{CuP_2} = 7.6 \times 10^4$).

To prove this even further, titrations of mixtures Cu/Zn and Cu/Pb at pH 8 were made. The graphs obtained are shown in Figs. 19b and 19c. In the first case a single break corresponding to the mixture of metals is obtained; for Cu/Pb mixtures two

FIGURE 19. TITRATION GRAPHS FOR THE MIXTURE OF METALS. PAR $= 1.0 \times 10^{-3}$ M. 1-cm cell. λ 500 nm.

a) Cu/Pb/Zn Mixtures

1) pH=2

Cu $= 1.0 \times 10^{-5}$ M.

Pb $= 1.0 \times 10^{-5}$ M.

Zn $= 1.0 \times 10^{-5}$ M.

2) pH=8

Cu $= 0.5 \times 10^{-5}$ M.

Pb $= 0.5 \times 10^{-5}$ M.

Zn $= 0.5 \times 10^{-5}$ M.

b) Cu/Zn Mixture at pH=8.

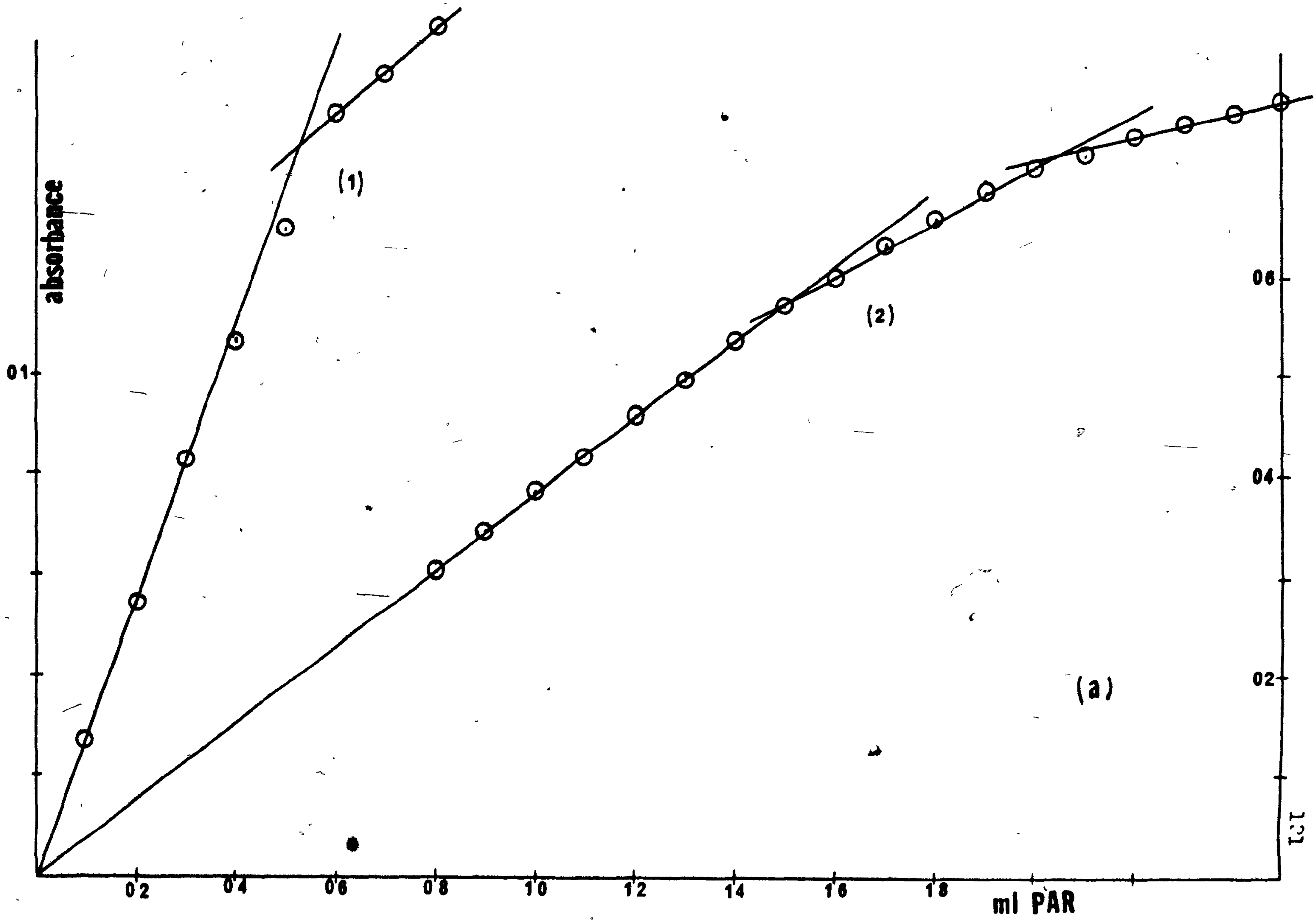
Cu $= 0.485 \times 10^{-5}$ M.

