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SPECTRAL DATA FOR THE DETERMINATION OF DISSOCIATION

CONSTANTS OF ORGANIC NITROGENOUS BASES

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Ultraviolet spectroscopic methods for the determination of dissociation constants can only be applied to those compounds having protonatable sites conjugated with or inherent in a chromophoric group of the compound.

The determination of the dissociation constants of organic nitrogenous bases by ultraviolet spectroscopic methods was found to be only reliable for those compounds having a single protonatable site in or conjugated with the chromophoric group of the heterocycle.

With such compounds both methods, (I) those based on taking the extinction coefficient profile over the entire pH range at selected wavelengths, and (II) those based on a measurement of the pH at which the λ_{max} . value was approximately the average for the protonated and unprotonated forms at a selected wavelength, were in fair agreement with one another and with dissociation

constants determined by potentiometrics, conductometric and other methods.

With those compounds having two protonatable sites, both weakly basic, there was found to be approximately fair agreement between methods I and II and with those determined by other procedures, but not in all cases. Method II did not lend itself to the measurement of more than a single constant when several constants were present in a compound.

Those compounds having two protonatable sites, one weakly basic and the other weakly acidic, also gave approximately fair agreement between methods I, II and published data.

The amino acids likewise gave only fair approximations with methods I and II and those recorded in the literature.

With compounds having three or more protonatable sites in the chromophore there was poor agreement between methods I and II as well as with those determined by other procedures.

Method I was found to be capable of measuring several dissociation constants when more than one occurred with a given compound. Moreover, the most reliable information was obtained by taking the extinction coefficient profile over the entire pH range at 10 μ intervals over the entire ultraviolet spectra.

This was especially helpful for measuring dissociation constants which were of approximately the same order associated with a given chromophoric group.

Method I gave a number of dissociation constants for compounds having several protonatable sites within the chromophoric group for certain compounds which had not been measurable by other procedures. Included in these observations was evidence of the deprotonation of amino substituent in alkaline media in a fairly large number of instances.

A number of unreported dissociation constants of known compounds are herein documented.

A STUDY OF THE LIMITATIONS OF
ULTRAVIOLET SPECTRAL DATA FOR THE
DETERMINATION OF DISSOCIATION CONSTANTS
OF ORGANIC NITROGENOUS BASES

by

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A STUDY OF THE LIMITATIONS OF
ULTRAVIOLET SPECTRAL DATA FOR THE
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INTRODUCTION

Interest in the possibilities of employing ultraviolet spectral data as a means of determining dissociation constants of certain organic acids and bases stems from the early work of Stenström and Reinhard (36) who reported the influence of the pH upon the ultraviolet absorption spectra of certain cyclic compounds.

This approach appeared to be especially attractive due to the great sensitivity of organic compounds to ultraviolet radiation which would allow these determinations to be made at high dilution. This provides the only means of measuring dissociation constants for those fairly insoluble compounds which absorb energy in the ultraviolet and whose chromophores are either protonable or are conjugated with either acid and/or basic group.

In 1926 Stenström and Goldsmith (37) described a method for the determination of the dissociation constants of phenol and tyrosine based on observations of Stenström and Reinhard (36) using extinction data taken at a given wavelength in the ultraviolet over a span of pH values ranging from pH 4 to pH 13. The selection of the given wavelength for this determination was based on

ease with which the change in extinction coefficient with pH could be most readily followed.

Their procedure was based on the assumption that for certain compounds two forms of absorbing species existed, one in acidic medium, and the other in basic medium, each of which was capable of yielding its own absorption curve in the ultraviolet. Thus at a given wavelength there should be a significant difference between the extinction coefficients of the two structures taken at a fixed pH. It was also assumed that a mixture of two types of absorbing units coexisting at a given pH would have an extinction coefficient lying between those two values and that the relationship between them would be:

$$x(1-a) + ya = E$$

where a = fraction of tyrosine molecules ionized at the hydroxyl group

$1-a$ = fraction of tyrosine molecule not ionized at hydroxyl group

x = extinction coefficient of molecules not ionized at hydroxyl group

y = extinction coefficient of molecules ionized at hydroxyl group

E = extinction coefficient for a mixture of the two species

c = original concentration

K_a = dissociation constant

Since $\left[\text{H}^+\right] \times [\text{anion}] = K_a \times [\text{acid}]$
 $\left[\text{H}^+\right] \times ac = K_a \times c(1-a)$

Where $a = \frac{K_a}{\left[\text{H}^+\right] + K_a}$

and $E = x \left[\frac{\left[\text{H}^+\right]}{\left[\text{H}^+\right] + K_a} \right] + y \left[\frac{K_a}{\left[\text{H}^+\right] + K_a} \right]$

and $K_a = \frac{(E - x)}{(y - E)} \left[\text{H}^+ \right]$ eq. (1)

The dissociation constant could be calculated when x and y are known and the value of E lying between x and y has been determined for a certain pH.

To determine a value of K_a one constructs the entire curve showing relationship of pH and extinction coefficient at a selected and given wavelength.

For example, in the case of phenol (37) with measurements taken at wavelength 2825\AA one obtains the data shown in Table I. To calculate the dissociation constant, a point of the curve was used for which E was approximately the arithmetical mean of the highest value (y) and the lowest value (x) of the extinction coefficient.

$$x = 380, y = 2822, E = 1600, \text{pH} = 9.86$$

$$\text{Calculated value of } K_a = 1.38 \times 10^{-10}.$$

$$\text{p}K_a = 9.86$$

Table I. Phenol: Figure 1 $\lambda = 2825 \text{ \AA}$

pH	Extinction Coefficient	pH	Extinction Coefficient
4.5	380	9.95 to 9.8	1550
6 approx.	380	10.0 to 10.1	1830
7.5	435	10 \pm .05	2100 approx.
8.75	540	10.15 to 10.2	2125
8.9	610	10.2	2160
8.95 \pm .05	600	10.45	2465
9.25	790 approx.	11.	2630
9.3	690	11.7 \pm .05	2800
9.3	755	12.75	2822
9.5	1215	13	2970

In 1935 Flexser and co-workers (13) published a second procedure based on the use of ultraviolet spectroscopic data for the determination of dissociation constants of very weak bases having chromophoric groups.

The determination of dissociation constants by the first procedure had been based on observation of changes in the extinction coefficient at a selected wavelength caused by variations in pH of the solution. This new approach was based on data obtained by taking the spectral transmission curve in the ultraviolet of a 0.1 N acidic, a 0.1 N basic and in a buffered solution at an appropriate pH.

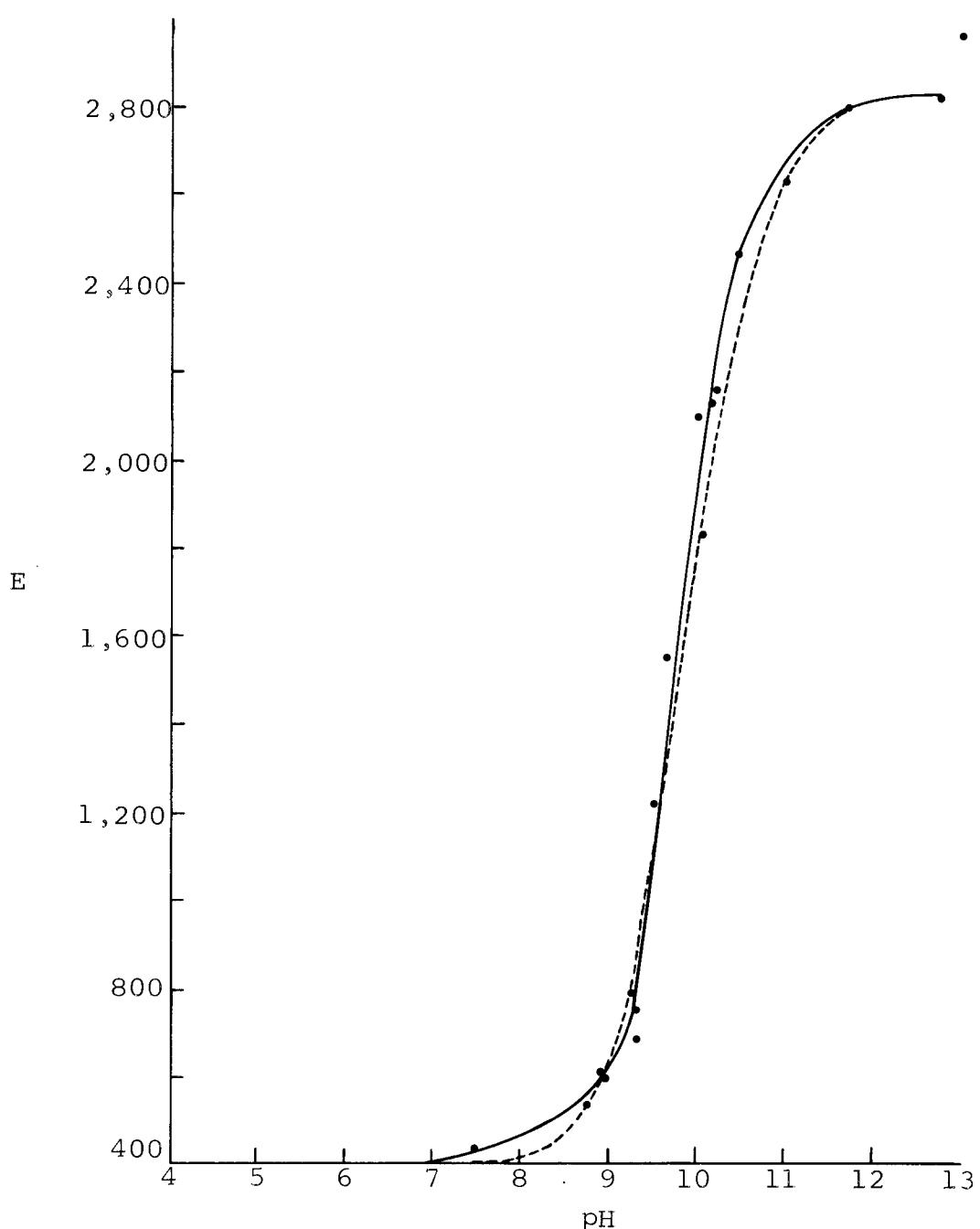


Figure 1. Dissociation of phenol by method of Stenström and Goldsmith (37).

Full curve experimental, broken curve theoretical. $\lambda = 2825 \text{ \AA}$

The calculation of acid or base strength was made as follows. The extinction coefficient k for a given wavelength was obtained by Beer's law.

$$k = -\log T/c l \quad \text{eq. (2)}$$

where T = absorbancy or optical density

l = length of cell (normally 1 cm. width)

c = concentration of the sample in mole/liter.

If a solute exists in two forms, say B and BH^+ , so that the total concentration c is equal to the sum of the concentrations of these two forms,

$$\text{therefore } c = c_B + c_{BH^+} \quad \text{eq. (3)}$$

and if, as seems generally to be the case, each substance absorbs independently of the presence of the other, then

$$-\log T = (k_B c_B + k_{BH^+} c_{BH^+}) l \quad \text{eq. (4)}$$

and it follows from equations (2), (3), and (4) that

$$(c_{BH^+})/(c_B) = (k - k_B)/(k_{BH^+} - k). \quad \text{eq. (5)}$$

In a dilute aqueous solution, k_B may be determined by reducing the acidity to the point where the concentration of BH^+ is vanishingly small; k_B similarly by increasing the acidity. Knowing these, a measurement of k in some solution of intermediate acidity permits the calculation of c_{BH^+}/c_B and from this, if the pH of the solution is known, of the dissociation constant of the base. The modifications of the above considerations, necessary if the dissociation constant of a weak acid HA which

ionizes to H^+ and A^- is to be measured, are obvious. In the measurement of the strengths of very weak bases in strong sulfuric acid solutions, certain complications arise from the fact that the change of acidity involves necessarily a significant change in the nature of the medium with a concomitant change in the absorption spectrum.

Measurements in Dilute Aqueous Solution

The Acid Strength of Benzoic Acid. The absorption of benzoic acid was determined in the following solvents: (1) 0.1 N. sulfuric acid; (2) a buffer containing 0.10 M. sodium acetate and 0.35 M. acetic acid (this solvent is transparent in most of the range of wavelengths available); (3) 0.1 M. sodium hydroxide. The results are plotted in Figure 2, and the extinction coefficients are given in Table II.

The logarithmic dissociation constant pK_a was calculated by the equation

$$pK_{HB} = pK_{HA} + \log c_{A^-}/c_{HA} - \log (k - k_{HB})/(k_{B^-} - k) \quad \text{eq. (6)}$$

derived from substitution of equation (5) in the equation

$$pK_{HB} = pK_{HA} + \log c_{A^-}/c_{HA} - \log c_{B^-}/c_{HB} \quad \text{eq. (7)}$$

which is an obvious combination and transformation of

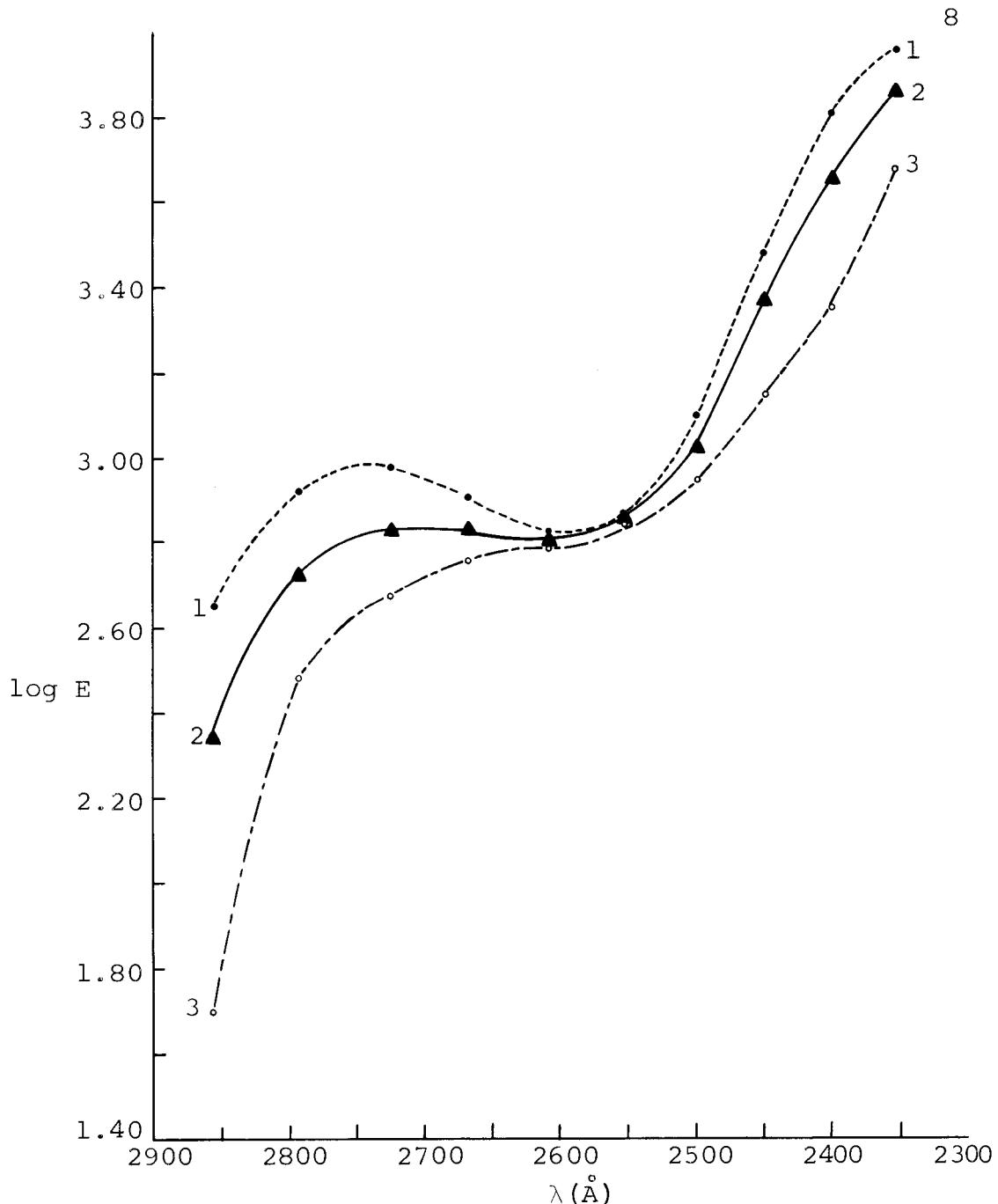


Figure 2. Dissociation of benzoic acid as an acid by method of Flexser *et al.* (13):
 Curve 1, 0.1N. H_2SO_4 ; curve 2, buffer;
 curve 3, 0.1N. NaOH .

Table II. Benzoic Acid.

Wave-length, Å	Extinction Coefficients in			pK_a
	0.1 N. H_2SO_4	0.1 M. NaOH	Buffer	
2857	450	50	225	4.11
2791	840	300	540	4.13
2727	950	475	680	4.10
2667	820	575	680	4.09
2609	675	620	640	-
2553	740	700	720	-
2500	1250	900	1050	4.09
2449	3050	1400	2350	4.35
2400	6450	2300	4500	4.27
2353	9200	4800	7200	4.30
Average 4.18				
± 0.09				

the equilibrium expressions for the dissociation of acetic and benzoic acids. The subscript A refers to acetate, and the subscript B to benzoate. For the calculations, values of k_{HB} were taken from curve 1, those of k_{B^-} from curve 3, and those of k from curve 2. The value of pK_{HA} was taken as 4.76. This equation assumes that the quantity $f_A f_{HB} / f_{HA} f_{B^-}$ is unchanged by a transfer from infinite dilution to an ionic strength of 0.1.

Within the precision of this assumption, therefore, the pK_{HB} obtained is the value in terms of activities referred to infinite dilution in water as the standard state

$$pK_{HB} = -\log a_{H^+} a_{B^-} / a_{HB} \quad . \quad \text{eq. (8)}$$

Table II gives the values of pK_a thus obtained at various wavelengths, omitting those in the neighborhood of the isobestic point, the point where all three curves meet. The average value of 4.16 thus obtained is in satisfactory agreement with the value of 4.20 found in the recent measurements by the conductivity method of Brockman and Kilpatrick (7) and of Saxton and Meier (33).

The conclusion of Flexser and co-workers (13) that ultraviolet colorimetry cannot be applied to the measurement of the dissociation of benzoic acid was apparently due to the limitations of their measurements. They did not determine the complete absorption spectra of benzoic acid but instead measured the wavelengths at which benzoic acid has an extinction coefficient of 800 ($\log k = 2.9$). They thereby determined three points of the curve for benzoate ion and three for molecular benzoic acid. Four of these six points happen to fall on the isobestic point where of course no change takes place. The other two points are not in agreement with our measurements.

The significant difference between the two methods is in the selection of the pH which is used in the determination of the dissociation constants.

Flexser et al. used a pH which would give the arithmetic mean of the extinction coefficient of the acidic and basic solutions. Stenström and Goldsmith used the pH at the inflection point of a curve obtained by plotting the pH versus the extinction coefficient.

The determination of a dissociation constant of a protonated chromophore of an organic compound depends upon securing accurate data (a) in regard to the extinction coefficients of the protonated and deprotonated species, and (b) the assumption that the absorption of a mixture of the two species are additive. With this information it is possible to calculate the ratio of two species knowing the extinction coefficients of the two forms and its mixture at a given wavelength together with the pH of the mixture of two species, provided these measurements are taken at a meaningful region of the spectra. In our work this method will be referred to as Method II.

In Figure 3 is an example of a typical illustration of spectral transmission curves of a simple protonated, deprotonated chromophore, together with a spectrum of a mixture of the two species.

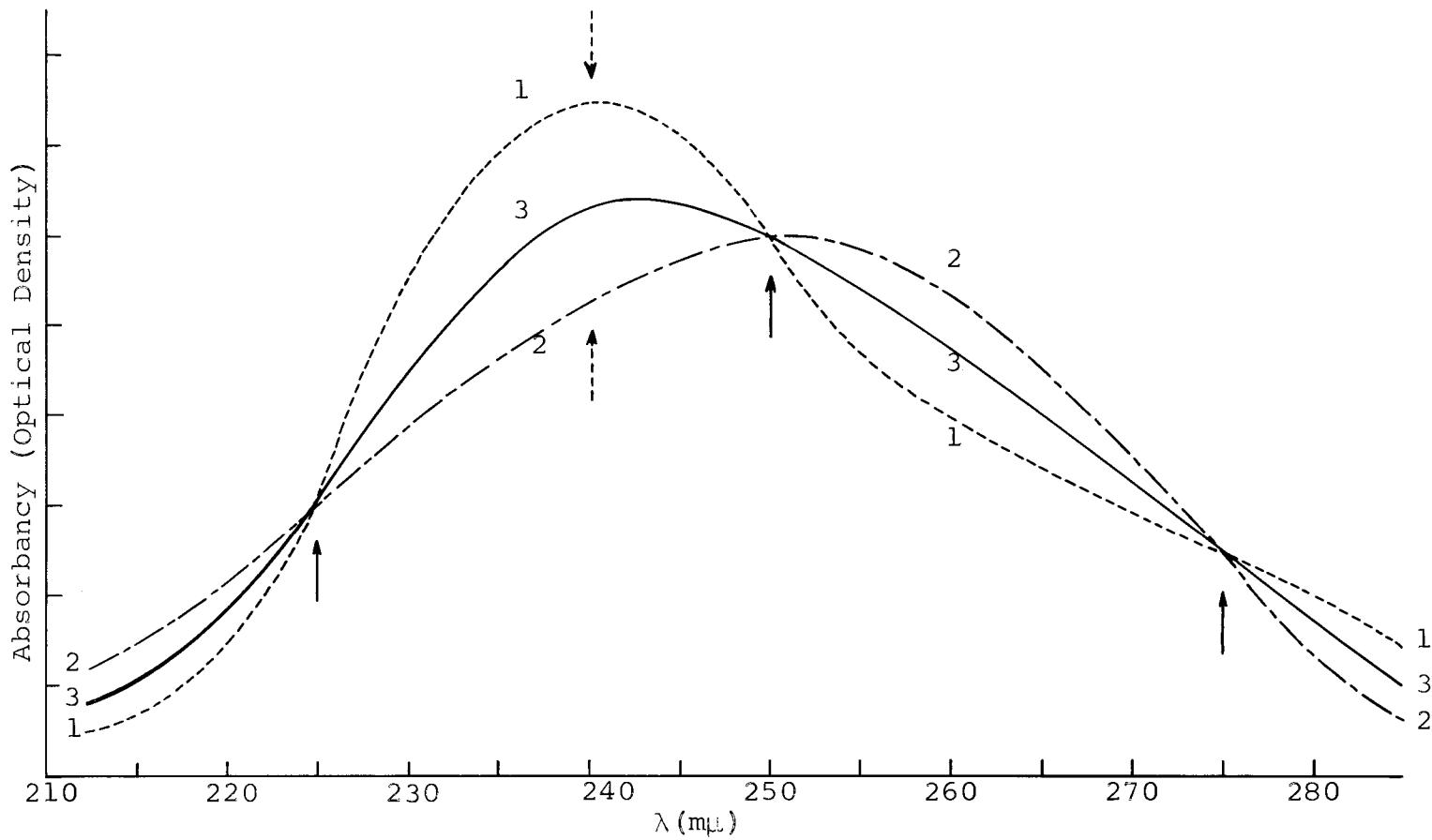


Figure 3. A Typical Spectral Transmission Curve.

- (1) a protonated or deprotonated chromophore
- (2) a deprotonated or protonated chromophore
- (3) a mixture of the two species

It is obvious that no determination of dissociation constants in this case (Figure 3) can be obtained with measurements taken at the isosbestic points or close proximity to wavelengths 225, 250, and 275 m μ . Furthermore, the data in region 250 to 275 m μ would not be very reliable due to the similarity in absorption characteristics of both species in this range.

At $\lambda_{\text{max.}}$ 240 m μ one finds the greatest deviation in extinction coefficients between the two species and consequently in the region 235-245 m μ one obtains the most accurate data for dissociation constant measurements.

On the other hand if one plots the extinction coefficients at wavelength 240 m μ (the most sensitive point of the spectra to pH changes) versus acidity over the entire pH range, one would obtain a curve (similar to potentiometric titration curve) with a typical inflection point. From this data one can calculate the dissociation constant of the compound. In our work this will be referred to as Method I.

If the compound plotted in Figure 3 had two reactive sites in its chromophoric group then one might obtain two inflection points indicative of two distinct dissociation constants.

However, if two dissociation constants should be indicated from the plot of pH versus extinction

coefficients it is evident that three distinct species of the molecule must have been involved as the pH changes from 0 to 14.

In this case the measurement of dissociation constant from extinction coefficients of the protonated, deprotonated, partially protonated at a given wavelength together with pH of the partially protonated form (Method II) would be suspect. It is possible that more than two species of the molecule could have been involved in absorbance measurements and hence calculations would only lead to approximate values for dissociation constants for compounds having more than a single reactive site in the chromophore.

When Method I is used in conjunction with Method II, it should be possible to obtain the highest degree of precision for a spectral method. For example, it is possible to determine the number of protonated and deprotonated forms of a given molecule that are responsible for the absorption at a given wavelength, using the technique of Method I. If results of such an investigation indicate that only two forms are responsible for the absorption at a given wavelength, and if the differences in the magnitude of the extinction coefficients of these forms are significant, then the technique of Method II should lead to the measurement of dissociation constants

with greatest precision. However, the data in Table IV does not substantiate this hypothesis; apparently the differences due to possible presence of a third molecular species, where so indicated, are so minimal as to be negligible in most cases.

In order to accurately determine the dissociation constants of compounds having chromophoric groups with two protonatable sites using Method II, it would be necessary to obtain the spectral transmission curve of the half protonated chromophore. If both sites are weakly acidic or strongly acidic, it would be difficult to distinguish between constants due to difficulty of obtaining the extinction coefficient of the half protonated form. However, if one site was weakly acidic and the other strongly basic (i.e., p-aminophenol), one should be able to secure more reliable measurements.

Another indication of the accuracy of these measurements is the magnitude of the differences in extinction coefficients taken at the most favorable region of the spectra. These differences will be indicated on the following tables of data.

One would assume from the work of Flexser that calculations of pK_a from ultraviolet data for compounds having several λ_{max} values in ultraviolet spectra of the protonated and unprotonated form would yield the

same values of pK_a as determined over the entire range of the usable spectra. This has never been established experimentally and furthermore should be questionable in the case of compounds having more than one reactive site in the chromophore.

The procedure of Stenström and Goldsmith, on the other hand, which was based on the measurement of changes in extinction coefficient at an easily followed wavelength over the entire pH range, should give a curve such as illustrated in Figure 1 for simple compound with a single reactive site. The behavior of compounds having more than one reactive site has not been investigated.

For these reasons a study of the limitations and other aspects of the use of ultraviolet absorption data for the determination of dissociation constants of organic bases was undertaken.

RESULTS AND DISCUSSION

Using these procedures, a group of simple organic acids and bases (having only one reactive site in the chromophore) were studied. The spectral transmission curves of both the protonated and deprotonated form were determined to ascertain the $\lambda_{\text{max.}}$ and their respective extinction coefficients. Having determined the $\lambda_{\text{max.}}$ values of both forms, the extinction coefficients were calculated and plotted over the entire pH range for each value of $\lambda_{\text{max.}}$. This gave an inflection point which in turn provided the pH used to calculate the dissociation constant as described for Method I.

For Method II the pH of the curve which gave approximately the arithmetical mean of the optical density of the protonated or deprotonated form, at a wavelength at which a significant difference in extinction coefficient values occurred (usually at $\lambda_{\text{max.}}$ value of either form), was used in the calculations of dissociation constants.

In Table III are tabulated the results of these studies.

In general there was very little change in $\lambda_{\text{max.}}$ values at pH's seven, thirteen and fourteen as would be expected for a moderately weak organic base. Moreover, the pH of the inflection points was the same for all wavelengths at $\lambda_{\text{max.}}$ values exhibited by the compound

Table III. λ_{max} , pH at Inflection Point and Isosbestic Point of Compounds in Group I (having one reactive site in the chromophore).

Compound	pH 1	pH 7	pH 13	pH 14	Inflection Point $\lambda_{\text{max.}}$	pH	Isosbestic Point
Acetanilide	238	238	238	238	238		0.20
Aniline	-	230	230	230	230		4.70
	-	280	280	280	280		4.70
Benzoic Acid	230	224	224	224	230		4.15
	273	270 sh	270 sh	270 sh	270		4.15
Diphenyl-amine	279	279	214 279	218 279	279		0.90
3-Indole-acetic Acid	217	219	219	219	219		13.10
	275	280	280	280			
Isoquinoline	226	215	215	218	215	5.30	222 241 307
N,N-Dimethyl-aniline	-	242.5	214	218	242.5		5.06
	-	285 sh	242.5 288 sh	242.5 288 sh			

Table III. (Continued)

Compound	pH 1	pH 7	pH 13	pH 14	Inflection Point $\lambda_{\text{max.}}$	pH	Isosbestic Point
p-Aminophenyl -	236	236	236	236	236	5.00	
Acetic Acid -	285	285	285	285	285	5.00	
Pyridine	250 sh	244 sh	244 sh	244 sh	249.5	5.00	
	255	250	249	249	255	5.10	
		255	255	255	262	5.15	
		262	262	262			
Quinoline	232	224	224	224	224	4.90	228
	312.5	228 sh	228	228 sh	232	4.80	243
		312.5	275	275	275	4.80	289
			312.5	312.5	312.5	4.80	

in both acid and basic media.

The extremely weak bases, diphenylamine and acetanilide, gave inflection points at the expected level. The graphical data for the determination of the inflection point of acetanilide was not clear-cut. There was considerable fluctuation in E value in ranging from pH 4 to pH 14. Since acetanilide should be an extremely weak base the inflection point at approximately pH 0.2 could be meaningful. The second inflection point at about pH 4 may be due to aniline resulting from hydrolysis of the amide.

Having established the pH of the inflection point, the dissociation constants were then calculated by Method I at wavelengths of the $\lambda_{\text{max.}}$ values in the acid and basic regions. Moreover, the pH of the solution whose spectral transmission curve gave an approximate mean value for extinction coefficient at the $\lambda_{\text{max.}}$ value either of the protonated or deprotonated form of the compounds, was used to calculate the dissociation constants by Method II.

The results of these studies are tabulated in Table IV.

In all cases there was reasonably good agreement between the pK_a values as determined by other methods and the ultraviolet spectral methods using either

Table IV. Comparison of pK_a of Compounds in Group I by Method I and Method II.

Compound	pK_a from literature	$\lambda_{max.}$	Method I				$\lambda_{max.}$	Method II	
			pH	pK_a	$pK_a - pH 7$	$pK_a - pH 13$			
Acetanilide	0.61(9)	238	1	7	13	14	0.16		
Aniline	4.58C(18)	230	-	7	13	14	4.62	230	4.77
	4.60C(32)	280	-	7	13	14	4.65	280	4.66
Benzoic Acid	4.18P(24)	224	-	7	13	14	-	225	4.23
	4.20C(7)	230	1	-	-	-	4.18	230	4.16
		270	1	7sh	13sh	14sh	4.26	270	4.28
Diphenyl-amine	0.85P(18)	218	-	-	13	14	-	220	1.33
		279	1	7	13	14	0.88	279	1.35
3-Indole-acetic Acid		219	1	7	13	14	13.12	219	4.11
		275	1	-	-	-	-	275	-
		280	-	7	13	14	-	280	-

Table IV. (Continued)

Compound	pK _a from literature	$\lambda_{\text{max.}}$	Method I					Method II		
			pH		pK _a	$\lambda_{\text{max.}}$	pK _a -pH 7	pK _a -pH 13		
Iso-quinoline	5.40P(30)	215 226	- 1	7 -	13 -	14 -	5.33 -	215 225	5.33 5.44	5.33 5.42
N,N-Dimethyl-aniline	5.06C(18)	214 242.5	- -	- 7	13 13	14 14	5.06 5.06	215 242.5	5.01 5.03	5.04 5.07
p-Amino-phenylacetic Acid		236 285	- -	7 7	13 13	14 14	5.00 5.03	236 285	5.04 5.03	5.05 5.04
Pyridine	5.16S(19) 5.16P(2) 5.23P(2)(15)	249.5 255 262	1 1 -	7 7 7	13 13 13	14 14 14	5.05 5.12 5.16	249.5 255 262	5.32 5.38 5.36	5.32 5.39 5.37
Quinoline	4.93S(3)	224 232 275 312.5	- 1 1 1	7 - 7 7	13 - 13 13	14 - 14 14	4.83 4.80 4.89 4.77	224 235 275 312.5	4.78 4.82 4.79 4.84	4.91 4.82 4.82 4.84

Method I or Method II. Furthermore, there is good agreement between (a) the pK values as determined at the different $\lambda_{\text{max.}}$ values of a given compound and (b) calculations using Method II based on species existing either at pH 7 and pH 13 (same specie).

The case of diphenylamine is one in which there is some deviation between the two methods. This compound would appear to have two absorption peaks so close to one another as to be unresolvable by the spectrometer. If this were the case the $\lambda_{\text{max.}}$ value that we would see would be proportioned somewhat differently (more blunt) than the usual absorption peak in the ultraviolet. This would lead less precise dissociation constant as calculated by Method II.

The dissociation constants of 3-indoleacetic acid as determined by Method I appear reasonable in contrast to the unlikely values obtained by Method II. However, the spectra in the region of 220 m μ was such as to make this determination questionable.

Compounds having two protonatable sites on the chromophore could exhibit two dissociation constants, the magnitude of which would be dependent on the acidity of the protonated function. Thus within a given chromophoric group there could exist both strong and weak acidic functions or a combination of both.

Method II, however, would not be capable of yielding both constants unless a given compound had more than one absorption peak each whose existence was dependent on a different dissociation constant, and provided it was possible to measure the distinction coefficient of the half protonated chromophoric group. Otherwise it will only give a single value which might be only an approximation for the dissociation constant. However, it may be possible to determine both dissociation constants using Method I. In the case of compounds having only strongly acidic functions (protonated form) the deprotonated form (weak base) would be expected to exhibit the same structure at pH 7 through pH 13.

If this were the case, the solutions should give the same absorption over this pH range if no other reactions occurred as a consequence of the basicity. To test this hypothesis the spectral transmission data in the range 210 to 320 m μ of a number of nitrogenous bases having two weakly basic functions (protonated function would be strongly acidic) were obtained in which the pH varied from one to fourteen. The results of these studies are tabulated in Tables V and VI.

It is apparent from Table VI that practically all the compounds having two reactive weakly basic functions remain unaltered in aqueous solution as judged by λ_{max} .

Table V. $\lambda_{\text{max.}}$, pH at Inflection Point and Isosbestic Point of Compounds in Group II (having two similar reactive sites in the chromophore).

Compound	pH 1	pH 7	pH 13	pH 14	Inflection Point		Isosbestic Point
					$\lambda_{\text{max.}}$	pH	
5-Acetyl-2,4-Dimethyl-pyrimidine(16)	223 252sh	233.5	233.5	234	223 233.5	13.50 1.70	253
2-Aminopyridine	228 299	228 289	228 287	228 287	228 287	6.70 6.70	280 284
Benzamidine Hydrochloride	228	228	228	228	228	11.30	245 270
Hydrazobenzene	245 318b	239 290b 318b	213 239sh 318b	318b	213 239 245 290 318	0.90 2.30 1.65 1.80 8.75	245 8.88 8.40 8.80 13.10
4-Methyl-pyrimidine(14)	244	242	242	242	242 244	2.30 2.35	267.5

Table V. (Continued)

Compound	pH 1	pH 7	pH 13	pH 14	Inflection Point		Isosbestic Point
					$\lambda_{\text{max.}}$	pH	
m-Phenylene-diamine Dihydrochloride	240b	210	212	219	210	4.80	13.00
	-	240sh	235sh	235sh	235sh	2.25	4.90
	-	290	290	290	240	2.25	4.90
					290	2.20	4.85
o-Phenylene-diamine	230	206	213	218	230	0.75	4.25
	280	230sh	230sh	238sh	290	0.75	4.20
		290	290	290			
p-Phenylene-diamine	240	240	213	218	240	2.68	6.10
		305	240	240	305	2.60	5.80
			305	305			
Phenylhydrazine	221	230sh	230	230	230	6.20	
	270	274	270sh	285sh	274	5.30	7.50 10.50 13.10
Phthalic Acid	203	225sh	216	220	216	2.85	5.30
	229	275sm	275sm	275sm	229	2.85	5.30
	275sm				275	3.00	5.20
Pyrimidine(14)	242	242	242	242	242	1.40	266

Table VI. Comparison of pK_a of Compounds in Group II by Method I and Method II.

Compound	pK_a from literature	$\lambda_{max.}$	Method I				Method II		
			pH	pK_{a1}	pK_{a2}	pK_{a3}	$pK_a - pH$	7	$pK_a - pH$
5-Acetyl-2,4-dimethyl-pyrimidine(16)		223 233.5	1 -	- 7 13 14	- 1.56	13.48 13.68		1.75	1.72
2-Amino-pyridine	6.86P(2)(6)	228 287	1 -	7 13 7 13	14 -	6.62 6.76		6.51	-
Benzamidine hydrochloride	11.60P(2) 11.60S(29)	228	1	7 13 - -	14	11.32		-	11.27
Hydrazo-benzene		213 239 245 290 318	- - 1 - 1	- 7 - - -	13 - - 1.70 -	0.93 2.30 8.37 8.75 8.80	8.87 13.15	1.72 - - 1.75 -	1.60 - - 1.86 -
4-Methylpyrimidine(14)	1.98P(2)	242 244	- 1	7 -	13 - -	14 - -	2.24 2.30	2.13 2.10	2.14 2.09

Table VI. (Continued)

Compound	pK_a from literature	$\lambda_{max.}$	Method I				Method II			
			pH			pK_{a1}	pK_{a2}	pK_{a3}	pK_a -pH 7	pK_a -pH 13
m-Phenylene-	4.88C(26)	210	-	7	-	-	4.80	12.97	-	-
diamine	2.50C(32)	235	-	-	13sh	14sh	2.20	4.92	2.19	2.21
Dihydro-	5.20C(32)	240	1b	7sh	-	-	2.24	4.86	2.28	2.29
chloride		290	-	7	13	14	2.20	4.85	2.64	2.64
o-Phenylene-	4.37 (9)	230	1	7sh	13sh	14sh	0.65	4.45	13.63	-
diamine	4.47C(26)	290	1	7	13	14	0.65	4.26	4.50	4.40
p-Phenylene-	2.54 (9)	240	1	7	13	14	2.62	6.10	5.87	-
diamine	6.04 (9)	305	-	7	13	14	2.60	5.62	5.87	6.06
	6.08C(26)									
Phenyl-	5.21(9)	230	-	7sh	13	14	6.20		-	-
hydrazine		274	-	7	-	-	5.30	10.50	13.10	-
							7.50			-
Phthalic	2.95T(25)	216	-	-	13	-	2.84	5.22	12.23	-
Acid	5.41T(25)	229	1	-	-	-	3.00	5.39		4.99
		275	1	7	13	14	3.00	5.40	5.23	5.12
Pyrimidine	1.30P(2)	242	1	7	13	14	1.43		1.58	1.60
(14)										

and E values as the pH of the solutions varied from seven to fourteen. It is interesting to note the presence of a λ_{max} , which cannot be assigned to either the completely protonated or deprotonated chromophoric group. This must be due to the presence of the third species (half protonated form).

The spectral transmission curve of o-phenylenediamine at wavelength 205 m μ (pH 7), phthalic acid at wavelength 212 m μ (pH 5.48), hydrazobenzene at wavelength 260 m μ (pH 1.8), and p-phenylenediamine at wavelength 233 m μ (pH 6.95) are illustrations of the effect of the absorbance of the intermediate form.

In general those compounds whose chromophores have two weakly basic active sites yield dissociation constants by Method II, which are in approximate agreement with one of the values obtained by Method I or with literature data despite having no information on the extinction coefficient of the half protonated compound. This may be due to the fact that one of the protonated forms is so acidic that the extinction coefficient at pH 1 is a close approximation of that half protonated chromophore.

In the case of nitrogenous bases Method II will yield the dissociation constant of the more acidic form of the protonated base if the value does not fall below a pK_a of one.

The only exception to this expected behavior (same $\lambda_{\text{max.}}$ and E values at pH 7 and 13) was that of the compound hydrazobenzene in which the weakly basic functions are adjacent to one another. It is apparent that the structure of hydrazobenzene in dilute aqueous solution of pH 7 is not the same as that of pH 13 which in turn is different from that of pH 1.

One must conclude that the spectral transmission curve obtained at pH 1 represents the protonated form, that at pH 13 the deprotonated form and that at pH 4 - 6 the composite of both forms (protonated and half-protonated). Protonated hydrazobenzene therefore behaves as a relatively strong acid having at least one highly acidic (protonated) function.

In order to confirm this hypothesis the experiments were undertaken with phthalic acid. In this case, as would be expected, the structure of phthalic acid in dilute aqueous solution of pH 7 was not the same as that of pH 13; moreover, the structure in dilute aqueous solution pH 1 was not the same as that of pH 13. The relative changes in structure of these two compounds with pH were very much alike.

The agreement of values of dissociation constants as obtained from ultraviolet spectral data for compounds having two protonable sites is not as consistent as those

having a single protonatable site group. Moreover, there are more extended regions where pK values cannot be obtained by Method II. It is interesting to note that optical density of the compounds of Tables IV and VI (having two reactive sites in their chromophores) was approximately one-half the value of those having only a single reactive site in the chromophore. Consequently, the data in Table VI was the less accurate of the two.

Only a few of the compounds (pyrimidine and 4-methyl-pyrimidine) gave dissociation constants by both Methods I and II at all $\lambda_{\text{max.}}$ values which were in only approximate agreement with the literature values.

2-Aminopyridine gave dissociation constants by both Methods I and II which agree approximately with literature value but not for all $\lambda_{\text{max.}}$ values. The dissociation constant was not calculated by Method II at $\lambda_{\text{max.}}$ 228 due to small differences in extinction coefficient values.

p-Phenylenediamine gave two dissociation constants by Method I which were in fair agreement with literature or with one another. At one wavelength (305 m μ) agreement was obtained with the literature values by Method II, while at the other wavelength (240 m μ) the dissociation constant was not calculable at pH 13.

o-Phenylenediamine gave constants by both procedures

which were in fair agreement with literature value.

However, Method I yielded two other constants, one of which (pK 13.63) must be due to other factors.

m-Phenylenediamine gave three different dissociation constants by Method I, one of which was in agreement with dissociation constant reported earlier. The second constant was in approximate agreement with that obtained by Method I. The third constant must arise from structural changes due to other considerations.

Hydrazobenzene gave four dissociation constants as determined by Method I, with poor agreement between two constants measured at different wavelengths. Good agreement was obtained between values at λ_{max} . 290 m μ and Method II.

5-Acetyl-2,4-dimethylpyrimidine, however, gave only rough agreement between values obtained by Methods I and II.

The phthalic acid experiments indicated fair agreement between literature values and Method I values. The values yielded by Method II at wavelength 229 m μ were rather poor. The other constant (pK_a 12.23) yielded by Method I must be due to other factors.

Benzamidine hydrochloride gave a fair agreement with the literature value by both methods. The difficulty is that the pH meter can be used up to pH 11 only, in order

to adjust the intermediate pH for Method II.

Phenylhydrazine gave only one value by Method I that agreed with that from literature data. The reasons for other higher values were unknown.

A number of bifunctional compounds in which (a) the acid or basic site was inherent in the chromophore or conjugated with it, and (b) both acidic and basic functions were involved in the given chromatophoric system, were examined.

The results of these studies are tabulated in Tables VII and VIII.

The results of those experiments employing Method I gave anywhere from one to three dissociation constants (where two were expected). The agreement between constants obtained at one $\lambda_{\text{max.}}$ with that of another $\lambda_{\text{max.}}$ of a given compound in general was reasonably good.

Sulfanilic acid gave only one dissociation constant, that for the amino function, which was in good agreement with the literature. The dissociation constant for the sulfonic acid moiety was not obtainable (as expected).

In the initial work p-aminobenzoic acid gave only what appeared to be one dissociation constant, in which the values determined at two different wavelengths ($\lambda_{\text{max.}}$ values) were only in approximate agreement. This may be due to the superimposing of one inflection point

Table VII. $\lambda_{\text{max.}}$, pH of Inflection Point and Isosbestic Point of Compounds in Group III (having two different reactive sites in the chromophore).

Compound	pH 1	pH 7	pH 13	pH 14	Inflection Point		Isosbestic Point	
					$\lambda_{\text{max.}}$	pH		
p-Amino- benzoic Acid	225	265	215	218	215	2.90	13.10	
	275b		265	265	225	2.10		
					235	2.30		
					245			
					255	2.30		
					265	2.20		
					275	2.30		
					285	2.30		
					295	2.25		
					305	2.25		
					315	2.25	4.90	
m-Amino- phenol	215	231sh	213	218	231	4.25	9.85	13.35
	270	281	235sh	235sh	281	4.25		260
			290	290				275
o-Amino- phenol	210	228	213	218	228	4.55	9.20	13.60
	270	281	240	240sh	281	4.50		255
			295	295				272
p-Amino- phenol	218	231	212	220	231	5.45	9.70	13.05
	270	296	240	240sh	296	5.40	9.60	222
			312	312				280

Table VII. (Continued)

Compound	pH 1	pH 7	pH 13	pH 14	Inflection Point		Isosbestic Point	
	$\lambda_{\text{max.}}$	pH						
Anthra- nilic Acid	226	240	216	220	216	2.05	4.65	12.85
	270sh	310	240	240	220	2.00	5.00	13.00
			310	310	226	3.10	5.50	12.85
					240	2.05	4.90	
					310	2.10	4.90	
Nicotinic Acid	212.5	212.5	220	220	212.5	4.60	12.30	247
	255sh	255	255sh	255sh	220	4.80	12.30	270
	260	262	262	262	255	4.65		
	265	269	269	269	260	4.80		
					262	4.80		
					269	4.90		
Sulpha- nilic Acid	212.5	247.5	247.5	247.5	247.5	3.20		211
	250b							223

Table VIII. Comparison of pK_a of Compound in Group III (having two different reactive sites in the chromophore) by Method I and Method II.

Compound	pK_a from literature	$\lambda_{max.}$	Method I				Method II		
			pH	pK_a	$pK_a - pH$	$pK_a - pH$	7	13	
			13	-	13.08	2.96	-	-	
p-Amino- benzoic Acid	2.29S(27)	215	-	-	2.90	-	13.08	2.96	-
	4.86S(27)	225	1	-	2.13	4.38		3.06	3.10
		235	-	-	2.30	4.65		-	-
		245	-	-		4.56		-	-
		255	-	-	2.32	4.77		-	-
		265	-	7	2.21	4.50		2.92	2.92
		275	1b	-	2.29	5.00		-	-
		285	-	-	2.31	4.99		-	-
		295	-	-	2.25	4.85		-	-
		305	-	-	2.26	4.86		-	-
		315	-	-	2.25	4.92		-	-
m-Amino- phenol	4.17C(26)	231	-	7sh	4.23	9.82	13.41	4.26	4.46
	9.87C(26)	281	-	7	4.27			-	-
o-Amino- phenol	4.72C(26)	228	-	7	4.50	9.28	13.78	4.46	4.43
	9.71C(26)	281	-	7	4.42			4.51	4.41
p-Amino- phenol	5.50C(26)	231	-	7	5.42	9.70	13.00	5.45	5.54
	10.30C(26)	296	-	7	5.38	9.57		-	-

Table VIII. (Continued)

Compound	pK _a from literature	$\lambda_{\text{max.}}$	Method I						Method II		
			pH						pK _a -pH 7	pK _a -pH 13	
Anthra- nilic Acid	2.05T(25)	216	-	-	13	-	2.04	4.63	12.85	-	-
	4.95T(25)	220	-	-	-	14	1.99	4.96	12.97	-	-
	6.46C(22)	226	1	-	-	-	3.04	5.58	12.85	-	-
	2.14S(27)	240	-	7	13	14	2.05	4.87		4.70	4.76
	4.80S(27)	310	-	7	13	14	2.10	4.90		4.55	4.59
Nicotinic Acid	2.07P(17)	212.5	1	7	-	-	4.49	12.22		4.65	-
	4.81P(17)	220	-	-	13	14	4.74	12.30		4.95	-
	2.09S(20)	255	lsh	7	13sh	14sh	4.71			4.73	4.79
	4.78S(20)	260	1	-	-	-	4.92			4.70	4.73
	2.09S(12)	262	-	7	13	14	4.83			4.82	4.84
	4.75S(12)	269	-	7	13	14	4.80			-	-
Sulpha- nilic Acid	3.23C(28)	247.5	-	7	13	14	3.17			3.13	3.13

on another in the cases where dissociation constants were of approximately the same magnitude.

For this reason the relationship of pH versus extinction coefficients were determined at 10 m μ intervals over the range 215 to 315 m μ . A plot of this data was much more informative, showing that indeed there were two dissociation constants of approximately the same magnitude, as well as a third dissociation of a very weakly acidic function.

All three of the aminophenols gave three dissociation constants by Method I, as determined using one of the wavelengths of λ_{max} . at pH 7, while the other wavelength of the second λ_{max} . value at pH 7 provided only one or two dissociation constants which were in good agreement with those obtained at the other λ_{max} . value. The reason for a third dissociation constant is not known.

Since Method II is only capable of yielding one dissociation constant value, in contrast to Method I, it was interesting to note that the dissociation value obtained by two methods were in approximate agreement. Moreover, this agreement of Method II values could involve either the higher or lower value obtained from Method I, depending upon the compound in question.

Certain amino acids having protonatable chromophores

were examined by Methods I and II, inasmuch as this was one method by which it might be possible to determine their respective dissociation constants. The results of these studies are tabulated in Tables IX and X.

Since spectral procedures can only determine dissociation constants which are an integral part of chromophoric groups or conjugated with it, only certain amino acids would be responsive to this procedure. Thus, one may determine the dissociation constant of phenolic group of tyrosine or protonated amino ring nitrogen of tryptophane or histidine.

Using Method I, dissociation constants were obtained for the chromophoric groups which are only in approximate agreement in the case of tyrosine, although in somewhat better agreement in the case of L-histidine with literature values. In both instances other apparent constants were indicated which are unexplainable.

The data from Method II yielded values which were either indeterminate or in reasonably good agreement with literature. Although p-hydroxyphenoxyacetic acid is not an amino acid, the dissociation of the phenolic group should behave similarly to that of tyrosine. Determinations employing Method I, however, give two constants at two $\lambda_{\text{max.}}$ values which are not in very good agreement. Furthermore, it is difficult to explain the constant

Table IX. $\lambda_{\text{max.}}$, pH at Inflection Point and Isosbestic Point of Compounds in Group IV (Amino Acids and p-Hydroxyphenoxyacetic Acid).

Compound	$\lambda_{\text{max.}}$				Inflection Point		Isosbestic Point	
	pH 1	pH 7	pH 13	pH 14	$\lambda_{\text{max.}}$	pH		
l-Histidine	210	210sh	215	218	210 215	9.85 5.60	13.00 9.40	
							13.20	
p-Hydroxy-	222	222	235	235	222 235 285 287	3.10 3.10 3.10 2.80	10.30 10.30 10.40 10.50	12.75
phenoxy-	285	287	305	305				262
acetic								294
Acid								
dl-Tryptophane	217 278	218 278	221 278	221 278	218 221 278	2.70 3.05 undeterminable	11.90 13.10	280
l-Tyrosine	222.5 274	222.5 274	240 292	240 292	222.5 240 274 292	9.60 9.75 undeterminable 9.80	13.40	

Table X. Comparison of pK_a of Compounds in Group IV by Method I
and Method II.

Compound	pK _a from literature	$\lambda_{\text{max.}}$	Method I					Method II pK _a -pH 13	
			pH			pK _a			
L-Histidine	6.06, 9.41T(35)	210	1	7sh	-	-	9.85	13.02	-
	5.85, 9.45T(21)	215	-	-	13	-	5.60	9.33 13.16	-
p-Hydroxy-phenoxy-acetic Acid		222	1	7	-	-	3.13	10.30	12.75
		235	-	-	13	14	3.15	10.29	10.24
		285	1	-	-	-		10.38	10.41
		287	-	7	-	-	2.92	10.43	10.42
		305	-	-	13	14	3.22	10.28	10.24
dl-Tryptophane	9.39, 11.62P(34)	218	-	7	-	-	2.65	11.88	-
		221	-	-	13	14	3.08		-
		278	1	7	13	14	undeterminable		9.31
L-Tyrosine	9.56, 10.07S(38)	222.5	1	7	-	-	9.65	13.33	-
	10.05S(4)	240	-	-	13	14	9.73		10.07
	9.15, 10.15P(10)	274	1	7	-	-	undeterminable		-
	11.77, 12.40P(23)	292	-	-	13	14	9.74		9.84

around 3.20, 2.90 which is unreasonable.