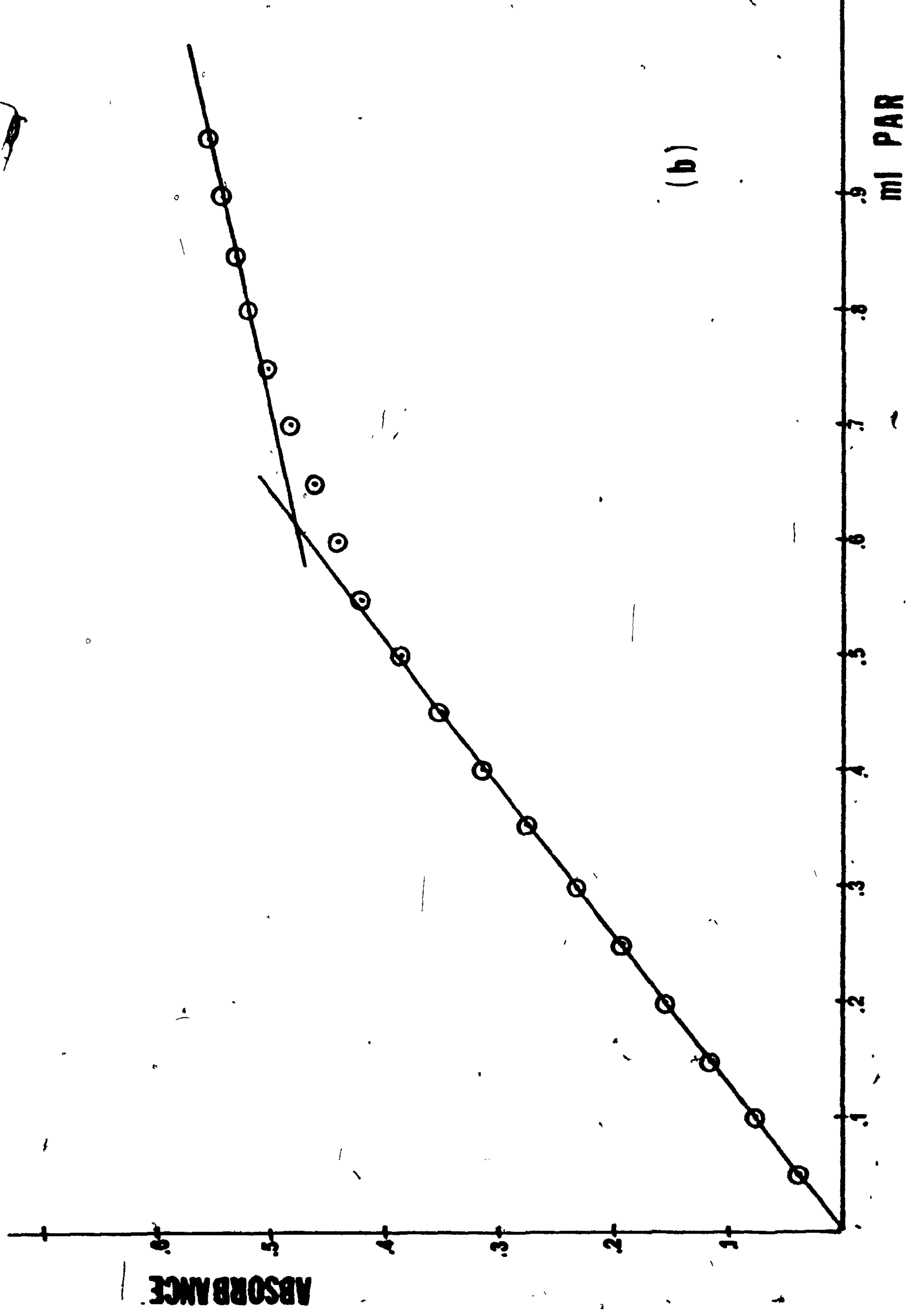
Zn $= 0.385 \times 10^{-5}$ M.

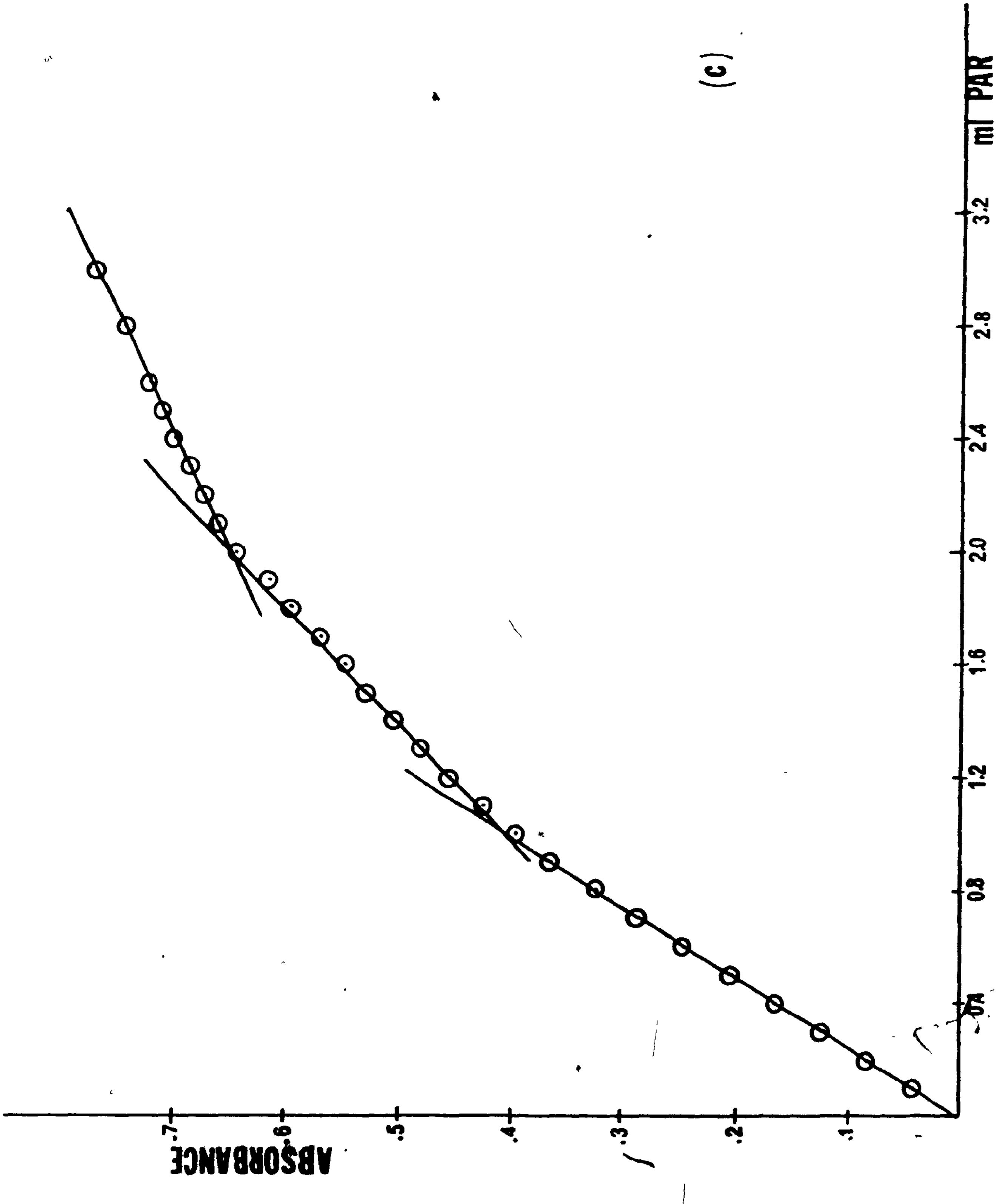
c) Cu/Pb Mixture at pH=8.