Method II, however, gives a series of values based on the extinction coefficient of structure existing in aqueous solution at pH 7 which are in approximate agreement with those of the more acidic constants obtained by Method I, while those based on structures existing at pH 13 are incalculable.

It is interesting to note that dissociation constants for these compounds as determined by Method II were frequently incalculable or unreasonable. Moreover, much better agreement was obtained in those cases where calculations were based on the extinction coefficient of the structure existing at pH 7.

Anthranilic acid behaved in much the same manner as p-aminobenzoic acid in that it had a similar pH profile (pH versus extinction coefficient) at various wavelengths which indicated the presence of two dissociation constants in close proximity to one another. However, it also gave a third constant which might arise from the deprotonation of the amino substituent.

Nicotinic acid gave two dissociation constants, one of which was in approximate agreement with published data, the other so low as to be suspect.

p-Hydroxyphenoxyacetic acid gave three constants. The first constant was of such a magnitude as to imply

that dissociation of the carboxyl function was capable of altering the chromophoric group, thus making it possible to measure the dissociation constant using spectroscopic methods. The second constant gave a reasonable value for phenolic hydrogen. The third constant can only be accounted for on the possible deprotonation of the methylene moiety of the acetic acid.

Finally, compounds having three or more active sites associated with their chromophoric groups were examined. The results of these studies are tabulated in Tables XI and XII.

In general the agreement between dissociation constants reported for other methods were not in good agreement with values found in these studies.

4,5,6 Triaminopyrimidine, which has five protonatable sites associated with its chromophore, gave three constants by Method I. One of the constants (pK_a 13.4) must have resulted from the dissociation of the amino substituent.

Both 2-amino-4-methylpyrimidine and 2-amino-4,6-dimethylpyrimidine gave dissociation constants which must have been the consequence of deprotonation of the amino substituent. It is interesting to note the effect of a methyl substituent on the magnitude of the dissociation constants.

Table XI. $\lambda_{\text{max.}}$, pH at Inflection Point and Isosbestic Point of Compounds in Group V (having three or more reactive sites in the chromophore).

Compound	$\lambda_{\text{max.}}$				Inflection Point			Isosbestic Point
	pH 1	pH 7	pH 13	pH 14	$\lambda_{\text{max.}}$	pH		
2-Amino-4,6-Dichloro-pyrimidine (8)	207 232	232 297.5	232 297.5	232sh 297.5	232 297.5	0.96 0.40	13.50	248 280
2-Amino-4,6-Dimethyl-pyrimidine (11)	222 295	225 286	225 286	218 286	218 222 225 286 295	4.25 4.20 4.60 4.30 4.20	12.60 13.55 13.50	227 284
2-Amino-4-Methyl-pyrimidine (5)	222 299	224 288	224 288	218 288	218 288 299	3.60 - 3.50	13.80	290
4,5,6-Tri-aminopyrimidine (31)	216 267b	210 277	215 277	215 277	210 215 277	0.85 0.85 0.85	5.65 5.70 13.25 13.40	221 226

Table XII. Comparison of pK_a of Compounds in Group V by Method I and Method II.

Compound	pK_a from literature	$\lambda_{max.}$	pH	Method I			Method II	
						pK_a	$pK_a - pH_7$	$pK_a - pH_{13}$
2-Amino-4,6-Dichloro-pyrimidine (8)	232	1 7 13 14sh	0.92	13.50	-	-		
	297.5	- 7 13 14	0.57		-	-		
2-Amino-4,6-Dimethyl-pyrimidine (11)	4.85P(2)	218	- - - 14	4.18	12.60	3.96	-	
		222	1 - - -	4.28	13.57	3.89	-	
		225	- 7 13 -	4.30	13.52	3.82	-	
		286	- 7 13 14	4.48		3.95	-	
		295	1 - - -	4.20		3.87	3.90	
2-Amino-4-Methyl-pyrimidine (5)	4.15P(2)	224	- 7 13 -	3.47	13.85	3.31	3.76	
		288	- 7 13 14	undeterminable		3.32	3.32	
		299	1 - - -	3.45		3.62	3.62	
4,5,6-Tri-amino-pyrimidine (31)	1.47S(29)	210	- 7 - -	0.88	5.66	13.27	5.69	-
	5.78S(29)	215	- - 13 14	0.87	5.66	13.39	5.93	-
		277	- 7 13 14	0.87		-	-	

2-Amino-4,6-dichloropyrimidine gave essentially the same spectral transmission curve over the entire pH spectrum. This no doubt accounts for the poor precision for dissociation constants determined at two different wavelengths.

EXPERIMENTAL

Preparation of Samples

All chemical reagents used in this investigation were reagent grade. The stock solution, in each case, was prepared using either distilled water or 95% ethanol, depending on the solubility of the compound under investigation. However, the aqueous stock solutions were preferable. The concentration of the stock solution ranged from 0.05×10^{-5} to 0.5×10^{-5} mole/ml. in order to avoid error in weighing. If the stock solution was unstable a new one was prepared daily.

The working solution was pipetted out from the stock solution into 100 ml. volumetric flask, using volumetric pipette, then diluted with distilled water and adjusted to the desired pH with hydrochloric acid or sodium hydroxide solution of suitable concentration to avoid dilution of the sample. From pH 0 to 2 and pH 11.5 to 14, either the hydrochloric acid or sodium hydroxide solution of known normality was used in dilution, instead of water.

In the case of benzoic acid, each working solution for Method II was prepared independently in 1000 ml. volumetric flask with the concentration about 10 mg. per liter.

Determination of pH

The pH of the working solution was determined before and after the spectrum was taken, using a Beckman Zero-matic pH meter, model 9600, with glass and calomel electrodes. Accuracy is 0.1 pH and reproducibility 0.02 pH. The original and final pH of each working solution were determined at about ten minute intervals. The reported pH was the average of the above.

Determination of Spectra

The ultraviolet absorption spectra of the compound being investigated were taken with a Cary 15 spectrophotometer and recorded on the chart paper. The instrument was set for sensitivity at 4 and dynode voltage at 2 all through the course of study. Chart gears were No. 7 and 8, which corresponded to 5 m μ per chart division. Matched silica cells No. 1242 (1 cm. width) with polystyrene cell-covers were used. The temperature was maintained between 20°-25°C.

Scanning from 320 m μ to 200 m μ was done in most cases; except when the base line was too high, scanning from 360 m μ to 200 m μ was made instead. It took about two minutes to scan each sample.

For Method I, spectra of the compound were recorded at various pH from 0 to 14, with about 0.5 pH scale

interval. On the other hand, spectra of the compound at pH 1, 7, and 13 were taken for Method II. Besides, the spectrum (of the intermediate pH) which lay between those of pH 1 and 7 and 13 or between 1 and 13 were also recorded.

In the case of benzoic acid and pyridine, the intermediate pH values were obtained by adding half equivalent of sodium hydroxide or hydrochloric acid solution respectively. All others were by adjustment to the desired intermediate pH (which corresponded to the pH of the inflection point yielded from Method I).

Table XIII. Dissociation Constants of Acetanilide
by Method I.

No.	pH	E at 238 m μ
1	0.00	10516
1A	0.25	10699
2	0.65	10760
3	1.25	10760
4	1.98	10760
5	2.85	10729
6	3.58	10729
7	4.30	10881
8	5.06	10851
9	5.60	10942
10	6.24	10912
11	7.00	10851
12	7.45	10790
13	7.98	10912
14	8.44	10760
15	8.82	10851
16	9.44	10790
17	9.91	10820
18	10.47	10760
19	11.00	10912
20	11.50	10881
21	12.00	10912
22	12.50	10912
23	13.00	10973
24	13.50	10851
25	14.00	10881

$$\lambda = 238 \text{ m}\mu, \quad x = 10520, \quad E = 10650$$

$$y = 10770, \quad \text{pH} = 0.20, \quad \text{pK}_a = 0.16$$

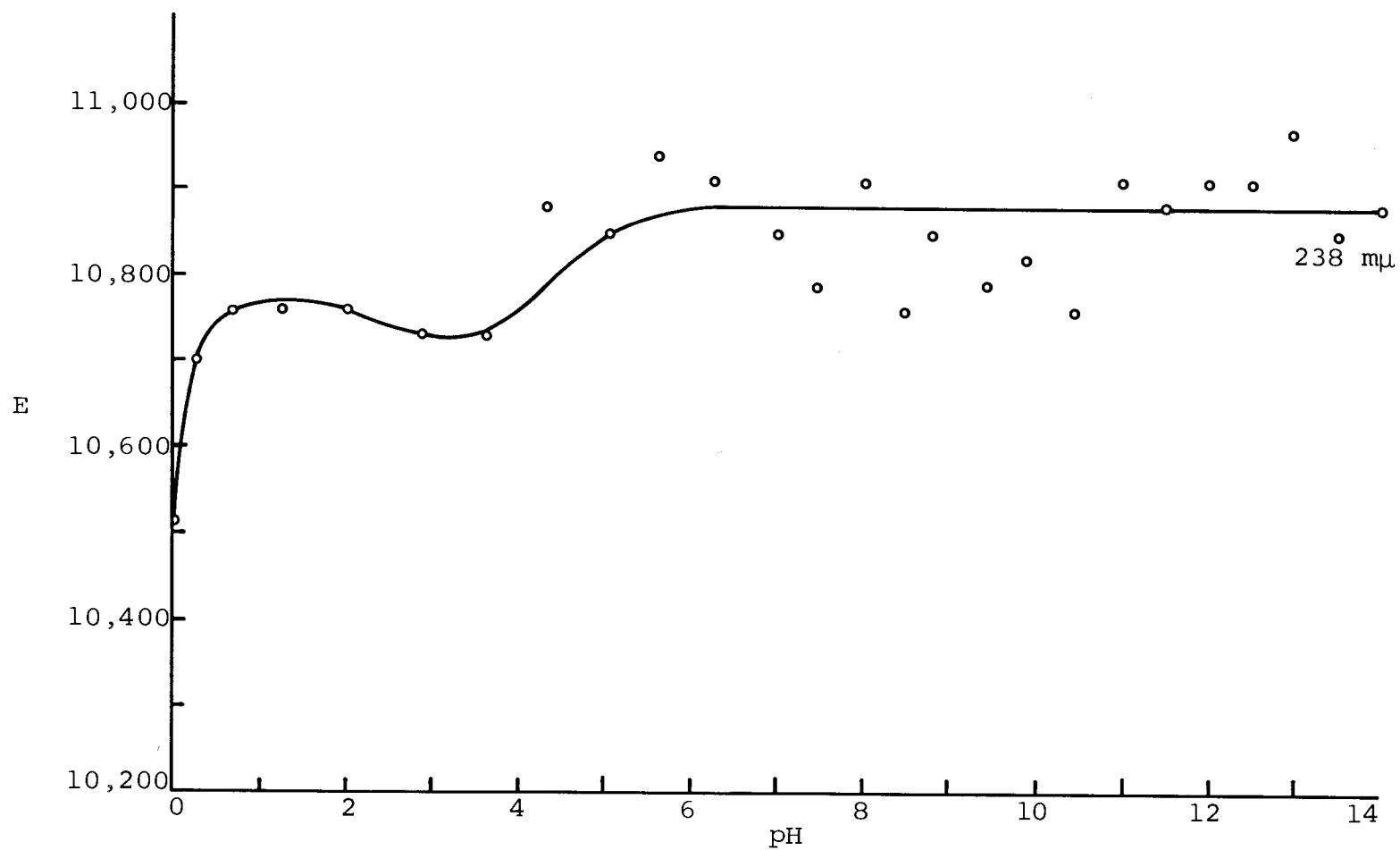


Figure 4. E versus pH of Acetanilide by Method I.

Table XIV. Dissociation Constants of p-Aminophenylacetic Acid by Method I.

No.	pH	E at 236 m μ	E at 285 m μ
1	0.15	303	177
2	0.57	303	202
3	0.95	329	202
4	1.50	303	202
5	2.00	329	202
6	2.50	379	202
7	3.00	480	202
8	3.45	859	253
9	3.75	1213	303
10	4.05	1643	379
11	4.32	2249	455
12	4.59	2982	556
13	4.95	4296	758
14	5.30	6015	986
15	5.55	7076	1137
16	5.75	7708	1264
17	5.98	8188	1289
18	6.50	8971	1390
19	7.03	9275	1440
20	7.60	9199	1415
21	7.95	9148	1390
22	8.45	9148	1390
23	9.11	9123	1390
24	9.45	9174	1390
25	10.00	9224	1415
26	10.56	9224	1390
27	10.95	9224	1390
28	11.50	9199	1415
29	12.00	9300	1390
30	12.50	9199	1415
31	13.00	9325	1440
32	13.50	9426	1415
33	14.00	9856	1440

$$\lambda = 236 \text{ m}\mu, \quad x = 300, \quad E = 4800$$

$$y = 9300, \quad \text{pH} = 5.00, \quad pK_a = 5.00$$

$$\lambda = 285 \text{ m}\mu, \quad x = 200, \quad E = 800$$

$$y = 1450, \quad \text{pH} = 5.00, \quad pK_a = 5.03$$

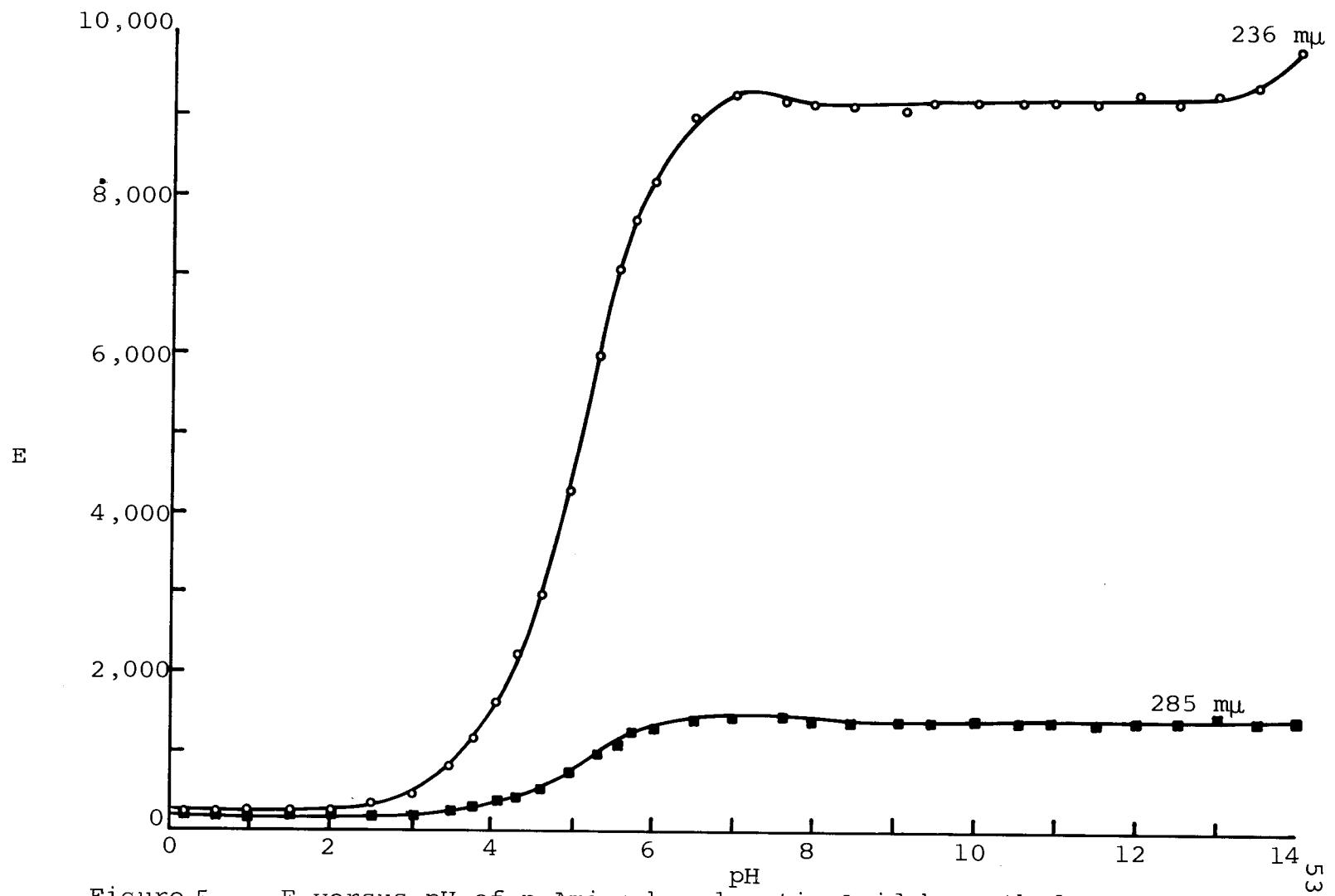


Figure 5. E versus pH of *p*-Aminophenylacetic Acid by Method I.

Table XV. Dissociation Constants of p-Amino-phenylacetic Acid by Method II.

λ (m μ)	E at	E at	pH 7.04		pH 13	
	pH 1.00	pH 5.10	E	pK _a	E	pK _a
200	0	20596	31590	-	5054	-
205	6697	11625	15921	5.04	5206	-
210	6065	6065	5812	-	5257	-
215	3285	4625	3993	-	5257	-
220	1112	4094	4599	-	5383	-
225	505	4069	6192	4.88	6596	4.95
230	354	4675	8087	5.00	8340	5.03
235	354	5105	9227	5.04	9300	5.04
236	354	5080	9119	5.04	9275	5.05
240	354	4625	8415	5.05	8415	5.05
245	354	3311	6015	5.06	5939	5.05
250	354	1946	3386	5.05	3311	5.03
255	354	1011	1643	5.08	1617	5.06
260	329	632	960	5.13	885	5.02
265	278	556	783	5.01	758	4.96
270	253	607	885	5.00	885	5.00
275	253	733	1112	5.00	1112	5.00
280	237	834	1365	5.05	1365	5.05
285	202	859	1415	5.03	1440	5.04
290	152	809	1314	5.00	1314	4.99
295	101	581	1011	5.05	986	5.02
300	76	354	607	5.06	581	5.01
305	76	202	329	5.10	303	5.00
310	51	126	152	-	152	-
315	25	25	51	-	25	-
320	0	0	0	-	0	-

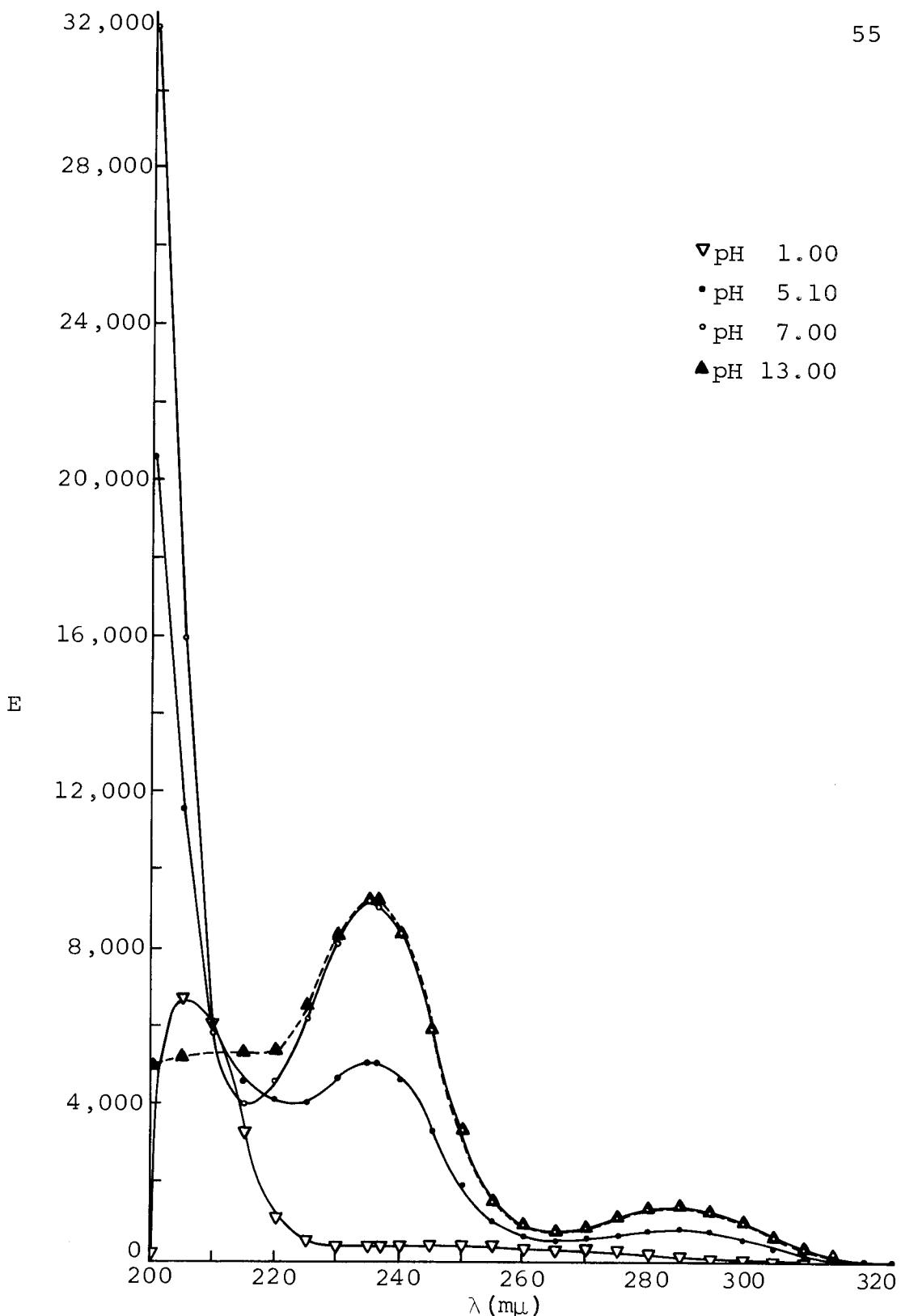


Figure 6. E versus λ of *p*-Aminophenylacetic Acid by Method II.

Table XVI. Dissociation Constants of Aniline Hydrochloride by Method I.

NO.	pH	E at 230 m μ	E at 280 m μ
0	0.80	89	0
1	1.55	114	0
2	2.10	114	0
3	2.68	216	25
4	3.20	546	76
5	3.93	1815	305
6	4.25	3122	520
7	4.58	3845	635
8	5.03	3807	635
9	5.38	7792	1320
10	5.70	7970	1345
11	6.62	8147	1371
12	7.53	8046	1371
13	8.65	8160	1383
14	9.80	8147	1383
15	11.00	8338	1421
16	12.00	8249	1409
17	13.00	8236	1396
18	14.00	8236	1396

$\lambda=230 \text{ m}\mu$, $x=100$, $E=4500$, $y=8200$, $\text{pH}=4.70$, $\text{pK}_a=4.62$

$\lambda=280 \text{ m}\mu$, $x=0$, $E=750$, $y=1450$, $\text{pH}=4.70$, $\text{pK}_a=4.65$

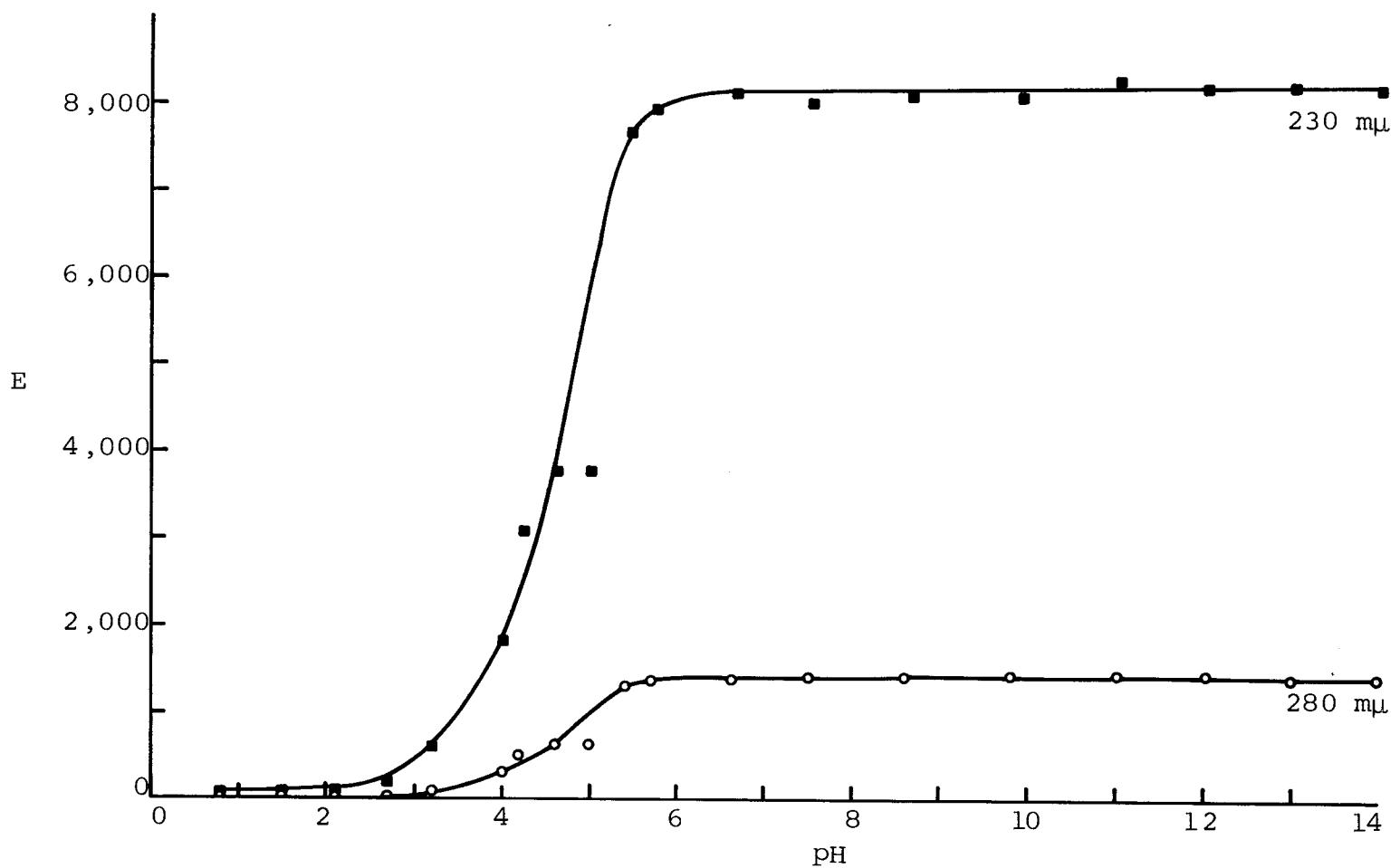


Figure 7. E versus pH of Aniline Hydrochloride by Method I.

Table XVII. Dissociation Constants of Aniline Hydrochloride by Method II.

λ (m μ)	E at pH 1.17	E at pH 4.80	E	pH 7.00 pK _a	E	pH 13 pK _a
210	1576	0	3919	-	0	-
215	113	0	4110	-	0	-
220	45	957	5518	-	2703	-
225	34	2984	7264	-	6025	-
230	56	4167	7995	4.77	7489	4.71
235	68	3886	6869	4.69	6588	4.65
240	79	2590	4482	4.68	4302	4.63
245	113	1363	2252	4.65	2252	4.65
250	113	687	1070	4.63	1070	4.63
255	113	394	563	4.58	563	4.58
260	101	360	563	4.69	552	4.67
265	0	439	709	4.59	698	4.57
270	11	597	991	4.63	957	4.59
275	11	732	1273	4.68	1227	4.64
280	11	800	1374	4.66	1284	4.59
285	11	732	1250	4.66	1160	4.57
290	11	552	901	4.61	800	4.55
295	11	282	518	4.74	439	4.56
300	0	146	248	4.65	191	-
305	0	56	113	-	56	-
310	0	23	56	-	23	-
315	0	0	23	-	0	-
320	0	0	11	-	0	-

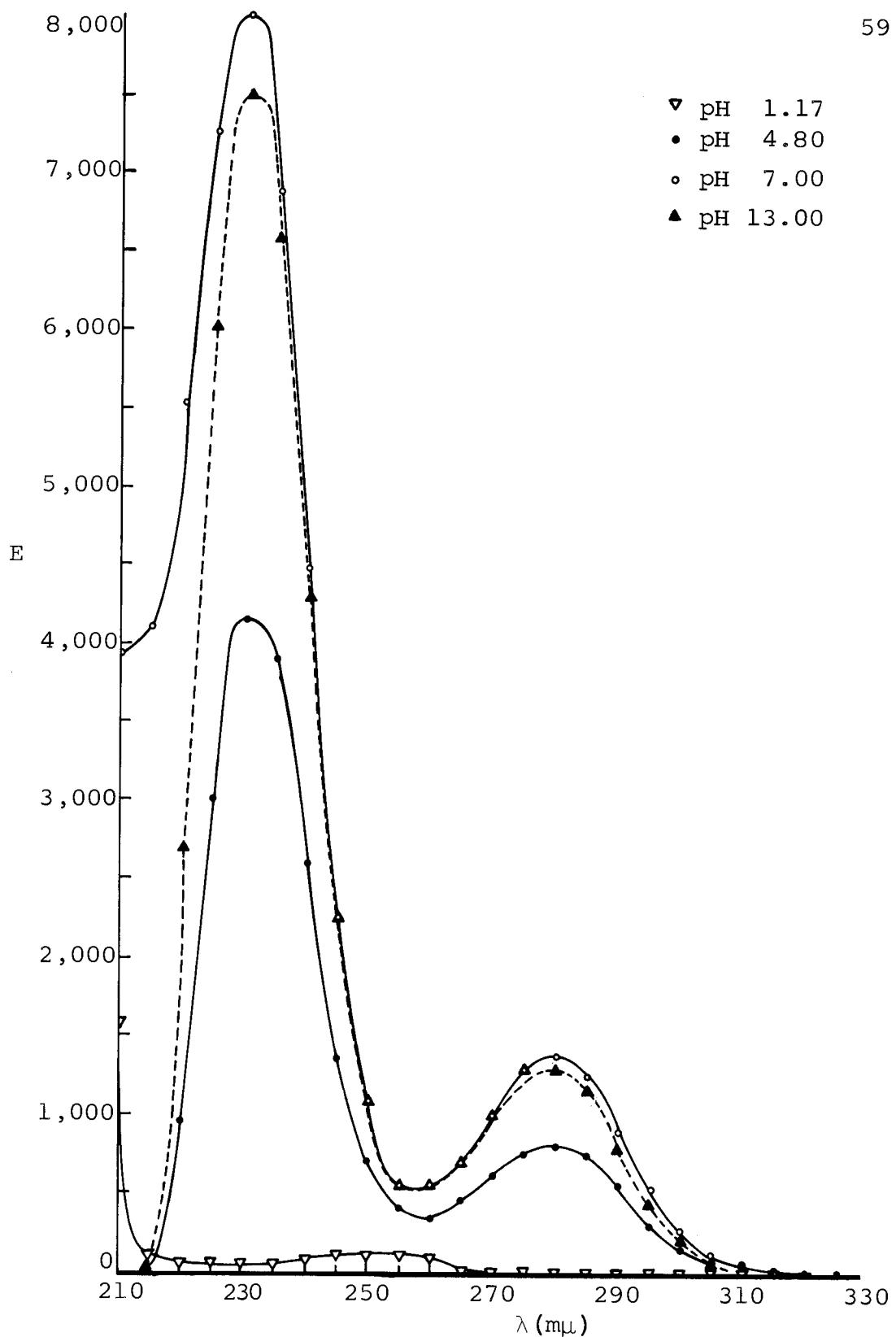


Figure 8. E versus λ of Aniline by Method II.

Table XVIII. Dissociation Constants of Benzoic Acid
by Method I.

No.	pH	E at 230 m μ	E at 270 m μ
1	0.80	11124	899
2	1.59	11043	899
3	2.28	11075	899
4	3.15	10819	899
5	3.97	9310	770
6	4.60	8266	674
7	4.78	7673	626
8	6.10	7079	562
9	7.03	7063	562
10	7.84	7223	546
11	8.94	6982	578
12	10.04	7047	562
13	11.05	7095	594
14	12.00	7095	562
15	13.00	6934	546
16	14.00	7095	578

$\lambda=230 \text{ m}\mu$, $x=7600$, $E=9100$, $y=10700$, $\text{pH}=4.15$, $\text{pK}_a=4.18$

$\lambda=270 \text{ m}\mu$, $x=562$, $E=710$, $y=900$, $\text{pH}=4.15$, $\text{pK}_a=4.26$

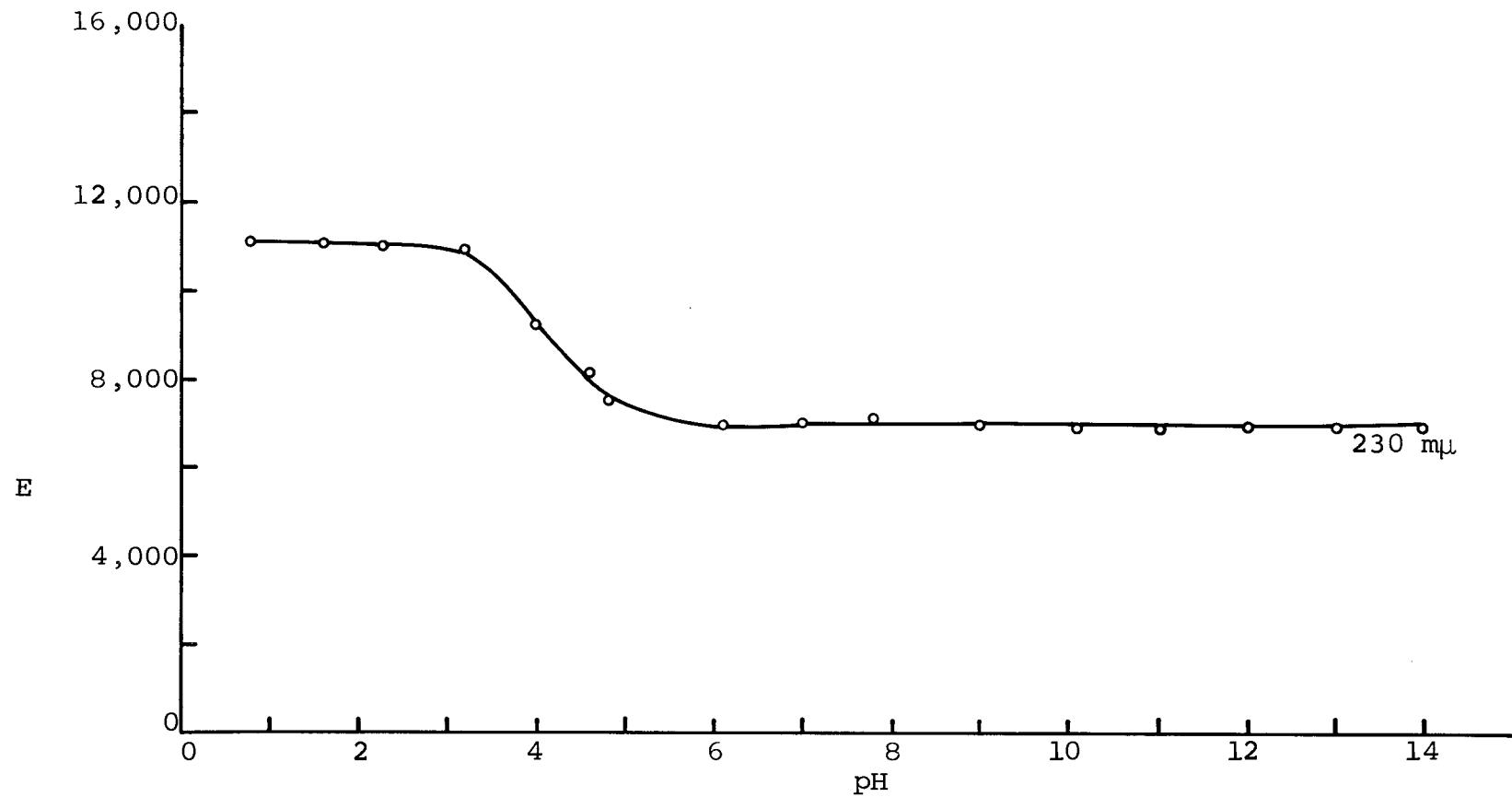


Figure 9. E versus pH of Benzoic Acid by Method I.

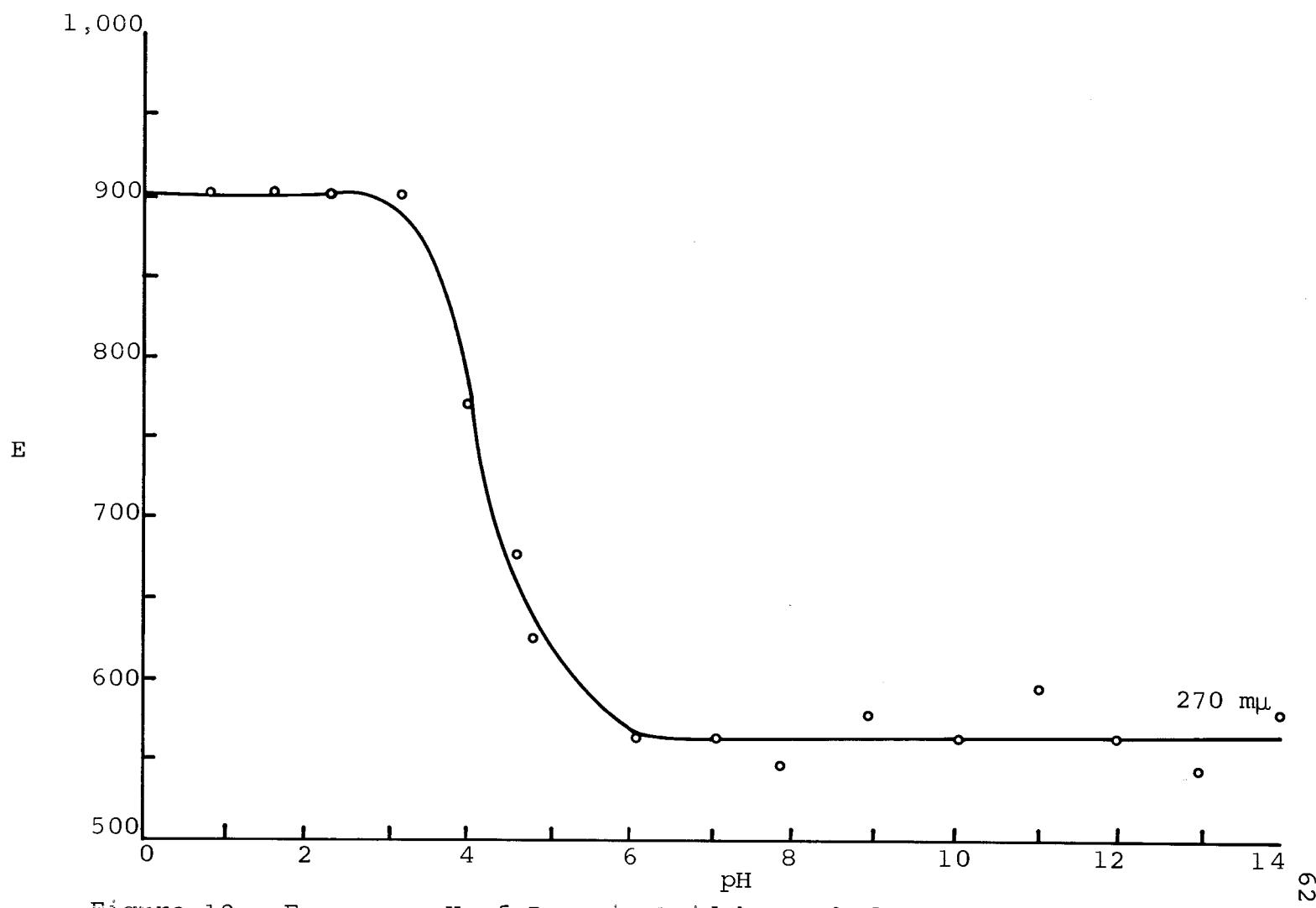


Figure 10. *E* versus pH of Benzoic Acid by Method I.

Table XIX. Dissociation Constants of Benzoic Acid by Method II.

λ (m μ)	E at	E at	<u>pH 7.03</u>		<u>pH 13</u>	
	pH 1.05	pH 4.80	E	pK _a	E	pK _a
210	3303	5355	5827	4.16	5415	-
215	4663	6197	6421	-	6046	-
220	7521	7897	7897	-	7912	-
225	10108	8724	8347	4.23	8093	-
230	11161	7822	7063	4.16	7010	4.19
235	9702	5641	4848	4.10	4844	4.10
240	6393	3309	2600	4.16	2587	4.20
245	3008	1729	1396	4.22	1474	4.10
250	1339	1038	915	-	1023	-
255	797	752	706	-	752	-
260	752	692	626	-	692	-
265	842	662	562	-	647	-
270	963	662	562	4.28	647	-
272.5	1009	617	465	-	526	4.17
275	978	572	417	-	496	4.10
280	842	376	225	-	271	4.15
285	526	165	32	-	90	4.12
290	150	45	0	-	45	-
295	30	15	0	-	15	-
300	15	15	0	-	0	-
305	15	0	0	-	0	-
310	15	0	0	-	0	-
315	15	0	0	-	0	-
320	15	0	0	-	0	-

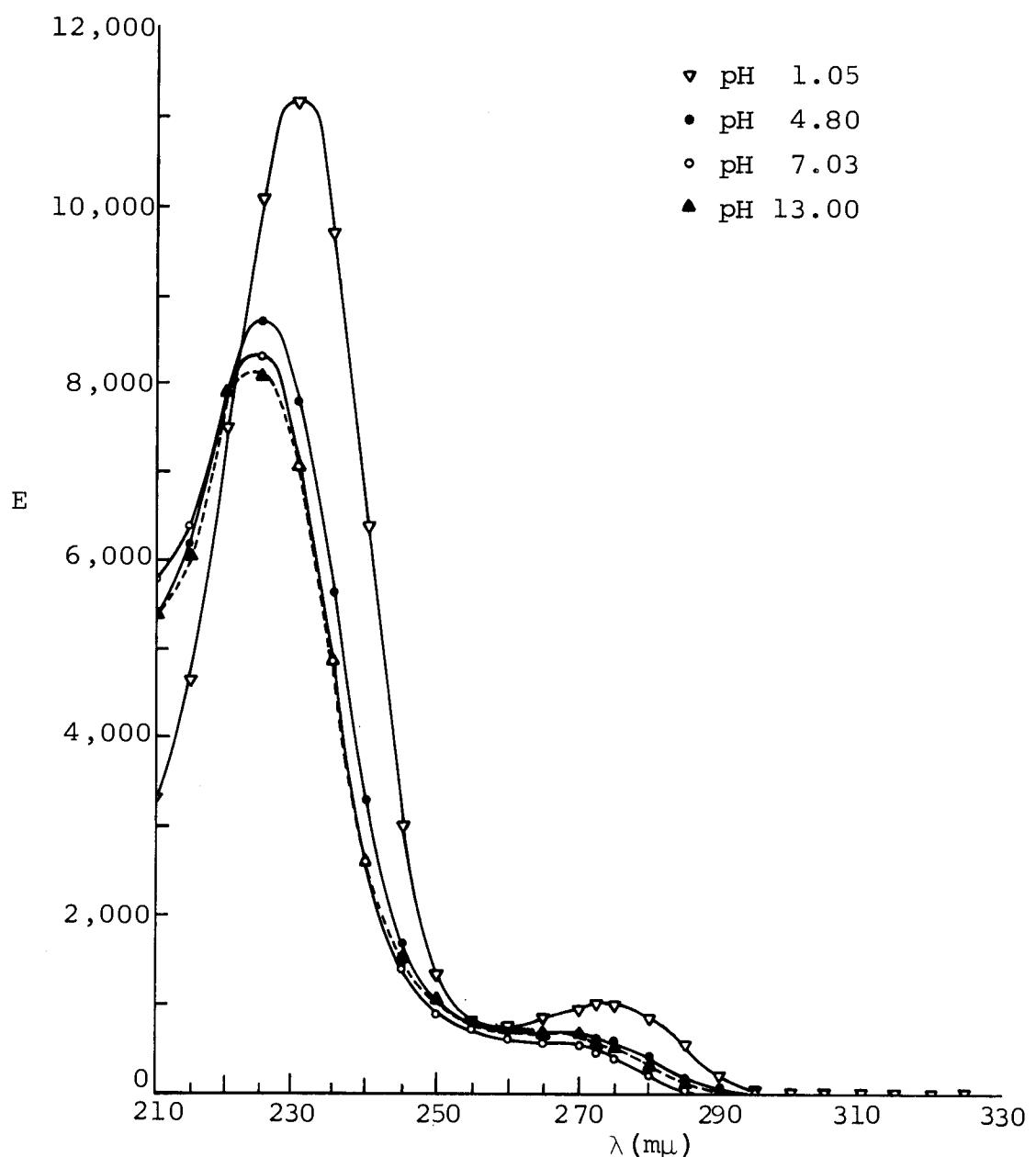


Figure 11. E versus λ of Benzoic Acid by Method II.

Table XX. Dissociation Constants of N,N-Dimethyl-aniline by Method I.

No.	pH	E at 242.5 m μ
1	0.00	471
2	0.45	471
3	0.85	471
4	1.44	471
5	1.84	471
6	2.50	508
7	3.00	659
8	3.48	791
9	3.84	1318
10	4.02	1902
11	4.15	2241
12	4.35	3126
13	4.51	3729
14	4.66	4991
15	4.85	6328
16	5.05	7815
17	5.20	8927
18	5.42	10810
19	5.65	12260
20	5.85	12618
21	6.11	14576
22	6.37	14896
23	6.70	15782
24	7.04	16064
25	7.31	15800
26	7.68	15725
27	8.45	15424
28	9.21	15198
29	9.91	15706
30	10.75	15989
31	11.50	16460
32	12.00	16497
33	12.50	16460
34	13.00	16422
35	13.50	16403
36	14.00	16441
$\lambda=242.5$,		$x=450$,
$y=15900$,		$pK_a=5.10$,
		$E=8500$
		$pK_a=5.06$

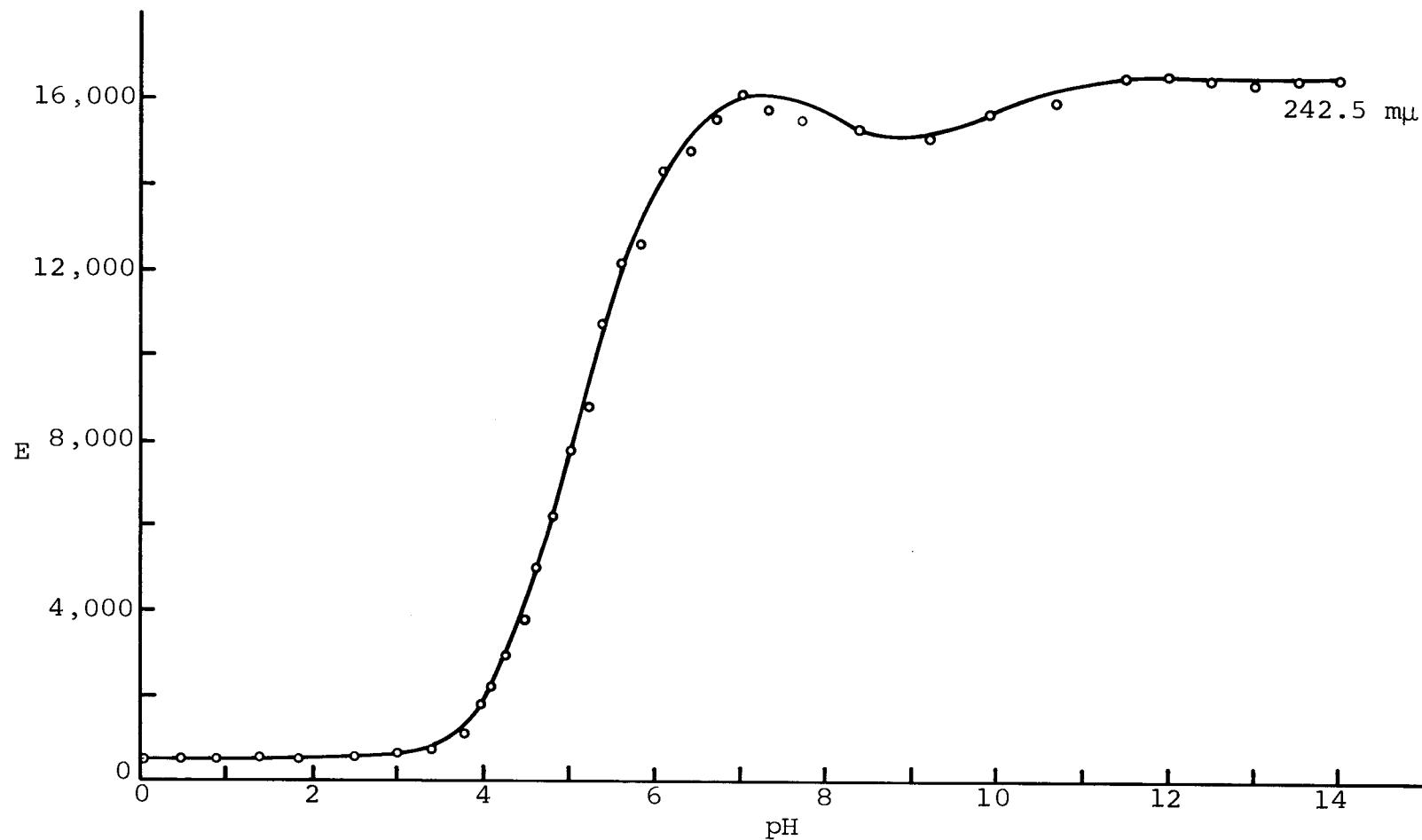


Figure 12. E versus pH of N,N -Dimethylaniline by Method I.

Table XXI. Dissociation Constants of N,N-Dimethyl-aniline by Method II.

λ (m μ)	E at	E at	<u>pH 7.08</u>		<u>pH 13</u>	
	pH 1.00	pH 5.08	E	pK _a	E	pK _a
210	4331	10358	14124	-	7458	-
215	471	4237	7439	5.01	7646	5.04
220	132	3277	6026	5.02	7062	5.15
225	151	4143	7721	5.03	8380	5.11
230	282	5593	10546	5.05	11017	5.09
235	320	7156	13371	5.04	13936	5.08
240	377	8286	15311	5.03	16008	5.07
242.5	414	8437	15612	5.03	16290	5.07
245	414	8343	15348	5.02	16083	5.07
250	414	7401	13446	5.02	14124	5.06
255	414	5650	10264	5.02	10716	5.07
260	320	3766	6949	5.04	7062	5.06
265	132	2448	4369	5.00	4539	5.03
270	94	1695	3126	5.03	3258	5.07
275	75	1412	2693	5.06	2731	5.08
280	94	1337	2637	5.10	2561	5.07
285	94	1281	2373	5.04	2599	5.13
290	94	1149	2090	5.03	2166	5.06
295	94	942	1751	5.06	1789	5.08
300	94	791	1394	5.02	1412	5.03
305	113	659	1130	5.01	1149	5.03
310	113	527	885	5.01	923	5.06
315	113	414	697	5.05	716	5.08
320	94	282	452	5.03	471	5.08

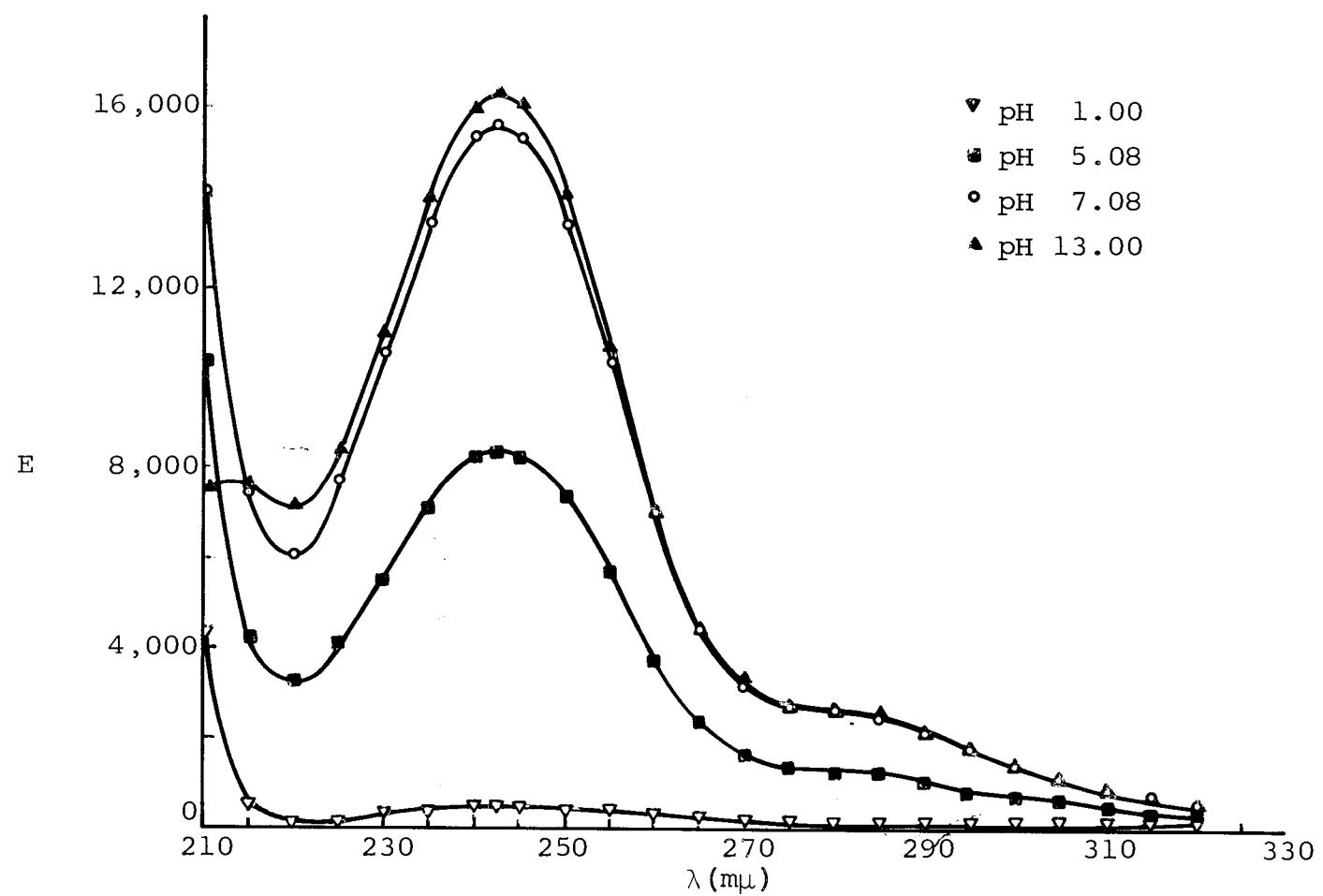


Figure 13. E versus λ of N,N-Dimethylaniline by Method II.

Table XXII. Dissociation Constants of Diphenylamine
by Method I.

No.	pH	E at 279 m μ
1	0.00	1358
2	0.20	1790
3	0.40	2901
4	0.57	4599
5	0.76	6296
6	0.90	7685
7	1.06	9383
8	1.27	11080
9	1.35	11574
10	1.59	12747
11	1.82	13364
12	2.00	13642
13	2.25	14012
14	2.62	14167
15	3.00	14352
16	3.50	14352
17	4.00	14352
18	4.57	14414
19	5.05	14352
20	5.48	14475
21	6.10	14383
22	6.57	14290
23	6.99	14506
24	7.60	14352
25	8.20	14444
26	8.95	14414
27	9.65	14352
28	10.30	14506
29	10.95	14537
30	11.50	14506
31	12.00	14568
32	12.50	14660
33	13.00	14568
34	13.50	14660
35	14.00	14660

$\lambda=279 \text{ m}\mu$; $x=1350$, $E=8000$

$y=14300$, $\text{pH}=0.90$, $\text{pK}_a=0.88$

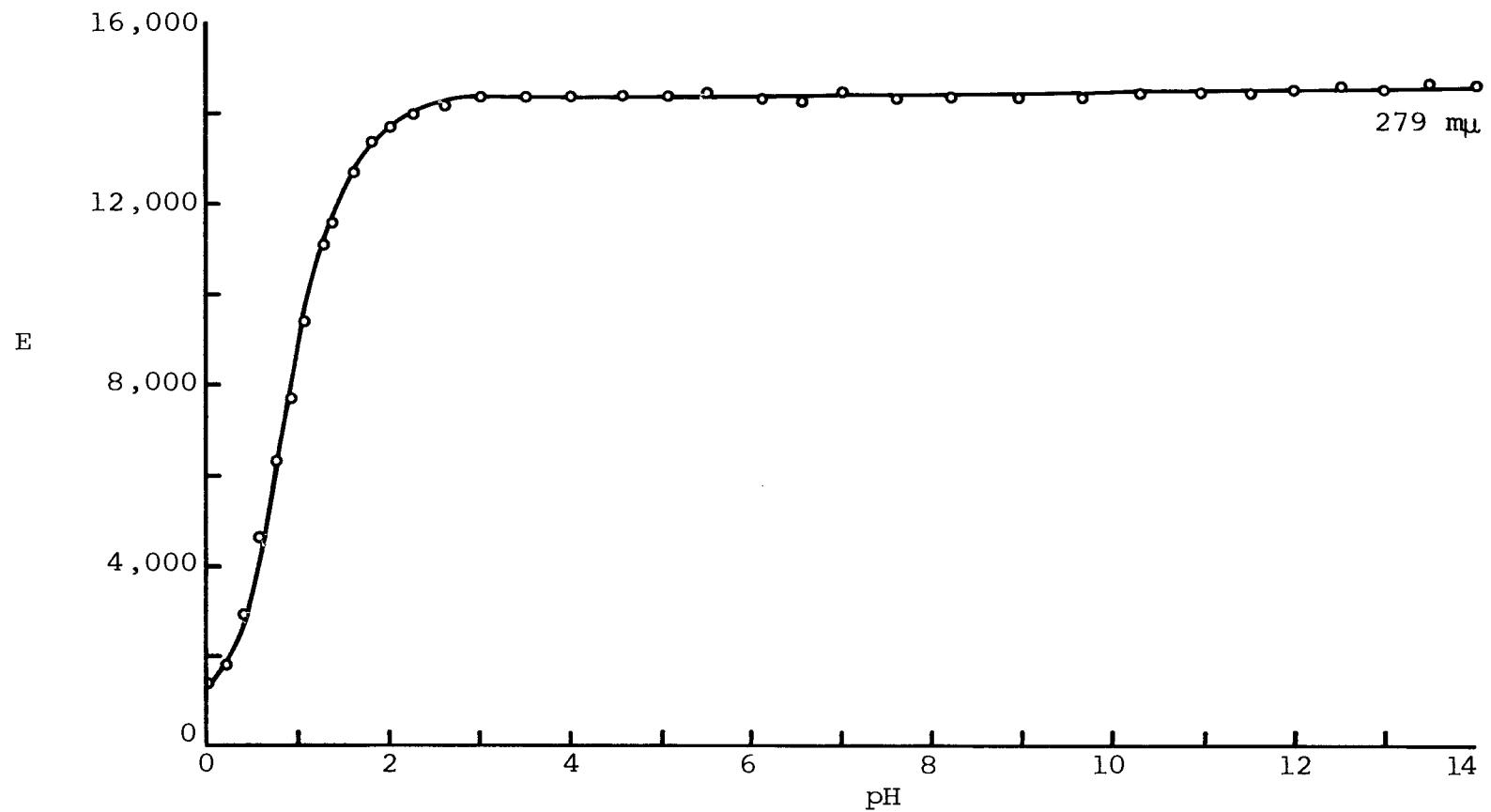


Figure 14. E versus pH of Diphenylamine by Method I.

Table XXIII. Dissociation Constants of Diphenylamine
by Method II.

λ (m μ)	E at	E at	<u>pH 7.00</u>		<u>pH 13</u>	
	pH 1.01	pH 1.38	E	pK _a	E	pK _a
210	15123	15741	16049	-	15741	-
215	7377	8488	9043	-	8981	-
220	4475	5864	7099	1.33	7130	1.34
225	3457	4938	6019	1.24	6049	1.26
230	3086	4475	5494	1.24	5494	1.24
235	2901	4290	5093	1.14	5093	1.14
240	2901	4136	4938	1.19	4969	1.21
245	3025	4321	5093	1.16	5093	1.16
250	3488	4753	5864	1.32	5895	1.33
255	4321	5648	7284	1.47	7377	1.49
260	5062	7037	9074	1.39	9105	1.40
265	5895	8457	10957	1.37	10957	1.37
270	6821	9753	12685	1.38	12747	1.39
275	7531	10833	14043	1.37	14074	1.37
279	7716	11204	14444	1.35	14444	1.35
280	7685	11173	14414	1.35	14414	1.35
285	7253	10617	13611	1.33	13673	1.34
290	6296	9259	11759	1.30	11821	1.31
295	5031	7407	9414	1.30	9444	1.31
300	3765	5494	6914	1.29	6944	1.30
305	2469	3673	4599	1.27	4630	1.28
310	1543	2160	2778	1.38	2747	1.36
315	833	1173	1389	1.19	1358	1.12
320	340	463	586	1.38	586	1.38

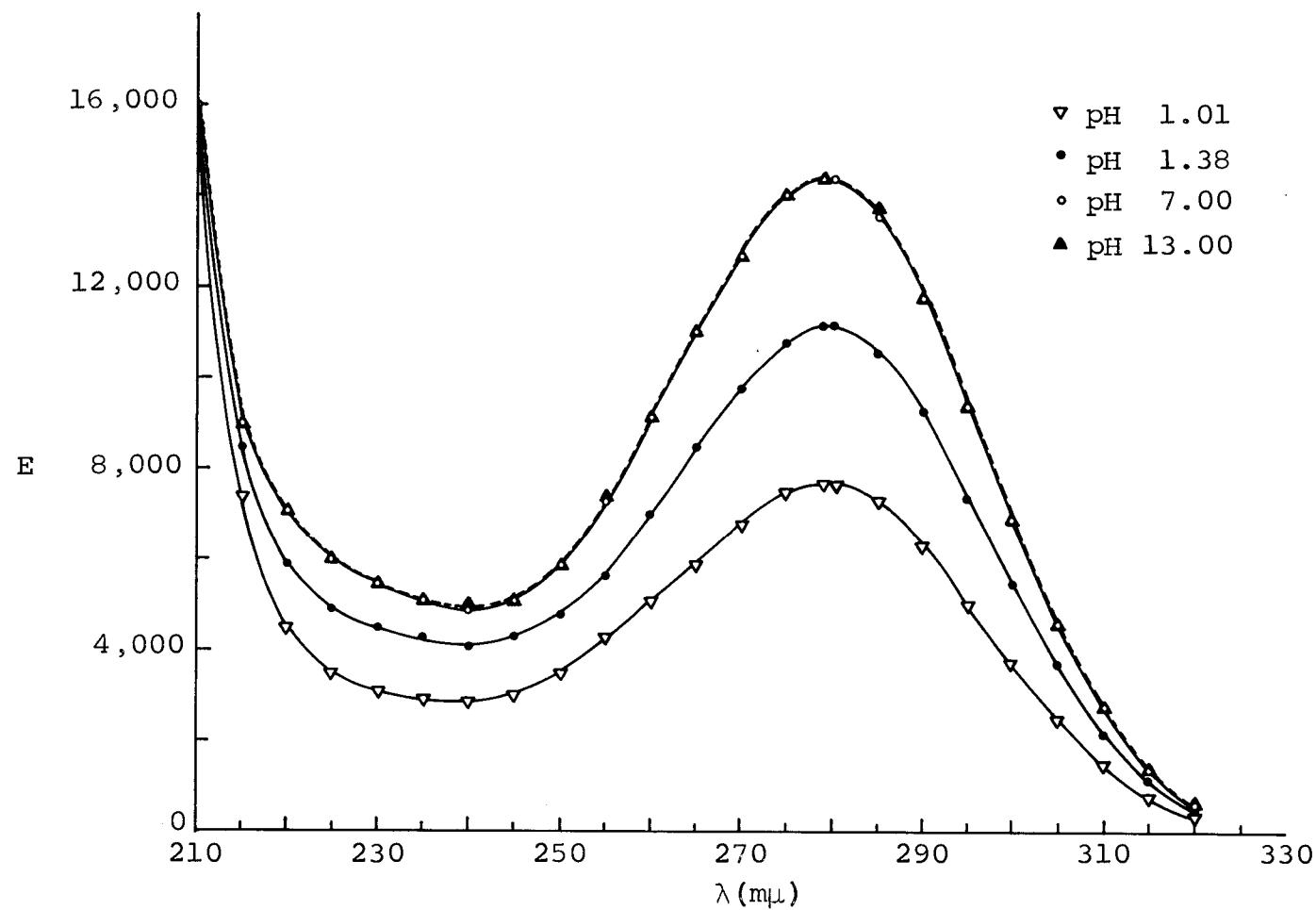


Figure 15. E versus λ of Diphenylamine by Method II.

Table XXIV. Dissociation Constants of 3-Indoleacetic Acid by Method I.

No.	pH	E at 219 m μ	E at 280 m μ
1	0.00	32824	5732
2	0.50	30998	5732
3	1.00	32909	5648
4	1.45	30998	5648
5	1.95	32824	5945
6	2.51	31847	5945
7	2.75	32696	5732
8	2.95	30149	5435
9	3.39	32272	5732
10	3.79	32484	5945
11	4.26	31423	5478
12	4.65	33715	5732
13	5.11	30998	5223
14	5.56	31762	5308
15	6.20	30701	5180
16	6.57	30828	5180
17	6.99	32059	5478
18	7.50	32654	5520
19	8.06	30701	5138
20	8.52	32187	5393
21	8.95	32144	5350
22	9.56	30488	5096
23	10.05	30870	5223
24	10.51	30531	5138
25	11.00	32569	5478
26	11.50	30786	5223
27	12.00	29936	5053
28	12.50	30573	5180
29	13.00	33970	5478
30	13.50	36858	5563
31	14.00	39278	5393

$\lambda=219$ m μ , $x=30200$, $E=34600$, $y=39200$, $pH=13.10$, $pK_a=13.12$

$\lambda=280$ m μ , pK_a undeterminable

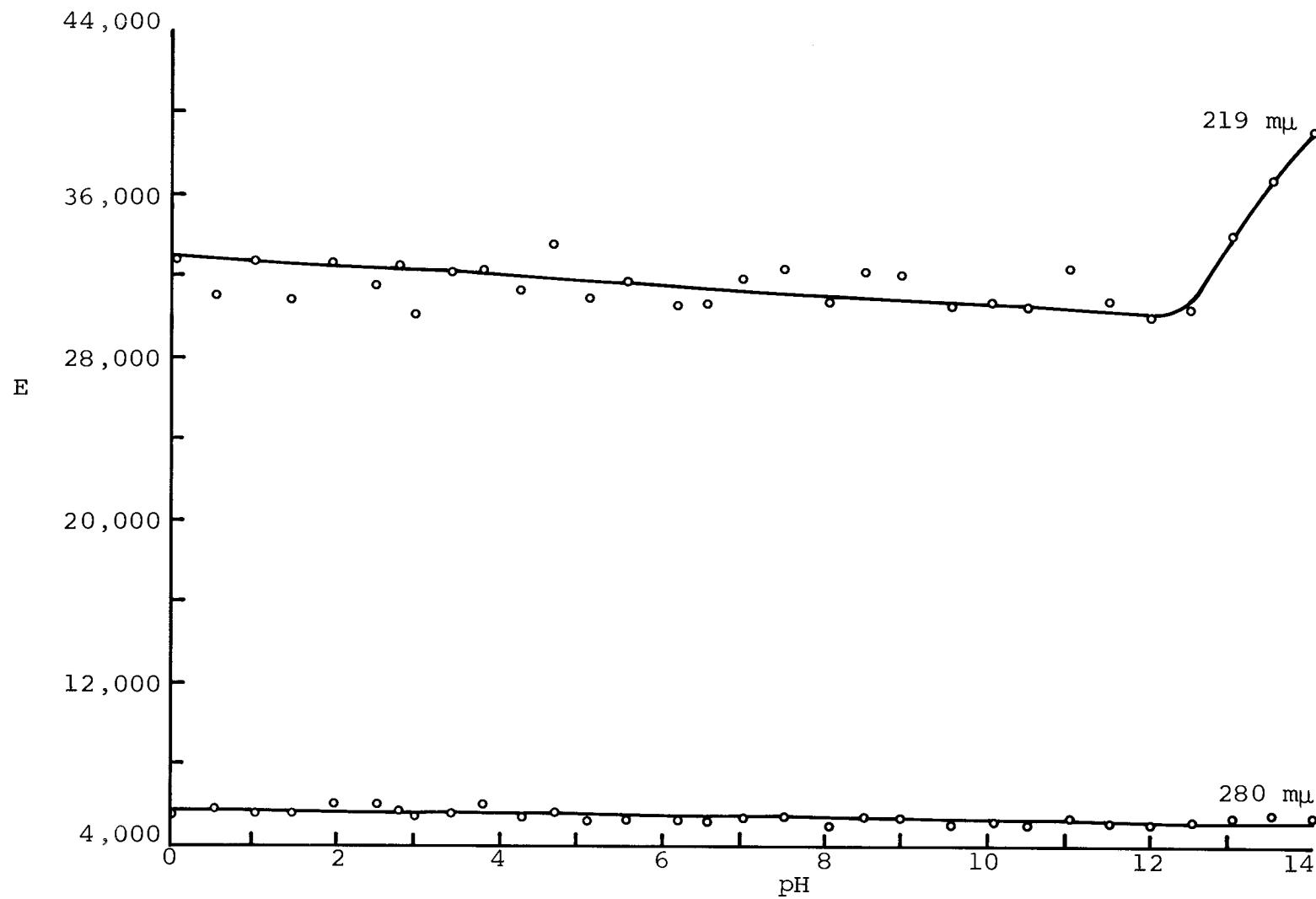


Figure 16. E versus pH of 3-Indoleacetic Acid by Method I.

Table XXV. Dissociation Constants of 3-Indoleacetic Acid by Method II.

λ (m μ)	E at	E at	<u>pH 7.02</u>		<u>pH 13</u>	
	pH 1.00	pH 4.40	E	pK _a	E	pK _a
200	23355	19193	19278	-	34013	-
205	20679	19448	18174	4.41	34862	-
210	25605	24416	22081	4.69	36008	-
215	31338	30786	28790	4.96	36263	-
219	29936	31847	32527	4.11	34183	4.49
220	28662	31210	32484	4.10	33673	4.39
225	15711	20807	25902	4.40	26115	4.42
230	5435	7643	10616	4.53	10616	4.53
235	2760	3057	3397	4.46	3355	4.40
240	2335	2251	2166	4.45	2081	4.71
245	2335	2251	2123	4.58	2038	4.81
250	2633	2548	2293	4.88	2251	4.94
255	3185	3057	2803	4.70	2760	4.77
260	3992	3907	3609	4.95	3524	5.05
265	4671	4671	4374	-	4289	-
270	5223	5223	5053	-	4926	-
275	5308	5435	5308	-	5223	-
280	5265	5520	5520	-	5435	-
285	4416	4671	4841	4.23	4765	-
290	3185	3864	4331	4.24	4246	4.15
295	1104	1699	2208	4.33	2123	4.25
300	382	594	1019	4.70	892	4.55
305	85	212	425	4.63	340	4.40
310	42	85	212	4.87	127	4.39
315	0	42	85	4.41	85	4.41
320	0	0	0	-	42	-

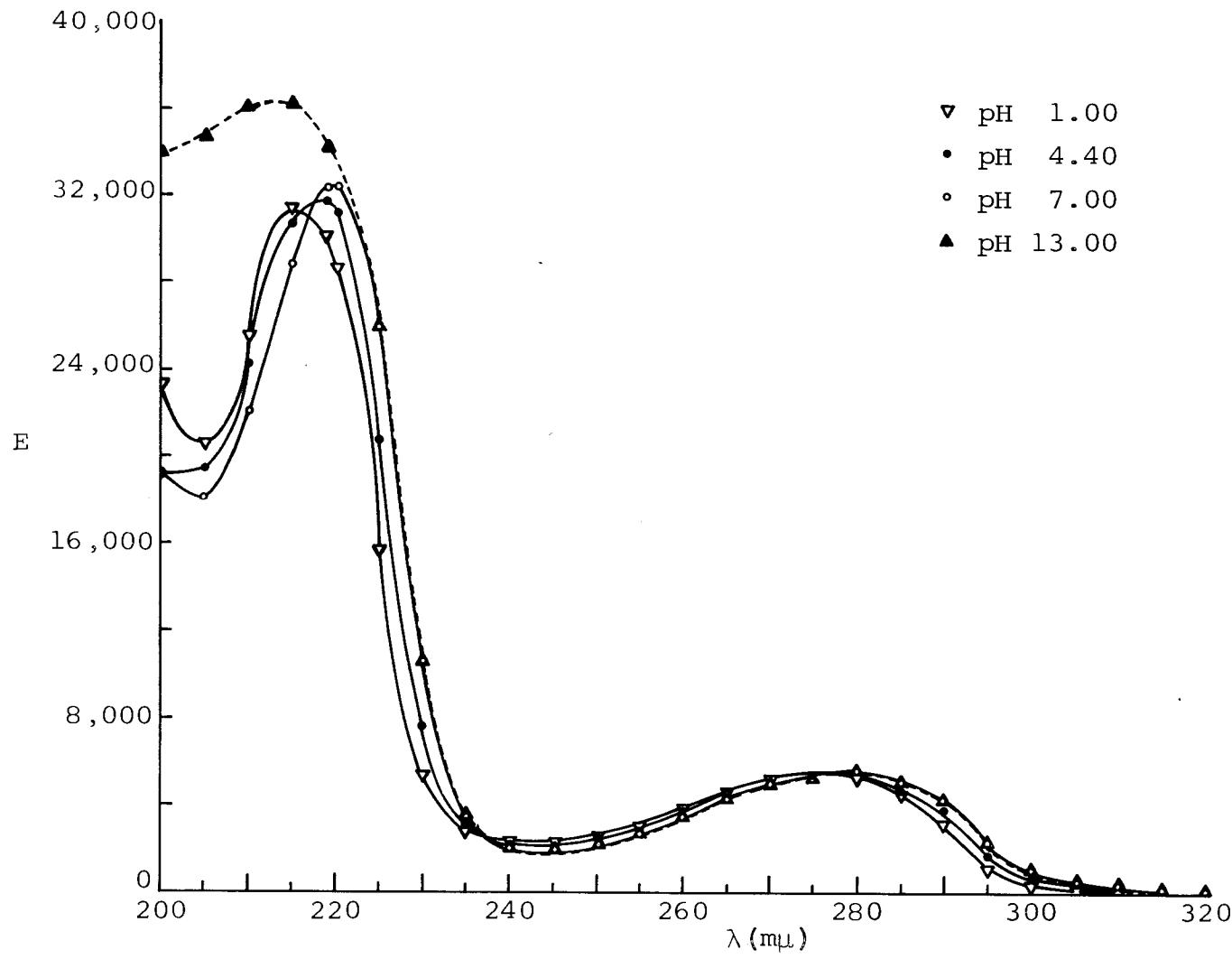


Figure 17. E versus λ of 3-Indoleacetic Acid by Method II.

Table XXVI. Dissociation Constants of Pyridine
by Method I.

No.	pH	E at 249.5 m μ	E at 255 m μ	E at 262 m μ
1	1.26	4757	5407	3443
2	2.17	4750	5282	3208
3	3.37	4710	5203	2973
3A	4.05	4499	4969	2895
4	4.48	3912	4296	2504
5	5.05	3607	3991	2465
5A	5.47	3091	3396	2222
6	5.90	2668	2934	1886
7	7.10	2527	2739	1800
8	7.58	2527	2739	1886
9	9.44	2512	2700	1878
10	10.37	2488	2660	1870
11	11.13	2512	2700	1878
12	12.00	2535	2778	1878
13	13.00	2543	2739	1878
14	14.00	2543	2778	1875

$\lambda=249.5 \text{ m}\mu$, $x=2500$, $E=3560$, $y=4760$, $\text{pH}=5.00$, $\text{pK}_a=5.05$

$\lambda=255 \text{ m}\mu$, $x=2700$, $E=3920$, $y=5200$, $\text{pH}=5.10$, $\text{pK}_a=5.12$

$\lambda=262 \text{ m}\mu$, $x=1780$, $E=2380$, $y=3000$, $\text{pH}=5.15$, $\text{pK}_a=5.16$

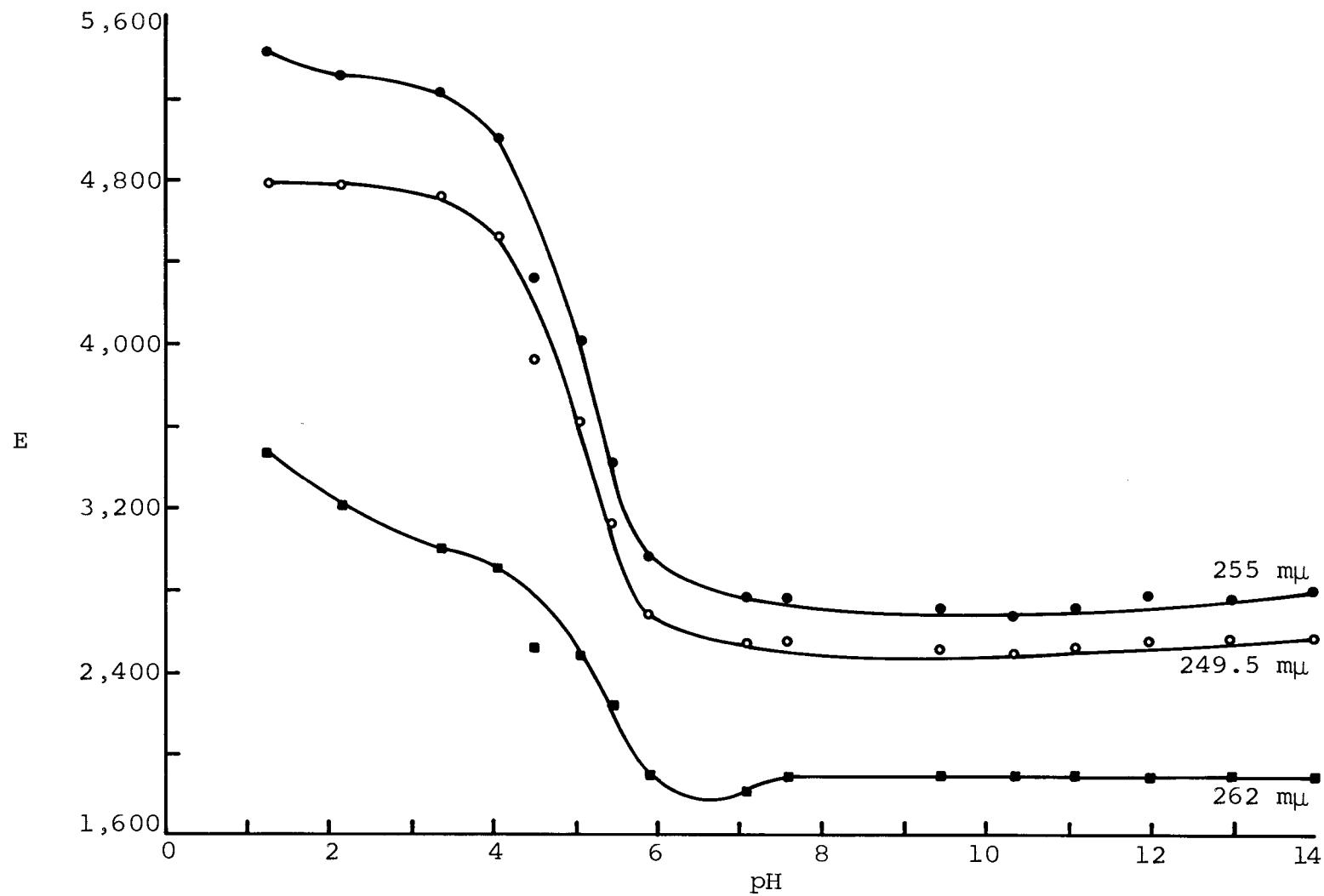


Figure 18. E versus pH of Pyridine by Method I.

Table XXVII. Dissociation Constants of Pyridine
by Method II.

λ (m μ)	E at pH 1.12	E at pH 5.78	<u>pH 7.02</u>		<u>pH 13</u>	
			E	pK _a	E	pK _a
200	3028	0	4089	-	0	-
205	2551	0	1498	-	0	-
210	1255	0	583	-	0	-
215	389	0	494	-	0	-
220	130	0	470	-	0	-
225	178	32	502	-	0	-
230	405	308	648	-	324	-
235	931	737	891	-	810	-
240	1822	1377	1239	5.27	1255	5.22
245	3150	2178	1806	5.36	1798	5.37
249	4534	2915	2348	5.32	2348	5.32
250	4688	3109	2518	5.35	2510	5.36
252.5	4858	2955	2186	5.38	2186	5.38
255	5328	3385	2607	5.38	2599	5.39
256.5	5182	3498	2834	5.38	2826	5.38
260	3603	2227	1628	5.42	1619	5.43
262.5	3093	2219	1887	5.36	1878	5.37
265	1174	972	972	-	972	-
270	105	105	81	-	81	-
275	40	0	0	-	0	-
280	32	0	0	-	0	-
285	24	0	0	-	0	-
290	24	0	0	-	0	-
295	16	0	0	-	0	-
300	8	0	0	-	0	-
305	0	0	0	-	0	-
310	0	0	0	-	0	-
315	0	0	0	-	0	-
320	0	0	0	-	0	-

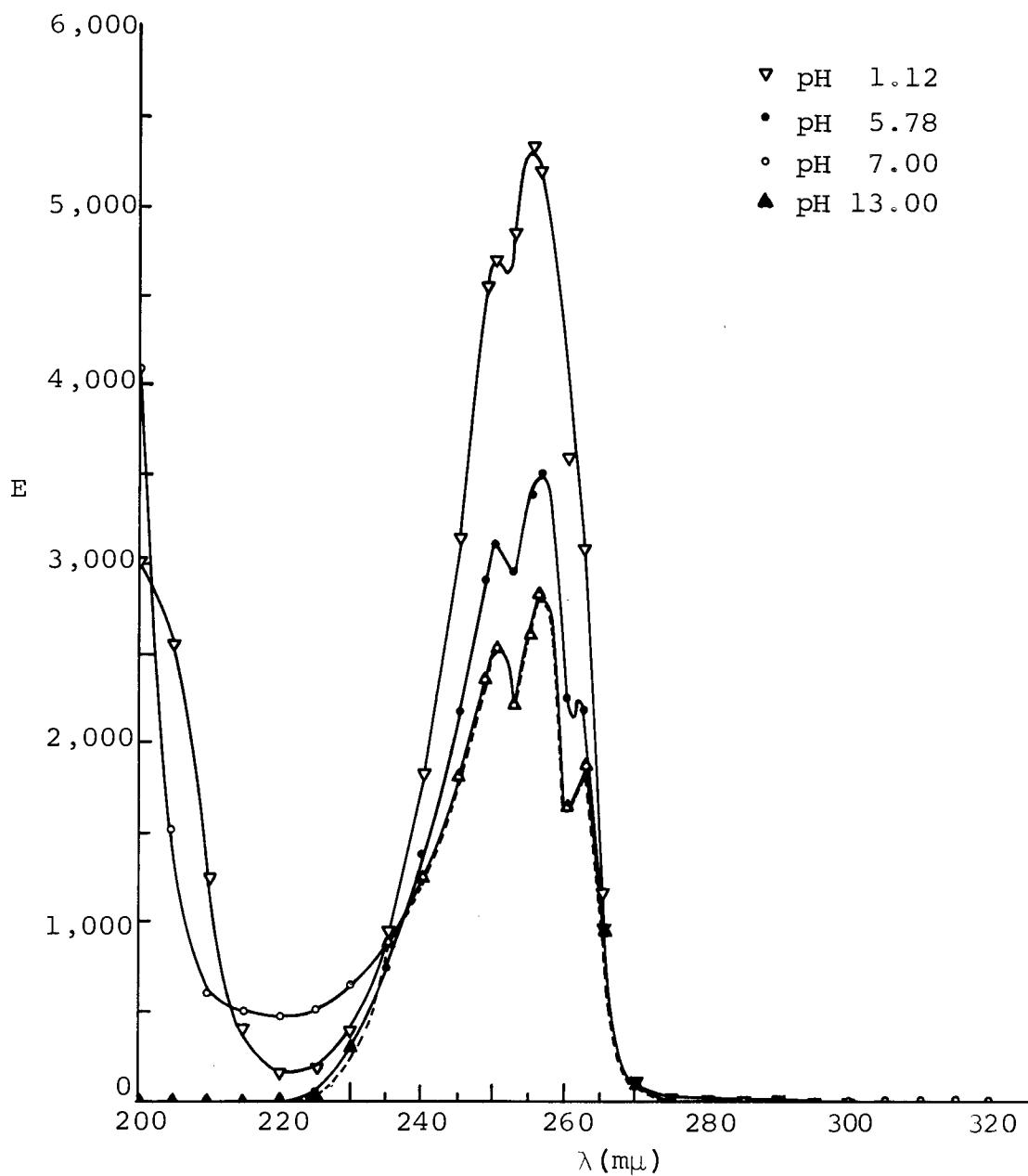


Figure 19. E versus λ of Pyridine by Method II.

Table XXVIII. Dissociation Constants of Quinoline
by Method I.

No.	pH	E at 224 m μ	E at 232 m μ	E at 275 m μ	E at 312.5 m μ
1	0.30	17892	38235	1667	7157
2	0.80	16667	36765	1569	6863
3	1.29	18137	38333	1716	7059
4	1.89	17647	37255	1667	6912
5	2.40	17647	37304	1667	6863
6	2.98	17647	37402	1716	6961
7	3.55	18137	35784	1716	6765
8	3.86	18627	34461	1863	6569
9	4.17	19265	32353	2108	6275
10	4.57	22206	27451	2353	5686
11	4.85	24510	23284	2745	5294
12	5.48	29314	15196	3382	4314
13	6.00	30294	11520	3578	3824
14	6.55	30441	10784	3578	3431
15	6.91	31471	10784	3824	3922
16	7.83	31275	10784	3676	3725
17	8.89	32010	10784	3676	3725
18	9.88	31176	10784	3627	3725
19	11.00	31373	10784	3824	3775
20	12.00	31520	10784	3676	3725
21	13.00	32353	10784	3676	3725
22	14.00	35294	11275	3627	3725

$\lambda=224 \text{ m}\mu$, $x=17400$, $E=25000$, $y=31400$, $\text{pH}=4.90$, $\text{pK}_a=4.83$
 $\lambda=232 \text{ m}\mu$, $x=10800$, $E=24200$, $y=37600$, $\text{pH}=4.80$, $\text{pK}_a=4.80$
 $\lambda=275 \text{ m}\mu$, $x=1700$, $E=2600$, $y=3700$, $\text{pH}=4.80$, $\text{pK}_a=4.89$
 $\lambda=312.5 \text{ m}\mu$, $x=3700$, $E=5400$, $y=7000$, $\text{pH}=4.80$, $\text{pK}_a=4.77$

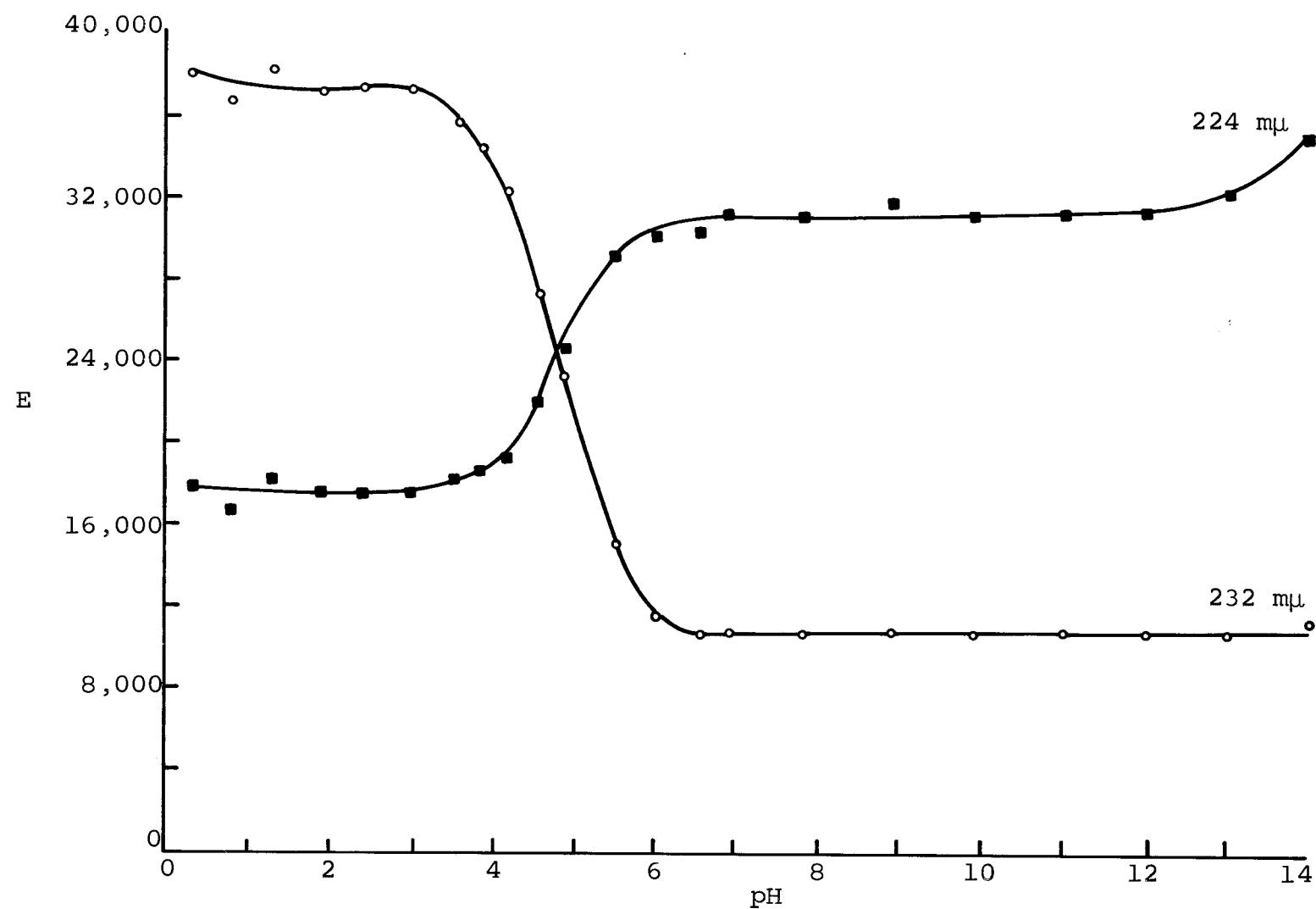


Figure 20. E versus pH of Quinoline by Method I.

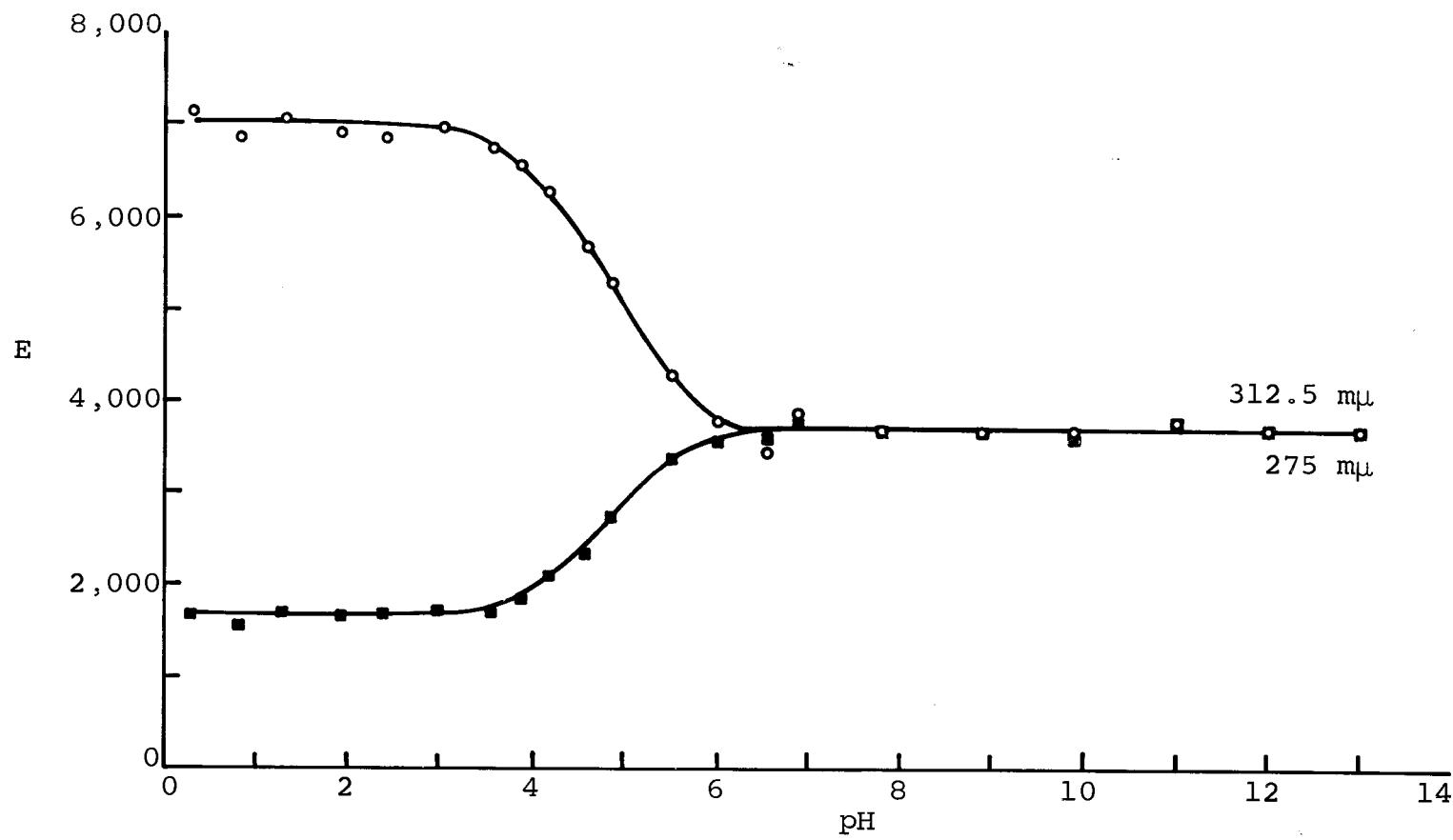


Figure 21. E versus pH of Quinoline by Method I.

Table XXIX. Dissociation Constants of Quinoline
by Method II.

λ (m μ)	E at pH 1.02	E at pH 5.07	E	pH 6.98 pK _a	E	pH 13 pK _a
210	9559	20098	26667	4.86	29216	5.01
215	9069	19559	25784	4.84	29557	5.05
220	11275	22059	28382	4.84	30392	4.96
224	17157	26029	30539	4.78	32108	4.91
225	18627	26422	29902	4.72	31618	4.89
228.5	27696	27451	26961	-	27696	-
230	31618	26275	22059	4.96	23039	4.85
235	35833	14902	3137	4.82	3088	4.82
240	8823	3676	1961	4.60	1961	4.60
245	882	1618	2010	4.80	2108	4.89
250	686	1716	2206	4.75	2402	4.89
255	637	1716	2451	4.90	2598	4.98
260	735	2108	2892	4.83	2941	4.85
265	833	2353	3137	4.78	3186	4.81
270	1176	2647	3431	4.80	3529	4.82
275	1569	2892	3578	4.79	3627	4.82
280	2010	3039	3578	4.79	3627	4.83
285	2647	3235	3529	4.77	3627	4.89
290	3431	3382	3284	-	3333	-
295	4412	3382	2794	4.83	2843	4.79
300	5539	4069	3137	4.87	3186	4.85
305	6373	3971	2696	4.80	2745	4.78
310	6569	4020	2549	4.83	2549	4.83
312.5	6912	4902	3725	4.84	3725	4.84
315	6471	3186	1471	4.79	1471	4.79
320	4167	1961	441	4.91	392	4.92
325	2843	1176	294	4.79	294	4.79
330	2206	980	294	4.82	294	4.82
335	1520	686	294	4.74	294	4.74
340	1078	539	294	4.73	294	4.73

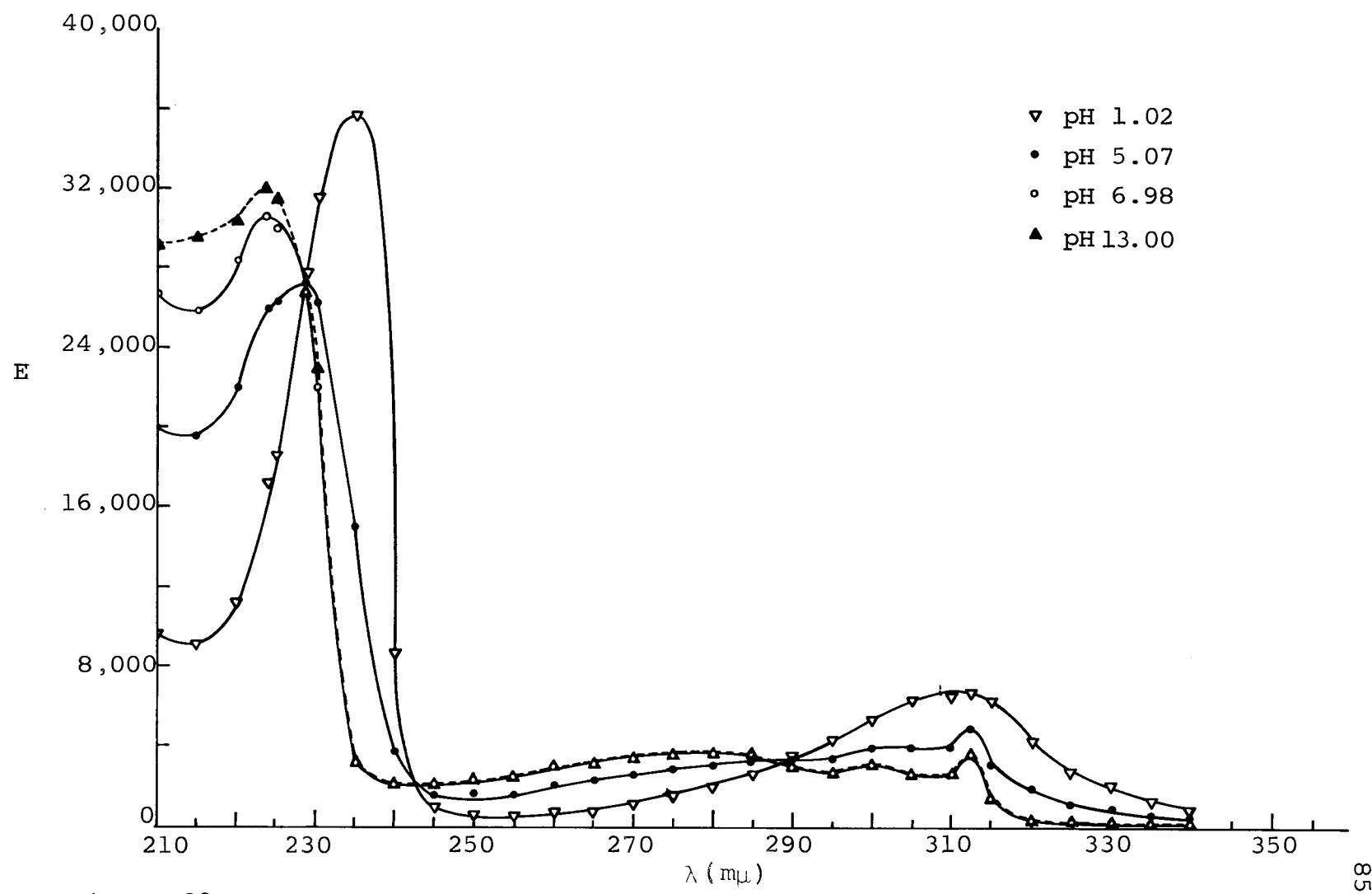


Table XXX. Dissociation Constants of Iso-Quinoline
by Method I.

No.	pH	E at 215 m μ
1	0.43	28788
2	1.01	26818
3	1.51	28030
4	2.01	28106
5	2.44	27348
6	3.13	28636
7	3.60	28712
8	4.15	29470
9	4.71	35606
10	5.28	43333
11	5.69	51818
12	6.50	61288
13	7.00	62045
14	7.66	59924
15	8.58	59924
16	9.13	62424
17	9.81	61061
18	10.52	60758
19	11.03	57652
20	12.00	60906
21	13.00	61136
22	14.00	40758

$\lambda=215 \text{ m}\mu$, $x=28000$, $E=44000$, $y=61000$, $\text{pH}=5.30$, $\text{pK}_a=5.33$

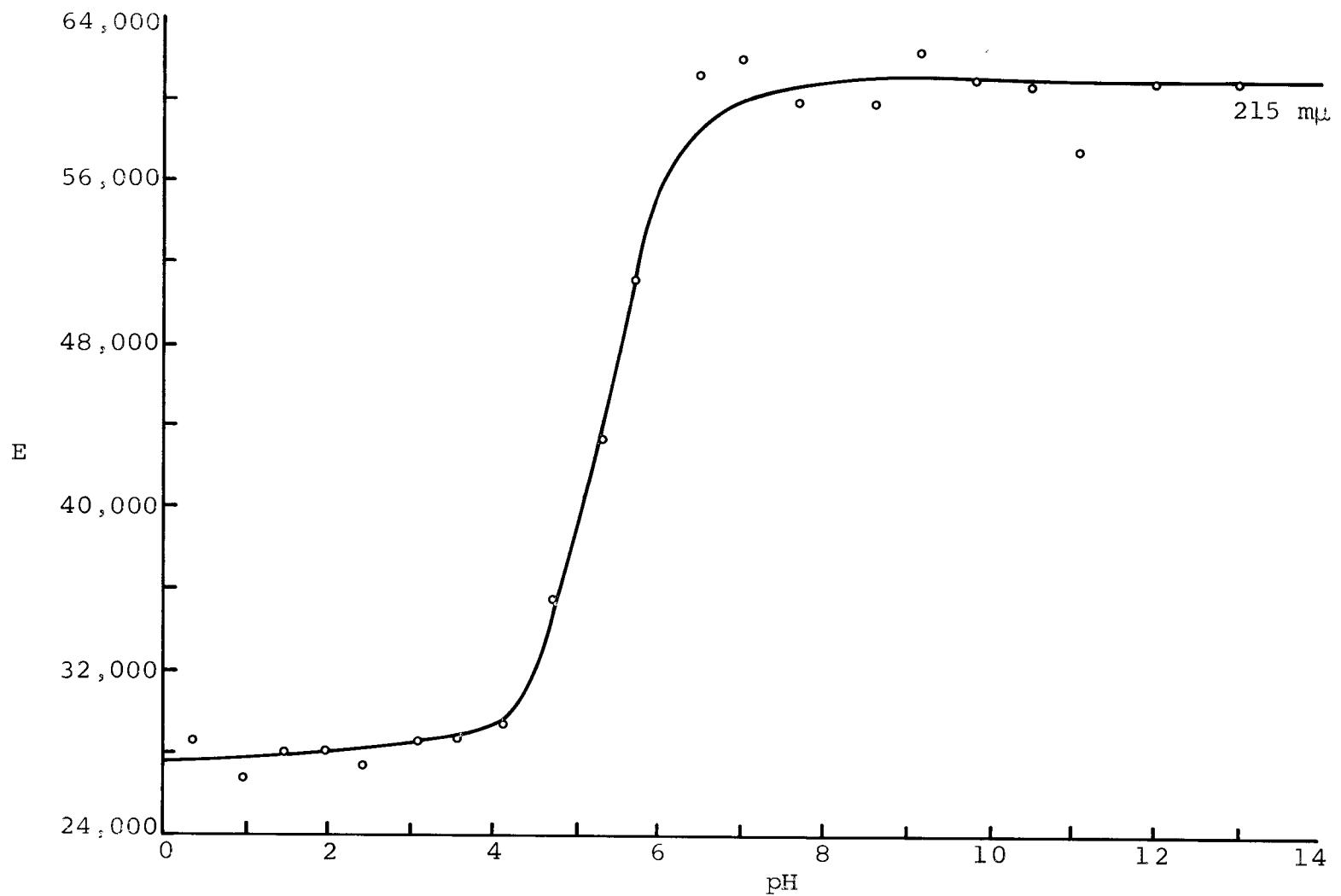


Figure 23. E versus pH of Iso-quinoline by Method I.

Table XXXI. Dissociation Constants of Iso-Quinoline
by Method II.