Cu $= 0.97 \times 10^{-5}$ M.

Pb $= 0.97 \times 10^{-5}$ M.


absorbance
01
06
04
02
02
04
06
08
10
12
14
16
18
ml PAR
(1)
(2)
(a)


(b)
ml PAR
.1
.2
.3
.4
.5
.6
.7
.8
.9
ABSORBANCE
.1
.2
.3
.4
.5
.6


(c)
ml PAR
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
ABSORBANCE
.1
.2
.3
.4
.5
.6
.7

two breaks, one for each metal, are observed.

Since at pH 8 it was not possible to determine the separate concentrations of copper and zinc present together, it was necessary to repeat the determination at another, more suitable pH. Therefore, the copper concentration was evaluated at pH 2, where zinc and lead PAR chelates do not form. Once the concentration of copper was known, it was possible to calculate the zinc concentration from the overall concentration of the mixture determined by the titration of it at pH 8. Two methods were used for the determination of the concentration of each metal in the mixture:

1) A sample containing a mixture of metals was adjusted to pH 2; the titration was then made taking care that the amount of ligand added was just enough to determine the end point for copper. The pH was then increased to 8, the sample diluted to twice its volume in order to have half the amount of copper chelate, due to the higher absorptivity of the copper-PAR chelate at pH 8. An aliquot of this solution was then taken, and the titration continued to past the end points first for copper and zinc, and finally for lead. A graph with the results obtained by this procedure is shown in Fig. 19a.

2) Two separate determinations were made, one at pH 2 for copper, and a second one at pH 8 to determine the end point first for copper plus zinc, then the end point for lead.

Of these two procedures the second one proved to be the better one. The first one is more elaborate and requires more handling of the sample which can produce larger errors. Besides, the short number of readings that can be taken after the copper end point before adjusting the pH from 2 to 8, are too few to be able to determine the copper end point very accurately.

Copper could be determined from pH 2 to 2.7 without interference from zinc and lead, even when these metals were present in high amounts. Determinations of copper were made in the presence of 100 fold excess of each of the metals without any effect on the results. This allowed a pH range for the determination of copper in mixtures with high concentrations of lead and zinc. If lead and zinc were present in lower concentrations (Pb:Zn:Cu = 10:10:1), the determination of copper can be made up to pH 5 without any interference.

In order to observe the precision and accuracy of this method, a determination of a sample of Cu-Pb-Zn mixture was repeated four times. The results are given in Table XVIII. They show that the accuracy and precision of the method are good. The determination is fast and it has the advantage of being in water.

TABLE XVIII

REPLICATE ANALYSIS OF A MIXTURE OF COPPER(II), ZINC, AND LEAD IN AQUEOUS SOLUTION AT 25°C, BY SPECTROPHOTOMETRIC TITRATION WITH PAR.

Concentration of PAR: 1.0×10^{-3} M.

Volume of solution: 50-ml

Wavelengths used: 520 nm for pH = 2, 500 nm for pH = 8

Concentrations of metal taken: Cu = 0.999×10^{-5} M
Zn = 1.020×10^{-5} M
Pb = 0.999×10^{-5} M

pH	Volume of titrant used.		mean concentration of metal found $M \times 10^{5}$			Standard deviation $\times 10^{5}$		
	To first end point ml	To second end point ml	Cu	Zn	Pb	Cu	Zn	Pb
2	0.098							
2	0.098							
2	0.098							
2	0.099		.98			.005		
8	0.150	0.250						
8	0.150	0.249						
8	0.151	0.250						
8	0.152	0.251						
				1.02	0.99		.010	.005

DISCUSSION

The analytical method developed for the determination of copper, lead, and zinc in mixtures proved to be precise and accurate.

Spectrophotometric titrations of metals with PAR are very sensitive in the visible region of the spectrum. The molar absorptivities of the complex are of the order of 39000 $l\text{-}m^{-1}cm^{-1}$ for M:PAR complexes and 77000 $l\text{-}m^{-1}cm^{-1}$ for the $M(PAR)_2$ complexes.

As the concentration of metal chelates used for the evaluation of the equilibrium never exceeded 2×10^{-5} M the activity coefficients of the metal chelates were taken in all cases to be unity.

There are disagreements in the literature, on the stoichiometry of complexes of several metals at the different pH values. Hnilickova and Sommer (17) reported that in an acidic solution of a divalent metal the species MHP^+ forms, whereas in alkaline solution $M(HP)_2$ forms. Nevertheless, species of the type MP have been reported to be present in alkaline solutions. Discrepancies found in the literature for the pH range in which the species reported in this work are significant are given in Table XIX.

The existence of the different chelate species in the pH range shown in Table XX was observed in the present work.

Due to the different species of PAR that co-exist in solution, the reported values for the stability constants of the chelates vary according to the PAR species used in the chemical equation. The stability constants of several metal complexes are shown in Table XXI. The stability constants reported are:

$$K_I = \frac{[MHP^+]}{[M^{++}][HP^-]} \qquad K_2 = \frac{[M(HP)_2]}{[MHP^+]\,[HP^-]}$$

TABLE XIX. SOME PHYSICOCHEMICAL DATA FOR METAL:PAR CHELATES

Metal ion.	M:L molar ratio	Absorption max. nm	pH	Reference
Cu(II)	1:1	520	2.3-5.0	17
	1:2	510	5.0	17
	1:1	517	3.2-10	21
	1:1			19
	1:2			19
Pb(II)	1:1	517	10	21
	1:1	520	10	26
	1:2			19
Zn(II)	1:1		10	21
	1:2	495	8.0	17
	1:1			19
	1:2			19

TABLE XX . pH RANGE OF PREDOMINANT M:PAR SPECIES IN AQUEOUS SOLUTION, OBSERVED IN THE PRESENT WORK.

Specie	M:L Molar Ratio	Absorption max. nm	pH
$CuHP^{+}$	1:1	500	1.5-4.0
CuP	1:1	500	7.0-10
$CuP_2^{=}$	1:2	500	9
$PbHP^{+}$	1:1	520	4.5
PbP	1:1	520	6.0-7.5
$ZnHP^{+}$	1:1	490	2.8-6.0
$Zn(HP^{-})_2$	1:2	490	2.8-6.0
$ZnP_2^{=}$	1:2	490	8

As chelation frequently occurs at pH values lower than those at which the two hydroxyl groups of PAR lose their hydrogen, protons are exchanged for metal in the ortho hydroxyl group. The species which chelates is (I), for which the dissociation constant is unknown.

Corsini (35) took this into account and made a correction to the values of the equilibrium constants reported in the literature for the metal-PAR chelates.

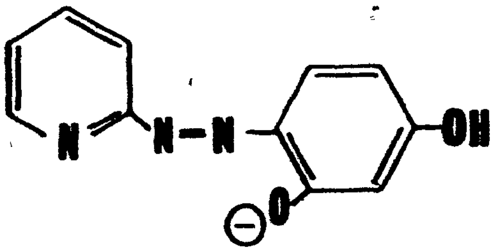
TABLE XXI . STABILITY CONSTANTS OF SOME PAR CHELATES.

Metal ion	log K_1	log K_1**	log K_2	Remarks	Reference
Cu(II)	14.8	2.5	9.1	Potentiometry water	19
	16.4	4.1	8.9	Potentiometry 1: 1 dioxane	19
	11.7*			Photometry	21
	17.5	5.2	20.7	Photometry	21
Pb(II)	12.9	0.59	13.7	Photometry	21
	6.5			Photometry	25
Zn(II)	10.5		6.6	Potentiometry water	35
	12.4	0.1	11.1	Potentiometry	35
	12.6	0.3	12.7	Photometry	35

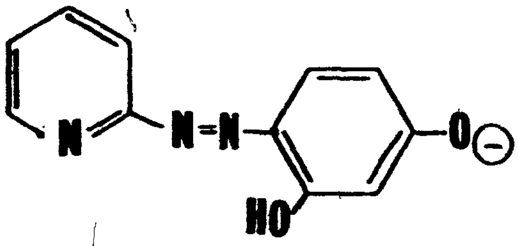
* The PAR species considered is $P^{=}$. Therefore:

$$K_1 = \frac{[MP]}{[M^{++}][P^{=}]}$$

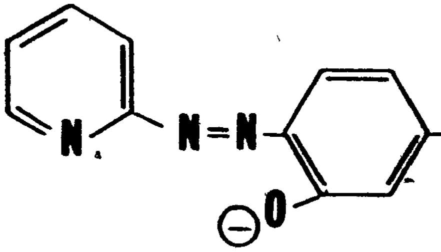
** Corrected value by applying Corsini's correction:



(I)



(II)



(III)

Corsini assumed that the value obtained for the dissociation of II to III was the same as the value for the dissociation of PAR to I, and he based this assumption on the fact that the dissociation constant of the ortho hydroxyl group was very close to the corresponding one for PAN, therefore he came to the conclusion that the ionization of the para hydroxyl group had no effects on the value of the ortho pK_{OH}.

In order to check the correctness of the chosen model at a given pH in the present work, the following derivations were made; considering the relationship of reactions I and II a value can be obtained to prove the correctness of the assumed model.

$$K_1 = \frac{[CuHP^+][H^+]^2}{[Cu^{++}][H_3P^+]} \quad \ldots (I) \qquad K_2 = \frac{[CuHP^+][H^+]}{[Cu^{++}][H_2P]} \quad \ldots (II)$$

$$K_{a1} = \frac{[H_2P][H^+]}{[H_3P^+]}$$

$$\frac{K_1}{K_2} = \frac{[H^+][H_2P]}{[H_3P^+]} = K_{a1}$$

$$pK_{a1} = pK_1 - pK_2$$

$$pK_{a1} = -1.43 - (-4.08) = 2.65$$

The literature value for pK_{a1} is 2.66; the agreement is therefore excellent and the chemical model is good.

Check on K_3 and K_4 in the copper-PAR system:

$$K_2 = \frac{[CuHP^+][H^+]}{[Cu^{++}][H_2P]} \qquad K_7 = \frac{[CuOH^+]}{[Cu^{++}][OH^-]}$$

$$K_3 = \frac{[CuP][H^+]}{[CuHP^+]} \qquad K_{a2} = \frac{[H^+][HP^-]}{[H_2P]}$$

$$K_4 = \frac{[CuP]}{[CuOH^+][HP^-]} \qquad K_w = [H^+][OH^-]$$

$$\frac{K_3}{K_w\ K_4} = \frac{[H][HP^-][CuOH^+]}{K_2\ [Cu^{++}][H_2P][OH^-]}$$

$$\frac{K_3}{K_w\ K_4} = \frac{K_{a2}}{K_2\ K_7}$$

$$K_7 = \frac{K_{a2}\ K_w\ K_4}{K_2\ K_3}$$

$$pK_7 = pK_{a2} + pK_w + pK_4 - pK_2 - pK_3$$

$$pK_7 = 5.48 + 14.0 - 8.76 + 4.08 - 5.08$$

$$pK_7 = 9.7$$

The literature value reported by Perrin (24) is $pK_7 = 8$. The value is not known precisely. The agreement is sufficiently good to support the chemical model chosen.