λ (m μ)	E at	E at	<u>pH 7.00</u>		<u>pH 13</u>	
	pH 1.01	pH 5.28	E	pK _a	E	pK _a
210	21818	34470	50000	5.37	61212	5.60
215	26894	43409	61742	5.33	62045	5.33
220	33333	37045	38636	-	40909	5.30
225	41288	30303	14394	5.44	15152	5.42
230	37879	23864	7500	5.35	6818	5.37
235	13258	8333	3788	5.24	3712	5.25
240	3106	3030	3030	-	2879	5.58
245	1591	2273	3182	5.40	2955	5.28
250	1591	2424	3333	5.32	3182	5.24
255	1742	2652	3636	5.31	3561	5.28
260	2121	2879	3636	5.28	3561	5.23
265	2197	2955	3712	5.28	3636	5.23
270	2273	2727	3561	5.54	3409	5.46
275	2273	2576	3030	5.46	2803	-
280	1667	2121	2803	5.46	2879	5.50
285	1515	1591	1742	5.58	1667	5.28
290	1364	1515	1742	5.46	1667	5.28
295	1364	1591	1894	5.40	1591	-
300	1742	1970	3030	-	2045	-
305	2500	2727	2879	-	2727	-
310	3030	3030	2727	-	2651	-
315	3788	3409	2879	5.43	2727	5.54
318	4091	3788	3409	5.38	3333	5.46
320	4242	3485	2652	5.32	2727	5.28
325	4318	2727	682	5.39	833	5.36
330	4394	2879	530	5.47	455	5.48
335	4167	2576	606	5.37	455	5.40
340	3030	1742	455	5.28	455	5.28
345	1515	1061	455	5.40	455	5.40

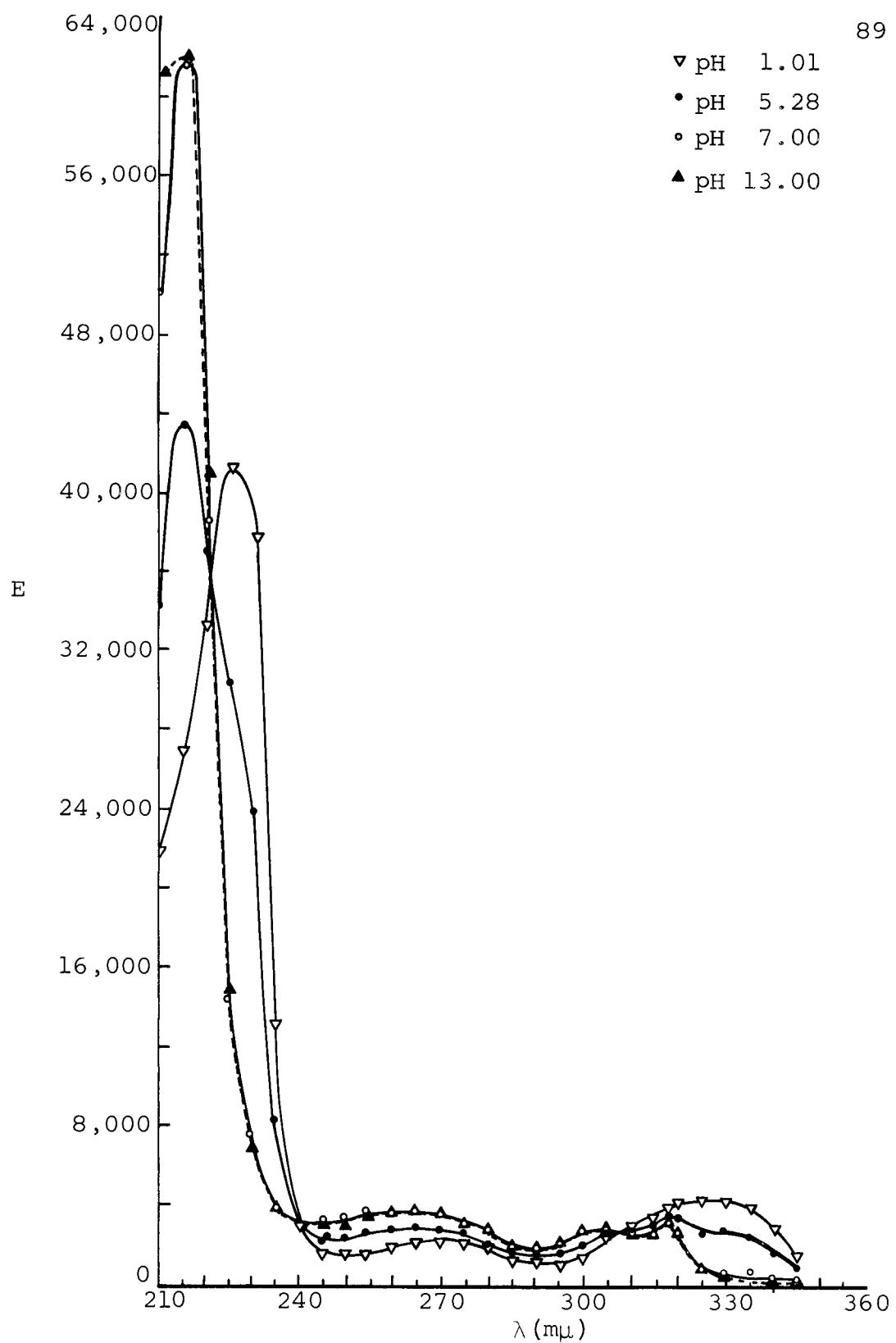


Figure 24. E versus λ of Iso-quinoline by Method II.

Table XXXII. Dissociation Constants of 5-Acetyl-2,4-Dimethylpyrimidine by Method I.

No.	pH	E at 223 m μ	E at 233.5 m μ
0	0.49	8792	7005
1	0.97	8426	6437
2	1.33	8528	7614
3	2.05	8305	9868
4	2.40	8447	10416
5	2.97	8447	10680
6	3.65	8284	10741
7	4.95	8284	10741
8	5.69	8122	10782
9	6.16	8183	10761
10	6.91	8122	10701
11	7.23	8345	10802
12	8.24	8162	10721
13	9.35	8142	10843
14	10.36	8122	10680
15	11.20	8081	10680
16	12.00	7919	10701
17	13.00	7147	10640
18	14.00	4467	10233

$\lambda=223$ m μ , $x=4500$, $E=6400$, $y=8200$, $pH=13.50$, $pK_a=13.48$

$\lambda=233.5$ m μ , $x=7000$, $E=9200$, $y=10800$, $pH=1.70$, $pK_a=1.56$
 $x=10200$, $E=10400$, $y=10700$, $pH=13.50$, $pK_a=13.68$

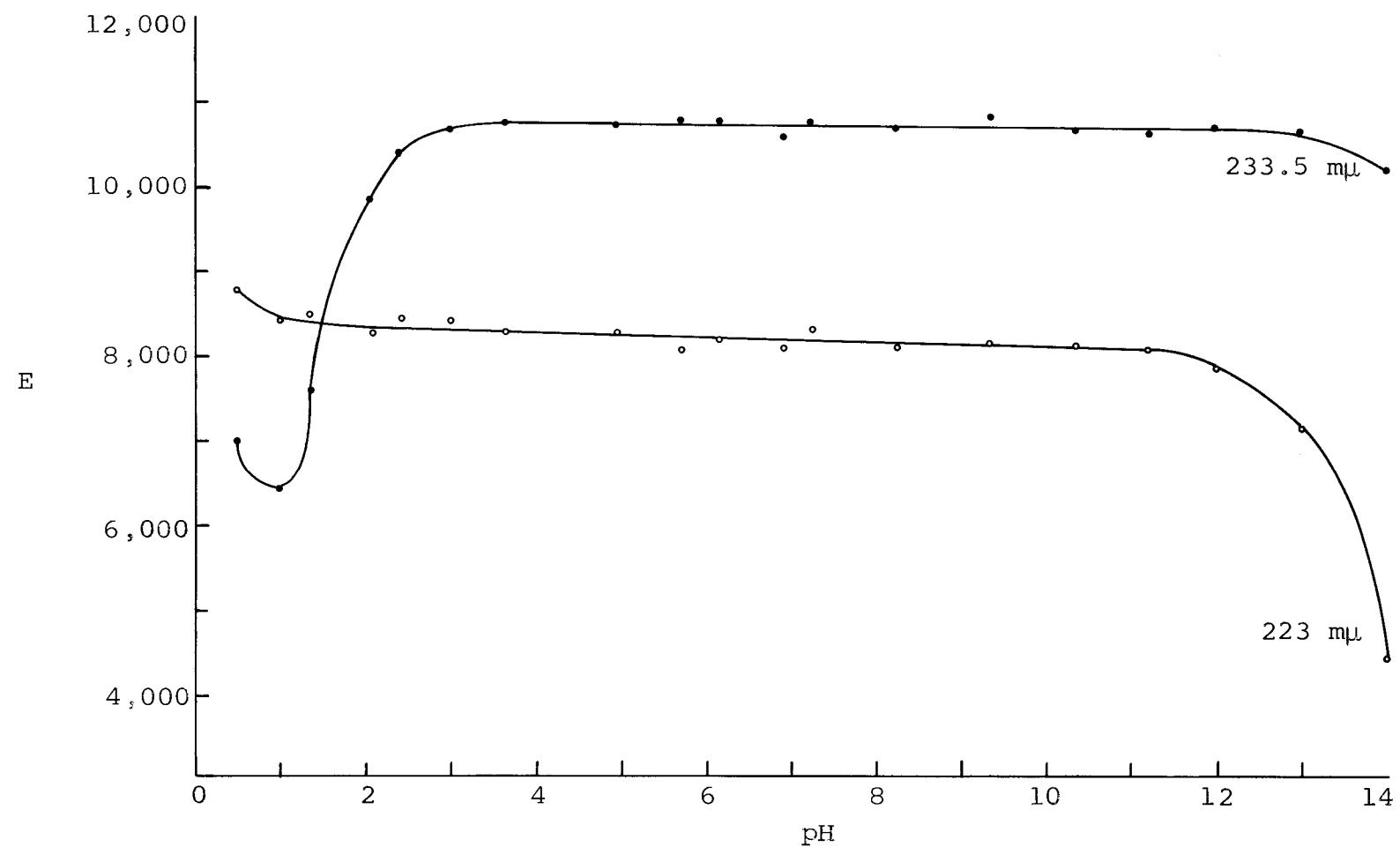


Figure 25. E versus pH of 5-Acetyl-2,4-Dimethylpyrimidine by Method I.

Table XXXIII. Dissociation Constants of 5-Acetyl-2,4-Dimethylpyrimidine by Method II.

λ (m μ)	E at	E at	pH 7.04		pH 1.3	
	pH 1.05	pH 1.67	E	pK _a	E	pK _a
200	0	4864	7035	-	0	-
205	1005	4121	3618	-	0	-
210	5307	4623	3638	1.83	0	-
215	6995	5910	4824	1.67	0	-
220	8040	7477	6734	1.79	4422	-
223	8322	8322	8040	-	7035	-
225	8241	8543	8824	1.64	8241	-
230	7417	8683	10231	1.76	9970	1.68
233.5	6292	8241	10550	1.75	10452	1.72
235	6030	7920	10493	1.80	10432	1.79
240	4724	6834	9407	1.76	9427	1.76
245	4261	5688	7417	1.75	7437	1.76
250	4281	4905	5588	1.71	5628	1.73
255	4281	4101	3920	1.67	3859	1.90
260	3819	3196	2412	1.77	2432	1.76
265	2854	1990	1065	1.70	1065	1.70
270	1668	1085	583	1.60	563	1.62
275	1065	784	462	1.73	442	1.76
280	864	663	362	1.85	382	1.82
285	764	603	322	1.91	342	1.88
290	704	543	241	1.94	281	1.88
295	603	462	201	1.94	221	1.90
300	482	362	141	1.93	161	1.90
305	422	302	121	1.85	141	1.80
310	302	241	101	-	101	-
315	201	201	80	-	60	-
320	101	100	40	-	20	-

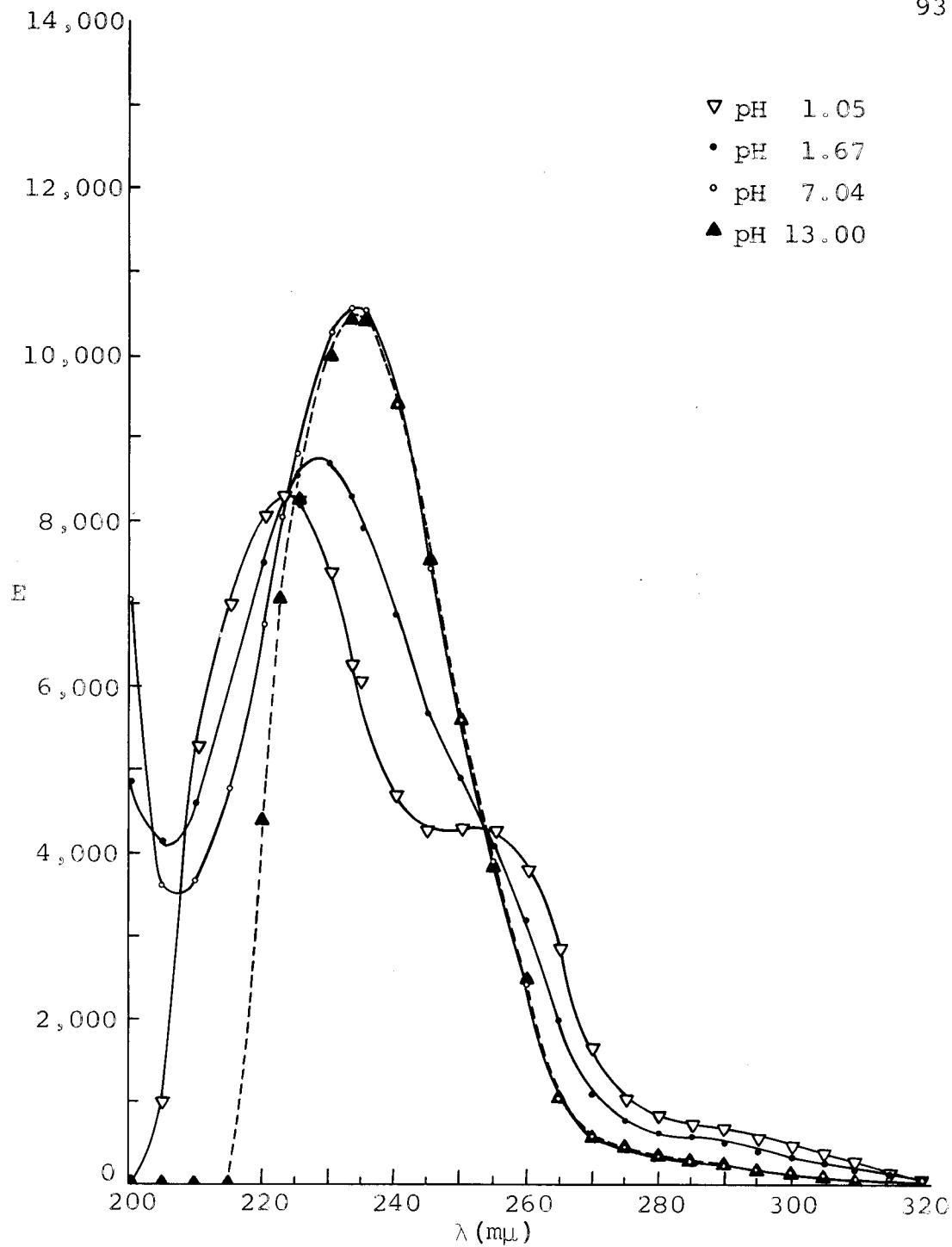


Figure 26. E versus λ of 5-Acetyl-2,4-Dimethylpyrimidine by Method II.

Table XXXIV. Dissociation Constants of 2-Aminopyridine
by Method I.

No.	pH	E at 228 m μ	E at 287 m μ	E at 292 m μ	E at 301 m μ
1	1.33	8538	4269	5023	5525
2	2.05	8739	4395	5073	5688
3	3.05	8903	4382	5148	5738
4	3.70	8890	4420	5148	5738
5	4.86	8802	4395	5148	5650
6	5.43	8802	4370	5035	5525
7	6.03	8852	4269	4884	5148
8	6.64	9103	4093	4357	3993
9	7.01	9129	3855	3842	3039
10	7.95	9267	3767	3616	2398
11	9.04	9329	3754	3553	2373
12	9.92	9292	3767	3528	2323
13	10.44	9329	3742	3516	2285
14	10.98	9292	3717	3553	2336
15	12.00	9017	3642	3415	2260
16	13.00	9042	3705	3528	2310
17	14.00	9042	3717	3528	2336

$\lambda=228 \text{ m}\mu$, $x=8800$, $E=9100$, $y=9350$, $\text{pH}=6.70$, $\text{pK}_a=6.62$

$\lambda=287 \text{ m}\mu$, $x=3750$, $E=4050$, $y=4400$, $\text{pH}=6.70$, $\text{pK}_a=6.76$

$\lambda=292 \text{ m}\mu$, $x=3500$, $E=4250$, $y=5150$, $\text{pH}=6.75$, $\text{pK}_a=6.75$

$\lambda=301 \text{ m}\mu$, $x=2500$, $E=3750$, $y=5250$, $\text{pH}=6.70$, $\text{pK}_a=6.78$

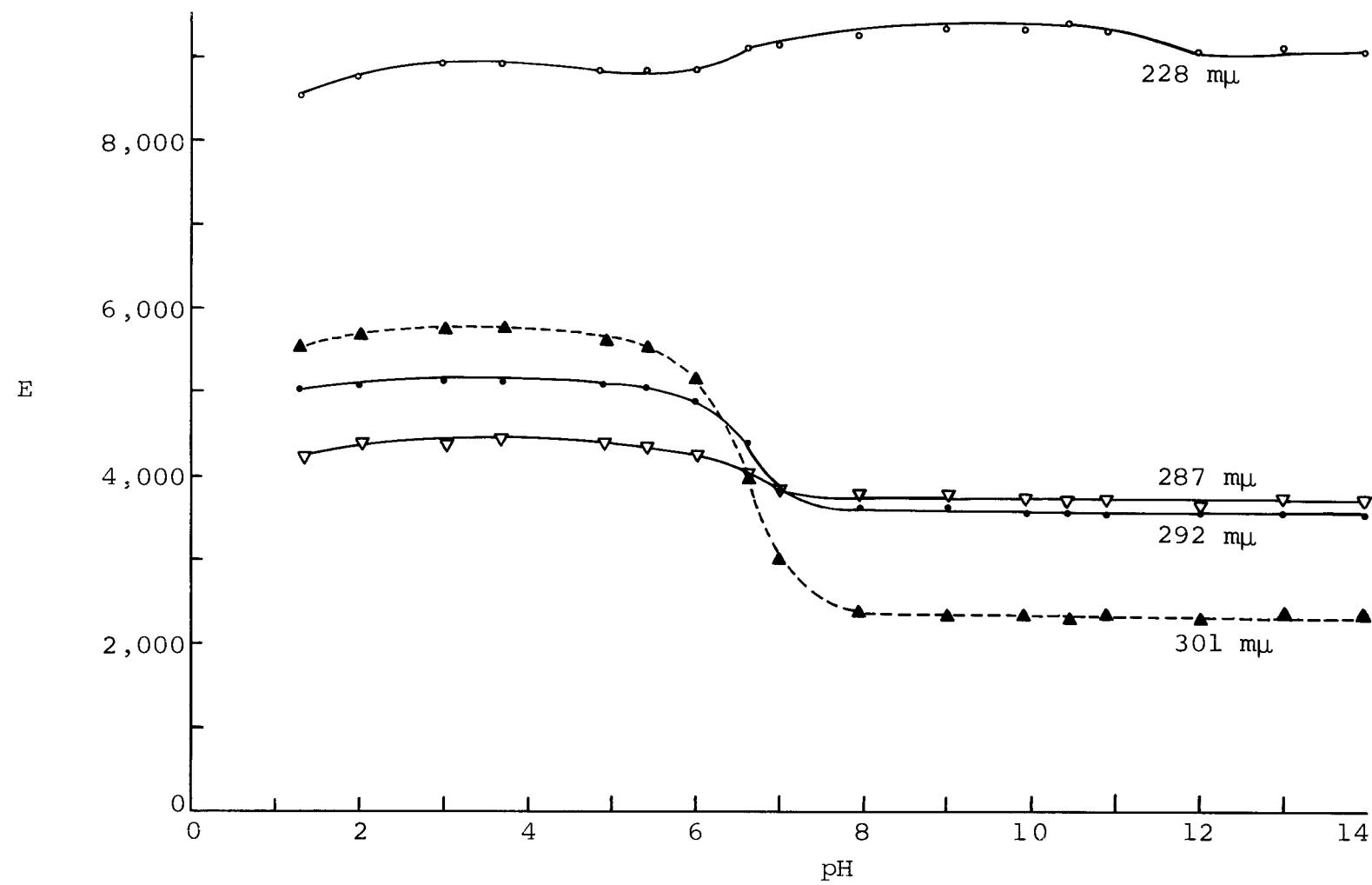


Figure 27. E versus pH of 2-Aminopyridine by Method I.

Table XXXV. Dissociation Constants of 2-Aminopyridine
by Method II.

λ (m μ)	E at	E at	pH 7.00		pH 13	
	pH 1.18	pH 6.11	E	pK _a	E	pK _a
200	7685	7887	5157	-	2750	-
205	1871	1921	2315	-	3347	-
207	1557	1608	2326	-	3640	-
210	1790	1871	2831	-	4146	-
215	3135	3236	4449	-	5460	-
220	5460	5561	6724	-	7887	-
225	8140	8889	8696	-	10111	-
228	9201	9100	9151	-	10566	-
230	9120	9080	8999	-	10415	-
235	6673	6775	6775	-	8291	-
240	1820	2224	3134	-	4803	-
245	354	526	1112	6.64	2123	-
250	384	394	536	-	1011	-
255	556	516	607	-	1011	-
260	859	819	910	-	1325	-
265	1274	1244	1365	-	1871	-
270	1871	1830	2022	-	2558	-
275	2629	2609	2730	-	3316	-
280	3539	3438	3438	-	3953	-
285	4449	4328	4014	-	4307	-
287	4853	4651	4146	6.51	4348	-
290	5359	5051	4277	6.52	4277	6.52
292	5561	5274	4287	6.65	4146	6.70
295	5986	5511	4206	6.55	3832	6.66
300	6168	5602	3842	6.60	3064	6.76
305	5966	5298	3286	6.59	2214	6.77
310	5137	4540	2558	6.63	1335	6.84
315	3953	3438	1820	6.61	708	6.83
320	2629	2275	1122	6.62	334	6.85

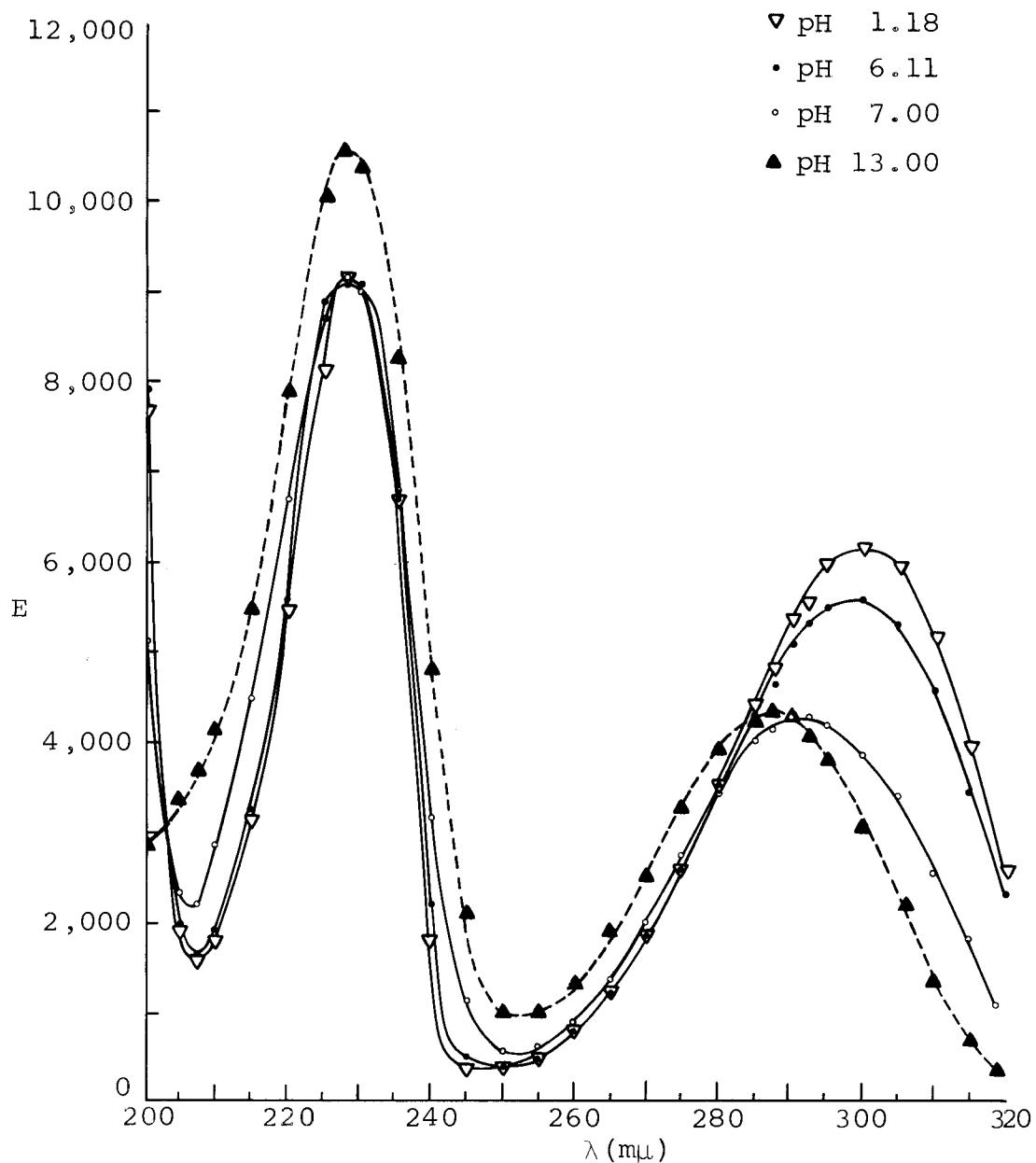


Figure 28. E versus λ of 2-Aminopyridine by Method II.

Table XXXVI. Dissociation Constants of Benzamidine Hydrochloride by Method I.

No.	pH	E at 228 m μ
1	0.00	10925
2	0.48	11040
3	1.00	11040
4	1.45	11012
5	2.00	10983
6	2.54	11012
7	3.04	11098
8	3.51	10925
9	4.00	10954
10	4.50	10954
11	5.00	10983
12	5.50	10983
13	5.96	10867
14	6.54	10954
15	7.00	11012
16	7.51	10896
17	8.10	10983
18	8.57	10983
19	9.22	10896
20	9.75	10751
21	10.13	10723
22	10.57	10607
23	11.00	10202
24	11.50	9682
25	12.00	9191
26	12.50	8873
27	13.00	8786
28	13.50	8526
29	14.00	8208

$\lambda=228 \text{ m}\mu$, $x=8850$, $E=9900$, $y=11000$, $\text{pH}=11.30$, $\text{pK}_a=11.32$

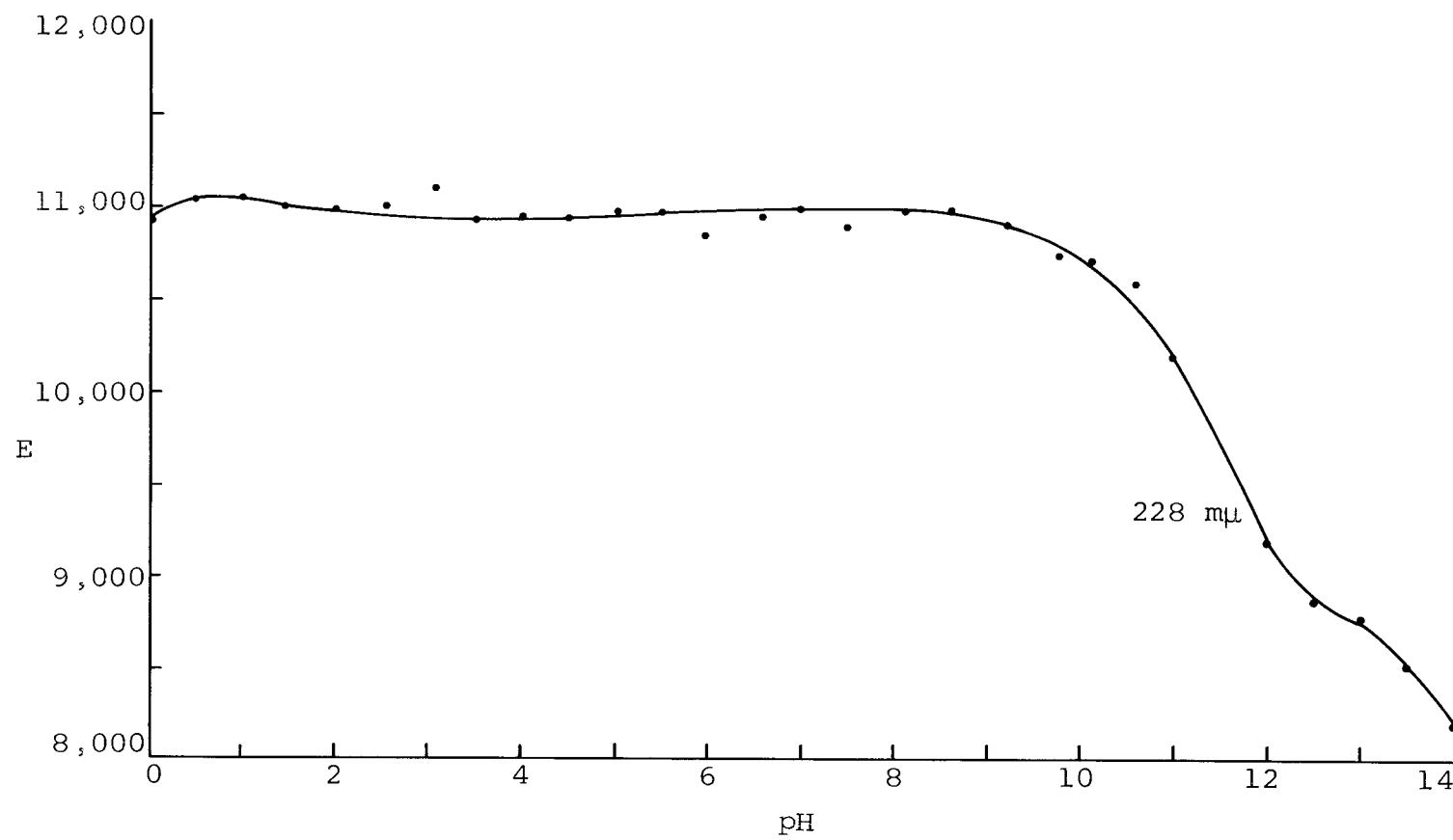


Figure 29. E versus pH of Benzamidine Hydrochloride by Method I.

Table XXXVII. Dissociation Constants of Benzamidine Hydrochloride by Method II.

λ (m μ)	E at pH 1.00	E at pH 11.00	pH 13	
			E	pK _a
200	21965	17486	5780	-
205	10405	10694	6156	-
210	6590	7312	6561	-
215	7399	7775	6936	-
220	9075	9075	7803	-
225	10549	10260	8786	-
228	10983	10231	8815	11.27
230	10925	9971	8613	11.15
235	9538	8526	7312	11.09
240	7023	6358	5780	10.94
245	4191	4191	4335	-
250	2023	2572	3353	11.15
255	1012	1561	2428	11.20
260	867	1243	1763	11.14
265	751	1012	1243	10.95
270	867	954	954	-
275	636	665	520	-
280	347	434	173	-
285	173	173	87	-
290	29	58	58	-
295	0	0	0	-
300	0	0	0	-
305	0	0	0	-
310	0	0	0	-
315	0	0	0	-
320	0	0	0	-

14,000

◦ pH 1.00

12,000

• pH 11.00

E

▲ pH 13.00

8,000

6,000

4,000

2,000

0

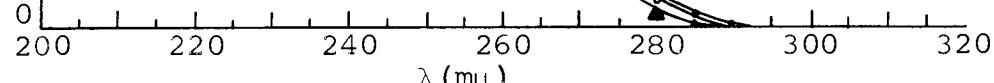
 λ (m μ)

Figure 30. E versus λ of Benzamidine Hydrochloride by Method II.

Table XXXVIII. Dissociation Constants of Hydrazobenzene
by Method I.

No.	pH	E at 213 m μ	E at 239 m μ	E at 245 m μ	E at 290 m μ	E at 318 m μ
1	0.00	10994	13742	14588	1564	2452
2	0.45	10148	13615	14757	1522	2410
3	0.95	9725	13784	14672	1649	2622
4	1.40	9725	13658	14419	1818	2748
5	1.86	9302	13827	13700	2622	2833
6	2.35	9091	14715	13277	3594	2706
7	2.70	8964	14926	13192	3636	2664
8	3.20	8879	14968	13319	3552	2791
9	3.74	9006	15180	13446	3679	2537
10	4.24	9091	15222	13531	3679	2537
11	4.79	9006	15053	13319	3636	2579
12	5.31	8753	14799	13066	3721	2875
13	5.65	8837	14757	13023	3679	2875
14	5.96	9091	15518	13742	3594	2283
15	6.55	8668	15180	13573	3510	2156
16	6.99	8964	14799	13108	3805	3002
17	7.30	9091	14715	13023	3848	3087
18	7.75	8964	14461	12854	3890	3214
19	8.20	8795	13784	12220	4017	3848
20	8.66	8457	13531	11628	4059	3890
21	9.05	8372	13277	11501	4059	4059
22	9.63	8457	13277	11416	4144	4186
23	10.17	8034	12727	10825	4313	4693
24	10.50	8372	12474	10613	4397	4989
25	11.00	8795	12685	10698	4355	4863
26	11.50	8879	12051	10106	4482	5666
27	12.00	8245	12262	10233	4482	5243
28	12.50	16279	12474	10571	4482	5201
29	13.00	31459	13235	11205	4397	4905
30	13.50	59197	12896	9937	4482	6131
31	14.00	-	13953	10359	4609	5877

Table XXXVIII. (Continued)

$\lambda=213 \text{ m}\mu$,	$x= 8900$,	$E= 9800$,	$y=11000$,	$pH=0.90$,	$pK_a = 0.93$
$\lambda=239 \text{ m}\mu$,	$x=13600$,	$E=14500$,	$y=15300$,	$pH=2.30$,	$pK_a = 2.30$
	$x=12100$,	$E=13500$,	$y=15150$,	$pH=8.80$,	$pK_a = 8.87$
	$x=12100$,	$E=13000$,	$y=14000$,	$pH=13.10$,	$pK_a = 13.15$
$\lambda=245 \text{ m}\mu$,	$x=13200$,	$E=13900$,	$y=14700$,	$pH=1.65$,	$pK_a = 1.70$
	$x=10400$,	$E=12000$,	$y=13500$,	$pH=8.40$,	$pK_a = 8.37$
$\lambda=290 \text{ m}\mu$,	$x= 1500$,	$E= 2500$,	$y= 3650$,	$pH=1.80$,	$pK_a = 1.86$
	$x= 3650$,	$E= 4100$,	$y= 4500$,	$pH=8.80$,	$pK_a = 8.75$
$\lambda=318 \text{ m}\mu$,	$x= 2400$,	$E= 3800$,	$y= 5400$,	$pH=8.75$,	$pK_a = 8.80$

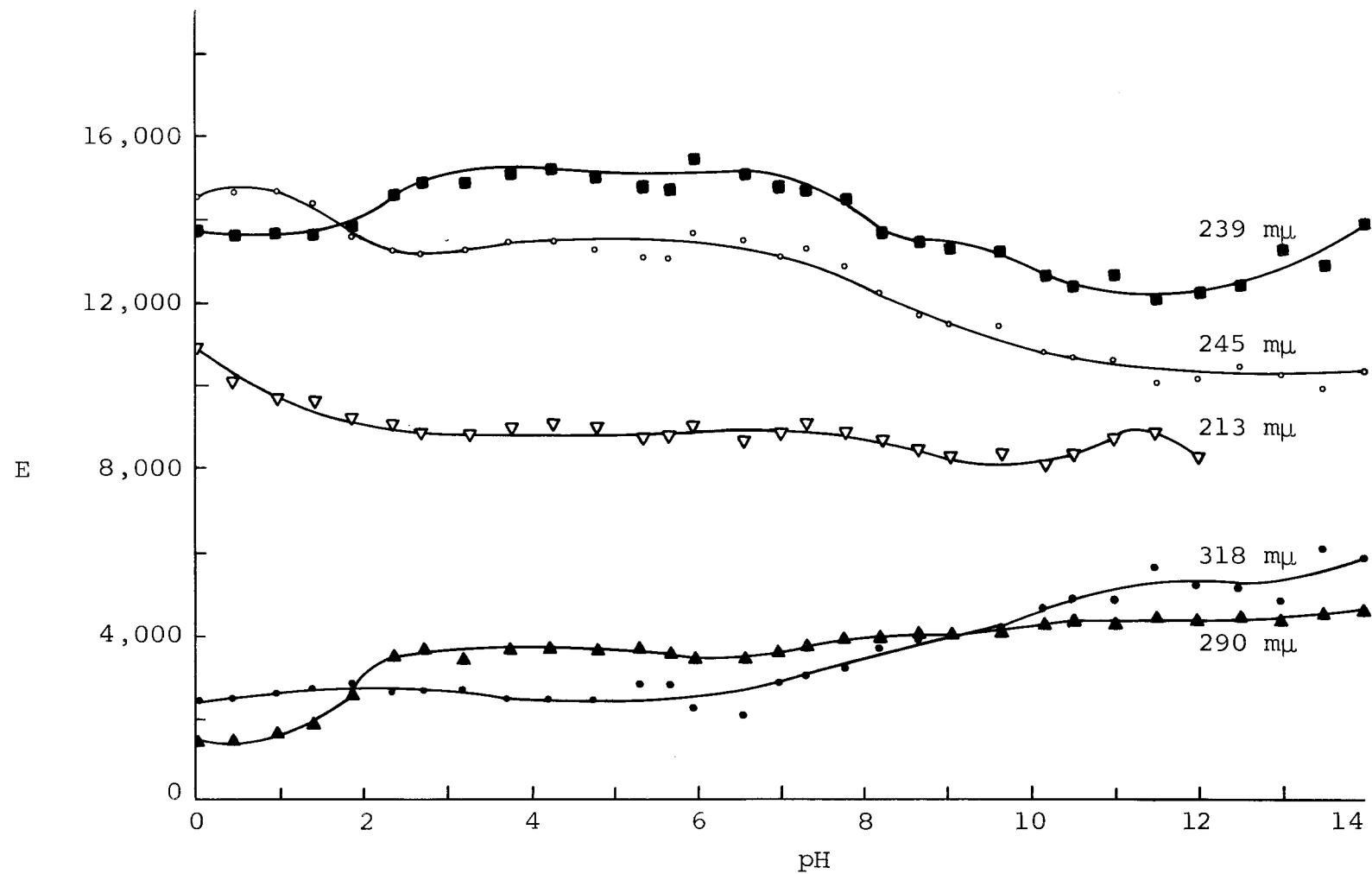


Figure 31. E versus pH of Hydrazobenzene by Method I.

Table XXXIX. Dissociation Constants of Hydrazobenzene
by Method II.

λ (m μ)	E at	E at	pH 7.00		pH 13	
	pH 1.00	pH 1.84	E	pK _a	E	pK _a
210	10359	14799	10994	-	29810	-
215	2748	7780	8161	-	30190	-
220	2283	6850	8795	-	23467	-
225	4863	8203	10359	1.65	16913	-
230	7611	10148	11966	1.70	14165	-
235	9979	11628	13066	1.78	13362	1.86
239	10825	12220	13277	1.72	13023	1.60
240	10825	12178	13192	1.72	12770	1.48
245	10444	11628	11416	-	10825	-
250	9006	10233	8118	-	7696	-
255	6089	8245	4693	-	4355	-
260	3044	5708	2664	-	2875	-
265	1268	4228	2072	-	1860	-
270	211	3383	2283	-	2114	-
275	1438	2918	2748	-	2622	-
280	1480	2791	3383	1.49	3383	1.49
285	1776	2960	3975	1.77	3975	1.77
290	2199	3298	4186	1.75	4440	1.86
295	2579	3510	4144	1.68	4651	1.93
300	3087	3805	4144	1.51	4136	1.95
305	3510	4101	4186	-	4989	-
310	3975	4313	4228	-	5159	-
315	4186	4482	4271	-	5201	-
320	4186	4440	4228	-	5201	-

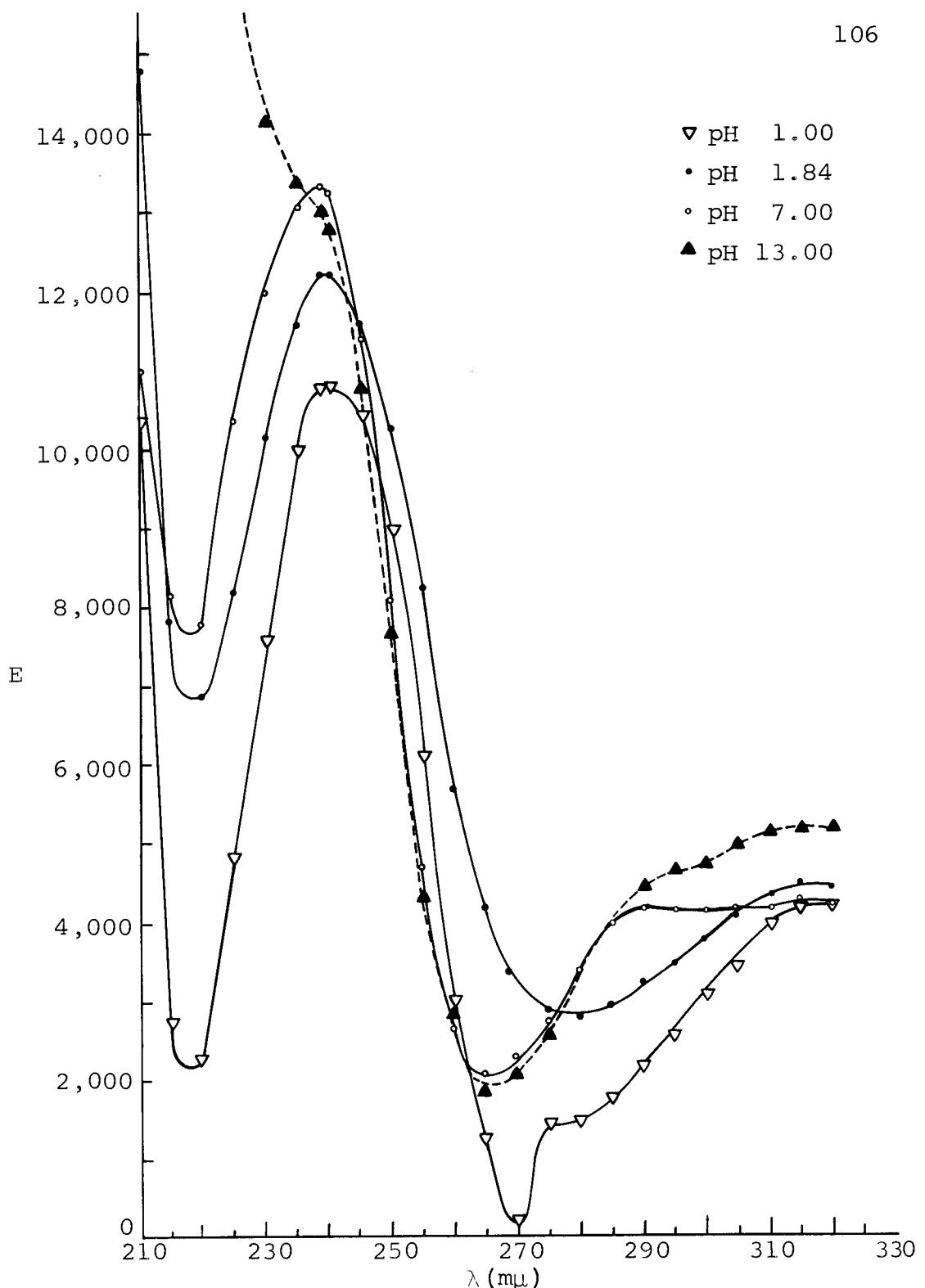


Figure 32. E versus λ of Hydrazobenzene by Method II.

Table XL. Dissociation Constants of 4-Methyl-pyrimidine by Method I.

No.	pH	E at 242 m μ	E at 244 m μ
0	0.38	4869	5192
1	1.17	5115	5253
2	1.49	5069	5161
3	2.43	4147	4209
4	3.36	3487	3518
5	4.40	3410	3425
6	5.16	3364	3379
7	5.97	3379	3364
8	7.09	3349	3333
9	7.63	3333	3303
10	8.40	3425	3425
11	9.23	3379	3395
12	10.33	3395	3379
13	11.20	3289	3287
14	12.00	3226	3257
15	13.00	3379	3303
16	14.00	3395	3349

$\lambda=242 \text{ m}\mu, x=3350, E=4300, y=5125, \text{pH}=2.30, \text{pK}_a=2.24$

$\lambda=244 \text{ m}\mu, x=3350, E=4350, y=5250, \text{pH}=2.35, \text{pK}_a=2.30$

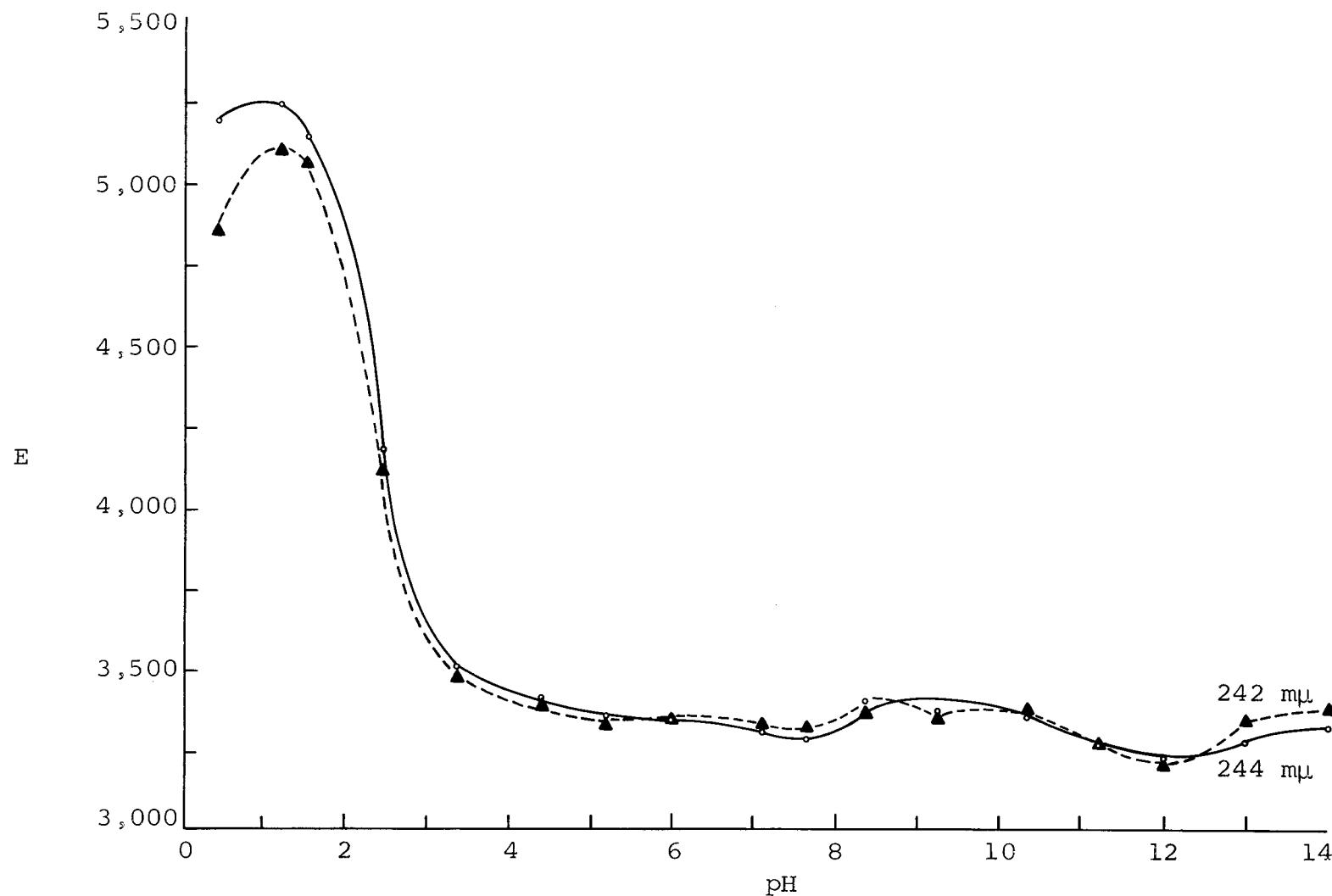


Figure 33. *E* versus pH of 4-Methylpyrimidine by Method I.

Table XLI. Dissociation Constants of 4-Methyl-pyrimidine by Method II.

λ (m μ)	E at	E at	<u>pH 6.95</u>		<u>pH 13</u>	
	pH 1.05	pH 2.21	E	pK _a	E	pK _a
200	1774	3879	3994	-	0	-
203	2074	3379	3149	-	0	-
205	2558	3034	2727	-	0	-
207.5	2849	2458	2151	2.10	0	-
210	2535	1882	1613	1.82	0	-
215	1551	937	730	-	0	2.28
220	1306	768	568	-	230	2.21
225	1659	1175	891	1.98	691	2.21
230	2496	1997	1559	2.05	1459	2.24
235	3725	3072	2458	2.20	2366	2.26
240	4892	3994	3226	2.14	3157	2.18
242	5108	4140	3333	2.13	3318	2.14
244	5207	4148	3333	2.10	3341	2.09
245	5177	4094	3303	2.07	3303	2.07
250	4155	3072	2381	2.02	2660	1.79
255	2465	1528	1006	1.96	1091	1.88
260	1068	691	530	1.89	545	1.80
265	530	422	422	-	422	-
270	307	338	369	2.21	361	2.08
275	192	269	292	-	300	1.81
280	107	184	215	1.81	215	1.81
285	69	123	138	-	138	-
290	38	77	77	-	77	-
295	23	31	31	-	31	-
300	8	0	0	-	0	-
305	0	0	0	-	0	-
310	0	0	0	-	0	-
315	0	0	0	-	0	-
320	0	0	0	-	0	-

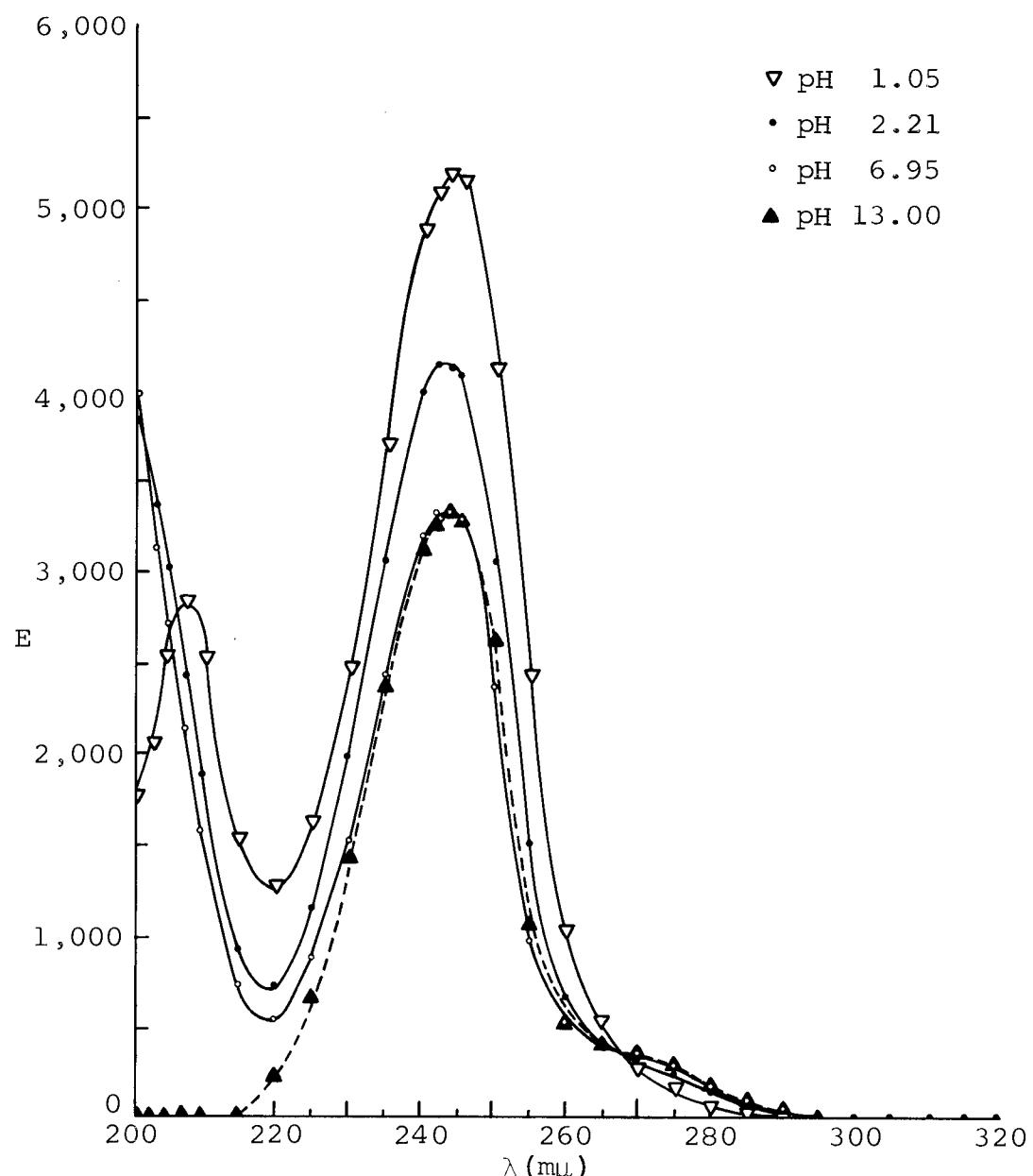


Figure 34. E versus λ of 4-Methylpyrimidine by Method II.