The procedure was the same for the lead-PAR system; the relationship of reactions VII, VIII and IX was considered:

$$K_1 = \frac{[PbHP^+][H^+]}{[Pb^{++}][H_2P]} \quad (VII)$$

$$K_2 = \frac{[PbP][H^+]}{[PbHP^+]} \quad (VIII)$$

$$K_3 = \frac{[PbP][H^+]}{[Pb^{++}][HP^-]} \quad (IX)$$

$$K_{a2} = \frac{[HP^-][H^+]}{[H_2P]}$$

$$\frac{K_1 \; K_2}{K_3} = K_{a2}$$

$$pK_{a2} = pK_1 + pK_2 - pK_3 = 5.5$$

The value obtained ($pK_{a2} = 5.5$) is in good agreement with the the literature reported value ($pK_{a2} = 5.48$).

By applying Corsini's suggestion the corrected values of K reported on the literature are compared with the ones obtained in this work. Results are shown in Table XXI. For the zinc-PAR system the values of the equilibrium constants reported so far in the literature, correspond to the formation of ZnHP and $Zn(HP)_2$ chelates, which takes place in the acid pH range, and was not evaluated in this work.

TABLE XXII

REPORTED VALUES OF M-PAR SYSTEMS IN THE LITERATURE AS COMPARE WITH THIS WORK.

K_n	This work	Literature	Reference
$K_2 = \frac{[CuHP^+][H^+]}{[Cu^{++}][H_2P]}$	4.08	5.1	23
$K_3 = \frac{[CuP][H^+]}{[CuHP^+]}$	-5.08	-5.5	17
$K_1 = \frac{[PbHP^+][H^+]}{[Pb^{++}][H_2P]}$	0.5	0.59	23

Appendix I

ABSORBANCE VALUES OBTAINED BY THE CONTINUOUS VARIATION METHOD.

A) Cu-PAR system

pH 2.1	Table I
pH 8.0	Table II
pH 10.0	Table III

B) Zn-PAR system

pH 4.0	Table IV
pH 5.0	Table V
pH 8.0	Table VI

$$\frac{M}{M+P} = \frac{\text{Conc. of metal}}{\text{Conc. of metal} + \text{Conc. of PAR}}$$

Both concentrations are stoichiometric values.

The numbers 400, 500, 510. 520 at the heads of the columns of absorbance values are the wavelengths in nm.

TABLE I

Absorbance values obtained by the Continuous Variation Method for copper-PAR system at pH 2.1 .

Solution Number	M / M+P	500	510	520
1	0.05	.031	.03	.03
2	0.1	.061	.062	.062
3	0.15	.092	.096	.096
4	0.20	.123	.129	.129
5	0.25	.152	.16	.16
6	0.30	.181	.191	.191
7	0.40	.234	.244	.244
8	0.50	.27	.273	.273
9	0.60	.231	.24	.24
10	0.70	.177	.187	.187
11	0.80	.121	.127	.127
12	0.85	.092	.095	.095
13	0.90	.06	.063	.063
14	0.95	.029	.032	.032

TABLE II

Absorbance values obtained by the Contimuous Variation Method for copper-PAR system at pH 8 .

Solution Number	M / M+P	500	520
1	0.05	.046	.034
2	0.10	.093	.073
3	0.15	.142	.11
4	0.20	.19	.148
5	0.25	.236	.186
6	0.30	.275	.227
7	0.40	.368	.305
8	0.50	.409	.344
9	0.60	.347	.282
10	0.70	.256	.217
11	0.80	.174	.148
12	0.85	.134	.11
13	0.90	.093	.075
14	0.95	.054	.035

TABLE III

Absorbance values obtained by the Continuous Variation Method for copper-PAR system at pH 10 .

Solution Number	M / M + L	500	520
1	0.05	.07	.052
2	0.10	.139	.105
3	0.15	.203	.162
4	0.20	.261	.205
5	0.25	.318	.25
6	0.30	.359	.278
7	0.40	.389	.31
8	0.50	.375	.311
9	0.60	.313	.259
10	0.70	.237	.196
11	0.80	.162	.136
12	0.85	.125	.104
13	0.90	.084	.07
14	0.95	.026	.022

TABLE IV

Absorbance values obtained by the Continuous Variation Method for zinc-PAR system at pH 4 .

Solution Number	M / M + P	400	500	520
1	0.047	.139	.024	.018
2	0.125	.236	.06	.045
3	0.25	.427	.119	.079
4	0.50	.409	.123	.081
5	0.75	.208	.08	.059
6	0.875	.109	.046	.034
7	0.95	.047	.019	.015

TABLE V

Absorbance values obtained by the Continuous Variation Method for zinc-PAR system at pH 5 .

Solution Number	M / M+P	400	500	520
1	0.047	.086	.04	.030
2	0.125	.209	.106	.091
3	0.25	.41	.206	.171
4	0.50	.399	.235	.195
5	0.75	.197	.126	.104
6	0.875	.101	.066	.055
7	0.95	.041	.027	.022

TABLE VI

Absorbance values obtained by the Continuous Variation Method for zinc-PAR system at pH 8 .

Solution Number	M / M+P	500	510	520
1	0.05	.077	.075	.053
2	0.10	.155	.139	.103
3	0.15	.227	.201	.152
4	0.20	.296	.262	.198
5	0.25	.368	.326	.243
6	0.30	.426	.373	.278
7	0.40	.437	.38	.27
8	0.50	.385	.333	.225
9	0.60	.315	.274	.18
10	0.70	.248	.216	.14
11	0.80	.168	.147	.095
12	0.85	.128	.112	.073
13	0.90	.084	.074	.048
14	0.95	.043	.038	.025

Appendix II

ABSORBANCE VALUES AS A FUNCTION OF pH USED FOR THE EVALUATION OF THE EQUILIBRIUM CONSTANTS.

A) Cu-PAR system

400 nm	Table I
500 nm	Table II
510 nm	Table III
520 nm	Table IV

B) Pb-PAR system

400 nm	Table V
500 nm	Table VI
510 nm	Table VII
520 nm	Table VIII

c) Zn-PAR system

400 nm	Table X
500 nm	Table XI
510 nm	Table XII
520 nm	Table XIII

TABLE I

Absorbance values for the evaluation of equilibrium constants in the Cu-PAR system at 400 nm.