Table XLII. Dissociation Constants of m-Phenylenediamine Dihydrochloride by Method I.

No.	pH	E at 210 m μ	E at 235 m μ	E at 240 m μ	E at 290 m μ
1	0.00	2536	222	254	0
2	0.45	1902	317	317	0
3	1.00	2061	476	444	0
4	1.42	1966	1110	951	127
5	1.60	1966	1554	1300	159
6	1.80	2473	2410	2029	317
7	2.00	2283	3171	2632	412
8	2.21	2790	4851	3932	698
9	2.45	2885	6309	5231	951
9A	2.55	2885	6817	5517	1046
9B	2.69	3171	7387	5897	1110
10	2.80	3361	7958	6563	1205
11	3.12	3868	8751	7292	1363
12	3.34	4280	9036	7292	1395
13	3.60	5073	9195	7451	1427
14	3.88	6658	9290	7578	1522
15	4.26	11097	9131	7578	1585
16	4.56	11034	9036	7356	1585
17	4.96	21972	8339	6975	1776
18	5.50	29423	7895	6848	1871
19	6.01	33925	7610	6722	1934
20	6.47	34750	7578	6627	1966
21	7.02	35794	7730	6894	2019
22	7.48	35724	7660	6755	2019
23	7.82	35933	7660	6895	2019
24	8.32	36421	7730	6964	2019
25	8.71	36072	7760	6825	1950
26	9.29	36281	7730	6894	2019
27	9.85	36212	7660	6775	1950
28	10.42	35794	7591	6685	1950
29	10.95	36560	7730	6894	1950
30	11.50	36630	7730	6964	2019
31	12.00	36490	7730	6894	2089
32	12.50	35376	7660	6964	2019
33	13.00	24861	7730	6894	2089
34	13.50	21031	7660	6755	1950
35	14.00	15320	7660	6894	1950

Table XLII. (Continued)

$\lambda=210 \text{ m}\mu$, $x= 2000$, $E=19000$, $y=36000$, $pH= 4.80$, $pK_a = 4.80$
 $x=14600$, $E=26000$, $y=36600$, $pH=13.00$, $pK_a = 12.97$

$\lambda=235 \text{ m}\mu$, $x= 225$, $E= 5000$, $y= 9275$, $pH= 2.25$, $pK_a = 2.20$
 $x= 7575$, $E= 8400$, $y= 9275$, $pH= 4.90$, $pK_a = 4.92$

$\lambda=240 \text{ m}\mu$, $x= 200$, $E= 4000$, $y= 7700$, $pH= 2.25$, $pK_a = 2.24$
 $x= 6600$, $E= 7200$, $y= 7750$, $pH= 4.90$, $pK_a = 4.86$

$\lambda=290 \text{ m}\mu$, $x= 0$, $E= 700$, $y= 1400$, $pH= 2.20$, $pK_a = 2.20$
 $x= 1400$, $E= 1700$, $y= 2000$, $pH= 4.85$, $pK_a = 4.85$

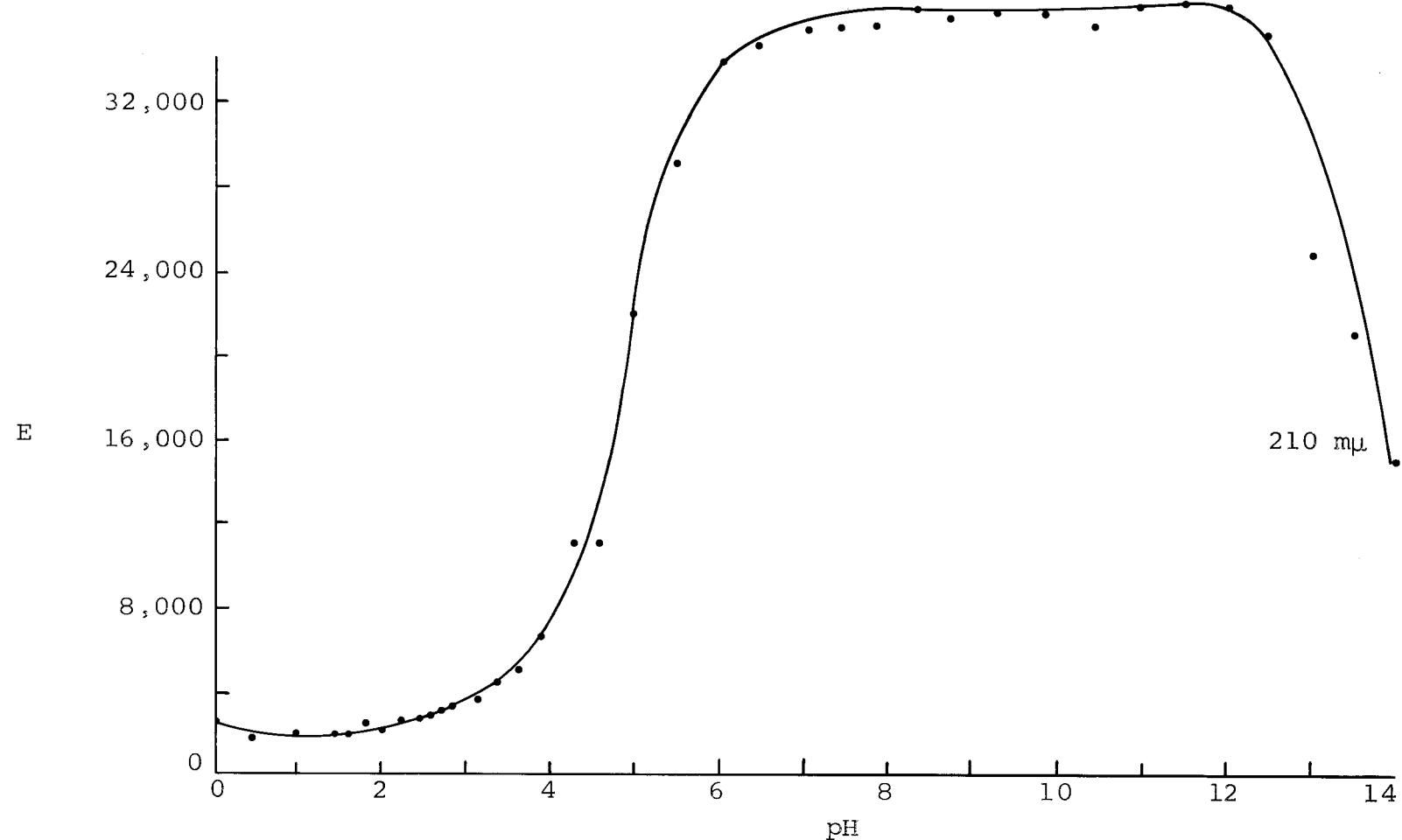


Figure 35. E versus pH of *m*-Phenylenediamine Dihydrochloride by Method I.

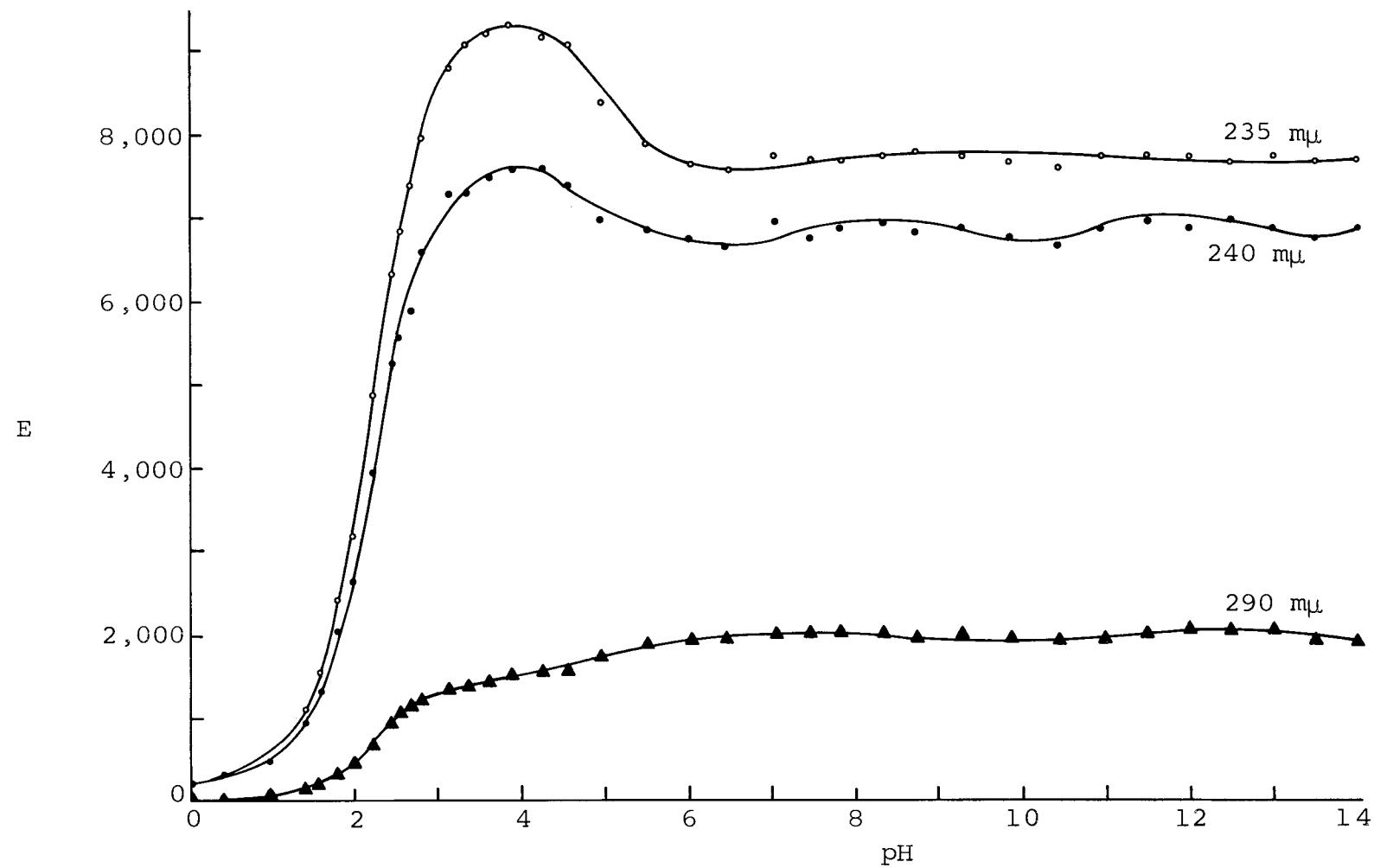


Figure 36. E versus pH of *m*-Phenylenediamine Dihydrochloride by Method I.

Table XLIII. Dissociation Constants of m-Phenylenediamine Dihydrochloride by Method II.

λ (m μ)	E at	E at	<u>pH 7.05</u>		<u>pH 13</u>	
	pH 1.05	pH 2.30	E	pK _a	E	pK _a
200	10028	18106	19638	-	23189	-
205	7660	8357	30641	-	23538	-
210	2298	2786	36072	-	30710	-
215	557	1950	28203	-	23189	-
220	348	2437	17409	-	15669	-
225	487	3621	10794	-	10306	-
230	766	4526	8565	2.33	8357	2.31
235	836	4666	7660	2.19	7799	2.21
240	766	3900	6894	2.28	6964	2.29
245	627	2437	5153	2.48	5223	2.49
250	418	1184	3343	-	3273	-
255	209	418	1532	-	1602	-
260	70	279	696	-	836	-
265	0	279	557	2.30	627	2.40
270	0	418	766	2.22	836	2.30
275	0	627	1114	2.19	1114	2.19
280	0	696	1602	2.41	1602	2.41
285	0	696	1950	2.56	2019	2.58
290	0	627	2019	2.64	2019	2.64
295	0	279	1671	-	1671	-
300	0	70	905	-	905	-
305	0	70	348	-	418	-
310	0	0	139	-	70	-
315	0	0	70	-	70	-
320	0	0	0	-	0	-

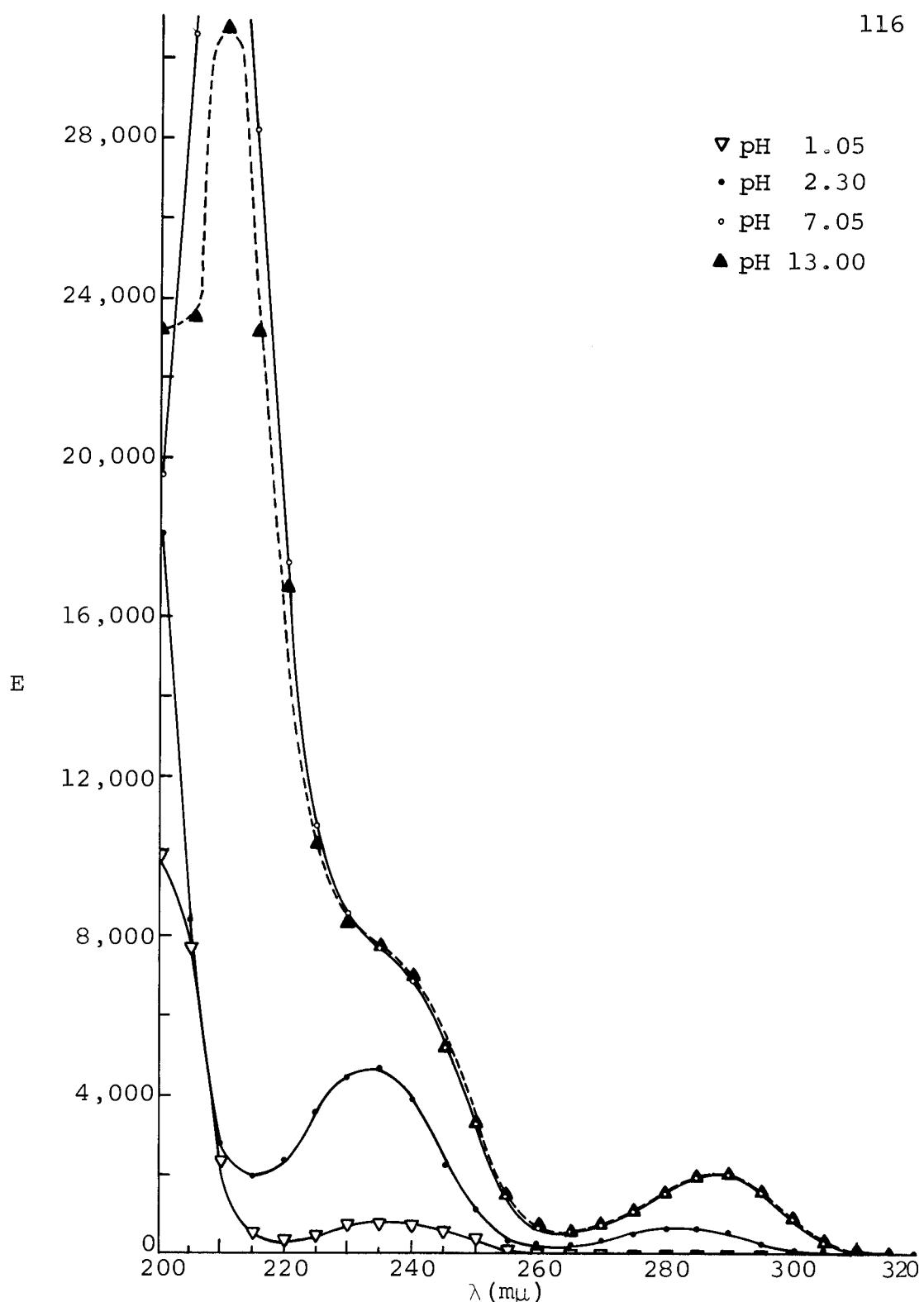


Figure 37. E versus λ of m-Phenylenediamine Dihydrrochloride by Method II.

Table XLIV. Dissociation Constants of o-Phenylenediamine by Method I.

No.	pH	E at 230 m μ	E at 290 m μ
1	0.00	1480	140
2	0.41	3855	587
3	1.03	7151	1061
4	1.34	8659	1257
5	1.84	9078	1397
6	2.60	9078	1368
7	3.55	8547	1620
8	4.55	7123	2514
9	5.00	6871	2793
10	6.05	6620	2905
11	6.95	6536	2877
12	8.13	6704	2961
13	9.14	6564	2933
14	10.30	6620	2905
15	11.00	6592	2877
16	12.00	6788	2961
17	13.00	6955	2933
18	14.00	8659	2933

$\lambda=230 \text{ m}\mu$, $x=1000$, $E=5500$, $y=9100$, $\text{pH}=0.75$, $\text{pK}_a=0.65$
 $x=6500$, $E=7500$, $y=9100$, $\text{pH}=4.25$, $\text{pK}_a=4.45$
 $x=6500$, $E=7400$, $y=8650$, $\text{pH}=13.50$, $\text{pK}_a=13.63$

$\lambda=290 \text{ m}\mu$, $x=150$, $E=850$, $y=1400$, $\text{pH}=0.75$, $\text{pK}_a=0.65$
 $x=1350$, $E=2100$, $y=2950$, $\text{pH}=4.20$, $\text{pK}_a=4.26$

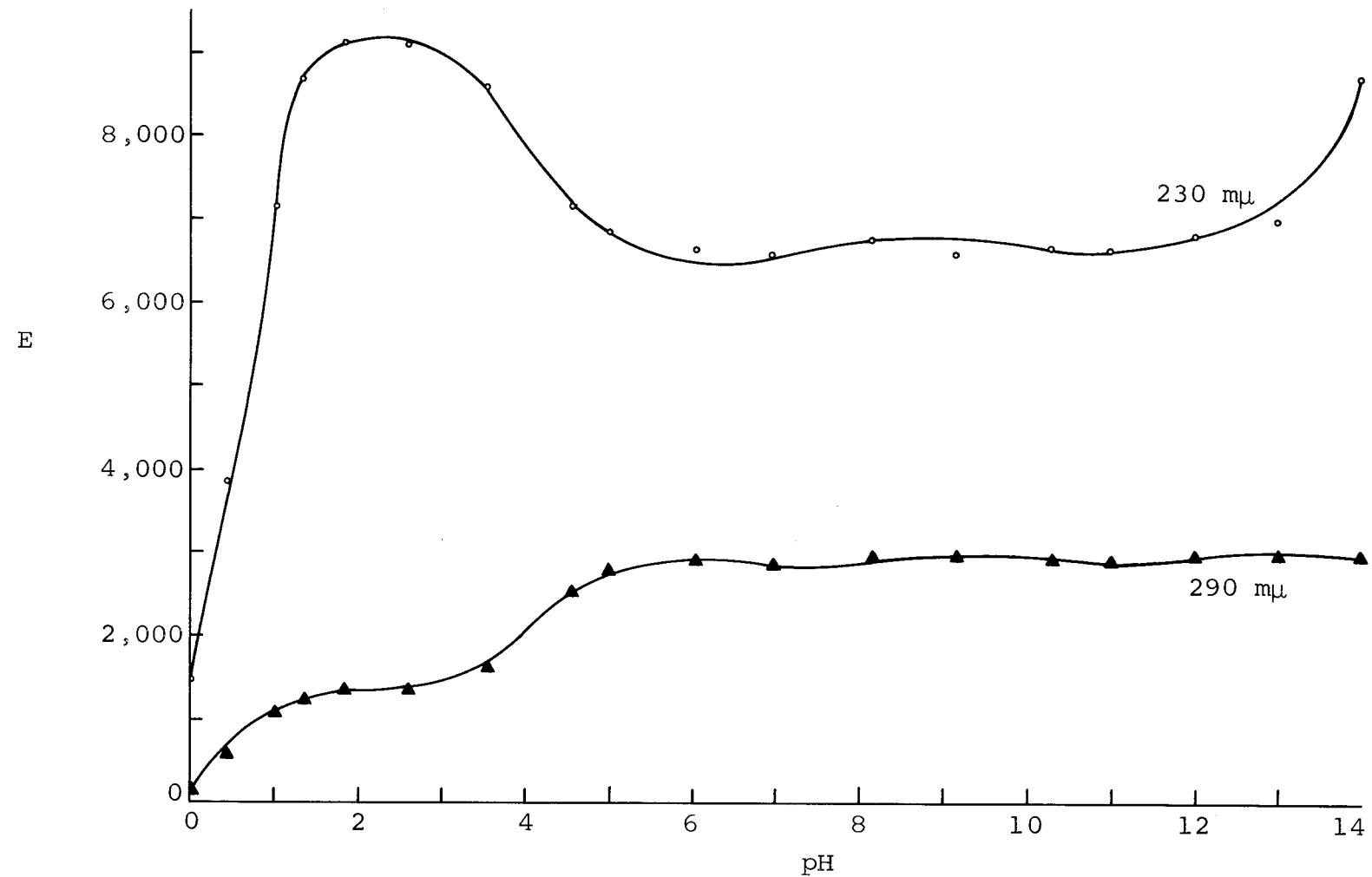


Figure 38. E versus pH of o-Phenylenediamine by Method I.

Table XLV. Dissociation Constants of α -Phenylenediamine by Method II.

λ (m μ)	E at pH 1.22	E at pH 4.87	pH 7.10		pH 13	
			E	pK _a	E	pK _a
200	16408	26763	27716	-	8891	-
205	7095	28204	37428	4.51	10754	-
210	3548	23392	31486	4.48	13348	-
215	3525	12195	16186	4.53	13348	-
220	4767	7539	8204	-	7982	-
225	6275	7095	6563	-	6208	-
230	6940	7251	6541	-	6098	-
235	5987	6674	6319	-	5920	-
240	3836	5255	5432	-	5100	-
245	1973	3326	3814	4.43	3547	-
250	887	1840	2328	4.54	2106	4.32
255	576	1131	1486	4.68	1330	4.43
260	687	998	1197	4.68	1020	-
265	865	1109	1175	-	998	-
270	1153	1330	1353	-	1197	-
275	1397	1729	1774	-	1574	-
280	1486	2106	2306	4.38	2195	-
285	1419	2395	2772	4.46	2661	4.31
290	1109	2350	2882	4.50	2772	4.40
295	710	1973	2550	4.53	2439	4.44
300	355	1330	1774	4.53	1663	4.40
305	155	732	1064	4.63	976	4.50
310	67	333	466	-	443	-
315	22	111	177	-	155	-
320	0	44	44	-	0	-

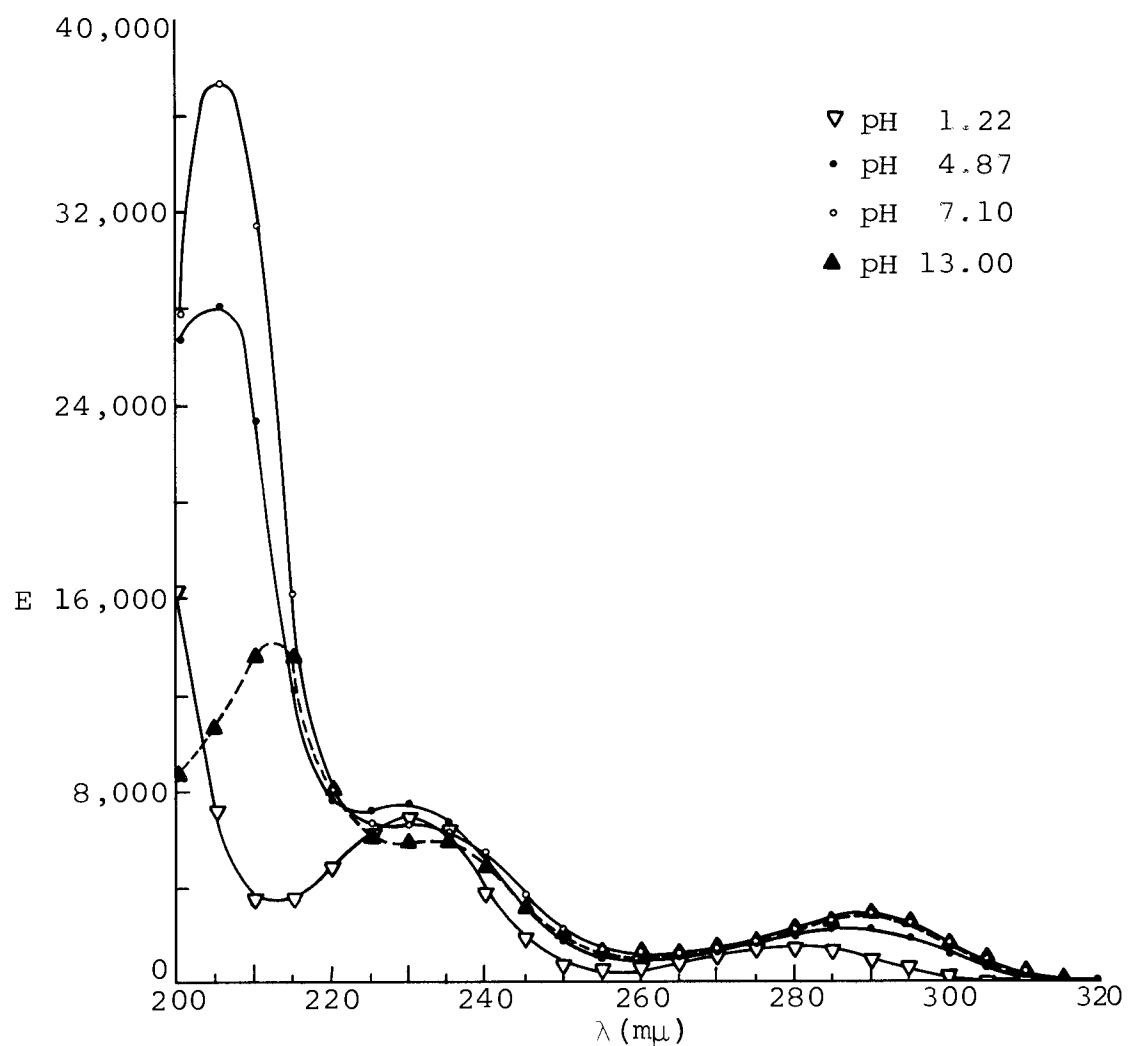


Figure 39. E versus λ of o-Phenylenediamine by Method II.

Table XLVI. Dissociation Constants of p-Phenylenediamine by Method I.

No.	pH	E at 240 m μ	E at 305 m μ
1	0.50	230	18
2	1.34	424	18
3	1.86	1131	18
4	2.29	2385	106
5	3.05	5724	247
6	3.65	7474	406
7	4.39	7650	601
8	4.89	7915	954
9	5.27	7650	495
10	6.45	8481	1431
11	6.96	8834	1502
12	8.03	8993	1572
13	9.08	8816	1502
14	10.13	8905	1555
15	11.12	8958	1572
16	12.00	8870	1555
17	13.00	9011	1572
18	14.00	9028	1555

$\lambda=240 \text{ m}\mu$, $x=250$, $E=4000$, $y=7500$, $\text{pH}=2.65$, $\text{pK}_a=2.62$
 $x=8000$, $E=8500$, $y=8900$, $\text{pH}=6.10$, $\text{pK}_a=6.10$

$\lambda=305 \text{ m}\mu$, $x=0$, $E=200$, $y=400$, $\text{pH}=2.60$, $\text{pK}_a=2.60$
 $x=1000$, $E=1300$, $y=1500$, $\text{pH}=5.80$, $\text{pK}_a=5.62$

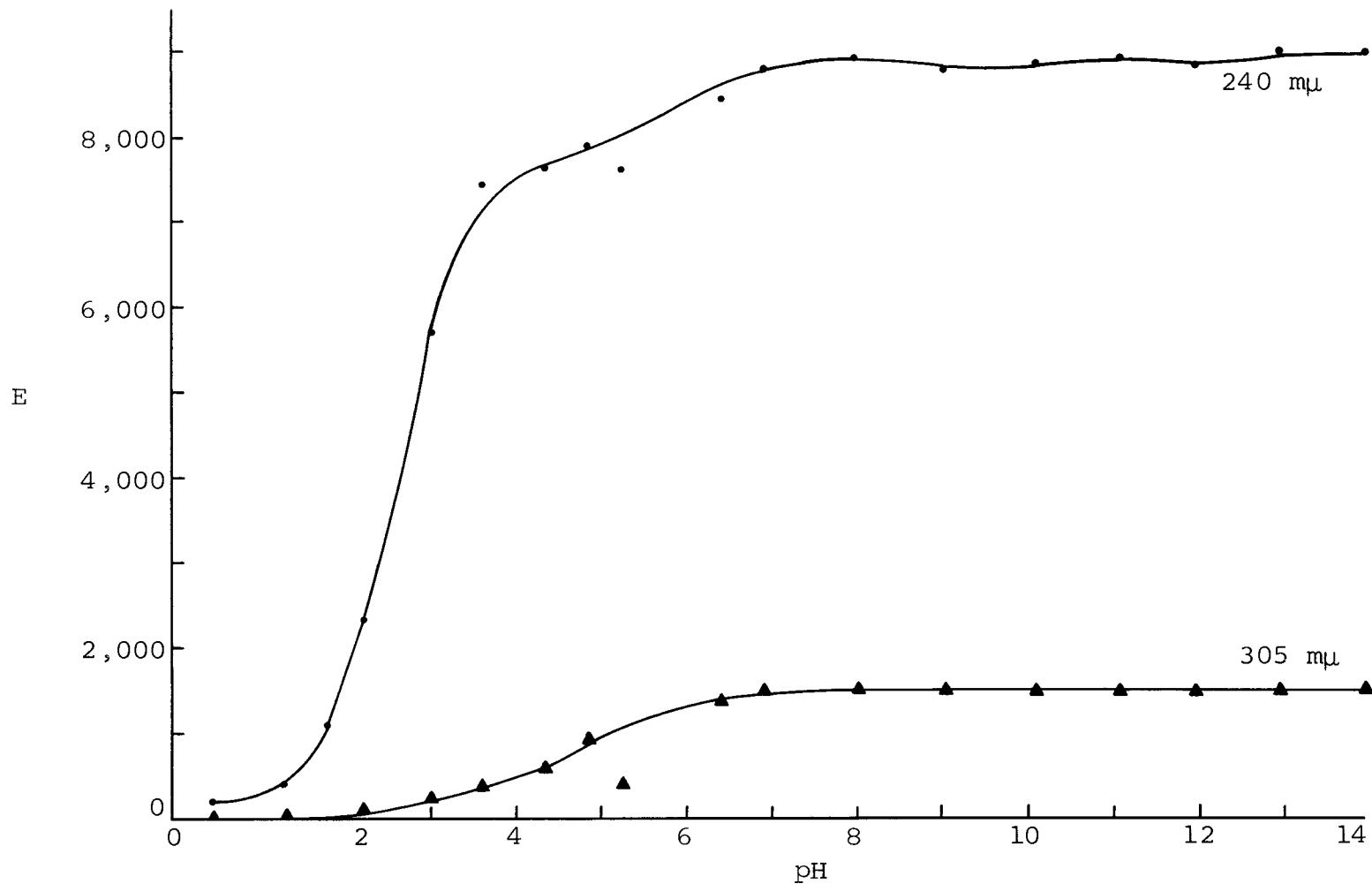


Figure 40. E versus pH of *p*-Phenylenediamine by Method I.

Table XLVII. Dissociation Constants of p-Phenylenediamine by Method II.

λ (m μ)	E at	E at	pH 6.95		pH 13	
	pH 1.14	pH 6.28	E	pK _a	E	pK _a
210	2059	4118	4632	5.68	4383	-
215	235	3132	3118	-	4691	6.01
220	147	3971	3794	-	4765	-
225	147	5735	5221	-	5662	-
230	191	7500	6985	-	6985	-
235	221	8500	8132	-	8235	-
240	221	8088	8397	5.87	8750	-
245	206	6324	7500	5.64	8088	-
250	191	4412	5662	5.75	6221	5.91
255	176	2500	3559	5.94	3897	6.06
260	132	1324	1941	5.99	2132	6.11
265	45	765	1029	5.85	1029	5.85
270	15	588	632	-	632	-
275	15	735	485	-	397	-
280	15	794	559	-	471	-
285	15	956	735	-	735	-
290	15	1029	955	-	955	-
295	15	1029	1147	-	1235	-
300	15	971	1265	5.77	1471	6.00
305	15	956	1324	5.87	1529	6.06
310	15	838	1206	5.93	1397	6.11
315	15	662	956	5.94	1074	6.08
320	15	441	603	5.86	706	6.07

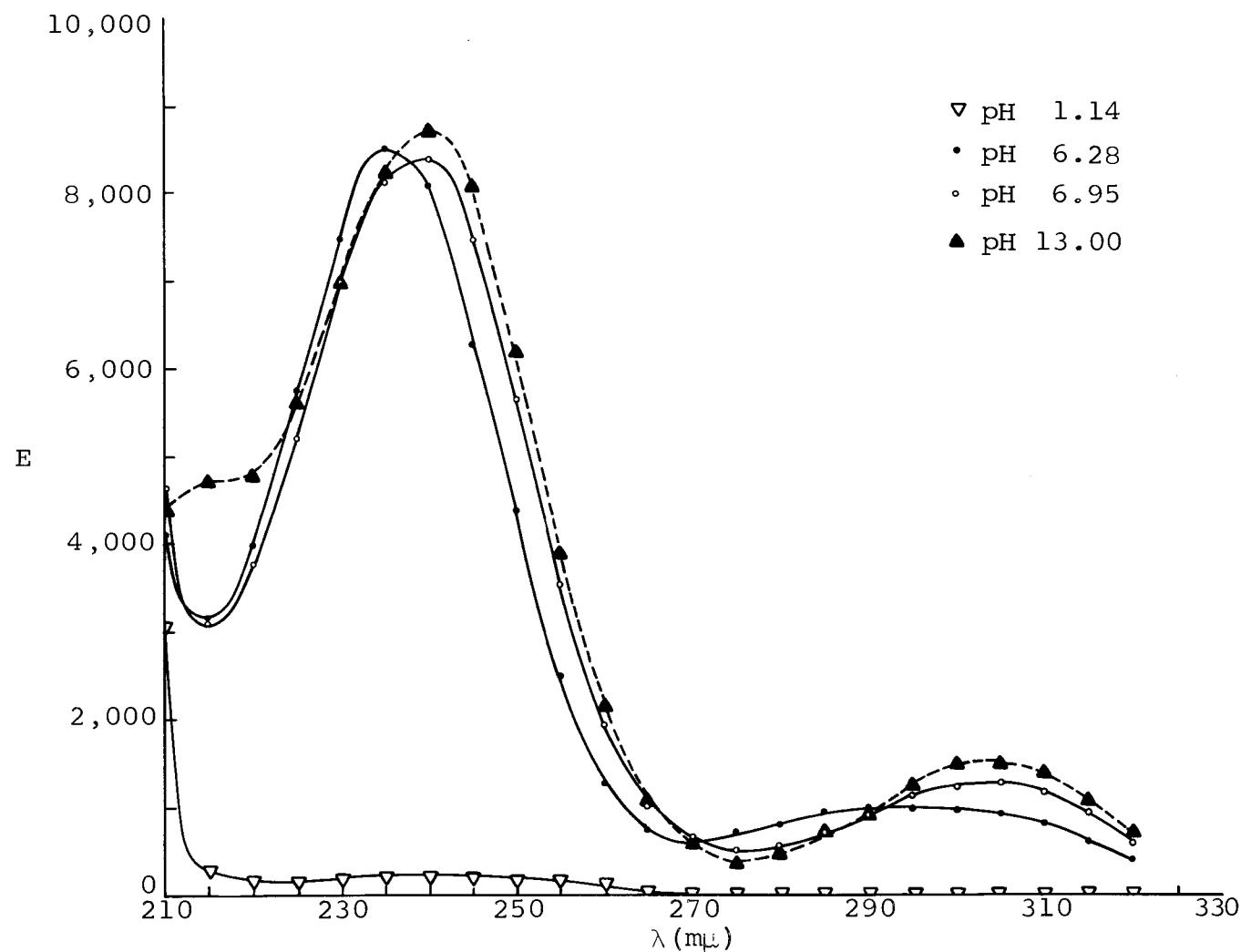


Figure 41. E versus λ of p-Pheneplenediamine by Method II.

Table XLVIII. Dissociation Constants of Phenylhydrazine
by Method I.

No.	pH	E at 230 m μ	E at 274 m μ
1	0.00	4967	1126
2	0.51	4901	1060
3	1.02	4283	993
4	1.34	4702	1060
5	1.85	4746	1038
6	2.44	4967	1214
7	2.89	4879	1192
8	3.52	4812	1170
9	4.08	4967	1214
10	4.58	4296	1589
11	4.81	5077	1214
12	5.15	4967	1413
13	5.50	5232	1347
14	5.86	6711	1788
15	6.25	5938	1788
16	6.65	5585	1700
17	7.02	5585	2141
18	7.25	4614	1766
19	7.46	5938	1567
20	8.15	6159	1435
21	8.80	6071	1435
22	9.40	6512	1391
23	9.78	6313	1435
24	10.26	6004	1788
25	10.91	5166	2605
26	11.50	6291	2208
27	12.00	5320	3135
28	12.50	6291	2318
29	13.00	6071	2384
30	13.50	6026	1965
31	14.00	5828	1766

$\lambda=230 \text{ m}\mu$, $x=4800$, $E=5450$, $y=6100$, pH= 6.20, pK_a= 6.20

$\lambda=274 \text{ m}\mu$, $x=1100$, $E=1450$, $y=1800$, pH= 5.30, pK_a= 5.30

$x=1400$, $E=1600$, $y=1800$, pH= 7.50, pK_a= 7.50

$x=1400$, $E=2000$, $y=2600$, pH=10.50, pK_a=10.50

$x=1750$, $E=2200$, $y=2600$, pH=13.10, pK_a=13.10

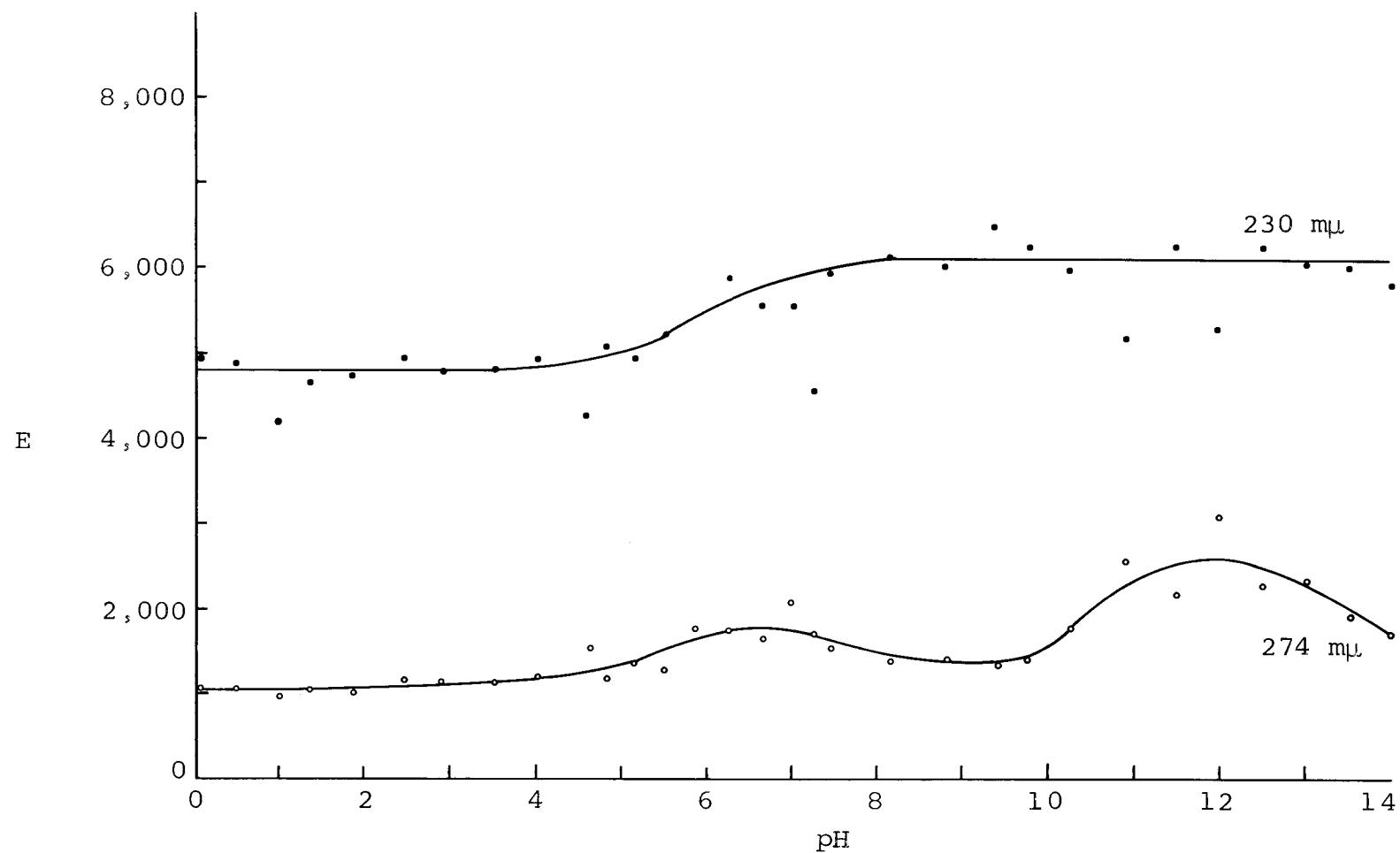


Figure 42. E versus pH of Phenylhydrazine by Method I.

Table XLIX. Dissociation Constants of Phenylhydrazine
by Method II.

λ (m μ)	E at	E at	<u>pH 7.02</u>		<u>pH 13</u>	
	pH 1.02	pH 5.86	E	pK _a	E	pK _a
200	9492	20971	19757	-	3532	-
205	5752	9934	10375	-	3797	-
210	4857	5298	5740	-	4018	-
215	5188	4746	4967	-	4415	-
220	5784	5188	5077	-	5077	-
225	5607	6291	5298	-	5519	-
230	4238	6711	5585	-	6049	-
235	2428	6181	5298	-	6004	-
240	1104	4857	4371	-	4989	-
245	662	3311	3201	-	3753	-
250	574	2141	2230	-	2980	5.58
255	662	1567	1810	5.29	2649	-
260	817	1479	1788	5.48	2517	-
265	927	1545	1898	5.62	2450	-
270	1038	1700	2097	5.58	2428	-
274	1015	1766	2141	5.56	2384	5.76
275	971	1766	2141	5.53	2362	5.74
280	883	1656	1987	5.49	2230	5.73
285	552	1413	1611	5.21	2053	5.73
290	331	1038	1214	5.26	1678	5.81
295	221	751	883	5.26	1280	5.86
300	221	552	640	5.29	905	-
305	221	353	530	-	684	-
310	221	243	331	-	552	-
315	221	199	221	-	486	-
320	199	132	199	-	397	-

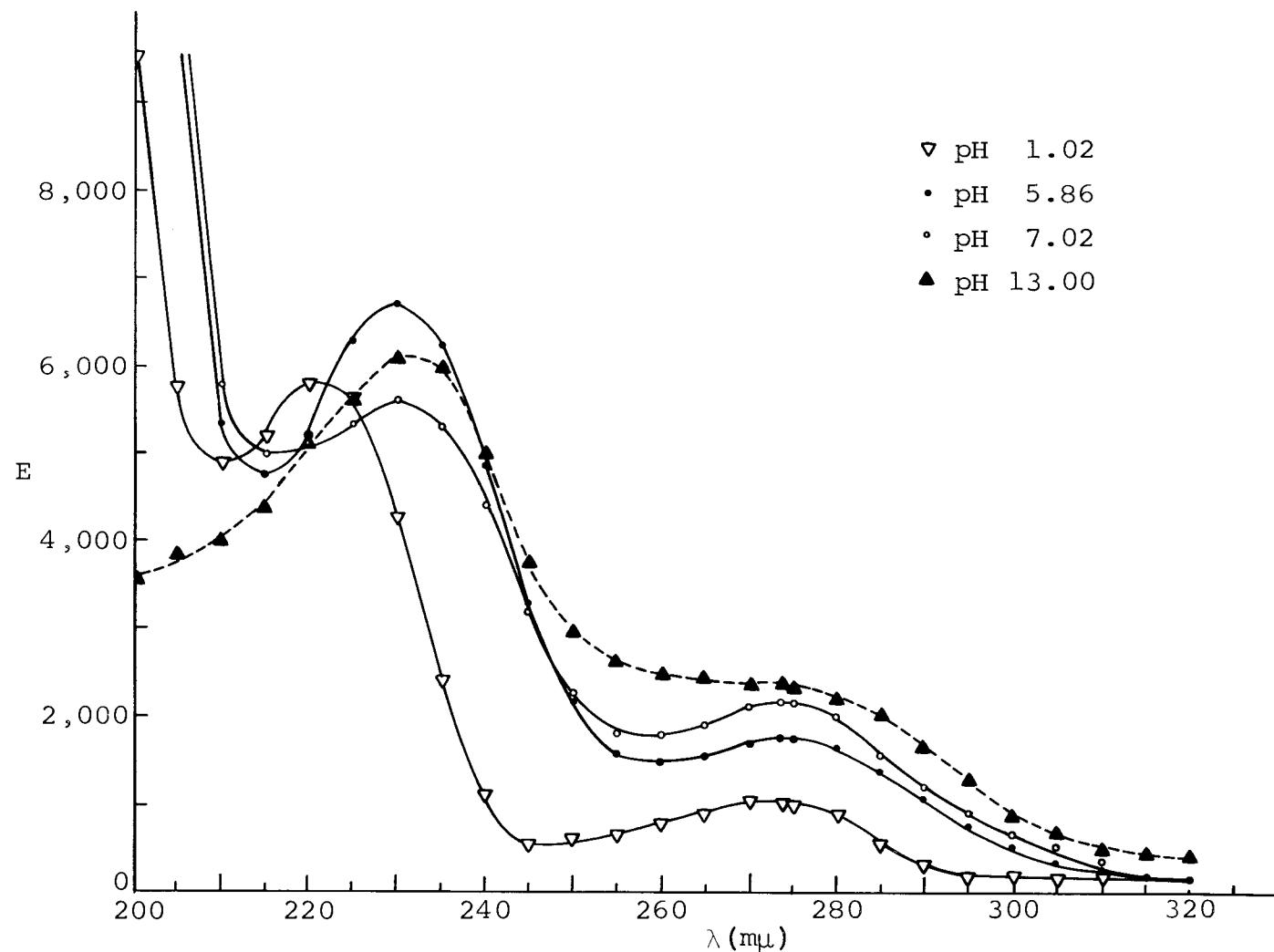


Figure 43. E versus λ of Phenylhydrazine by Method II.

Table L. Dissociation Constants of Phthalic Acid by Method I.

No.	pH	E at 216 m μ	E at 229 m μ	E at 275 m μ
1	1.06	6667	7975	1392
2	1.55	6709	7932	1392
3	1.87	6878	7848	1350
4	2.14	6962	7764	1308
5	2.62	7806	7637	1308
6	3.42	9283	7384	1435
7	3.65	9409	7300	1392
8	4.27	9747	7257	1392
9	4.67	9789	7131	1266
10	4.80	9705	7004	1224
11	5.23	9283	6624	1055
12	5.56	9747	6498	970
13	6.20	9536	6160	844
14	6.38	9536	6160	844
15	7.00	9578	6160	886
16	7.38	9620	6160	844
17	8.23	9494	6203	844
18	9.30	9283	6034	759
19	10.54	9241	5992	675
20	11.10	8439	5823	675
21	12.00	8903	5992	759
22	13.00	7004	5949	759
23	14.00	6793	6203	886

$\lambda = 216 \text{ m}\mu$, $x=6650$, $E=8250$, $y=9800$, $\text{pH}=2.85$, $\text{pK}_a=2.84$
 $x=9500$, $E=9650$, $y=9750$, $\text{pH}=5.30$, $\text{pK}_a=5.22$
 $x=6800$, $E=8000$, $y=9300$, $\text{pH}=12.20$, $\text{pK}_a=12.23$

$\lambda = 229 \text{ m}\mu$, $x=7150$, $E=7500$, $y=8000$, $\text{pH}=2.85$, $\text{pK}_a=3.00$
 $x=6100$, $E=6600$, $y=7250$, $\text{pH}=5.30$, $\text{pK}_a=5.39$

$\lambda = 275 \text{ m}\mu$, $x=1300$, $E=1375$, $y=1450$, $\text{pH}=3.00$, $\text{pK}_a=3.00$
 $x=800$, $E=1050$, $y=1450$, $\text{pH}=5.20$, $\text{pK}_a=5.40$

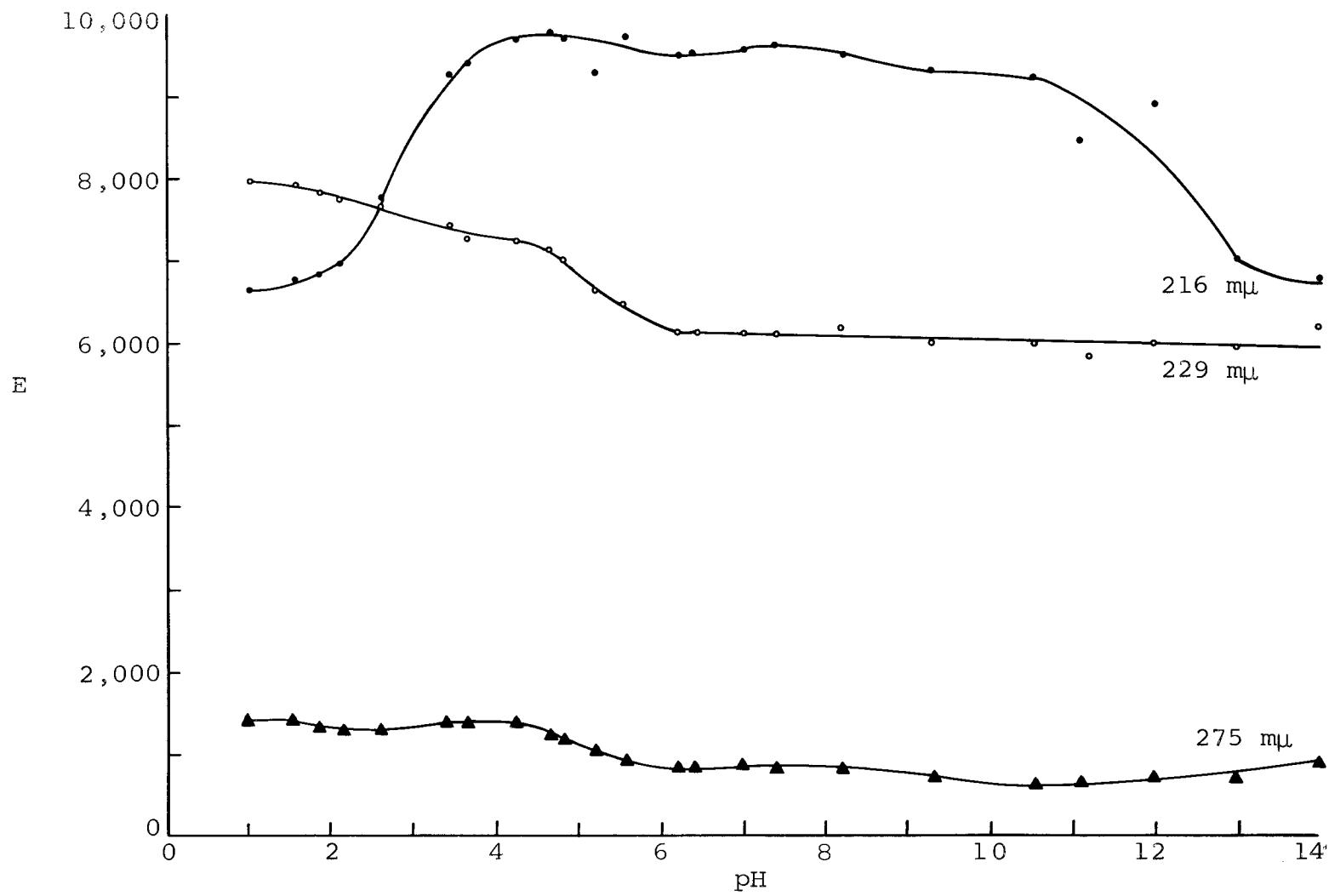


Figure 44. E versus pH of Phthalic Acid by Method I.

Table LI. Dissociation Constants of Phthalic Acid by Method II.

λ (m μ)	E at	E at	<u>pH 6.99</u>		<u>pH 13</u>	
	pH 1.17	pH 5.48	E	pK _a	E	pK _a
200	16557	31646	27848	-	8431	-
205	16076	22532	21519	-	8734	-
210	8861	14810	13924	-	9114	-
215	6582	9873	9570	-	8937	-
216	6633	9367	8987	-	8608	-
220	7165	7671	7468	-	7367	-
225	7823	6835	6456	5.06	6456	5.06
229	7949	6430	5924	5.00	5949	4.99
230	7924	6380	5797	5.06	5823	5.04
235	7139	5671	4835	5.24	4810	5.25
240	5620	4582	3722	5.40	3823	5.34
245	3418	3241	2785	-	2684	-
250	2101	2101	1772	-	1823	-
255	1342	1342	1215	-	1266	-
260	1114	937	937	-	962	-
265	1114	835	785	-	810	-
270	1241	886	810	-	835	-
275	1342	937	709	5.23	759	5.12
280	1266	911	608	5.41	633	5.37
285	987	709	329	5.62	354	5.59
290	430	456	101	-	76	-
295	101	203	25	-	0	-
300	25	51	0	-	0	-
305	0	0	0	-	0	-
310	0	0	0	-	0	-
315	0	0	0	-	0	-
320	0	0	0	-	0	-

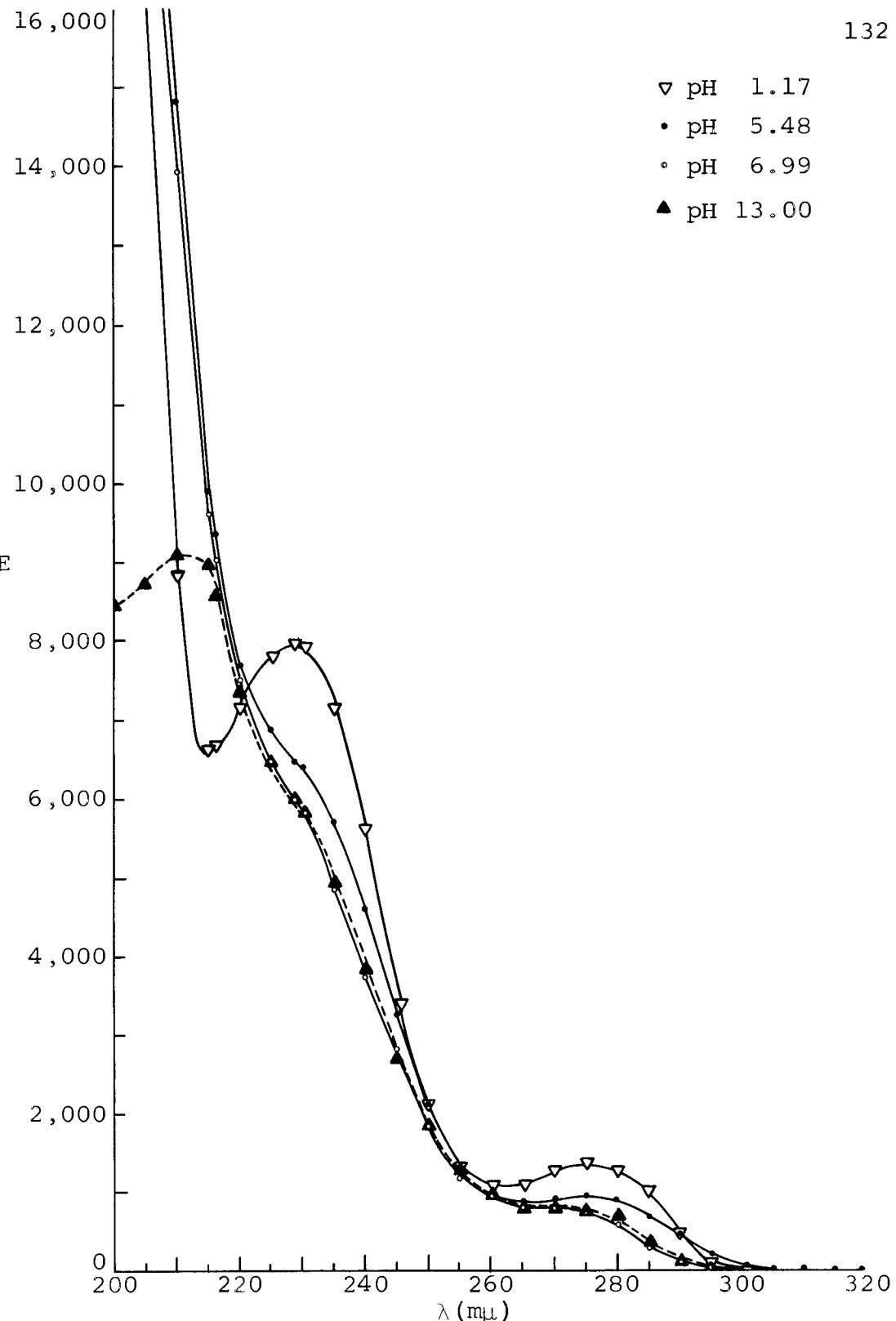


Figure 45. E versus λ of Phthalic Acid by Method II.

Table LII. Dissociation Constants of Pyrimidine
by Method I.

No.	pH	E at 242 m μ
1	0.00	3060
2	0.44	2982
3	1.10	2734
4	1.47	2448
5	1.80	2318
6	2.15	2188
7	2.40	2135
8	2.92	2057
9	3.70	2031
10	4.56	2057
11	5.62	2031
12	6.30	2057
13	6.99	2018
14	7.60	2070
15	8.20	2044
16	8.93	2031
17	9.73	2031
18	10.39	2044
19	11.10	2031
20	12.00	2031
21	12.50	2083
22	13.00	2096
23	13.50	2031
24	14.00	2096

$\lambda=242 \text{ m}\mu$, $x=2020$, $E=2520$, $y=3060$, $\text{pH}=1.40$, $\text{pK}_a=1.43$

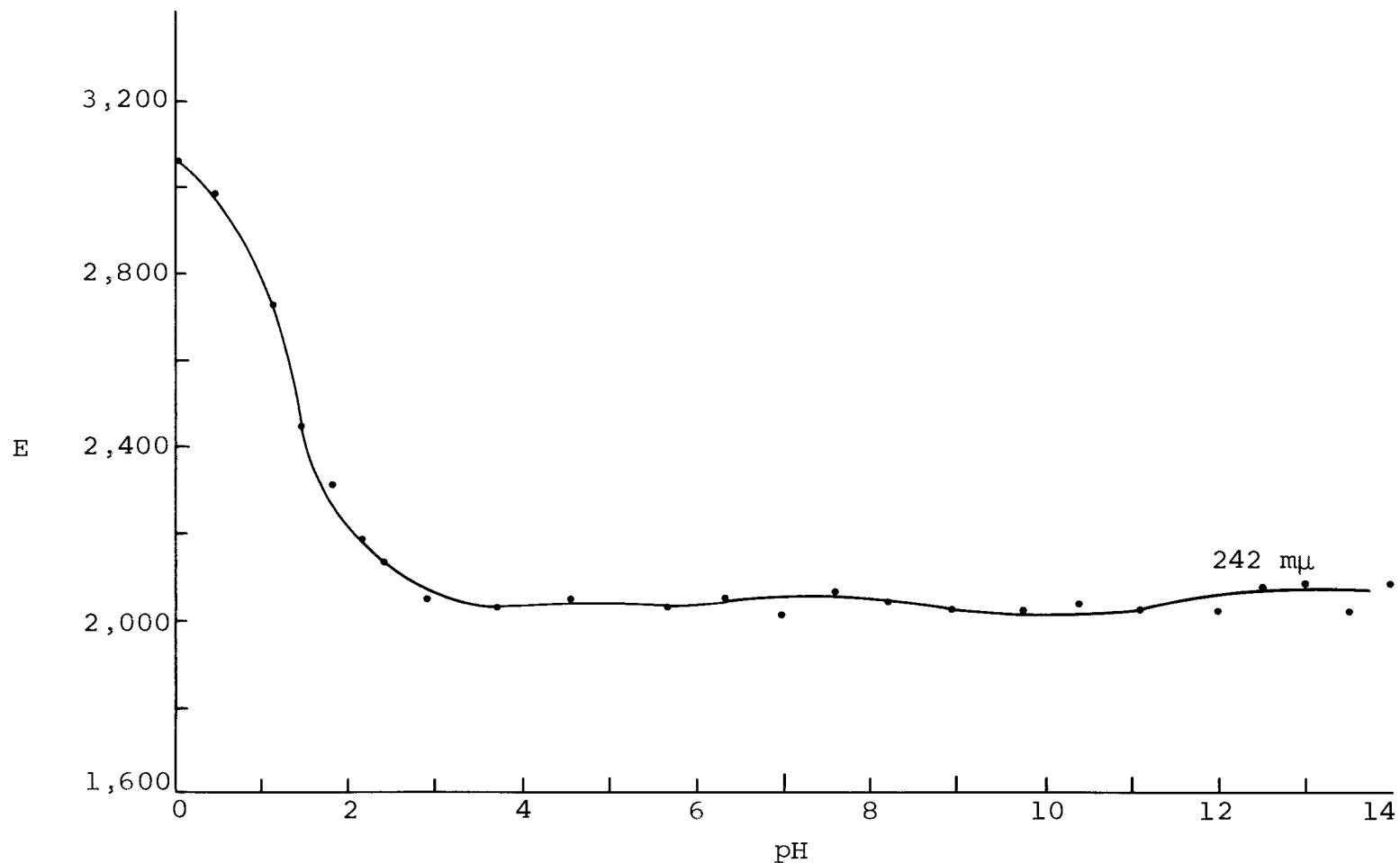


Figure 46. E versus pH of Pyrimidine by Method I.

Table LIII. Dissociation Constants of Pyrimidine
by Method II.

λ (m μ)	E at	E at	<u>pH 7.01</u>		<u>pH 13</u>	
	pH 1.07	pH 1.69	E	pK _a	E	pK _a
200	1888	1910	1910	-	0	-
205	1302	1172	1172	-	0	-
210	781	647	734	-	0	-
215	673	464	478	-	174	-
220	777	573	530	-	326	1.77
225	1016	820	694	1.50	634	1.67
230	1576	1311	1128	1.53	1085	1.62
235	2270	1910	1645	1.56	1628	1.58
240	2617	2192	1875	1.57	1866	1.58
242	2700	2305	1997	1.58	1984	1.60
245	2235	1866	1584	1.38	1584	1.38
250	1411	1172	1063	1.35	1050	1.40
255	516	412	352	1.45	347	1.49
260	313	278	265	1.26	256	1.49
265	260	243	260	-	260	-
270	221	239	265	1.88	260	1.80
275	191	230	256	1.61	252	1.54
280	143	191	221	1.49	226	1.55
285	109	161	178	1.21	178	1.21
290	78	109	126	1.43	122	1.31
295	43	61	65	-	74	1.55
300	22	39	43	-	39	-
305	9	13	13	-	13	-
310	0	0	0	-	0	-
315	0	0	0	-	0	-
320	0	0	0	-	0	-

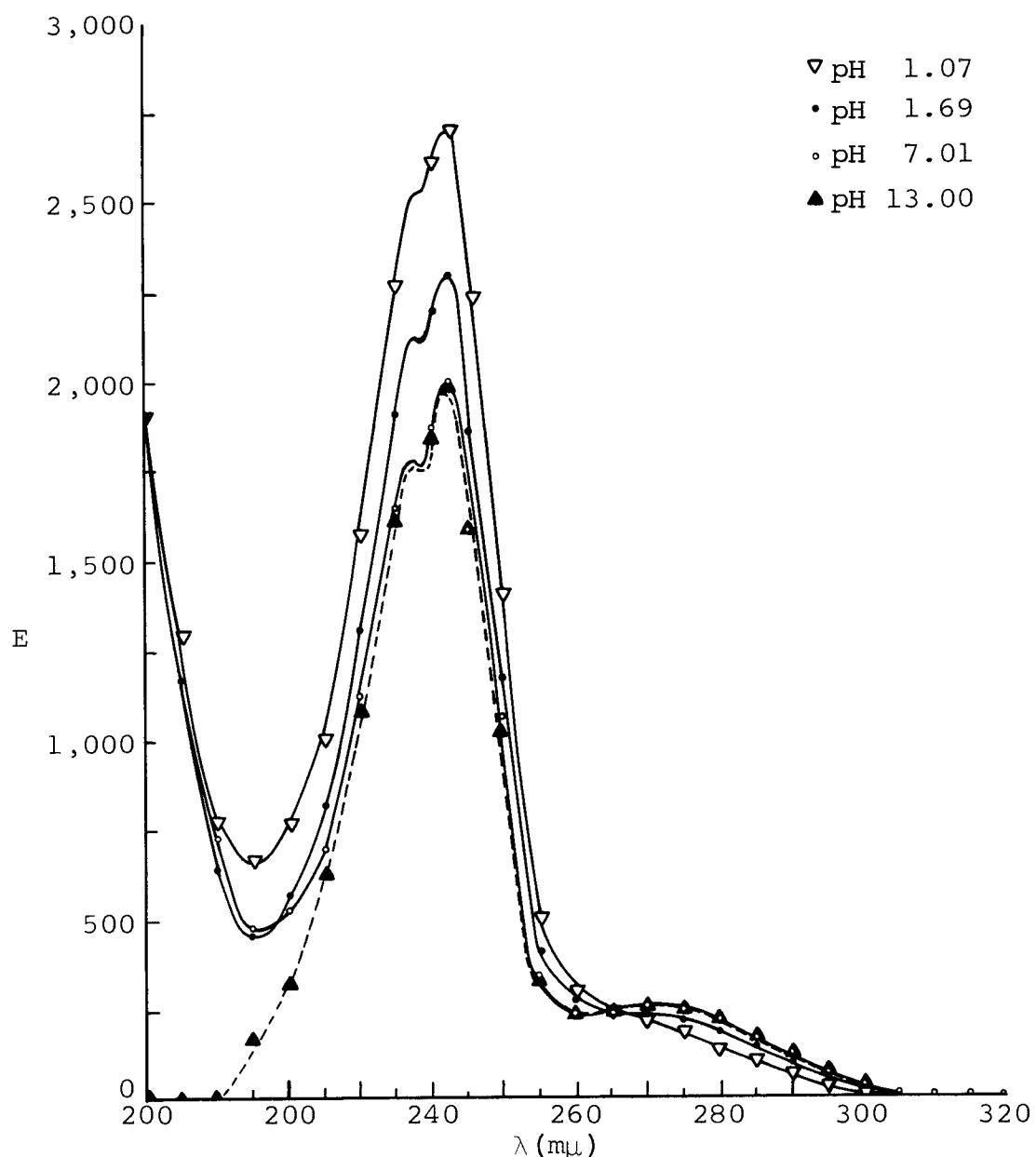


Figure 47. E versus λ of Pyrimidine by Method II.

Table LIV. Dissociation Constants of p-Aminobenzoic Acid by Method I.

No.	pH	E at 215 m μ	E at 225 m μ	E at 235 m μ	E at 245 m μ	E at 255 m μ	E at 265 m μ
1	0.00	6897	11379	6897	1379	690	805
2	0.46	7126	11471	6874	1379	736	874
3	1.13	7126	11241	6667	1402	943	1241
4	1.38	7356	11057	6207	1402	1080	1517
5	1.69	7126	10552	5977	1494	1471	2322
6	2.00	7356	10023	5471	1678	2161	3540
7	2.31	7540	9080	4437	1839	2989	5057
8	2.65	7793	8368	3678	2069	3793	6713
9	3.10	8046	7333	2759	2322	4828	8529
10	3.55	8138	6874	2414	2575	5402	9425
11	4.00	8276	6460	2414	3034	6092	10115
12	4.32	8299	5793	2414	3563	6966	10805
13	4.74	8437	5149	2874	4483	8276	11747
14	5.06	8529	4483	2989	5287	9425	12483
15	5.51	8621	3908	3149	6046	10621	13287
16	6.01	8736	3609	3333	6667	11310	13747
17	6.53	8736	3402	3218	6552	11379	13770
18	7.00	8851	3402	3310	6782	11517	13862
19	7.50	8506	3241	3356	6690	11609	13954
20	8.05	8736	3333	3287	6667	11540	13908
21	8.55	8782	3425	3218	6529	11494	13908
22	9.15	8621	3333	3333	6667	11494	13908
23	9.51	8391	3241	3333	6782	11632	13885
24	10.06	8713	3425	3287	6690	11540	13931
25	10.46	8736	3425	3218	6483	11379	13885
26	10.96	8644	3425	3287	6667	11494	13908
27	11.50	8506	3287	3218	6667	11563	13954
28	12.00	7839	3264	3195	6598	11379	13839
29	12.50	7586	3218	3195	6575	11494	13908
30	13.00	5540	2989	3218	6667	11494	13908
31	13.50	4092	2943	3195	6644	11494	14023
32	14.00	1954	2299	3011	6437	11379	13862

Table LV. Dissociation Constants of p-Aminobenzoic Acid by Method I.

No.	pH	E at 275 m μ	E at 285 m μ	E at 295 m μ	E at 305 m μ	E at 315 m μ
1	0.00	805	115	23	46	23
2	0.46	851	230	69	69	23
3	1.13	1379	851	644	414	138
4	1.38	1747	1264	1012	621	230
5	1.69	2989	2529	2115	1264	460
6	2.00	4598	4483	3908	2322	828
7	2.31	6644	6920	5862	3494	1149
8	2.65	8851	9517	8161	4874	1632
9	3.10	11356	12230	10414	6161	2000
10	3.55	12276	13149	11195	6667	2207
11	4.00	12644	13103	10805	6276	2069
12	4.32	12644	12483	9885	5517	1816
13	4.74	12621	11103	8069	4184	1333
14	5.06	12092	9862	6414	2989	897
15	5.51	11954	8782	4874	1839	506
16	6.01	11747	8046	3908	1195	230
17	6.53	11609	7816	3655	989	92
18	7.00	11678	7701	3471	989	92
19	7.50	11724	7793	3448	943	92
20	8.05	11655	7724	3448	943	69
21	8.55	11747	7908	3540	920	69
22	9.15	11724	7816	3448	943	92
23	9.51	11609	7701	3448	874	69
24	10.06	11724	7816	3471	920	92
25	10.46	11724	7862	3494	920	69
26	10.96	11724	7839	3517	920	92
27	11.50	11724	7839	3494	920	92
28	12.00	11724	7816	3494	920	69
29	12.50	11770	7931	3563	920	69
30	13.00	11747	7839	3517	920	69
31	13.50	11908	8046	3678	943	92
32	14.00	11839	8023	3678	943	69

Table LVI. Dissociation Constants of p-Aminobenzoic Acid by Method I.

λ (m μ)	x	E	y	pH at Inflection Point	pK _a
215	7100	7900	8700	2.90	2.90
	1950	5400	8700	13.10	13.08
225	8000	9700	11500	2.10	2.13
	3300	5700	8000	4.40	4.38
235	2300	4600	6900	2.30	2.30
	2300	2800	3250	4.70	4.65
245	1350	4000	6700	4.55	4.56
255	700	2800	5000	2.30	2.32
	5000	8400	11600	4.80	4.77
265	800	4600	8500	2.20	2.21
	8500	11200	13900	4.50	4.50
275	800	6800	12700	2.30	2.29
	11700	12200	12700	5.00	5.00
285	100	6600	13200	2.30	2.31
	6700	10000	13200	5.00	4.99
295	0	5600	11200	2.25	2.25
	3400	7300	11200	4.85	4.85
305	0	3300	6650	2.25	2.26
	1000	3800	6650	4.85	4.86
315	0	1100	2200	2.25	2.25
	100	1100	2200	4.90	4.92

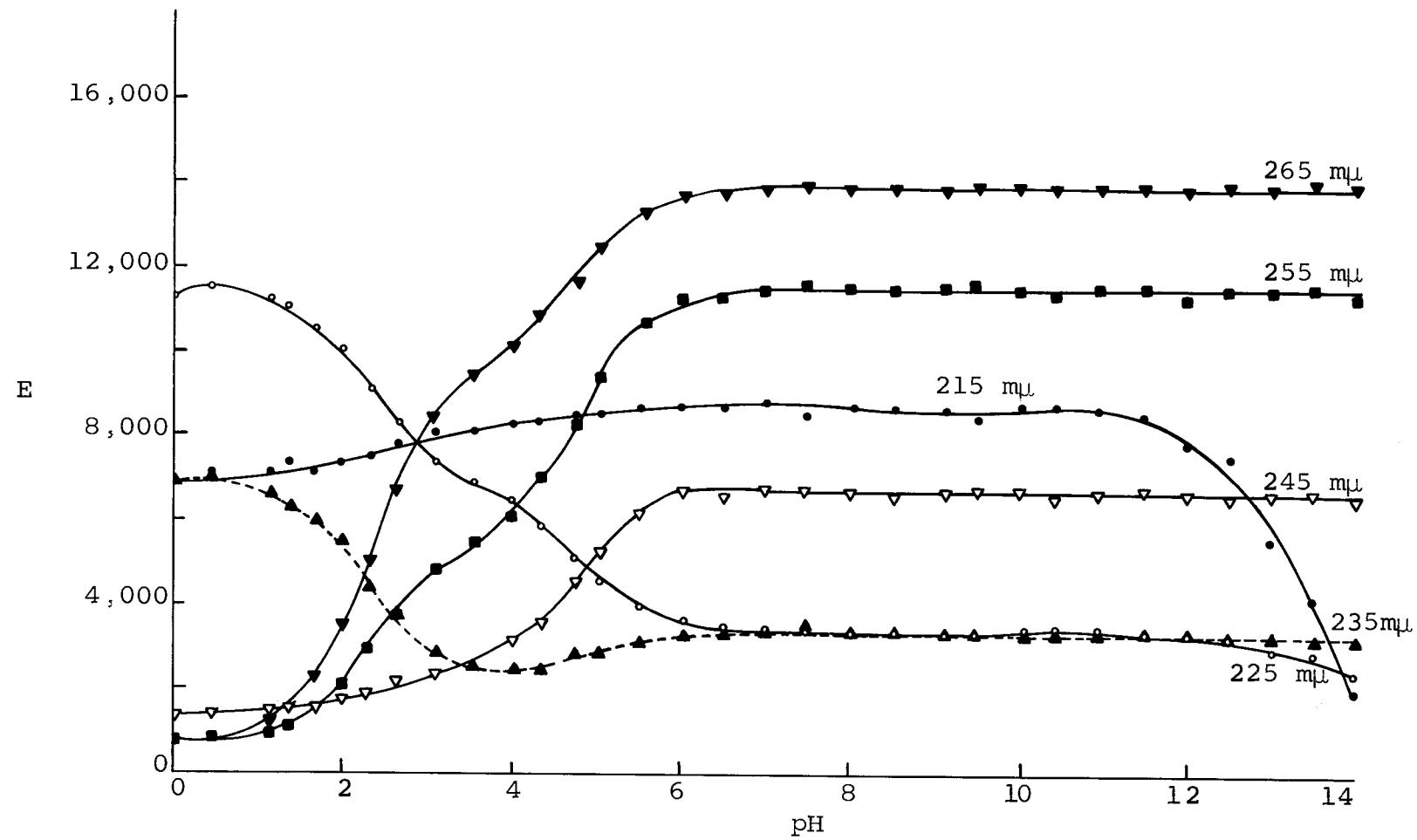


Figure 48. E versus pH of p-Aminobenzoic Acid by Method I.

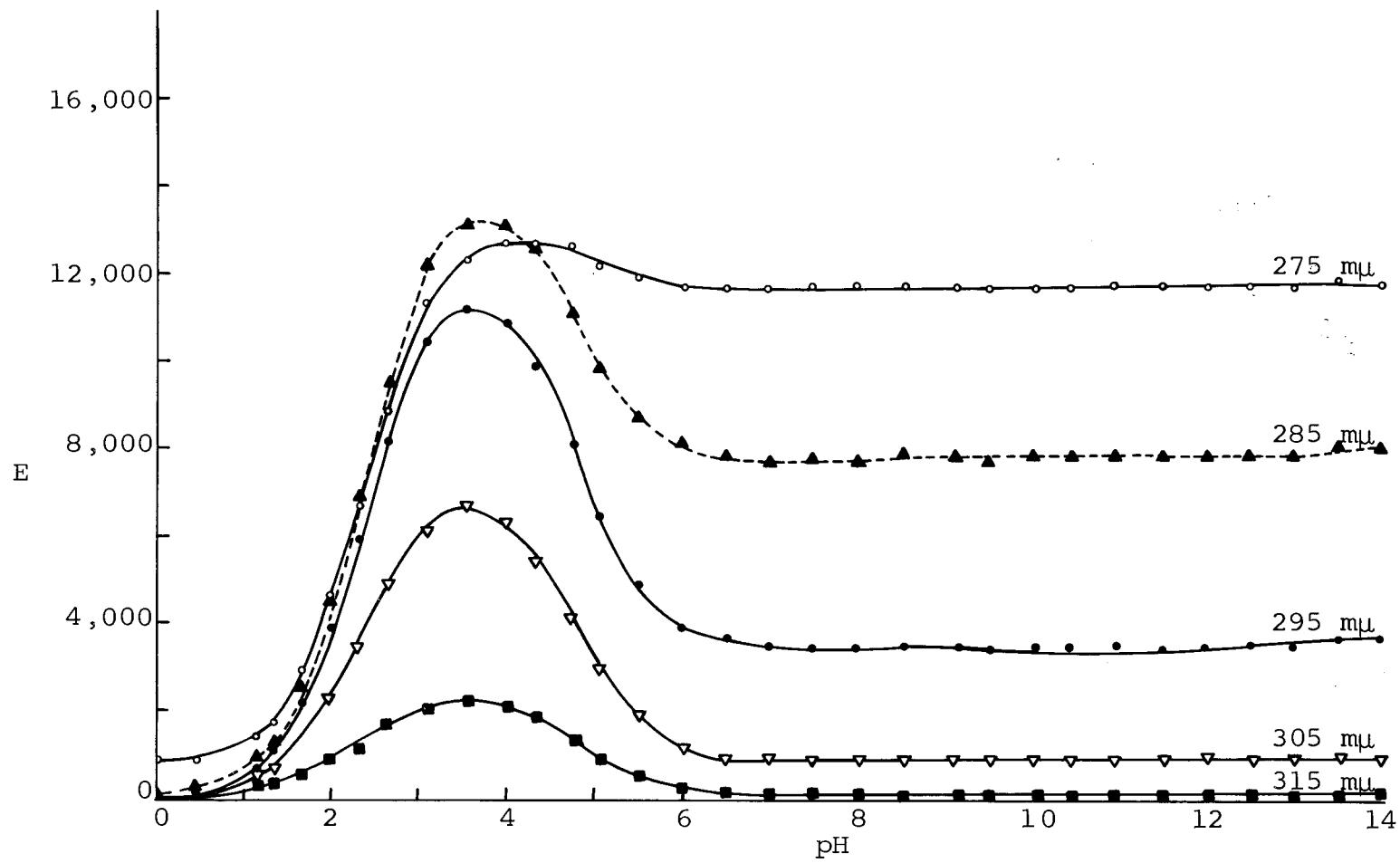


Figure 49. E versus pH of p-Aminobenzoic Acid by Method I.

Table LVII. Dissociation Constants of p-Aminobenzoic Acid by Method II.

λ (m μ)	E at	E at	<u>pH 7.10</u>		<u>pH 13</u>	
	pH 0.95	pH 3.00	E	pK _a	E	pK _a
210	4506	6207	11494	-	5402	-
215	6897	7862	8736	2.96	5632	-
220	9770	8690	5747	-	5598	-
225	11310	7609	3402	3.06	2989	3.10
230	10115	5172	2598	2.72	2414	2.75
235	6897	2989	3264	-	3218	-
240	3218	1977	4667	-	4598	-
245	1379	2184	6621	-	6621	-
250	851	3103	9080	-	8966	-
255	805	4460	11494	-	11471	-
260	851	6161	13333	-	13264	-
265	989	8000	13885	2.92	13885	2.92
270	1080	9540	13195	2.63	13149	2.63
275	1011	10690	11770	-	11724	-
280	851	11356	10023	-	9954	-
285	437	11563	7862	-	7885	-
290	345	11149	5655	-	5701	-
295	276	9908	3540	-	3540	-
300	230	8115	1977	-	1954	-
305	230	5954	966	-	920	-
310	115	3747	368	-	322	-
315	92	1977	115	-	115	-
320	23	828	23	-	46	-

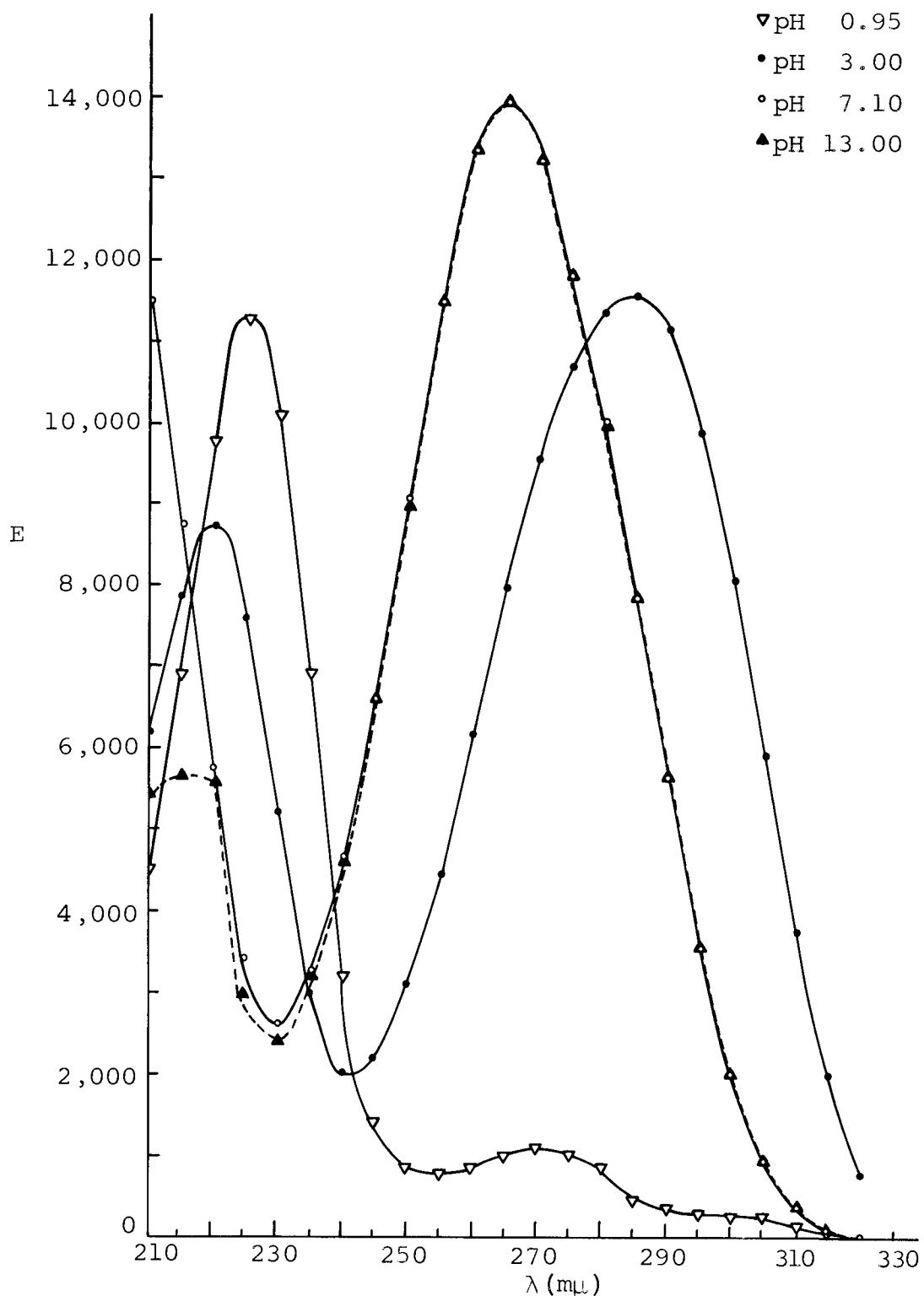


Figure 50. E versus λ of p-Aminobenzoic Acid by Method II.

Table LVIII. Dissociation Constants of m-Aminophenol
by Method I.

No.	pH	E at 231 m μ	E at 281 m μ
1	0.00	547	832
2	0.60	547	832
3	1.00	656	875
4	1.49	613	875
5	2.00	700	875
6	2.53	656	788
7	3.11	963	963
8	3.65	1860	985
9	4.25	3786	1400
10	4.79	5536	1707
11	5.30	6346	1838
12	5.68	6521	1860
13	6.31	6740	1904
14	6.65	6783	1947
15	7.01	6849	1969
16	7.50	6849	1969
17	8.12	6871	1969
18	8.59	6915	1969
19	9.15	7155	2035
20	9.70	7462	2013
21	10.06	7812	1991
22	10.54	8162	1991
23	11.00	8315	1991
24	11.50	8162	2035
25	12.00	8315	1991
26	12.50	8271	1991
27	13.00	8534	2035
28	13.50	8972	2013
29	14.00	9409	1751

$\lambda=231 \text{ m}\mu$, $x=500$, $E=3750$, $y=6850$, $\text{pH}=4.25$, $\text{pK}_a=4.23$
 $x=6850$, $E=7600$, $y=8300$, $\text{pH}=9.85$, $\text{pK}_a=9.82$
 $x=8275$, $E=8800$, $y=9400$, $\text{pH}=13.35$, $\text{pK}_a=13.41$

$\lambda=281 \text{ m}\mu$, $x=825$, $E=1400$, $y=2000$, $\text{pH}=4.25$, $\text{pK}_a=4.27$

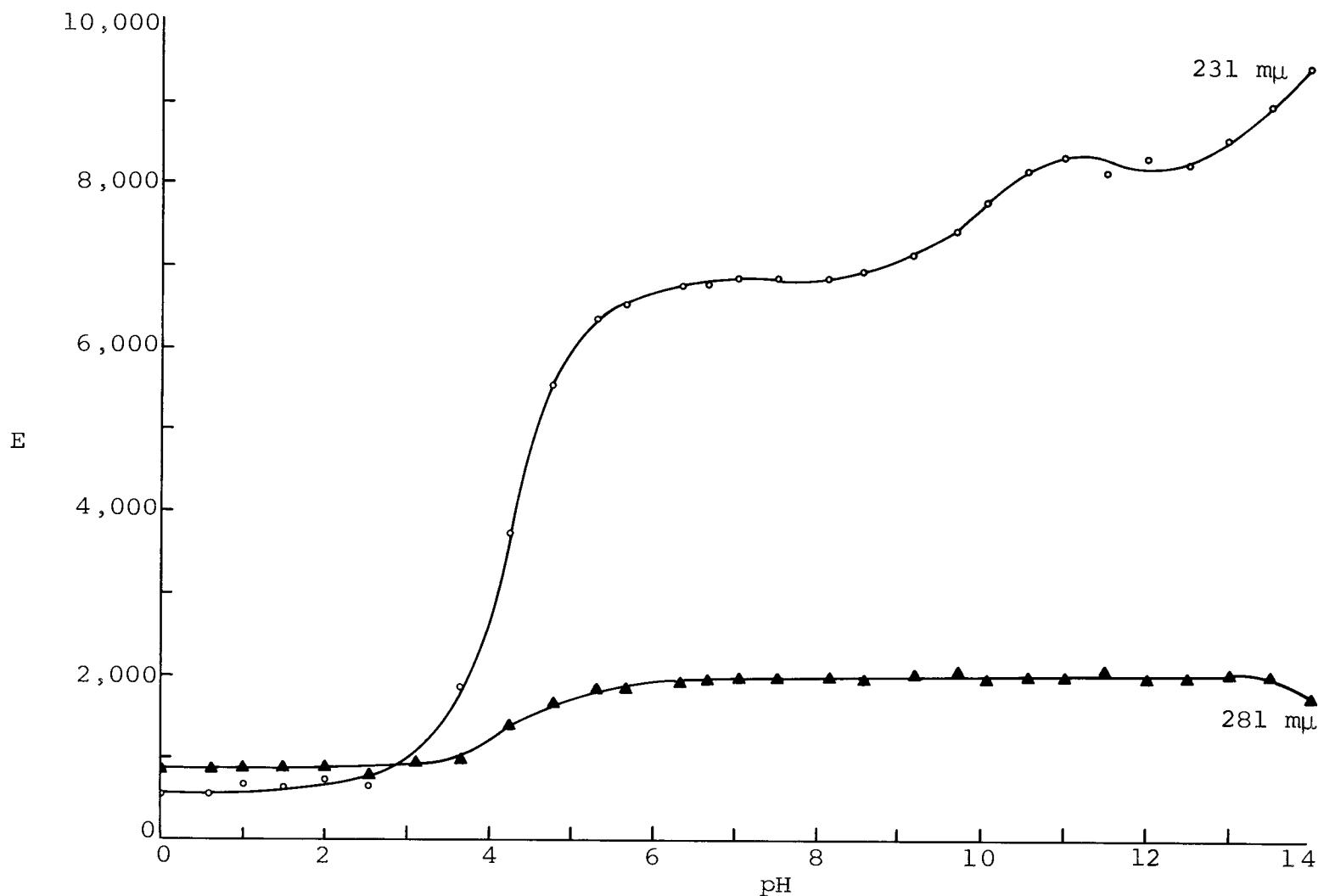


Figure 51. E versus pH of *m*-Aminophenol by Method I.

Table LIX. Dissociation Constants of m-Aminophenol by Method II.

λ (m μ)	E at pH 1.00	E at pH 4.34	pH 7.05		pH 13	
	E	pK _a	E	pK _a	E	pK _a
210	5777	12472	18381	4.28	29278	-
215	6214	8403	10722	4.37	28615	-
220	5689	6171	7090	-	19256	-
225	2845	4814	6652	4.31	12254	-
230	656	4114	7002	4.26	8972	4.49
231	438	4026	7002	4.26	8753	4.46
235	350	3720	6565	4.26	8140	4.46
240	394	2845	5252	4.33	7615	-
245	438	1838	2976	4.25	6127	-
250	656	1050	1532	4.43	3807	-
255	919	919	1444	-	1882	-
260	1751	1400	1400	-	1751	-
265	1751	1751	1532	-	1313	-
270	1969	1751	1751	-	1532	-
275	1882	1882	1882	-	1751	-
280	788	1751	1969	-	2188	-
281	613	1751	1969	-	2188	-
285	44	1094	1969	4.26	2670	4.52
290	0	700	1663	4.48	3063	-
295	0	263	613	4.46	2801	-
300	0	131	263	4.34	1969	-
305	0	88	131	-	875	-
310	0	44	88	-	219	-
315	0	0	44	-	175	-
320	0	0	0	-	44	-

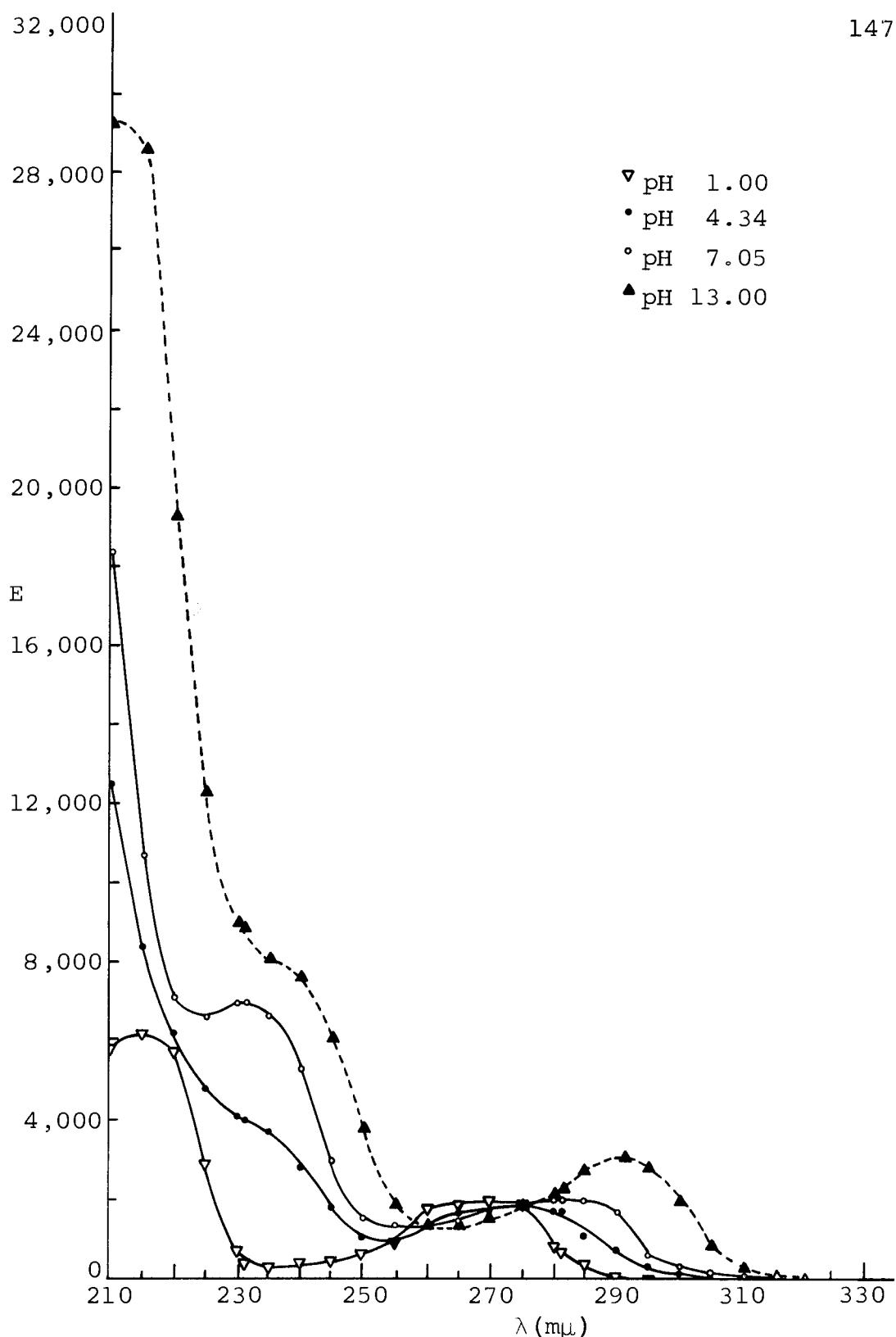


Figure 52. E versus λ of m-Aminophenol by Method II.

Table LX. Dissociation Constants of o-Aminophenol by Method I.

No.	pH	E at 228 m μ	E at 281 m μ
1	0.00	832	832
2	0.44	582	749
3	0.94	582	749
4	1.57	624	749
5	2.00	832	832
6	2.49	832	832
7	3.01	790	832
8	3.51	1165	1248
9	4.10	2121	1498
10	4.50	3286	1747
11	5.00	5616	2121
12	5.51	5824	2371
13	5.97	6198	2579
14	6.55	6364	2621
15	7.02	6531	2704
16	7.49	6531	2621
17	8.02	6572	2662
18	8.50	6572	2704
19	9.00	6448	2704
20	9.49	6160	2616
21	9.99	6076	2489
22	10.52	6076	2489
23	11.00	6034	2447
24	11.50	6076	2363
25	12.00	5907	2363
26	12.50	5696	2363
27	13.00	5992	2532
28	13.50	7511	2532
29	14.00	11392	2489

$\lambda=228 \text{ m}\mu$, $x=550$, $E=3750$, $y=6600$, $\text{pH}=4.55$, $\text{pK}_a=4.50$

$x=6075$, $E=6325$, $y=6600$, $\text{pH}=9.20$, $\text{pK}_a=9.28$

$x=5750$, $E=8000$, $y=11400$, $\text{pH}=13.60$, $\text{pK}_a=13.78$

$\lambda=281 \text{ m}\mu$, $x=725$, $E=1800$, $y=2700$, $\text{pH}=4.50$, $\text{pK}_a=4.42$

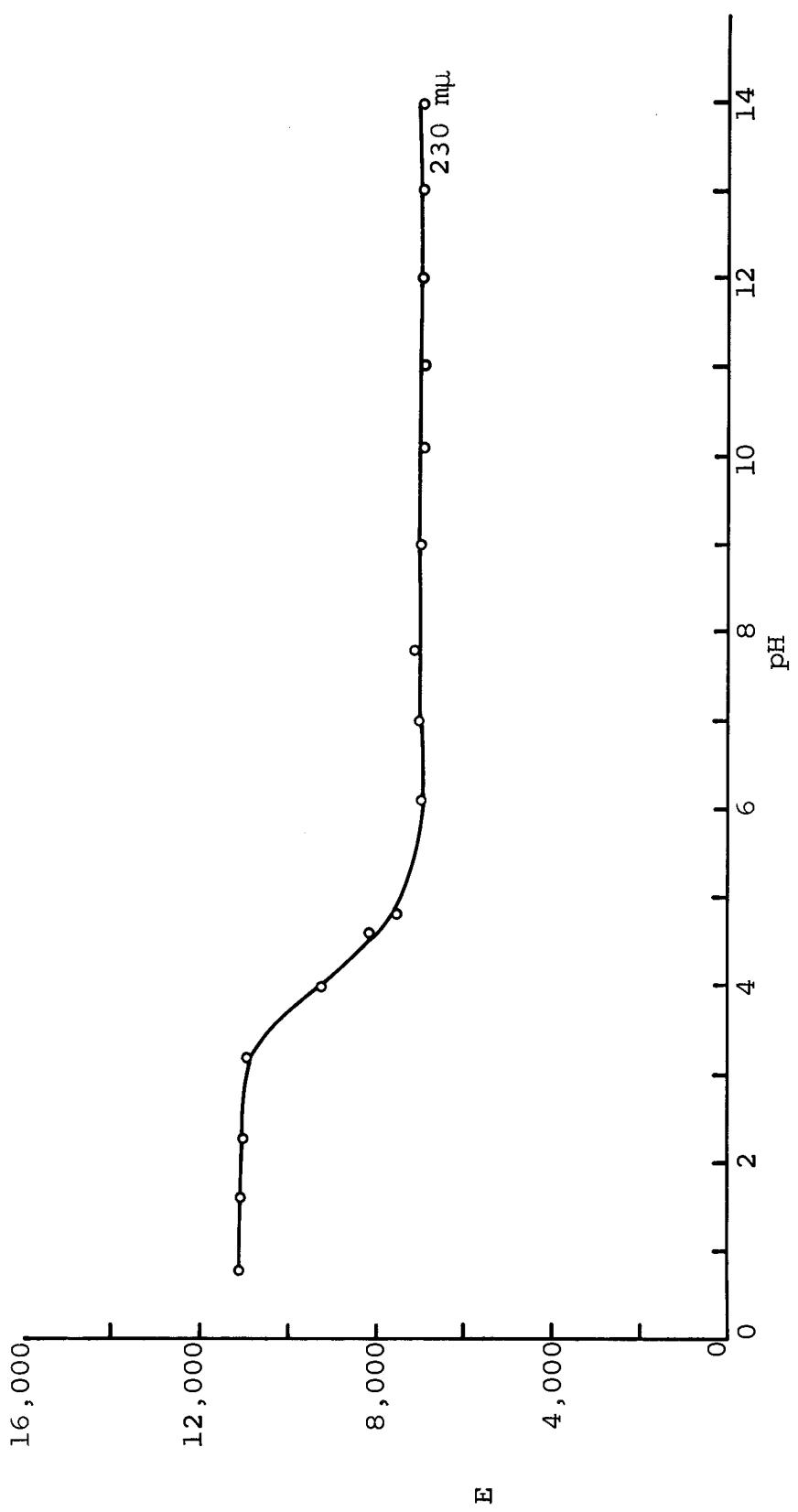


Figure 9. E versus pH of Benzoic Acid by Method I.

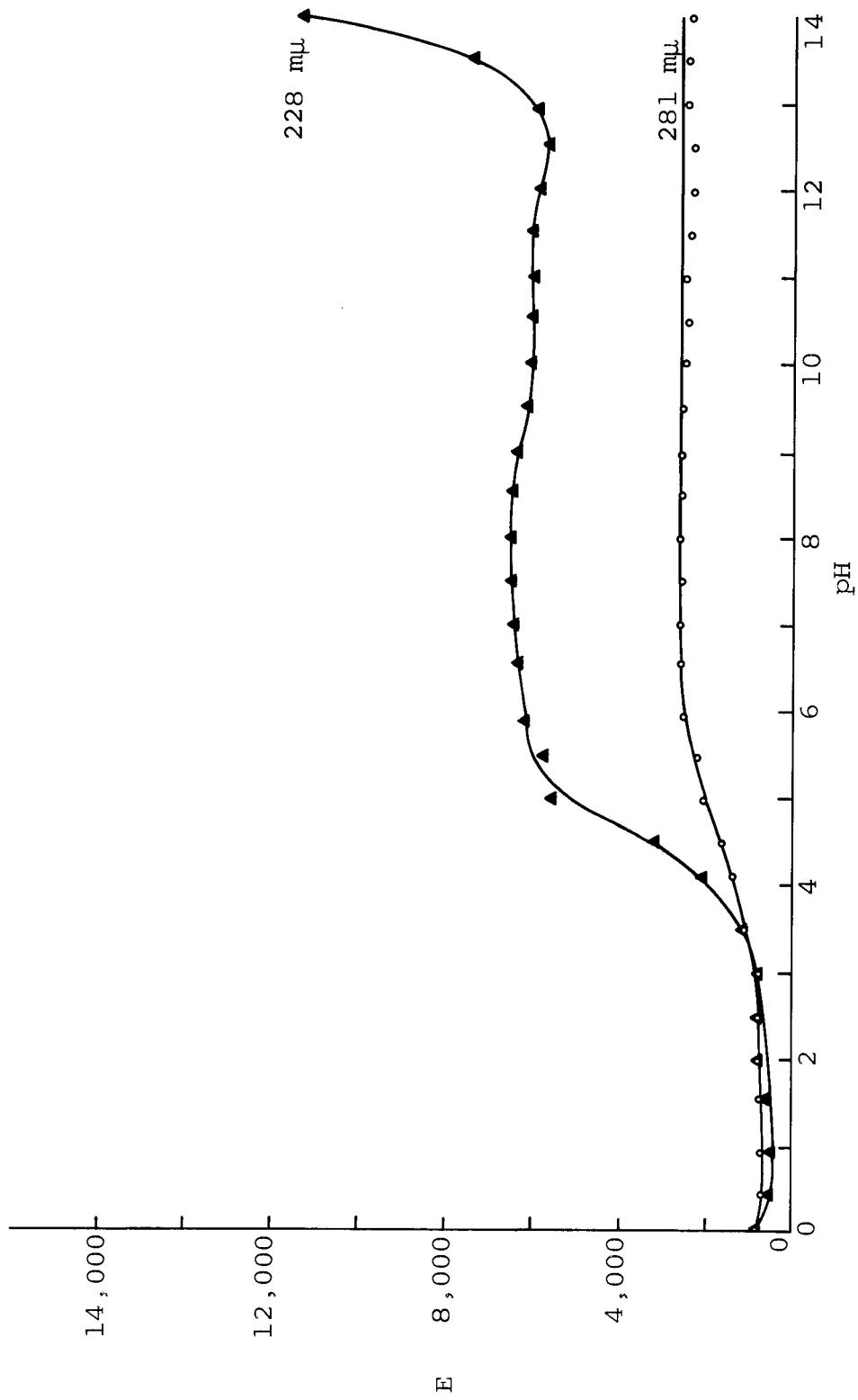


Figure 53. E versus pH of o-Aminophenol by Method I.