Solution	1	2	3	4	5	6	7
pH	A	A	A	A	A	A	A
1.0	.102	.208	.312	.418			
1.5	.094	.194	.291	.393			
2.0	.084	.167	.263	.365			
2.5	.068	.145	.241	.344			
3.2	.071	.142	.24	.342			
3.9	.067	.135	.23	.327			
4.5	.065	.119	.215	.315			
5.0	.038[1*]	.092	.20	.315			
5.5	.028	.056	.18[2*]	.316[3*]			
6.0	.021[4*]	.043	.184	.331	.649	.984	1.26
6.5	.018	.036	.183[5*]	.34			
7.0	.016	.035[6*]	.178	.339	.678	1.01	
7.5	.016	.032	.168	.328			
8.3	.017	.044	.176	.311[7*]	.65	.985	

TABLE I (continued)

9.0	.019	.033	.108	.227	.547	.859	1.78
10.0	.016	.034	.089	.19	.48	.823	1.19
11.0	.017	.034	.086	.165	.476	.813	
12	.018	.033	.086	.163			

1* pH = 5.2

2* pH = 5.4

3* pH = 5.7

4* pH = 6.3

5* pH = 6.4

6* pH = 6.9

7* pH = 8.1

TABLE II

Absorbance values for the evaluation of the equilibrium constants in the Cu-PAR system at 500 nm.

Solution	1	2	3	4	5	6	7
pH	A	A	A	A	A	A	A
1.0	.028	.0575	.087	.117			
1.5	.043	.083	.12	.155			
2.0	.069	.123	.165	.199			
2.5	.074	.144	.18	.208			
3.2	.082	.159	.188	.211			
3.9	.087	.172	.195	.212			
4.5	.102	.199	.224	.241			
5.0	.151[1*]	.27	.291	.304			
5.5	.175	.333	.345	.387[2*]			
6.0	.194[3*]	.378	.396	.409	.426	.452	.465
6.5	.194	.388	.417	.425			
7.0	.189	.385[4*]	.428	.445	.453	.476	.492
7.5	.188	.385	.431	.446			
8.3	.198	.38	.437	.477	.505[5*]	.542[5*]	.567[5*]

TABLE II(continued)

9.0	.196	.39	.503	.563	.615	.652	.681
10.0	.203	.40	.52	.61	.682	.717	.755
11.0	.202	.395	.51	.612	.682	.744	.783
12.0	.205	.40	.525	.63			

1* pH = 5.2

2* pH = 5.7

3* pH = 6.3

4* pH = 6.9

5* pH = 6.1

TABLE III

Absorbance values for the evaluation of the equilibrium constants in the Cu-PAR system at 510 nm .

Solution	1	2	3	4	5	6	7
pH	A	A	A	A	A	A	A
1.0	.0171	.0343	.054	.07			
1.5	.036	.069	.096	.124			
2.0	.07	.12	.156	.181			
2.5	.078	.148	.179	.197			
3.2	.086	.166	.19	.203			
3.9	.091	.181	.199	.211			
4.5	.104	.204	.226	.237			
5.0	.147[1*]	.268	.285	.295			
5.5	.168[2*]	.321	.331	.367[3*]			
6.0	.185[4*]	.363[5*]	.376	.387	.399	.421	.428
6.5	.185	.37	.395[6*]	.40[6*]			
7.0	.18	.37	.405	.41	.422	.44	.452
7.5	.181	.37	.41	.421			
8.3	.19	.36	.41	.442[7*]	.462	.485	.509

TABLE III (continued)

9.0	.19	.379	.471	.516	.551	.577	.598
10.0	.197	.388	.481	.548	.604	.633	.662
11.0	.196	.388	.48	.54	.621	.653	.686
12.0	.196	.39	.488	.568			

1* pH = 5.2

2* pH = 5.6

3* pH = 5.7

4* pH = 6.3

5* pH = 6.1

6* pH = 6.4

7* pH = 8.1

TABLE IV

Absorbance values for the evaluation of the equilibrium constants in the Cu-PAR system at 520 nm.

Solution	1	2	3	4	5	6	7
pH	A	A	A	A	A	A	A
1.0	.008	.022	.033	.045			
1.5	.032	.058	.083	.104			
2.0	.069	.118	.148	.168			
2.5	.078	.147	.175	.185			
3.2	.086	.167	.186	.193			
3.9	.089	.177	.191	.199			
4.5	.098	.194	.211	.217			
5.0	.128[1*]	.237	.249	.256			
5.5	.141	.27	.278[2*]	.306[3*]			
6.0	.151[4*]	.298	.31	.318	.333	.342	.35
6.5	.152	.305	.325[5*]	.33			
7.0	.149	.304[6*]	.33	.343	.356	.37	.377
7.5	.149	.304	.338	.348			
8.3	.155	.304	.337	.353[7*]	.377	.395	.417

TABLE IV (continued)

9.0	.155	.312	.39	.425	.455	.476	.677
10.0	.164	.322	.404	.455	.505	.523	.535
11.0	.162	.322	.40	.466	.515	.542	.562
12.0	.164	.323	.406	.471			

1* pH = 5.2

2* pH = 5.4

3* pH = 5.7

4* pH = 6.3

5* pH = 6.4

6* pH = 6.9

7* pH = 8.1

TABLE V

Absorbance values for the evaluation of the equilibrium constants in the Pb-PAR system at 400 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.099	.20	.302	.401
4.0	.093	.189	.285	.38
5.0	.092[1*]	.196[2*]	.298	.401
5.6	.092	.20	.319	.438
6.0	.081[3*]	.183[4*]	.314	.462
6.5	.06	.168	.295	.44
7.0	.042[5*]	.129	.258	.42
7.5	.032	.11	.25	.42
8.0	.024	.09	.236	.40
9.0	.027	.112	.26	.39
10.0	.022	.09	.248	.34
11.0	.029	.107	.23	
12.0	.043	.12	.219	

1* pH - 5.2
2* pH - 5.1
3* pH - 6.1
4* pH - 6.2
5* pH - 7.1

TABLE VI

Absorbance values for the evaluation of the Equilibrium constants in the Pb-PAR system at 500 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.022	.045	.067	.090
4.0	.019	.04	.061	.082
5.0	.043[1*]	.07[2*]	.092	.112
5.6	.054	.094	.12	.138
6.0	.088[3*]	.142[4*]	.176[3*]	.189
6.6	.118	.17	.225	.248
7.0	.141[5*]	.232[5*]	.278	.294
7.5	.153	.265	.314	.327
8.0	.165	.298	.33	.344
8.8	.165	.274	.312	.331
10.0	.168	.295	.334	.358
11.0	.172	.295	.35	.38
11.8	.146	.273	.365	.434

1* pH - 5.2

2* pH - 5.1

3* pH - 6.1

4* pH - 6.2

5* pH - 7.1

TABLE VII

Absorbance values for the evaluation of the equilibrium constants in the Pb-PAR system at 510 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.013	.026	.04	.053
4.0	.014	.031	.045	.06
5.0	.04[1*]	.066[2*]	.085	.10
5.6	.054	.094	.117	.131
6.0	.083[3*]	.147[4*]	.182	.19
6.5	.117	.178	.238	.257
7.0	.155[5*]	.246	.296	.308
7.5	.174	.282	.334	.348
8.0	.177	.318	.351	.365
9.0	.176	.294	.33	.35
10.0	.177	.306	.353	.368
11.0	.177	.30	.345	.386
12.0	.146	.273	.323	.42

1* pH - 5.2

2* pH - 5.1

3* pH - 6.1

4* pH - 6.2

5* pH - 7.1

TABLE VIII

Absorbance values for the evaluation of the equilibrium constants in the Pb-PAR system at 520 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.007	.014	.022	.029
4.0	.01	.022	.032	.042
5.0	.037	.060	.075	.088
5.6	.052	.087	.109	.121
6.0	.078[1*]	.144[2*]	.177	.19
6.5	.119	.176	.232	.253
7.0	.15	.245	.293	.306
7.5	.174	.281	.332	.345
8.0	.176	.315	.35	.364
9.0	.176	.291	.32	.345
10.0	.175	.31	.35	.361
11.0	.173	.308	.345	.365
12.0	.137	.253	.323	.38

[1*] pH - 6.1

[2*] pH - 6.2

TABLE IX

Absorbance values for the evaluation of the equilibrium constants in the Pb-PAR system for a M: L ratio 100: 1 .

Absorbance pH	400 nm	500 nm	510 nm	520 nm
3.0	.187	.067	.052	.041
3.5	.16	.097	.092	.082
4.05	.137	.129	.129	.121
4.5	.129	.141	.142	.136
5.0	.122	.153	.154	.148
5.7	.113	.18	.184	.178

TABLE X

Absorbance values for the evaluation of the equilibrium constants in the Zn-PAR system at 400 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.101	.202	.303	.403
4.0	.098	.197	.294	.391
4.5	.106	.213	.318[1*]	.423[1*]
5.0	.106	.213	.321	.428
5.5	.111	.225	.334	.452
6.2	.092	.199	.317	.43
6.7	.067	.158[2*]	.254	.382[3*]
7.0	.053	.122	.204	.305
7.5	.044	.085	.16	.249
8.0	.034	.065	.117	.201
9.0	.028	.06	.092	.164
10.0	.026	.056	.087	.168
11.0	.027	.058	.09	.162
12.0	.03	.061	.094	.139

1* pH - 4.6

2* pH - 6.5

3* pH - 6.6

TABLE XI

Absorbance values for the evaluation of the equilibrium constants in the Zn-PAR system at 500 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.022	.046	.069	.094
4.0	.019	.040	.061	.082
4.5	.026	.052	.078	.106
5.0	.034	.067	.097	.128
5.5	.053	.095	.128	.175
6.0	.103[1*]	.175[1*]	.323	-
6.5	.143[2*]	.244	.338[3*]	.385[4*]
7.0	.167	.308	.422	.517
7.5	.181	.363	.487	.603
8.0	.194	.385	.588	.72
9.0	.197	.39	.585	.718
10.0	.19	.388	.582	.715
11.0	.194	.39	.581	.718
12.0	.191	.387	.58	.756

1* pH - 6.2 3* pH - 6.65

2* pH - 6.7 4* pH - 6.6

TABLE XII

Absorbance values for the evaluation of the equilibrium constants in the Zn-PAR system at 510 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.013	.027	.041	.054
4.0	.014	.027	.043	.057
4.5	.021	.042	.062[1*]	.082[1*]
5.0	.028	.056	.082	.104
5.5	.046	.082	.108	.148
6.2	.089	.152	.199	.222
6.7	.123	.211[2*]	.29	.332[3*]
7.0	.146	.268	.368	.449
7.5	.154	.307	.412	.509
8.0	.171	.338	.481	.579
9.0	.174	.34	.501	.611
10.0	.165	.337	.501	.608
11.0	.172	.338	.50	.615
12.0	.168	.337	.50	.639

1* pH - 4.6

2* pH - 6.5

3* pH - 6.6

TABLE XIII

Absorbance values for the evaluation of the equilibrium constants in the Zn-PAR system at 520 nm.

Solution	1	2	3	4
pH	A	A	A	A
3.0	.005	.014	.022	.03
4.0	.008	.018	.027	.037
4.5	.015	.03	.045[1*]	.06[1*]
5.0	.023	.044	.063	.081
5.5	.035	.064	.086	.118
6.2	.062	.112	.15	.172
6.7	.088	.147[2*]	.209	.245[3*]
7.0	.096	.184	.262	.329
7.5	.10	.208	.292	.368
8.0	.108	.228	.338	.422
9.0	.116	.233	.359	.444
10.0	.124	.252	.374	.458
11.0	.128	.255	.377	.458
12.0	.132	.254	.373	.489

1* pH - 4.6

2* pH - 6.5

3* pH - 6.6

Appendix III

Data for the construction of the Distribution Diagram of lead as a function of pH.

The species to consider in water solutions (30) in addition to Pb^{++} are:

$PbOH^+$, $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$

$Pb(OH)_2$, $Pb(OH)_3^-$.