Table LXI. Dissociation Constants of o-Aminophenol by Method II.

λ (m μ)	E at		<u>pH 7.08</u>		<u>pH 13</u>	
	pH 1.00	pH 4.55	E	pK _a	E	pK _a
200	5443	23840	38144	-	18312	-
205	6245	17468	26793	4.47	19494	-
210	6414	9072	11814	4.56	20506	-
215	5485	5949	6371	4.51	20211	-
220	3840	4895	5738	4.45	11857	-
225	1308	3797	6118	4.52	6962	4.65
228	464	3671	6329	4.46	6076	4.43
230	338	3671	6329	4.45	5992	4.40
235	338	3122	5696	4.51	6160	4.59
240	422	2194	3755	4.49	6540	-
245	549	1392	2110	4.48	6076	-
250	633	928	1266	4.61	4557	-
255	886	928	886	-	2532	-
260	1350	1055	886	4.31	1477	-
265	1899	1435	1139	4.36	1224	-
270	1983	1899	1603	-	1350	4.36
275	1688	2025	2152	-	1688	-
280	844	1730	2616	4.55	2321	4.38
281	591	1688	2700	4.51	2489	4.41
285	84	1519	2616	4.43	3122	4.60
290	0	1266	2194	4.41	3840	-
295	0	675	1477	4.63	4177	-
300	0	295	591	4.55	3966	-
305	0	211	211	-	3080	-
310	0	169	127	-	2278	-
315	0	127	84	-	844	-
320	0	42	42	-	253	-

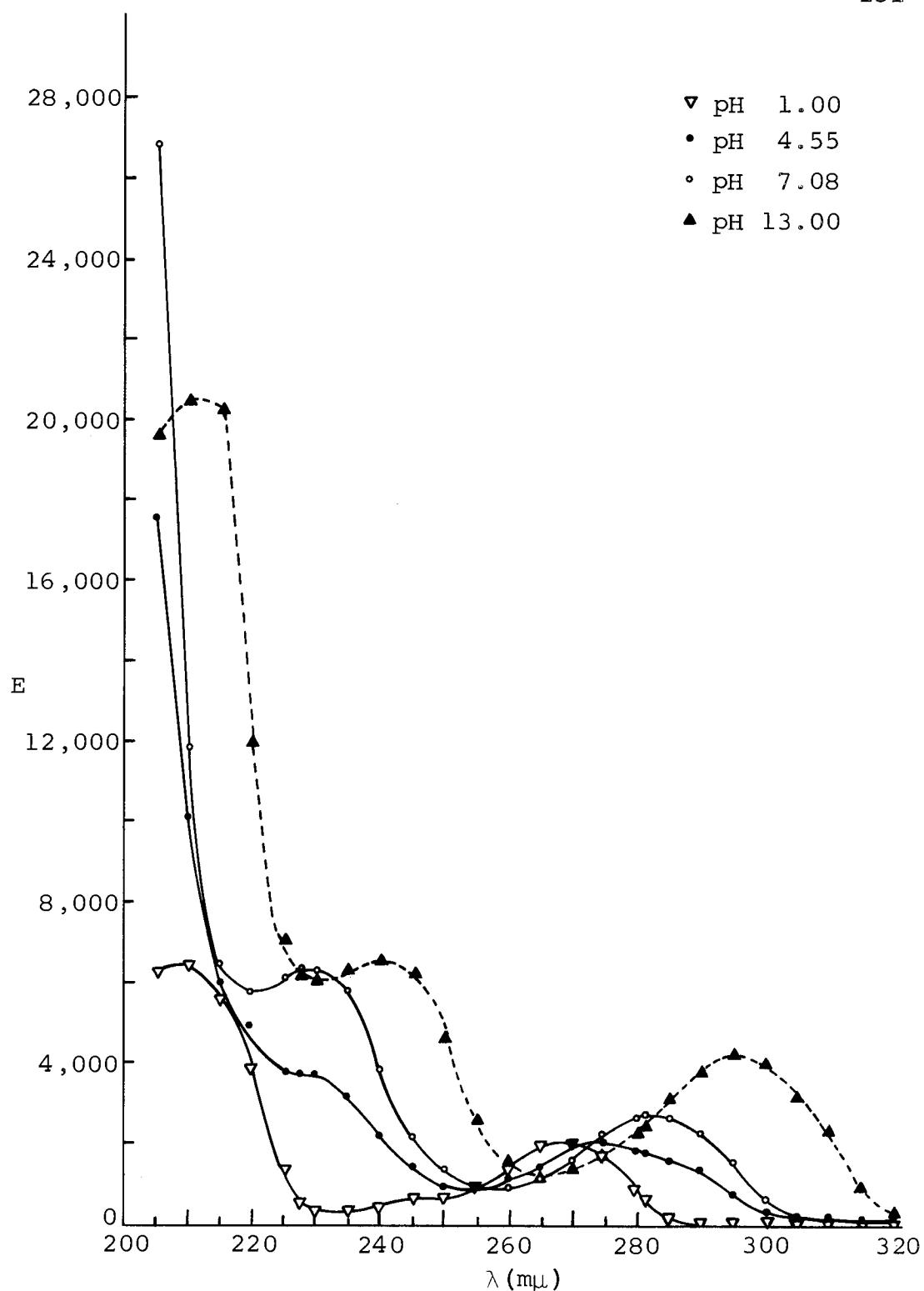


Figure 54. E versus λ of o-Aminophenol by Method II.

Table LXII. Dissociation Constants of p-Aminophenol
by Method I.

No.	pH	E at 231 m μ	E at 296 m μ
1	0.00	796	0
2	0.44	726	0
3	1.00	820	0
4	1.49	820	0
5	1.93	726	0
6	2.45	761	0
7	2.90	738	0
8	3.40	785	23
9	3.90	1066	59
10	4.40	1288	176
11	4.86	2166	457
12	5.13	2939	691
13	5.39	3864	995
14	5.74	4918	1323
15	6.05	5808	1581
16	6.40	6358	1803
17	6.66	6546	1862
18	6.96	6838	1897
19	7.30	6874	1920
20	7.77	7002	1956
21	8.27	6850	1897
22	8.61	6745	1814
23	9.10	6382	1639
23A	9.23	6329	1548
24	9.43	6011	1548
25	9.71	5920	1275
26	10.15	5510	956
27	10.58	4781	683
28	11.00	4781	729
29	11.50	4827	774
30	12.00	5100	501
31	12.50	5237	501
32	13.00	7013	637
33	13.50	8880	683
34	14.00	9472	546

Table LXII. (Continued)

$\lambda=231 \text{ m}\mu$, $x=700$, $E=3950$, $y=7000$, $pH=5.45$, $pK_a=5.42$
 $x=4750$, $E=5895$, $y=7000$, $pH=9.70$, $pK_a=9.70$
 $x=4750$, $E=7250$, $y=9475$, $pH=13.05$, $pK_a=13.00$

$\lambda=296 \text{ m}\mu$, $x=0$, $E=1000$, $y=1945$, $pH=5.40$, $pK_a=5.38$
 $x=700$, $E=1350$, $y=1950$, $pH=9.60$, $pK_a=9.57$

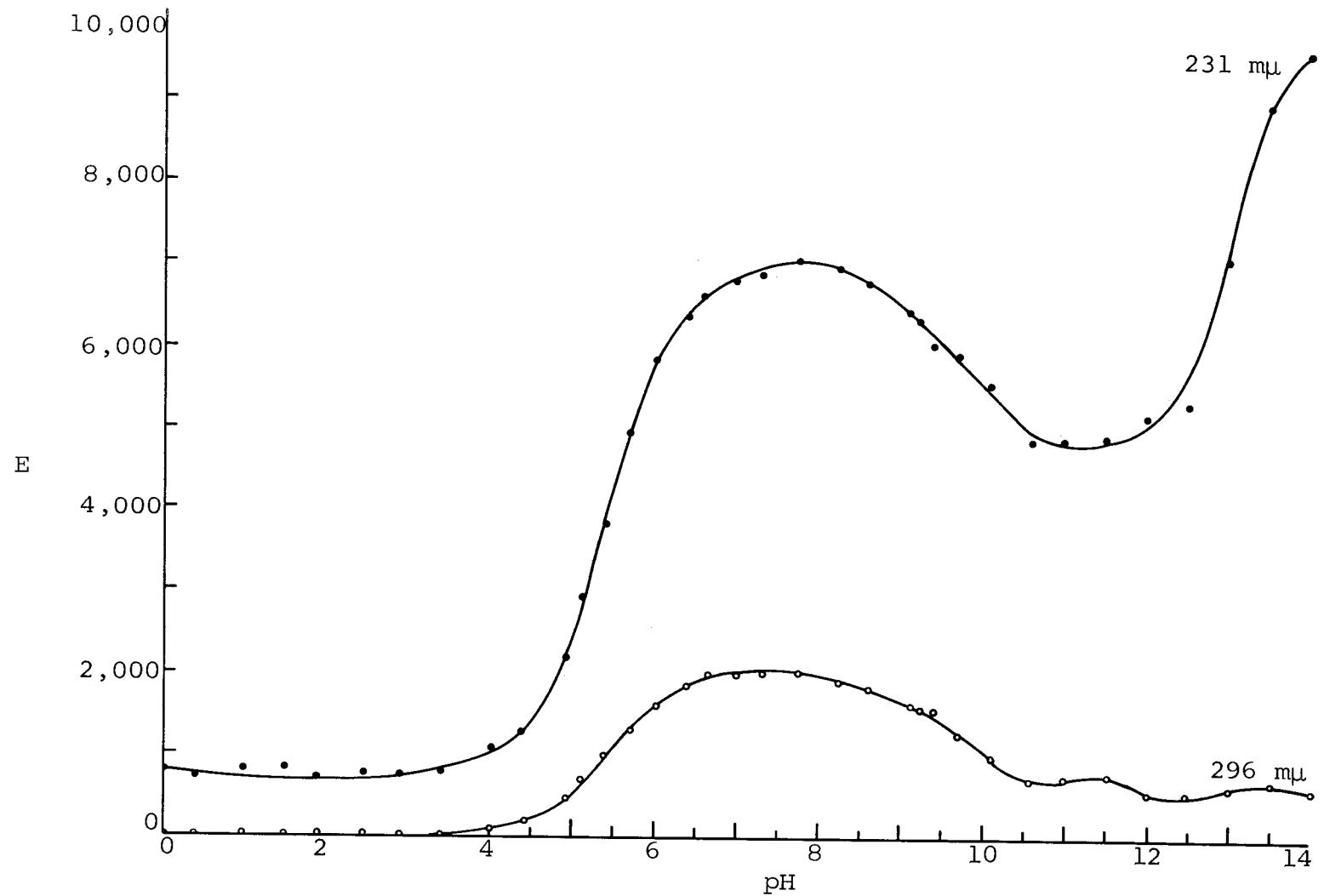


Figure 55. E versus pH of p-Aminophenol by Method I.

Table LXIII. Dissociation Constants of p-Aminophenol
by Method II.

λ (m μ)	E at	E at	<u>pH 7.06</u>		<u>pH 13</u>	
	pH 1.00	pH 5.45	E	pK _a	E	pK _a
210	6466	5738	5009	5.45	16940	-
215	6785	5692	4645	5.43	16667	-
220	6421	5920	5465	5.41	11430	-
225	3734	5237	6648	5.42	8379	-
230	1457	4508	7559	5.45	8151	5.53
231	1412	4463	7559	5.45	8197	5.54
235	1002	4007	7195	5.48	8880	5.66
240	1047	3142	6011	5.59	10246	-
245	1002	2095	3962	-	10838	-
250	1002	1457	2732	-	11384	-
255	1412	1093	1958	-	10337	-
260	1594	1366	1639	-	9381	-
265	2049	1184	1594	-	6557	-
270	1867	1412	1184	-	3643	-
275	1639	1412	1639	-	2049	-
280	1594	1594	1639	-	1594	-
285	546	1366	1913	5.28	1639	-
290	364	1548	2231	5.21	1685	-
295	273	1548	2322	5.24	1821	-
296	273	1594	2322	-	1821	-
300	319	1594	2277	-	2049	-
305	410	1275	2049	5.40	2322	5.53
310	455	1138	1639	5.31	2459	5.73
315	455	1002	1366	5.28	2368	5.85
320	319	455	911	-	2095	-

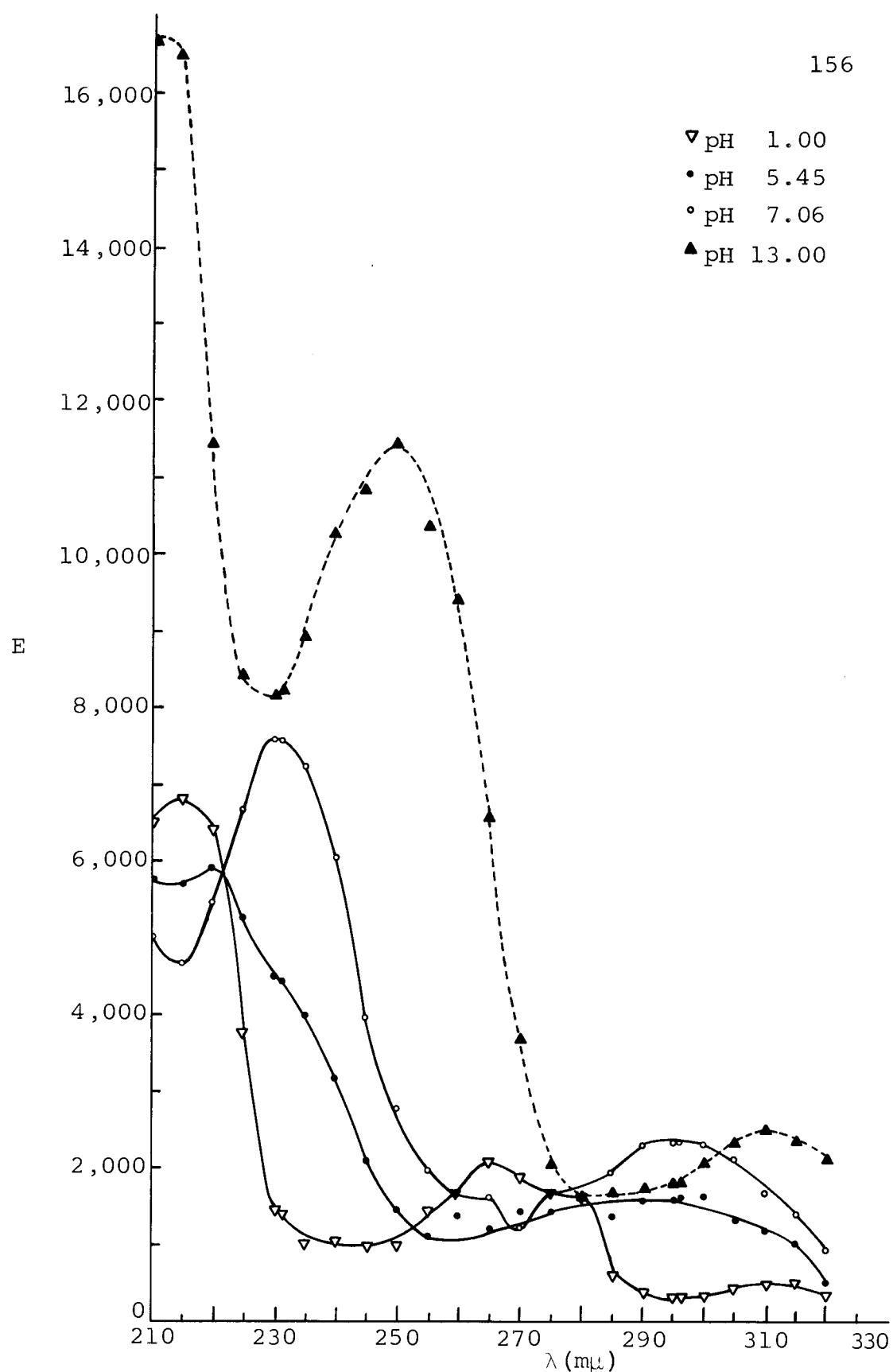


Figure 56. E versus λ of p-Aminophenol by Method II.

Table LXIV. Dissociation Constants of Anthranilic Acid by Method I.

No.	pH	E at 216 m μ	E at 220 m μ	E at 226 m μ	E at 240 m μ	E at 310 m μ
1	0.00	6513	8824	11093	4202	342
2	0.38	6513	8782	10756	3992	342
3	1.00	6933	9034	10714	3866	378
4	1.36	8403	10084	10840	3908	504
5	1.77	10504	11387	10504	3866	630
6	2.14	13025	13193	10504	4202	840
7	2.58	15504	14916	10420	4160	1008
8	3.20	17647	16176	9874	4244	1218
9	3.87	18067	15966	9244	4328	1303
10	4.45	18655	15672	9160	5000	1765
11	4.98	19328	15210	8950	5882	2227
12	5.65	19328	14286	8403	6975	2857
13	6.05	19748	14286	8403	7227	2983
14	6.48	19328	13655	8151	7311	3067
15	7.05	19748	13950	8319	7269	3067
16	7.52	19748	13655	8067	7311	3109
17	7.90	19748	13866	8109	7311	3067
18	8.52	19748	13782	8067	7353	3109
19	9.08	19748	13866	8193	7353	3067
20	9.72	20168	14286	8403	7437	3109
21	10.40	19538	13866	8193	7395	3151
22	10.95	19538	13782	8319	7395	3151
23	12.00	18950	13487	7983	7553	3109
24	12.50	16807	12395	7689	7553	3109
25	13.00	12899	11513	7647	7553	3109
26	13.50	8613	9076	7143	7553	3109
27	14.00	8193	8529	7353	7269	3235

Table LXV. Dissociation Constants of Anthranilic Acid by Method I.

λ (m μ)	X	E	Y	pH at Inflection Point	pK _a
216	6500	12300	18000	2.05	2.04
	18000	18900	19750	4.65	4.63
	8200	14000	19750	12.85	12.85
220	8800	12500	16100	2.00	1.99
	13800	15000	16100	5.00	4.96
	8500	11300	13900	13.00	12.97
226	9200	10000	10700	3.10	3.04
	8100	8600	9200	5.50	5.58
	7100	7700	8300	12.85	12.85
240	3800	4025	4250	2.05	2.05
	4250	5800	7300	4.90	4.87
310	350	775	1200	2.10	2.10
	1200	2150	3100	4.90	4.90

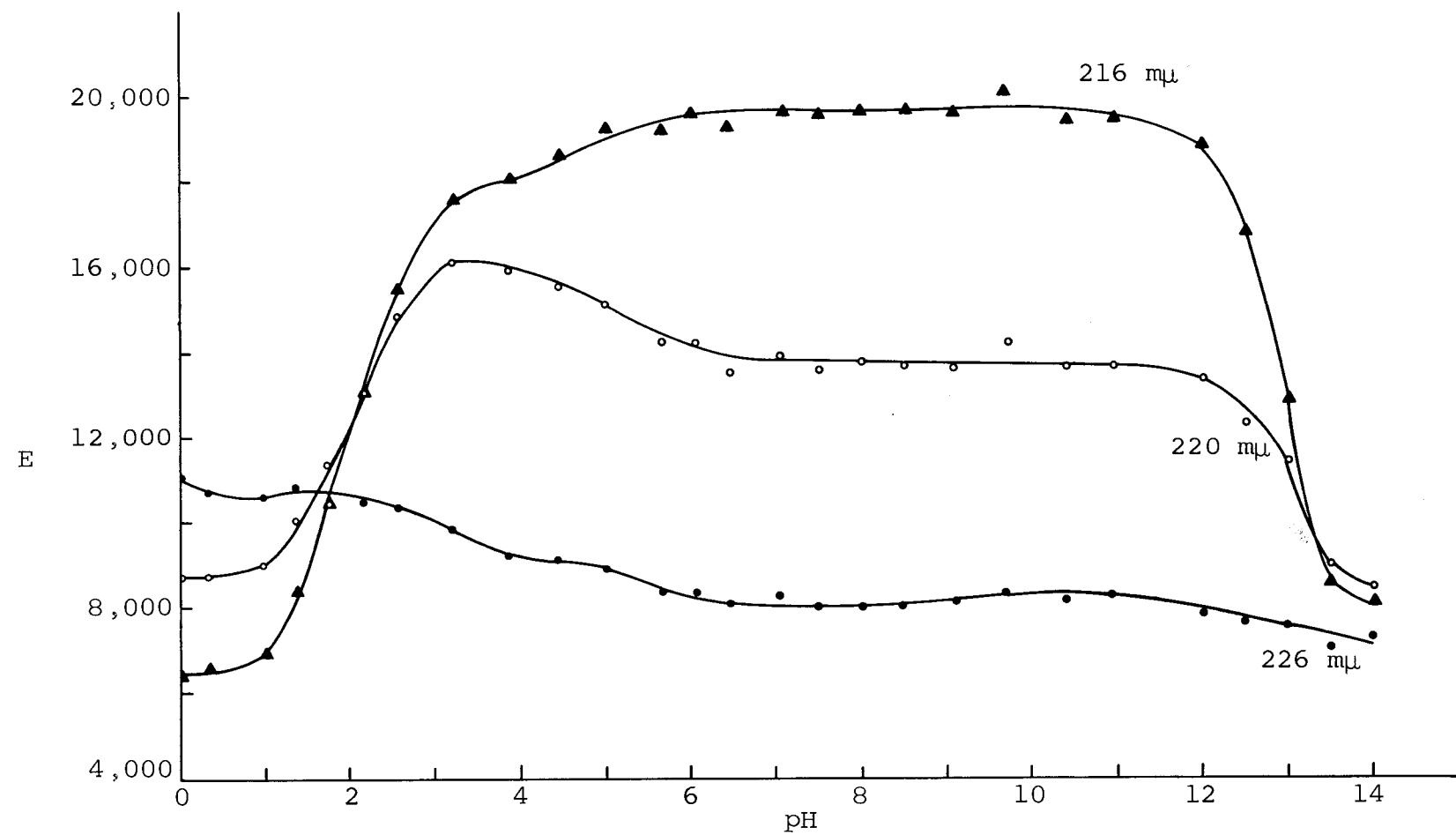


Figure 57. E versus pH of Anthranilic Acid by Method I.

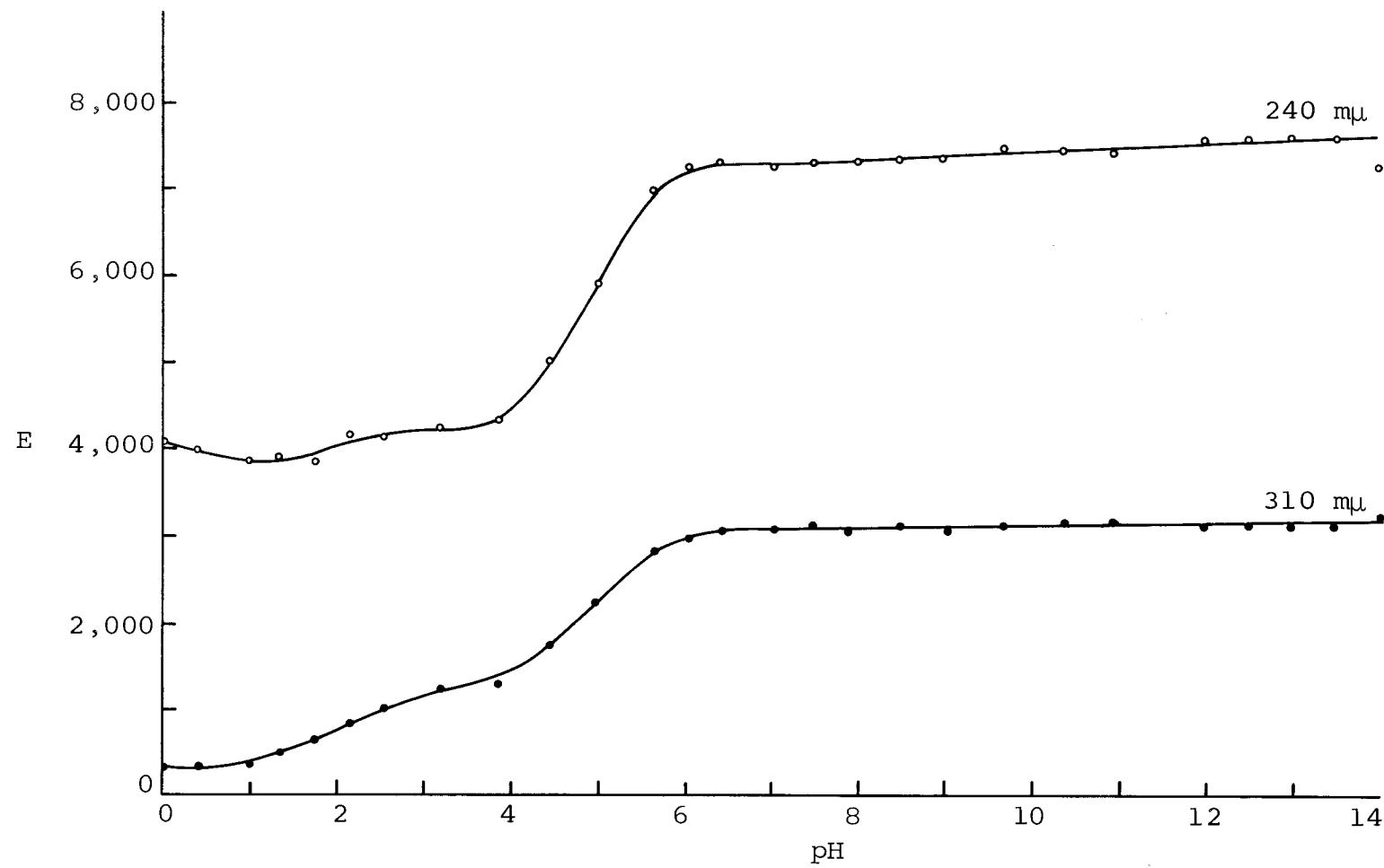


Figure 58. E versus pH of Anthranilic Acid by Method I.

Table LXVI. Dissociation Constants of Anthranilic Acid by Method II.

λ (m μ)	E at	E at	pH 7.05		pH 13	
	pH 1.00	pH 4.66	E	pK _a	E	pK _a
200	22899	15966	21639	-	13403	-
205	6849	17479	27312	-	14244	-
210	5462	20126	27731	-	15336	-
215	6849	18908	20798	-	16471	-
220	9160	15294	13403	-	12605	-
225	10840	9664	8361	4.71	8445	4.68
227	10840	7983	7563	-	7563	-
230	10168	6765	6975	-	7227	-
235	7437	5882	7185	-	7437	-
240	3782	5462	7311	4.70	7563	4.76
245	1849	4748	6387	4.42	6891	4.53
250	1218	3445	4580	4.37	5042	4.52
255	966	1681	2353	4.63	2689	4.81
260	1050	714	1050	-	1471	-
265	1050	126	588	-	714	-
270	1176	126	588	-	840	-
275	1092	210	714	-	924	-
280	966	294	1261	-	1303	-
285	714	714	1555	-	1681	-
290	252	966	2017	4.83	2059	4.84
295	168	1345	2395	4.61	2521	4.66
300	252	1471	2773	4.69	2857	4.72
305	336	1807	3109	4.61	3151	4.62
310	336	1891	3109	4.55	3235	4.59
315	336	1975	2941	4.52	3025	4.55
320	336	1933	2647	4.31	2689	4.33

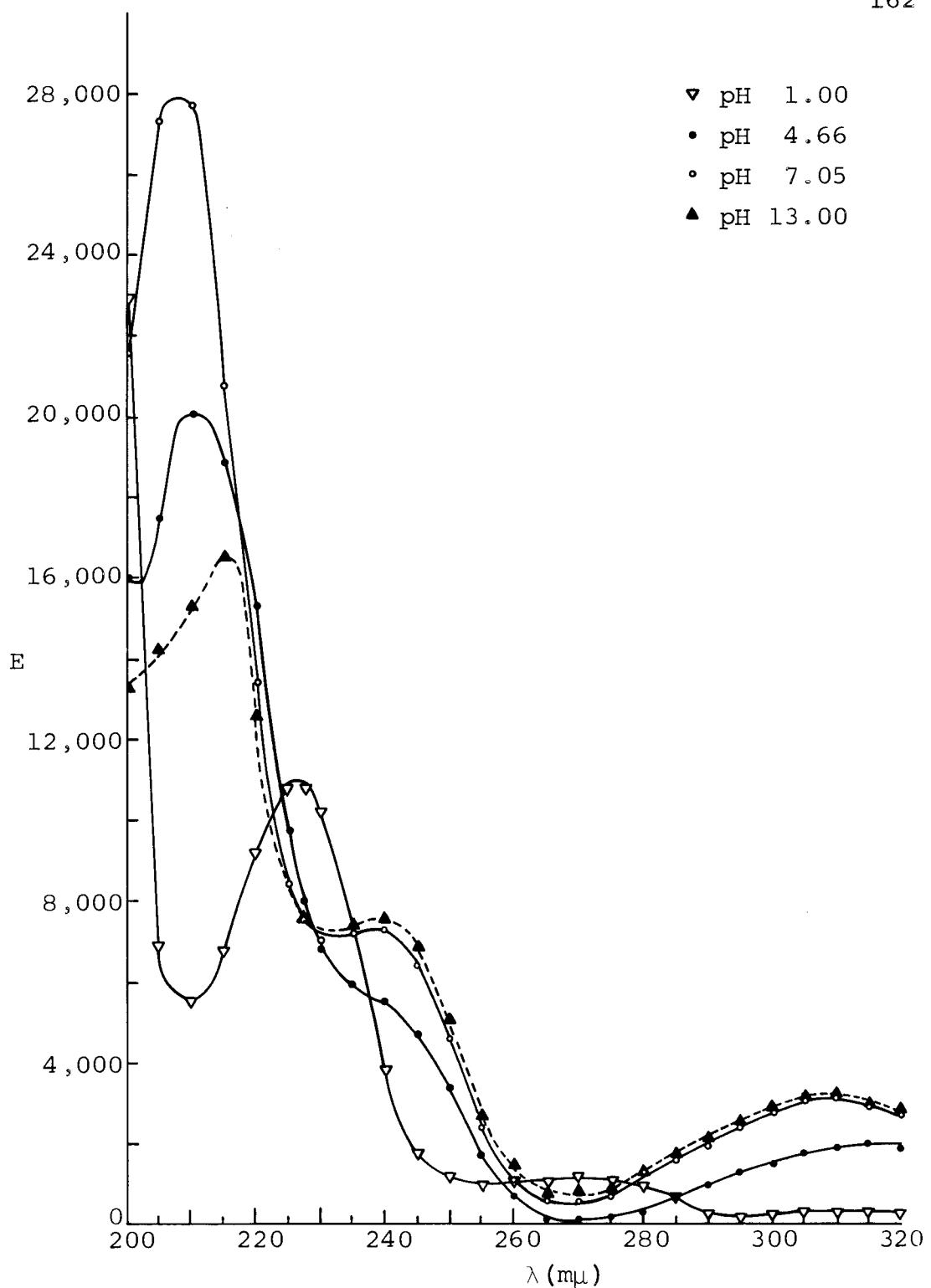


Figure 59. E versus λ of Anthranilic Acid by Method II.

Table LXVII. Dissociation Constant of Nicotinic Acid
by Method I.

No.	pH	E at 212.5 m μ	E at 220 m μ	E at 255 m μ	E at 260 m μ	E at 262 m μ	E at 269 m μ
1	1.13	5464	4286	4339	5179	4464	2679
2	1.40	5357	3964	4339	5161	4286	2679
3	2.40	5571	3839	4250	4982	4429	2679
4	3.12	5750	3750	4089	4750	4446	2768
5	4.09	6250	4161	3929	4464	4268	2768
6	4.48	6696	4732	3589	4036	3964	2732
7	5.14	7321	5250	3196	3482	3464	2500
8	6.04	7679	5804	2839	2964	3179	2321
9	7.03	7679	5857	2768	2911	3125	2321
10	7.82	7857	6071	2732	2893	3179	2375
11	9.17	7839	6071	2732	2875	3179	2375
12	10.20	7589	6071	2750	2857	3214	2375
13	11.18	6607	5536	2768	2911	3179	2339
14	12.00	6500	5714	2821	2893	3196	2357
15	13.00	2946	4732	2768	2875	3161	2357
16	14.00	3393	5214	2768	2857	3179	2357

$\lambda=212.5 \text{ m}\mu$, $x=5500$, $E=6800$, $y=7900$, $\text{pH}=4.60$, $\text{pK}_a=4.49$
 $x=2400$, $E=5400$, $y=7900$, $\text{pH}=12.30$, $\text{pK}_a=12.22$

$\lambda=220 \text{ m}\mu$, $x=3750$, $E=5000$, $y=6100$, $\text{pH}=4.80$, $\text{pK}_a=4.74$
 $x=4700$, $E=5400$, $y=6100$, $\text{pH}=12.30$, $\text{pK}_a=12.30$

$\lambda=255 \text{ m}\mu$, $x=2725$, $E=3500$, $y=4350$, $\text{pH}=4.65$, $\text{pK}_a=4.71$

$\lambda=260 \text{ m}\mu$, $x=2900$, $E=3800$, $y=5000$, $\text{pH}=4.80$, $\text{pK}_a=4.92$

$\lambda=262 \text{ m}\mu$, $x=3100$, $E=3750$, $y=4450$, $\text{pH}=4.80$, $\text{pK}_a=4.83$

$\lambda=269 \text{ m}\mu$, $x=2350$, $E=2600$, $y=2800$, $\text{pH}=4.90$, $\text{pK}_a=4.80$

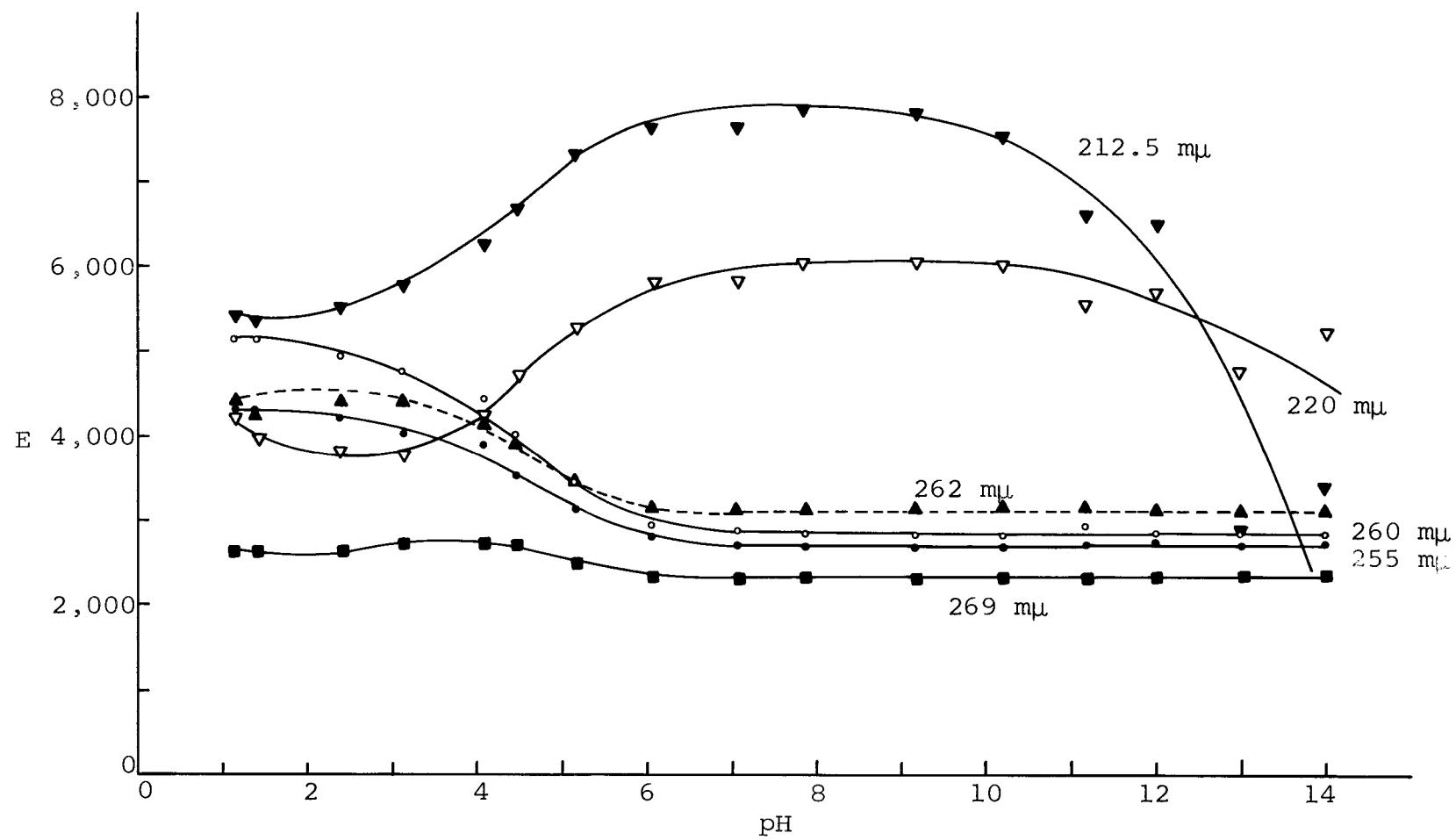


Figure 60. E versus pH of Nicotinic Acid by Method I.

Table LXVIII. Dissociation Constants of Nicotinic Acid
by Method II.

λ (m μ)	E at	E at	pH 7.06		pH 13	
	pH 1.28	pH 4.85	E	pK _a	E	pK _a
200	2571	7054	7545	-	3571	-
205	3482	6964	7411	-	3705	-
210	5196	7000	7723	-	3839	-
212.5	5348	6786	7679	4.65	4018	-
215	5179	6384	7321	4.74	4643	-
220	4107	4821	5714	4.95	5000	-
225	2411	3125	3661	4.73	3393	-
230	902	2045	2188	-	2054	-
235	759	1598	1598	-	1580	-
240	1143	1625	1607	-	1563	-
245	1875	1982	1795	-	1786	-
250	2947	2616	2223	4.93	2188	4.96
255	4197	3393	2768	4.73	2652	4.79
260	5089	3839	2947	4.70	2902	4.73
262	4732	3929	3179	4.82	3143	4.84
265	3982	3402	2536	5.02	2455	5.06
266.5	3964	3179	2304	4.90	2277	4.91
269	2321	2679	2321	-	2277	-
270	1964	2411	2143	-	2054	-
275	357	804	554	-	536	-
280	71	268	143	-	134	-
285	18	116	45	-	36	-
290	9	45	27	-	18	-
295	0	18	18	-	9	-
300	0	0	0	-	0	-
305	0	0	0	-	0	-
310	0	0	0	-	0	-
315	0	0	0	-	0	-
320	0	0	0	-	0	-

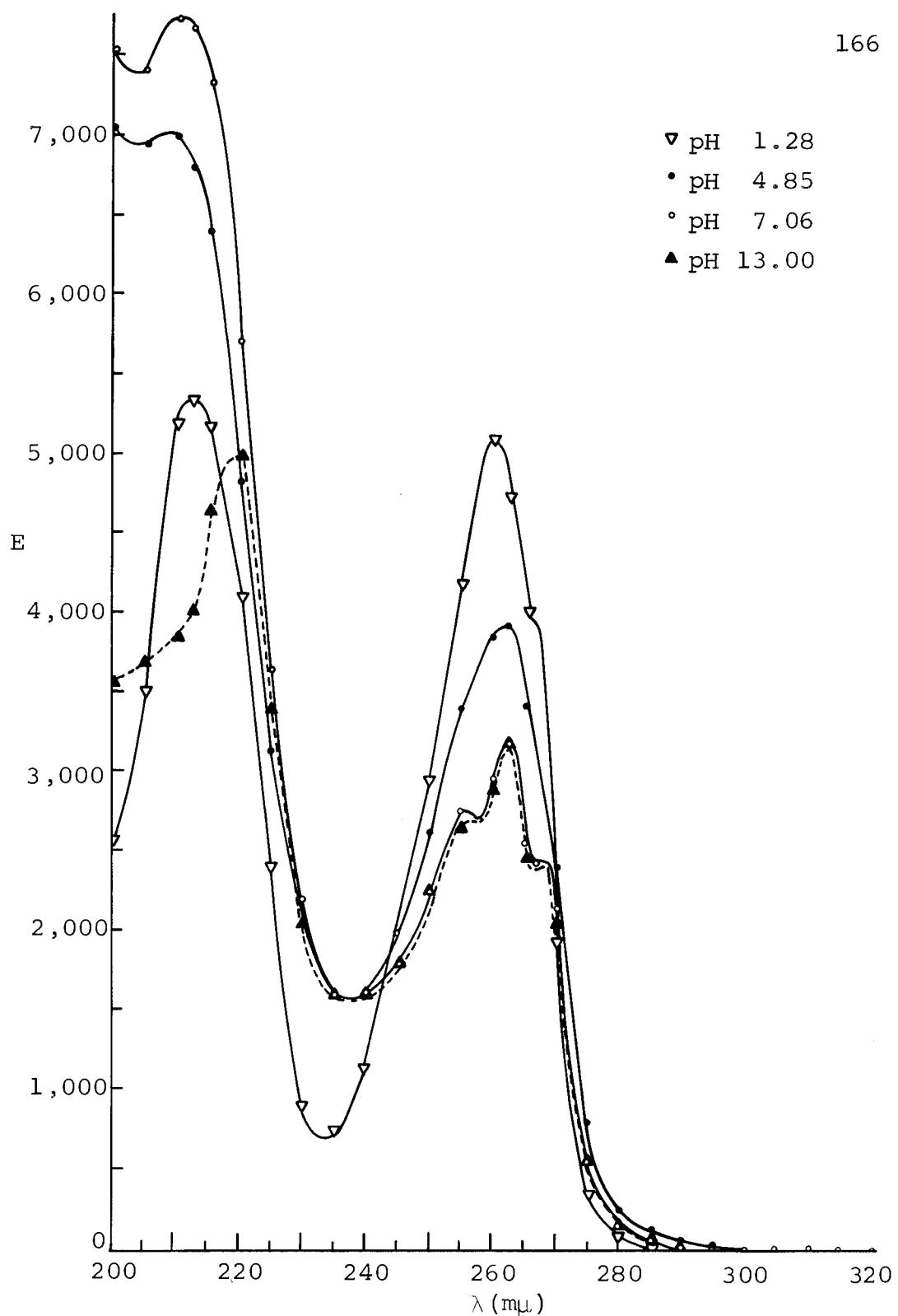


Figure 61. E versus λ of Nicotinic Acid by Method II.

Table LXIX. Dissociation Constants of Sulphanilic Acid by Method I.

No.	pH	E at 247.5 m μ
1	0.00	300
2	0.40	420
3	0.81	601
4	1.23	691
5	1.55	871
6	2.00	1471
7	2.13	1922
8	2.25	2162
9	2.44	3063
10	2.51	3363
11	2.75	4865
12	2.95	6036
13	3.10	7297
14	3.25	8529
15	3.50	10631
16	3.70	11802
17	3.97	13063
18	4.30	14174
19	4.58	14354
20	4.84	14745
21	5.22	14985
22	5.75	15015
23	6.35	15045
24	6.97	15045
25	7.75	15015
26	8.55	15045
27	9.66	15105
28	11.00	15045
29	12.00	15105
30	12.50	15225
31	13.00	15105
32	13.50	15255
33	14.00	15495

$\lambda=247.5$ m μ , $x=500$, $E=8000$, $y=15000$, $pH=3.20$, $pK_a=3.17$

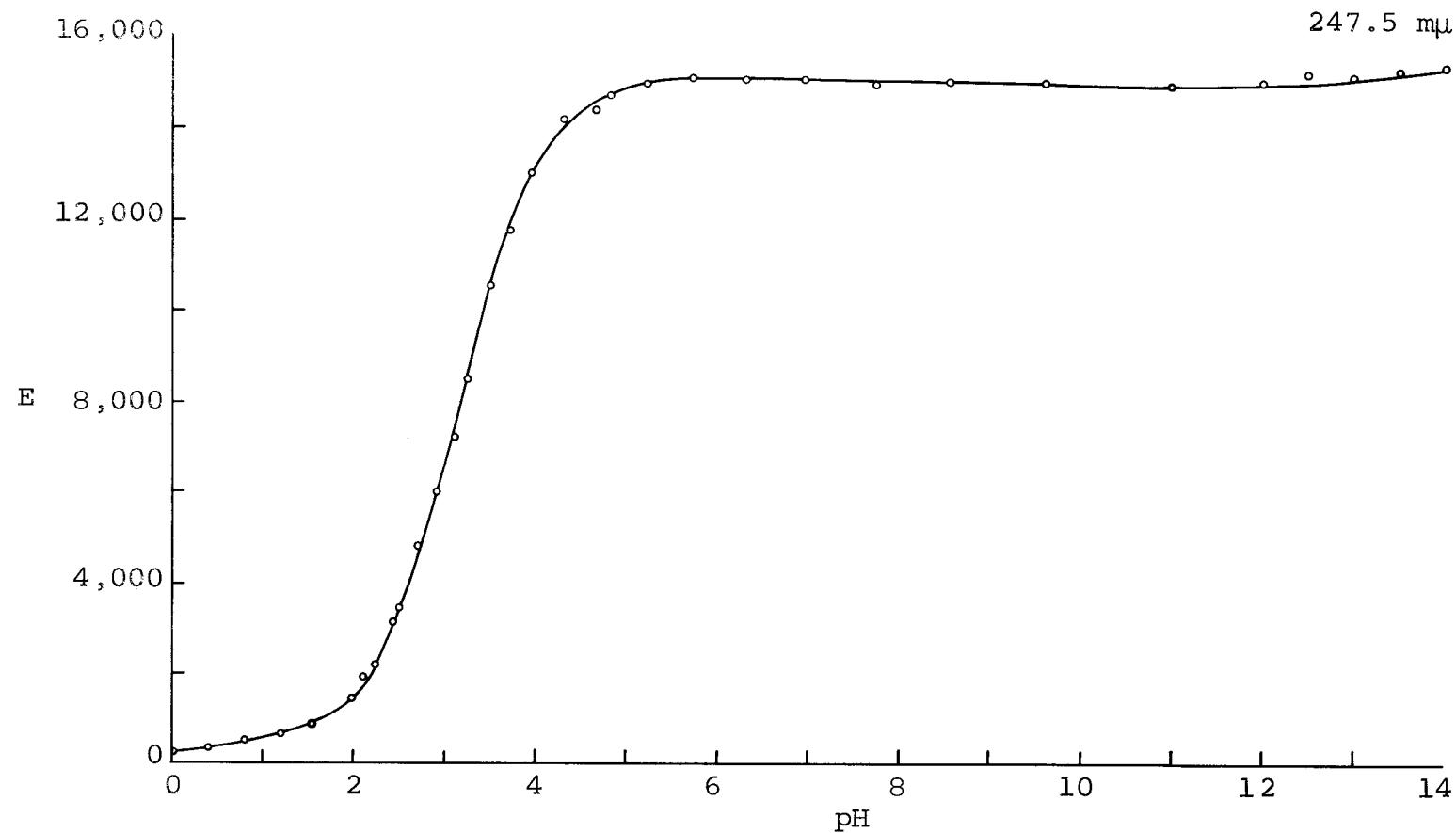


Figure 62. E versus pH of Sulphanilic Acid by Method I.

Table LXX. Dissociation Constants of Sulphanilic Acid by Method II.

λ (m μ)	E at	E at	<u>pH 7.01</u>		<u>pH 13</u>	
	pH 1.02	pH 3.15	E	pK _a	E	pK _a
210	9069	9910	9910	-	0	-
215	9069	6186	3363	3.14	0	-
220	5495	4084	2432	3.22	0	-
225	1051	2342	3604	3.14	3003	-
230	420	3153	5586	3.10	5465	3.08
235	511	4775	8709	3.11	8709	3.11
240	631	6577	12042	3.11	12102	3.12
245	661	7838	14685	3.13	14655	3.13
247.5	661	8048	15135	3.13	15135	3.13
250	661	7928	14955	3.14	14895	3.13
255	691	6727	12613	3.14	12582	3.14
260	661	4865	8979	3.14	8859	3.13
265	450	3003	5405	3.12	5435	3.13
270	420	1892	3303	3.13	3333	3.13
275	180	1351	2342	3.08	2372	3.09
280	180	1171	1952	3.05	1982	3.06
285	210	1051	1712	3.05	1772	3.08
290	180	871	1441	3.06	1502	3.11
295	150	601	1141	3.23	1141	3.23
300	180	420	721	3.25	721	3.25
305	180	330	480	3.15	511	3.23
310	180	300	330	-	300	-
315	150	210	210	-	240	-
320	150	150	180	-	180	-

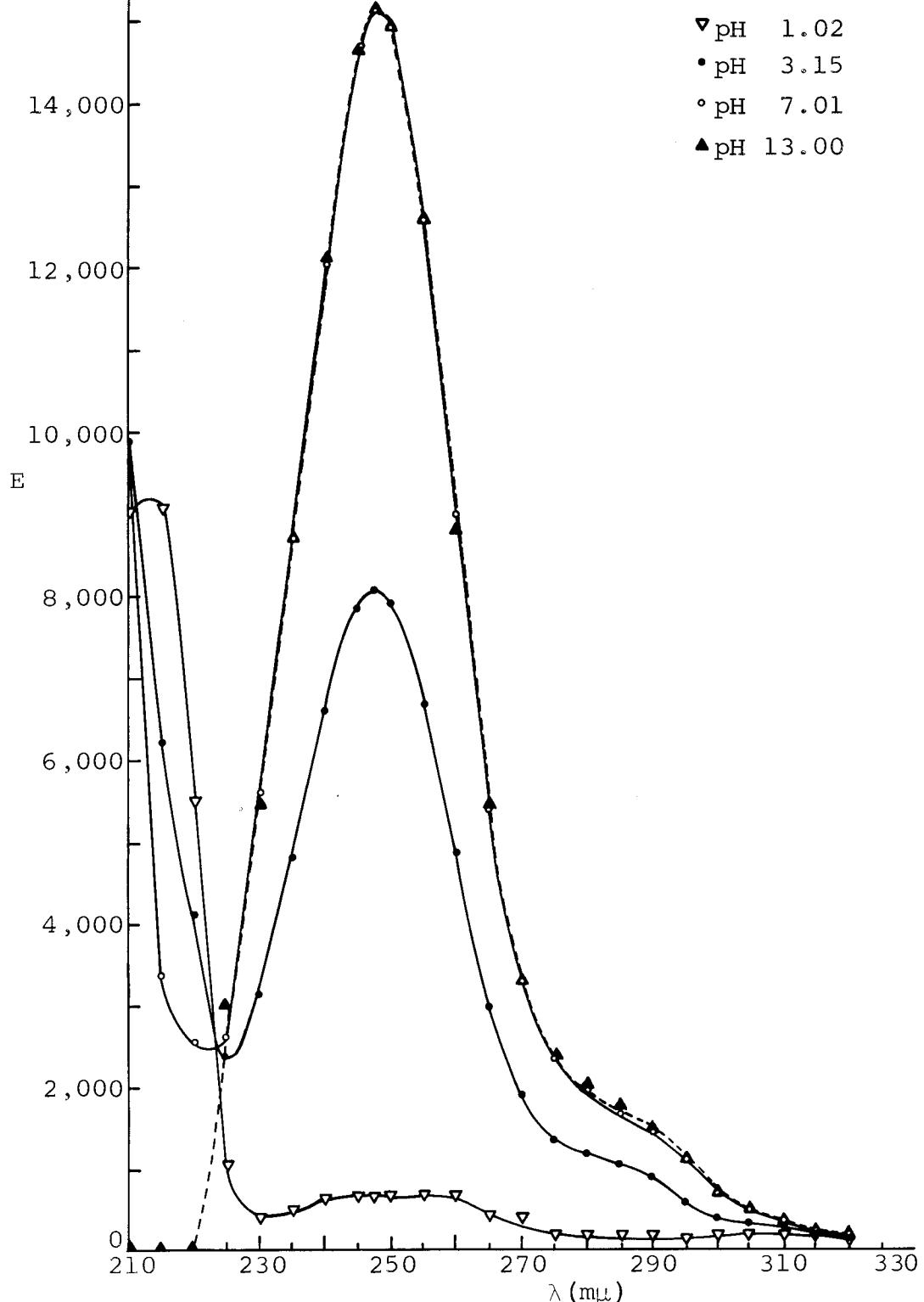


Figure 63. E versus λ of Sulphanilic Acid by Method II.