The species $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$ can be neglected at low concentrations of Pb^{++} as can be seen from the equilibrium constants reported by Olin (27). Therefore, the only species of interest are:

1) Pb^{++}
2) $PbOH^+$
3) $Pb(OH)_2$
4) $Pb(OH)_3^-$

The equilibria are:

1) $Pb^{++} + H_2O = PbOH^+ + H^+$ $\beta_{11} = 1.6 \times 10^{-8}$

$\log \beta_{11} = -7.8$

2) $Pb^{++} + 2\,OH^- = Pb(OH)_2$ $\beta_2 = 2.2 \times 10^{10}$

$\log \beta_2 = 10.34$

3) $Pb^{++} + 3\,OH^- = Pb(OH)_3^-$ $\qquad \beta_3 = 2. \times 10^{13}$

$\log \beta_3 = 13.29$

Let:

$$Pb_T = \left[Pb^{++}\right] + \left[PbOH^+\right] + \left[Pb(OH)_2\right] + \left[Pb(OH)_3^-\right]$$

$$1 = \frac{\left[Pb^{++}\right]}{Pb_T} + \frac{\left[PbOH^+\right]}{Pb_T} + \frac{\left[Pb(OH)_2\right]}{Pb_T} + \frac{\left[Pb(OH)_3^-\right]}{Pb_T}$$

$$1 = \alpha_o + \alpha_1 + \alpha_2 + \alpha_3$$

$$\frac{1}{\alpha_o} = 1 + \frac{\alpha_1}{\alpha_o} + \frac{\alpha_2}{\alpha_o} + \frac{\alpha_3}{\alpha_o}$$

$$\frac{1}{\alpha_o} = 1 + \frac{\beta_{11}}{\left[H^+\right]} + \beta_2(OH^-)^2 + \beta_3(OH)^3$$

$$\frac{1}{\alpha_o} = 1 + 1.6 \times 10^{6}\,(OH) + 2.2 \times 10^{10}\,(OH)^2$$

$$+ 2 \times 10^{13}\,(OH)^3$$

The values at different pH values are calculated and tabulated in Table I and in the graph Fig. 12 (page 90).

$$\alpha_0 = \frac{[Pb^{++}]}{[Pb]_T}$$

$$\alpha_1 = \frac{[PbOH^+]}{[Pb]_T}$$

$$\alpha_2 = \frac{[Pb(OH)_2]}{[Pb]_T}$$

$$\alpha_3 = \frac{[Pb(OH)_3^-]}{[Pb]_T}$$

TABLE I

Distribution values of lead species as a function of pH

pOH	pH	α_0	α_1	α_2	α_3
14.0	0	1.00	0	0	0
10.0	4.0	1.0	0	0	0
9.0	5.0	0.998	0.002	0	0
8.8	5.2	0.998	0.002	0	0
8.6	5.4	0.996	0.004	0	0
8.4	5.6	0.994	0.006	0	0
8.2	5.8	0.990	0.010	0	0
8.0	6.0	0.983	0.016	0	0
7.5	6.5	0.952	0.048	0	0
7.0	7.0	0.863	0.136	0	0
6.9	7.1	0.834	0.166	0	0
6.8	7.2	0.800	0.200	0	0
6.6	7.4	0.715	0.284	0.001	0
6.4	7.6	0.613	0.385	0.002	0
6.2	7.8	0.499	0.497	0.004	0
6.0	8.0	0.384	0.607	0.008	0
5.8	8.2	0.281	0.704	0.015	0
5.6	8.4	0.196	0.777	0.027	0
5.4	8.6	0.131	0.823	0.045	0
5.0	9.0	0.053	0.831	0.115	0.001
4.6	9.4	0.018	0.724	0.252	0.006

TABLE I (continued)

[a]pOH	pH	α_0	α_1	α_2	α_3
4.2	9.8	0.005	0.517	0.452	0.025
3.9	10.1	0.002	0.340	0.593	0.066
3.5	10.5	0	0.151	0.663	0.185
3.0	11.0	0	0.037	0.512	0.451
2.6	11.4	0	0.009	0.308	0.683
2.0	12.0	0	0.001	0.102	0.897
1.0	13.0	0	0	0.011	0.989

CLAIMS TO ORIGINAL RESEARCH

1) A new method has been developed for the quantitative analysis of mixtures of copper, lead, and zinc at trace level in aqueous solution.

2) Trace amounts of copper can be determined in the presence of large amounts of lead and zinc.

3) The following systems were studied as a function of pH:

Cu-PAR
Pb-PAR
Zn-PAR

and the equilibrium constants for the following reactions were evaluated:

$$Cu^{++} + H_3P^{+} = CuHP^{+} + 2\,H^{+}$$

$$Cu^{++} + H_2P = CuHP^{+} + H^{+}$$

$$CuHP^{+} = CuP + H^{+}$$

$$CuOH^{+} + HP^{-} = CuP$$

$$CuP + HP^{-} = CuP_2^{=} + H^{+}$$

$$CuP + P^{=} = CuP_2^{=}$$

$$Pb^{++} + H_2P = PbHP^{+} + H^{+}$$

$$PbHP^{+} = PbP + H^{+}$$

$$Pb^{++} + HP^{-} = PbP + H^{+}$$

$$Zn(OH)_2 + HP^{-} = ZnOHP^{-} + H_2O$$

$$ZnOHP^{-} + HP^{-} = ZnP_2^{=} + H_2O$$

SUGGESTIONS FOR FURTHER WORK

This has been an exploratory study to understand the behaviour of the metal-PAR systems in aqueous media as a function of pH. A further and more detailed study should be made to have a complete explanation of the system at every pH. It is suggested that:

1) More points be obtained with high accuracy for the pH-absorbance graphs, in order to be able to describe each system more exactly and more completely.

2) The behaviour of the system Zn-PAR in the pH range 5-7 be explained and the precipitate identified.

3) The equilibrium constants for the system Zn-PAR be evaluated for the reactions involved at pH values below 8.

4) The species be identified and the equilibrium constants evaluated for the Pb-PAR system at pH values above 8.

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