Table LXXI. Dissociation Constant of L-Histidine
by Method I.

No.	pH	E at 210 m μ	E at 215 m μ
1	0.10	5855	5362
2	0.48	5913	5188
3	1.11	5942	5130
4	1.58	6174	5304
5	2.17	6087	5478
6	2.77	5913	5246
7	3.40	6000	5362
8	4.00	6058	5449
9	4.48	6058	5362
10	4.90	6029	5304
11	5.29	5913	5217
12	5.79	6029	5217
13	6.25	5884	4928
14	6.64	5797	4841
15	7.00	5913	4957
16	7.40	5913	4870
17	7.90	5913	4957
18	8.30	5855	4928
19	8.95	5797	4928
20	9.60	6232	5449
21	10.16	6174	5536
22	10.79	6667	5623
23	11.50	6261	5478
24	12.00	6116	5217
25	12.50	5594	5159
26	13.00	4638	4812
27	13.50	3159	3507
28	14.00	3043	3420

$\lambda=210 \text{ m}\mu$, $x=5800$, $E=6200$, $y=6600$, $\text{pH}=9.85$, $\text{pK}_a=9.85$
 $x=3000$, $E=4750$, $y=6600$, $\text{pH}=13.00$, $\text{pK}_a=13.02$

$\lambda=215 \text{ m}\mu$, $x=4900$, $E=5150$, $y=5400$, $\text{pH}=5.60$, $\text{pK}_a=5.60$
 $x=4900$, $E=5300$, $y=5600$, $\text{pH}=9.40$, $\text{pK}_a=9.33$
 $x=3400$, $E=4550$, $y=5600$, $\text{pH}=13.20$, $\text{pK}_a=13.16$

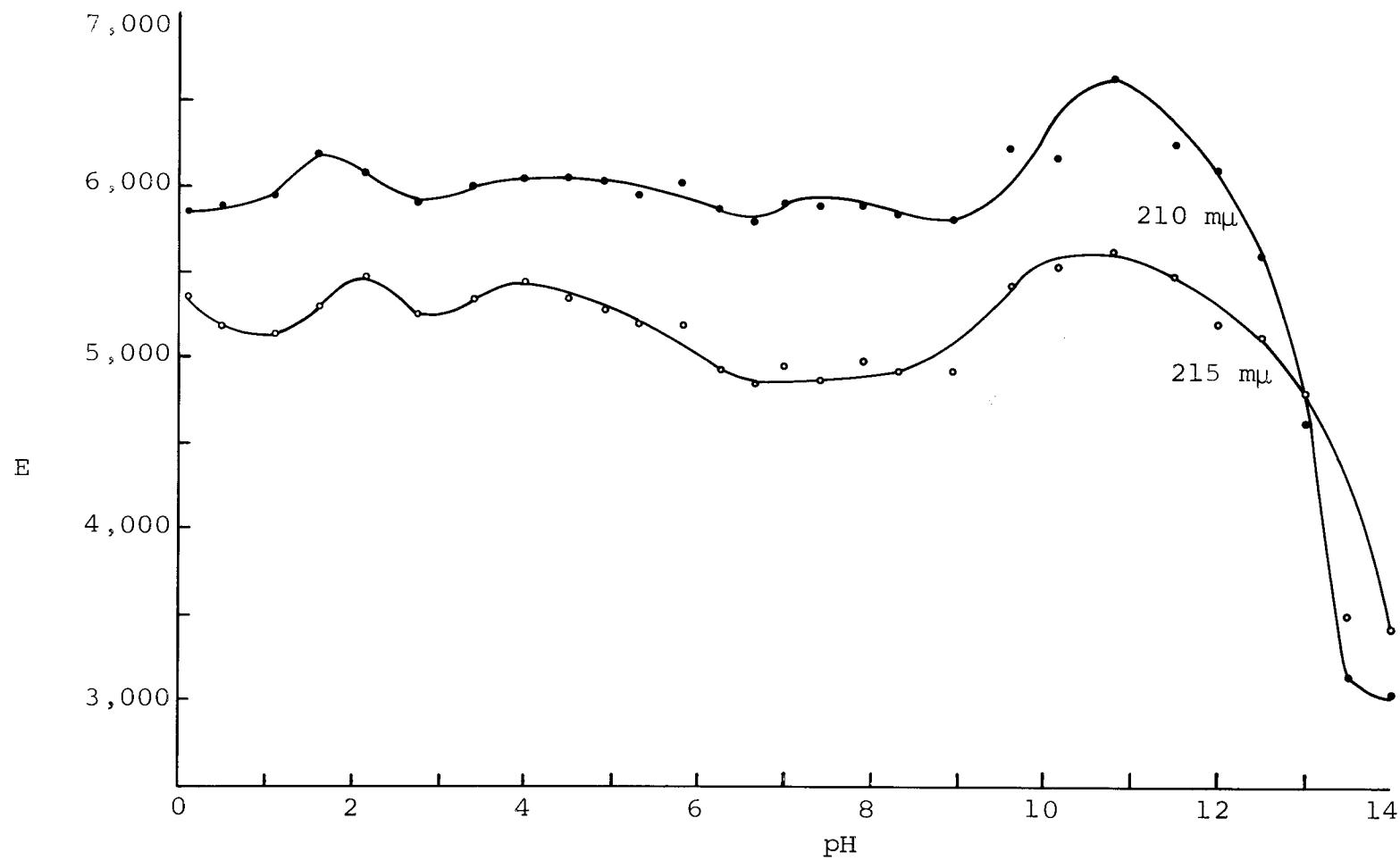


Figure 64. E versus pH of L-Histidine by Method I.

Table LXXII. Dissociation Constants of L-Histidine
by Method II.

λ (m μ)	E at pH 1.00	E at pH 9.48	E at pH 13	pK _a
200	3623	5638	3638	-
205	5145	5942	3768	-
210	5797	5899	3710	-
215	5014	5160	3986	-
218	3957	4304	4087	-
220	3217	3696	3783	-
225	1362	2029	2377	9.19
230	290	725	1000	9.28
235	72	217	362	9.48
240	72	116	217	9.84
245	43	101	174	9.58
250	14	72	130	9.48
255	0	43	87	9.49
260	0	0	72	-
265	0	0	29	-
270	0	0	14	-
275	0	0	14	-
280	0	0	0	-
285	0	0	0	-
290	0	0	0	-
295	0	0	0	-
300	0	0	0	-
305	0	0	0	-
310	0	0	0	-
315	0	0	0	-
320	0	0	0	-

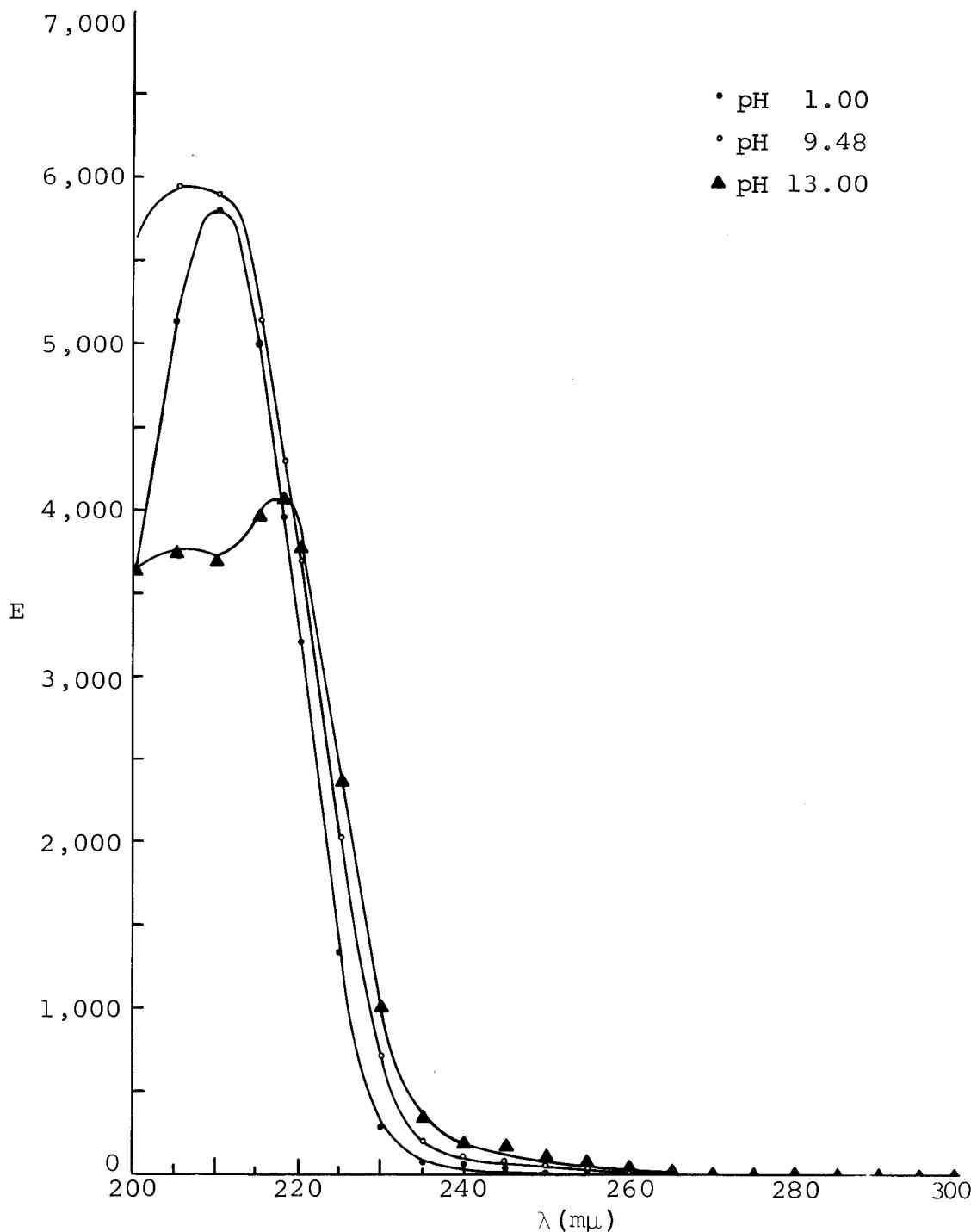


Figure 65. E versus λ of L-Histidine by Method II.

Table LXXIII. Dissociation Constants of p-Hydroxyphenoxyacetic Acid by Method I.

No.	pH	E at 222 m μ	E at 235 m μ	E at 285 m μ	E at 287 m μ	E at 305 m μ
1	0.00	6671	1228	2387	2360	164
2	0.45	6439	1228	2319	2265	136
3	1.05	6630	1228	2374	2319	136
4	1.65	6671	1228	2374	2319	164
5	2.28	6617	1228	2374	2319	150
6	2.77	6821	1296	2387	2387	191
7	3.20	6917	1432	2401	2401	205
8	3.70	7231	1637	2456	2483	273
9	4.14	7176	1637	2428	2456	286
10	4.40	7190	1610	2415	2456	300
11	5.05	7271	1637	2428	2469	300
12	5.55	7217	1637	2428	2469	300
13	6.02	7231	1569	2428	2456	273
14	6.51	7231	1569	2428	2456	300
15	7.05	7244	1637	2401	2456	300
16	7.41	7190	1569	2415	2456	286
17	7.90	7135	1637	2401	2428	314
18	8.31	7108	1637	2374	2387	286
19	8.96	7094	1896	2319	2374	396
20	9.61	6930	2797	2183	2251	682
21	9.92	6821	3684	2046	2142	928
22	10.52	6276	6385	1637	1746	1801
23	11.00	6003	8049	1296	1473	2265
24	11.50	5894	8186	1228	1378	2292
25	12.00	5593	9168	1023	1201	2578
26	12.50	5703	9263	1078	1228	2606
27	13.00	4775	9263	955	1132	2606
28	13.50	4911	9263	955	1160	2633
29	14.00	4502	9304	941	1132	2660

Table LXXIV. Dissociation Constants of p-Hydroxyphenoxyacetic Acid by Method I.

λ (m μ)	x	E	y	pH at Inflection Point	pK _a
222	6600	6900	7225	3.10	3.13
	6000	6550	7100	10.30	10.30
	4500	5250	6000	12.75	12.75
235	1225	1400	1600	3.10	3.15
	1600	5500	9300	10.30	10.29
285	950	1700	2425	10.40	10.38
287	2275	2350	2450	2.80	2.92
	1150	1850	2450	10.50	10.43
305	125	200	300	3.10	3.22
	300	1500	2650	10.30	10.28

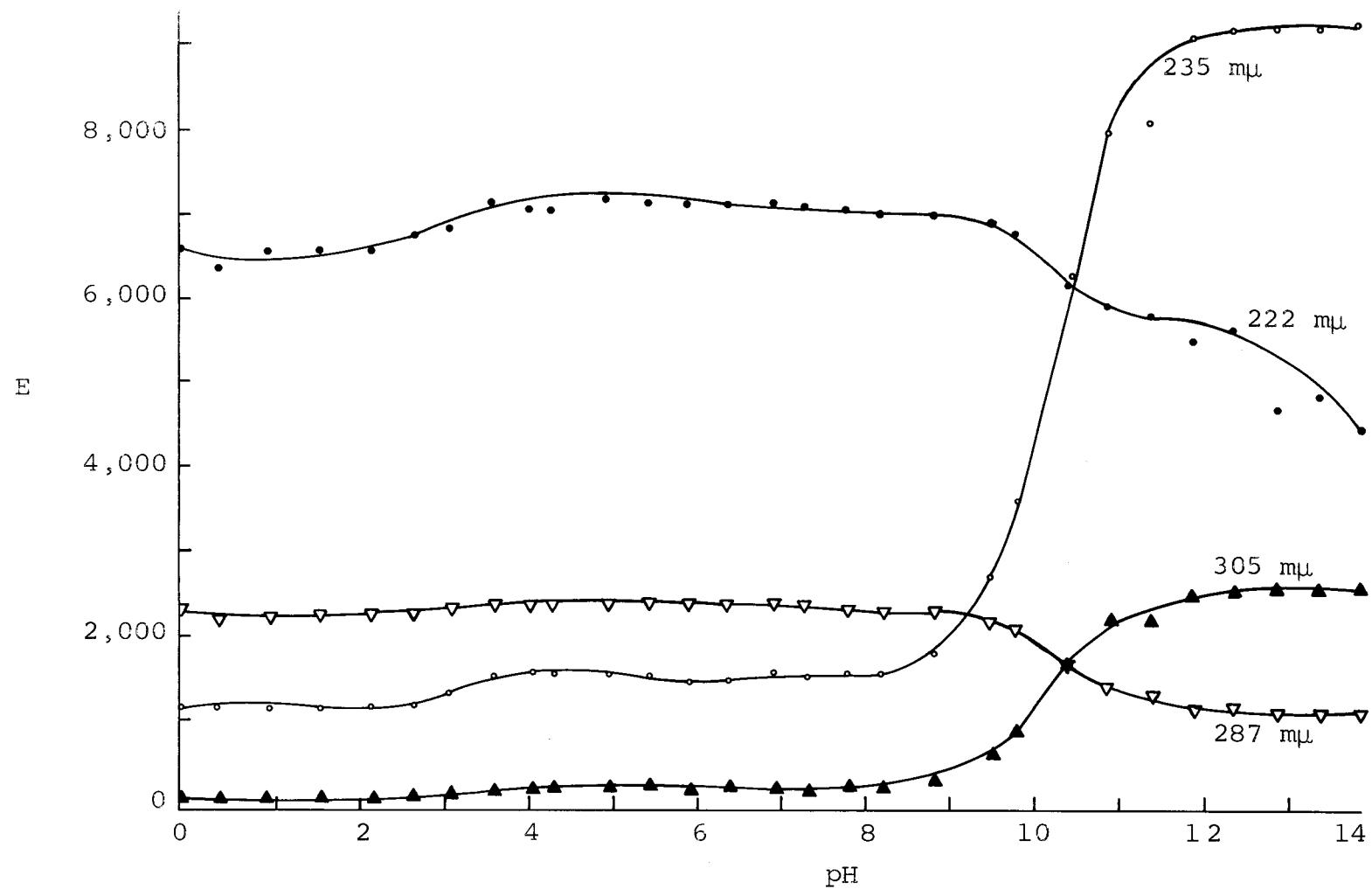


Figure 66. E versus pH of *p*-Hydroxyphenoxyacetic Acid by Method I.

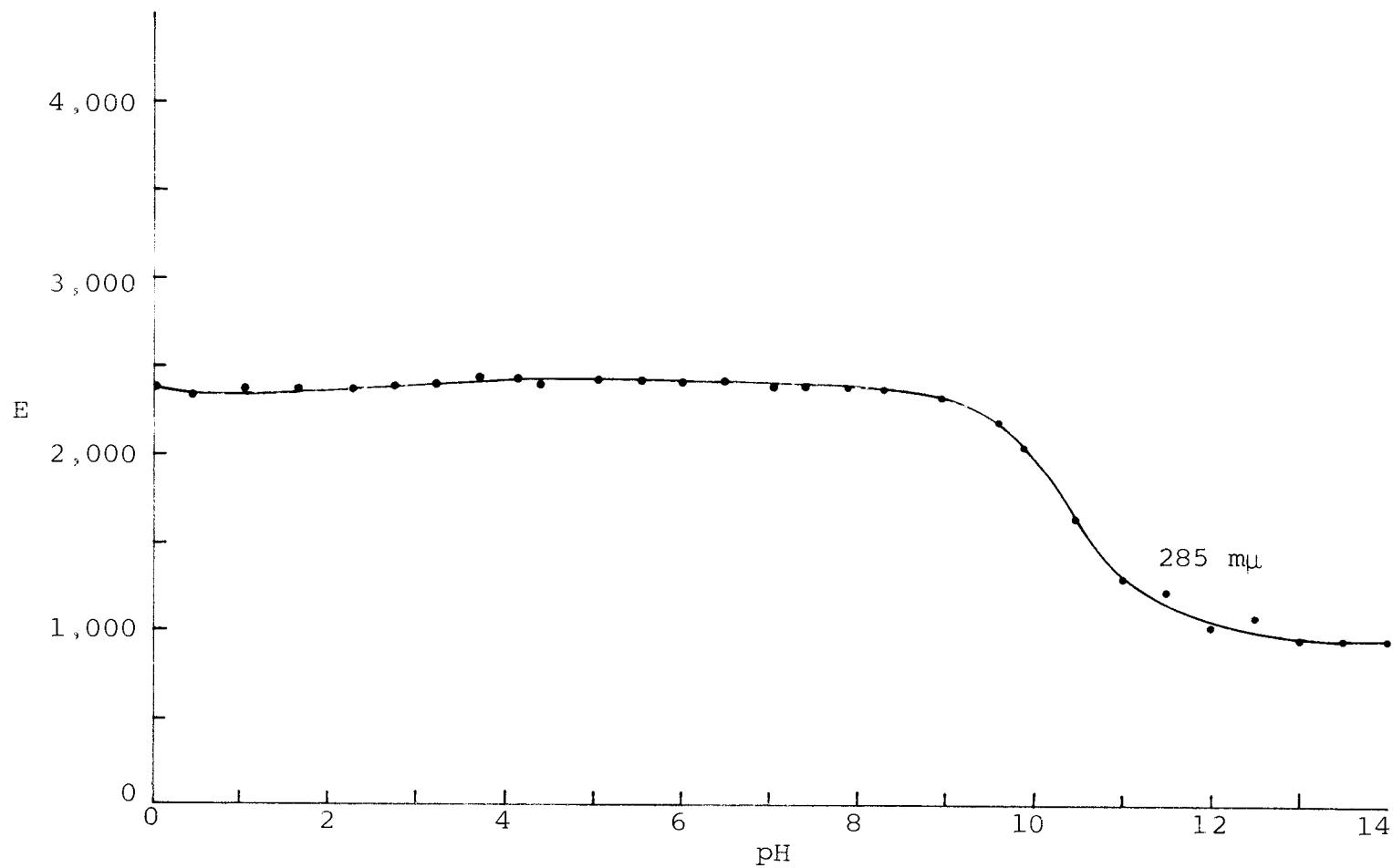


Figure 67. E versus pH of *p*-Hydroxyphenoxyacetic Acid by Method I.

Table LXXV. Dissociation Constants of p-Hydroxyphenoxyacetic Acid by Method II.

λ (m μ)	E at pH 1.05	E at pH 10.52	E	pH 13	
					pK _a
200	6821	19100	764	-	
205	4980	11596	996	-	
210	5307	6139	1173	-	
215	5771	5184	1610	-	
220	6671	5866	3683	-	
222	6630	6276	4502	-	
225	5771	6780	6139	-	
230	3138	6862	8322	-	
235	1214	6385	9140	10.24	
240	546	5321	8254	10.31	
245	287	3683	5798	10.31	
250	218	2046	3179	10.31	
255	287	982	1473	10.37	
260	437	573	682	10.42	
265	682	491	341	10.42	
270	1105	600	300	10.30	
275	1719	846	382	10.24	
280	2115	1187	600	10.32	
285	2360	1569	955	10.41	
287	2333	1678	1160	10.42	
290	2142	1828	1460	10.59	
295	1569	1951	1978	-	
300	696	1910	2428	-	
305	150	1774	2633	10.24	
310	41	1528	2469	10.32	
315	27	1132	1910	10.37	
320	14	655	1091	10.35	

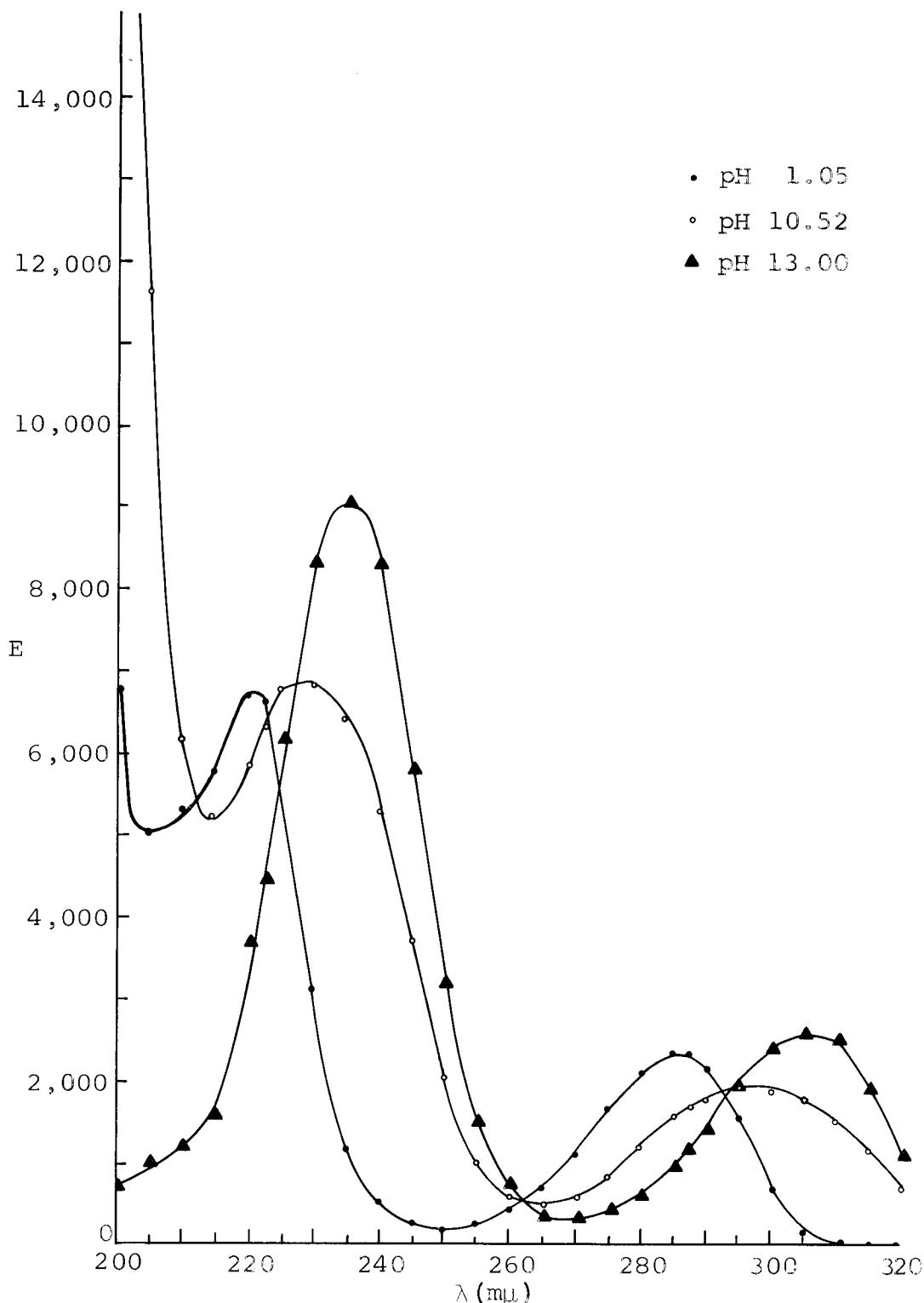


Figure 68. E versus λ of p-Hydroxyphenoxyacetic Acid by Method II.

Table LXXVI. Dissociation Constant of dl-Tryptophane
by Method I.

No.	pH	E at 218 m μ	E at 221 m μ	E at 278 m μ
1	0.15	33383	29895	5630
2	0.50	32885	29895	5531
3	0.90	33034	29895	5580
4	1.47	33134	29895	5580
5	1.88	33383	29895	5531
6	2.34	33632	30394	5481
7	2.80	33981	30891	5431
8	3.25	34429	31340	5580
9	3.78	34778	32387	5630
10	4.20	34629	31888	5531
11	4.77	34679	32387	5531
12	5.23	34928	32387	5630
13	5.71	34728	31888	5531
14	6.16	34679	32387	5531
15	6.55	34679	32387	5531
16	7.00	34629	32387	5531
17	7.52	34479	32387	5580
18	8.00	34380	31888	5481
19	8.41	34429	32387	5580
20	8.94	33433	32138	5481
21	9.46	33284	32387	5381
22	9.84	32636	32636	5282
23	10.18	32536	32885	5282
24	10.57	32387	32785	5381
25	10.85	31938	32885	5282
26	11.50	31839	32785	5232
27	12.00	30892	32785	5232
28	12.50	30892	31988	5232
29	13.00	29048	31141	5332
30	13.50	27554	29796	5332
31	14.00	27404	28301	5182

$\lambda=218 \text{ m}\mu$, $x=33000$, $E=34000$, $y=34900$, $\text{pH}=2.70$, $\text{pK}_a=2.65$
 $x=27400$, $E=31000$, $y=34400$, $\text{pH}=11.90$, $\text{pK}_a=11.88$

$\lambda=221 \text{ m}\mu$, $x=29900$, $E=31100$, $y=32400$, $\text{pH}=3.05$, $\text{pK}_a=3.08$
 $x=28300$, $E=30800$, $y=33000$, $\text{pH}=13.10$, $\text{pK}_a=13.05$

$\lambda=278 \text{ m}\mu$, pK_a undeterminable

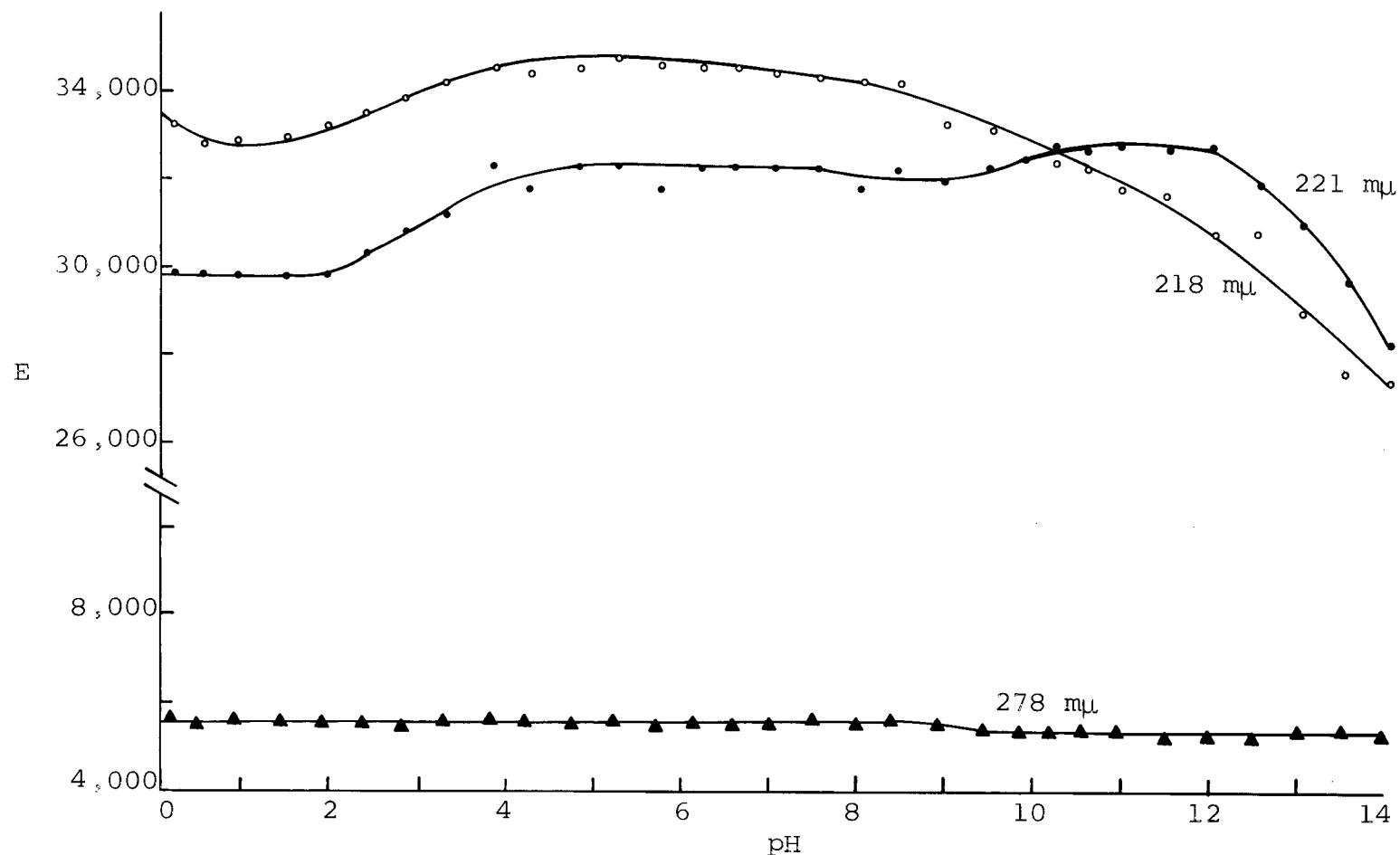


Figure 69. E versus pH of dl-Tryptophane by Method I.

Table LXXVII. Dissociation Constants of dl-Tryptophane
by Method II.

λ (m μ)	E at pH 1.00	E at pH 9.31	E at pH 13.00	pK _a
200	7474	20428	24415	-
205	20428	19831	25311	-
210	27653	23966	26158	-
215	33582	31141	27703	9.46
218	32885	33533	30643	-
220	30493	32985	31839	-
221	28401	31888	31734	-
225	16193	22920	26657	9.06
230	5481	7474	10463	9.49
235	2990	2740	3239	-
240	2392	2143	2143	-
245	2392	2192	2093	-
250	2691	2491	2242	9.41
255	3338	3039	2691	9.37
260	4235	3737	3338	9.21
265	5032	4484	4086	9.14
270	5481	5132	4783	9.31
275	5481	5282	5132	9.19
278	5630	5431	5232	9.31
280	5481	5431	5282	-
285	4484	4584	4637	9.01
290	3039	3737	4235	9.41
295	947	1744	2242	9.10
300	199	548	997	9.42
305	100	299	448	9.19
310	50	149	149	-
315	0	100	100	-
320	0	50	50	-

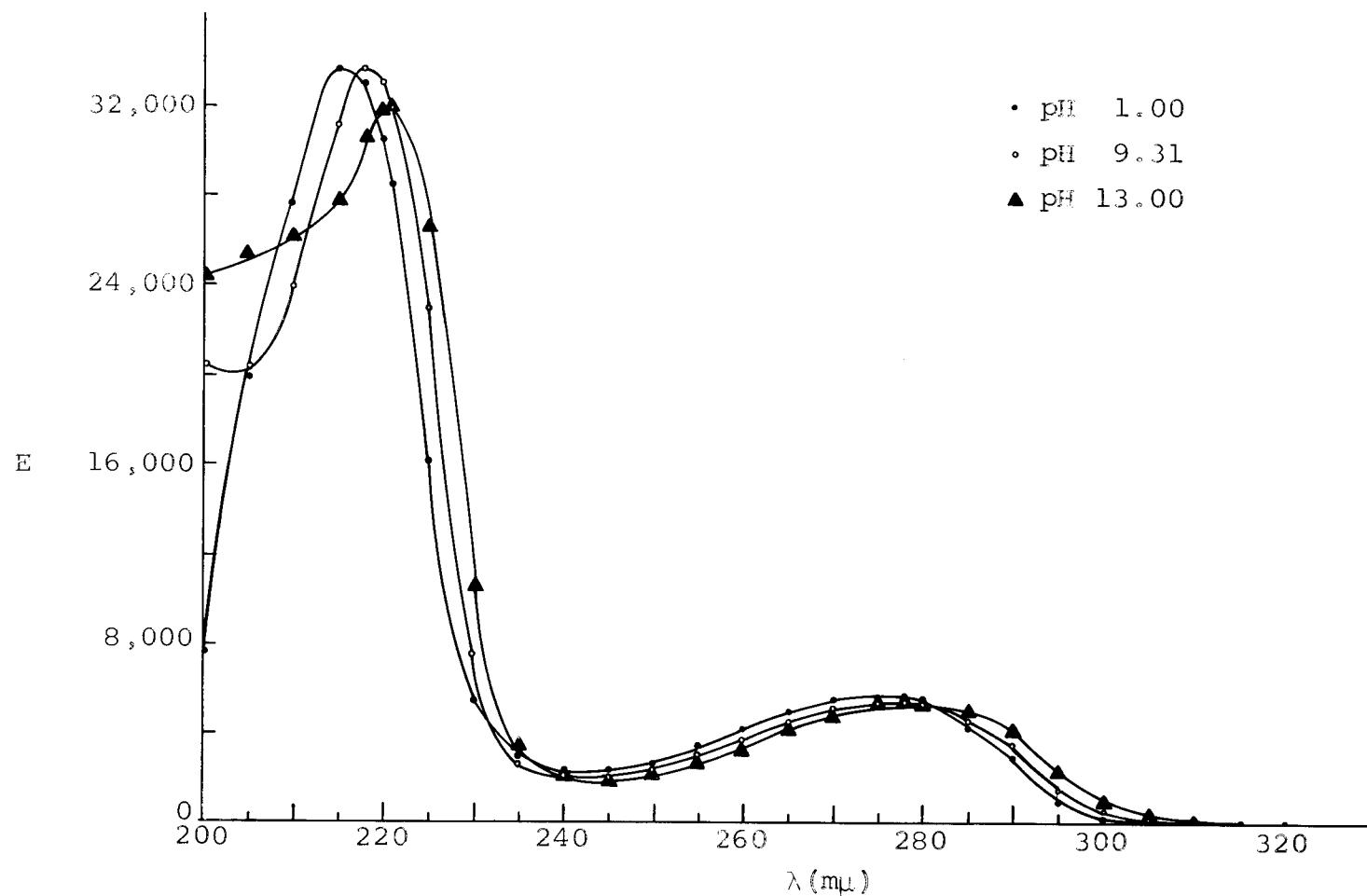


Figure 70. E versus λ of dl-Tryptophan by Method III.

Table LXXVIII. Dissociation Constant of L-Tyrosine
by Method I.

No.	pH	E at 222.5 m μ	E at 240 m μ	E at 274 m μ	E at 292 m μ
0	0.00	8005	510	1369	23
1	0.40	8121	534	1346	23
2	0.90	8121	510	1369	23
3	1.39	8121	510	1369	23
4	1.95	8190	464	1392	23
5	2.54	8190	394	1369	23
6	3.15	8306	394	1392	23
7	3.92	8283	348	1392	46
8	4.73	8329	371	1415	46
9	5.68	8329	371	1415	46
10	6.04	8329	464	1415	46
11	6.49	8306	464	1392	46
12	7.01	8329	487	1415	46
13	7.55	8306	510	1392	46
14	7.95	8237	743	1392	93
15	8.50	7935	1508	1369	232
16	9.05	7425	3016	1346	534
17	9.32	7123	3968	1346	835
18	9.61	6845	5197	1323	998
19	10.07	6262	7889	1299	1624
20	10.37	5800	9258	1230	1926
21	10.90	5429	10789	1137	2251
22	12.00	5452	11183	1160	2320
22A	12.50	5104	11369	1160	2390
23	13.00	4640	11323	1114	2343
23A	13.50	3944	11369	1137	2390
24	14.00	2784	11276	905	2297

$\lambda=222.5 \text{ m}\mu$, $x=5450$, $E=6800$, $y= 8300$, $\text{pH}= 9.60$, $\text{pK}_a= 9.65$
 $x=2800$, $E=4200$, $y= 5450$, $\text{pH}=13.40$, $\text{pK}_a=13.33$

$\lambda=240 \text{ m}\mu$, $x= 400$, $E=6000$, $y=11350$, $\text{pH}= 9.75$, $\text{pK}_a= 9.73$

$\lambda=274 \text{ m}\mu$, pK_a undeterminable

$\lambda=292 \text{ m}\mu$, $x= 50$, $E=1300$, $y= 2400$, $\text{pH}= 9.80$, $\text{pK}_a= 9.74$

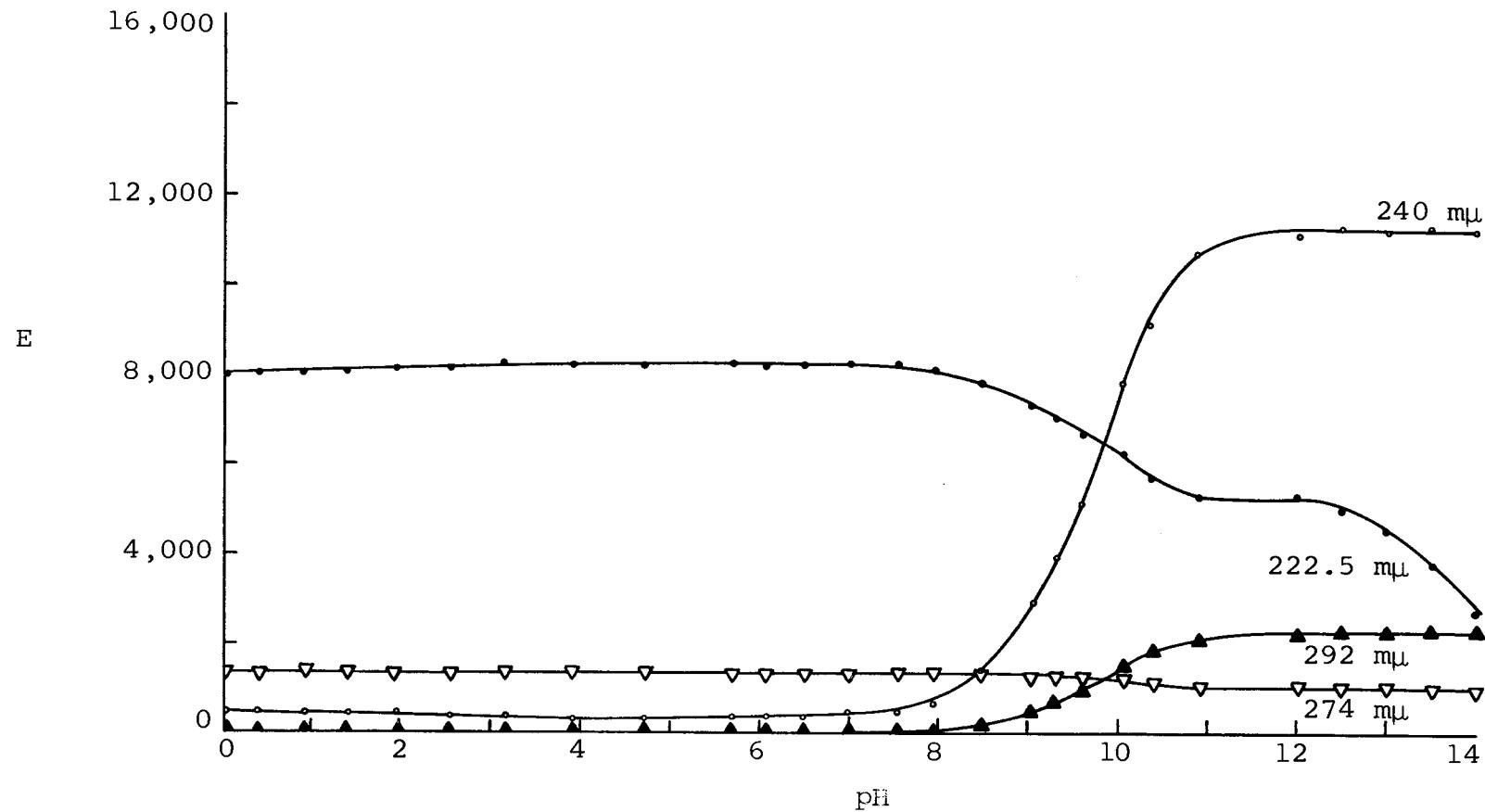


Figure 71. E versus pH of L-Tyrosine by Method I.

Table LXXIX. Dissociation Constants of L-Tyrosine
by Method II.

λ (m μ)	E at pH 5.73	E at pH 9.85	E at pH 13	pK _a
200	9165	20367	0	-
205	5397	10183	0	-
210	5295	6925	0	-
215	6110	6029	0	-
220	7454	6680	0	-
222.5	7821	7026	1018	-
225	7230	6925	2444	-
230	3666	5906	5499	-
235	978	3971	8187	10.00
240	122	3747	9776	10.07
245	81	3442	8452	10.02
250	143	2444	5214	9.93
255	305	1405	2424	9.82
260	550	937	754	-
265	855	916	81	-
270	1120	1120	0	-
274	1303	1303	81	-
275	1303	1303	122	-
280	1120	1303	570	-
285	570	1059	1018	-
290	81	815	1385	9.74
292	20	754	1466	9.84
295	20	713	1446	9.88
300	20	591	1181	9.86
305	20	367	672	9.79
310	0	143	244	-
315	0	41	102	-
320	0	0	20	-

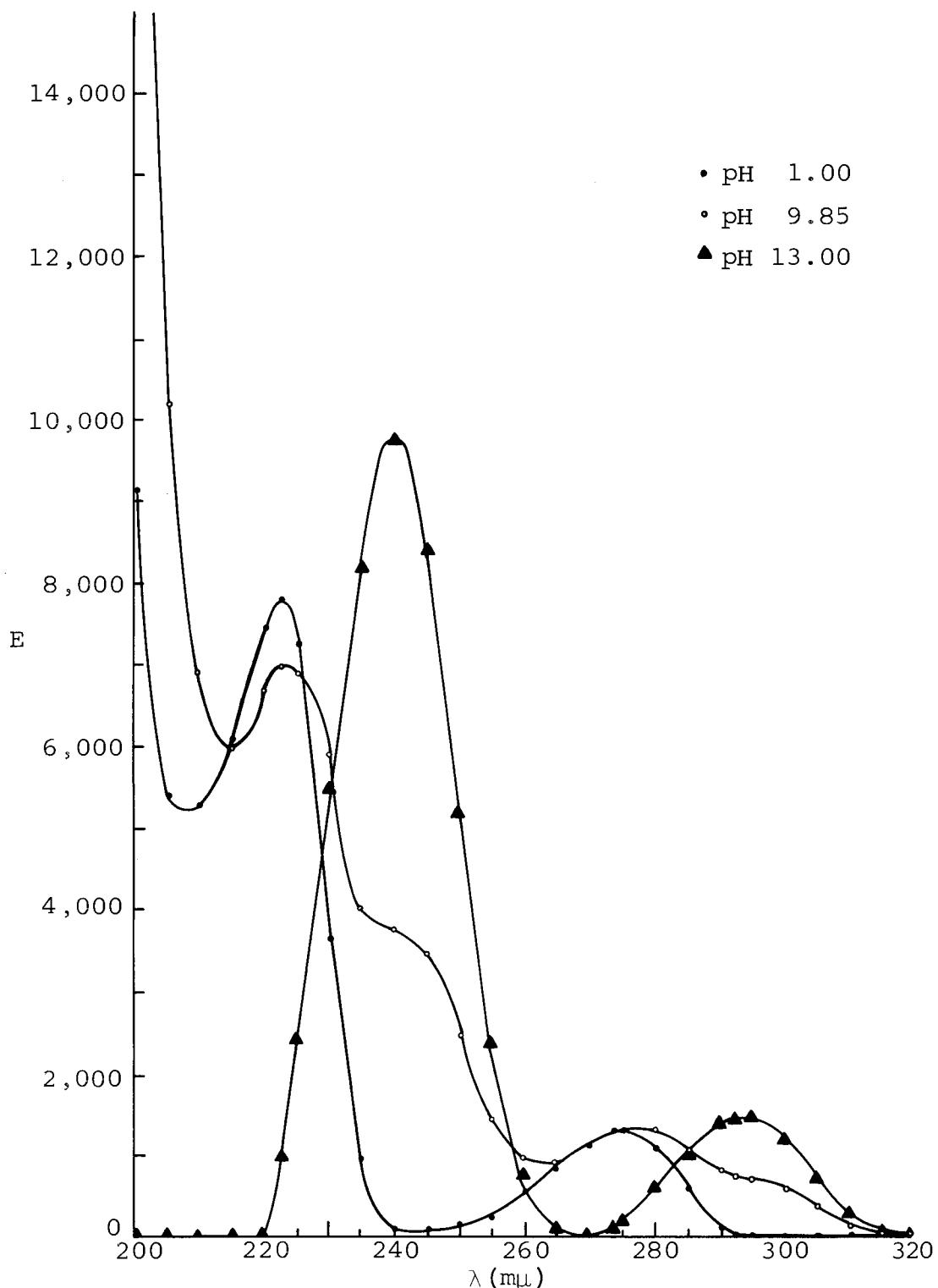


Figure 72. E versus λ of L-Tyrosine by Method II.

Table LXXX. Dissociation Constants of 2-Amino-4,6-Dichloropyrimidine by Method I.

No.	pH	E at 232 m μ	E at 297.5 m μ
0	0.00	10976	5163
1	1.18	12846	4451
2	1.87	13618	4756
3	2.58	13476	4654
4	3.20	13435	4634
5	3.86	13394	4614
6	4.65	13496	4654
7	5.30	13211	4614
8	6.18	13374	4634
9	7.00	13394	4634
10	7.65	13333	4614
11	8.84	13313	4593
12	9.95	13374	4634
13	11.03	13333	4634
14	12.00	13455	4634
15	13.00	13537	4593
16	14.00	15041	4472

$\lambda=232 \text{ m}\mu$, $x=10900$, $E=12200$, $y=13400$, $\text{pH}=0.96$, $\text{pK}_a=0.92$
 $x=13200$, $E=14100$, $y=15000$, $\text{pH}=13.50$, $\text{pK}_a=13.50$

$\lambda=297.5 \text{ m}\mu$, $x=4600$, $E=4800$, $y=5100$, $\text{pH}=0.40$, $\text{pK}_a=0.57$

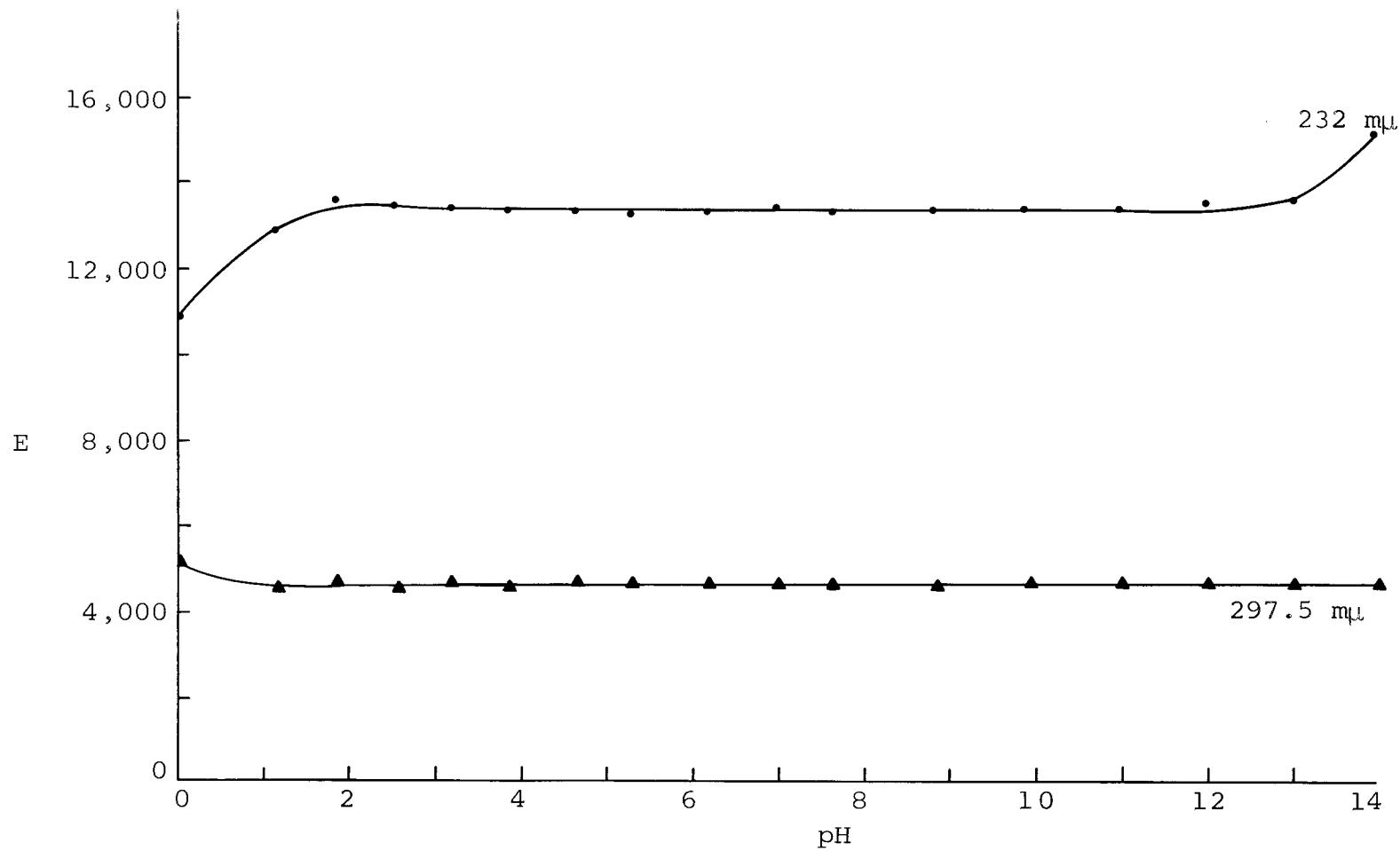


Figure 73. E versus pH of 2-Amino-4,6-Dichloropyrimidine by Method I.

Table LXXXI. Dissociation Constants of 2-Amino-4,6-Dichloropyrimidine by Method II.

λ (m μ)	E at	E at	pH 7.00		pH 13	
	pH 0.00	pH 1.18	E	pK _a	E	pK _a
200	13049	7114	18171	-	7175	-
205	13293	8740	15041	-	7358	-
207	13821	9797	12195	-	7439	0.95
210	15854	8028	7419	-	7520	-
212.5	16402	6504	5081	-	7602	-
215	13894	5752	4289	-	7602	-
220	13516	6504	5549	-	7825	-
225	12703	9756	9350	-	10549	-
230	11789	12602	12886	-	13252	1.08
232	10874	12846	13394	-	13537	-
235	8638	11890	12805	-	12642	-
240	4472	7927	8943	-	8638	-
245	2337	3354	3963	0.96	3760	-
250	1667	1159	1321	-	1341	-
255	1484	772	854	-	854	-
260	1524	813	915	-	955	-
265	1667	1016	1138	-	1179	-
270	1890	1362	1545	-	1626	-
275	2236	1911	2134	-	2154	-
280	2744	2541	2846	-	2846	-
285	3293	3333	3577	-	3598	-
290	4065	3964	4268	-	4268	-
295	4837	4390	4634	-	4593	-
297.5	5142	4431	4634	-	4573	-
300	5386	4411	4553	-	4512	-
305	5732	3923	3963	-	3902	-
310	5630	3069	3049	-	2947	-
315	5000	2012	1850	-	1809	-
320	3963	955	833	-	813	-

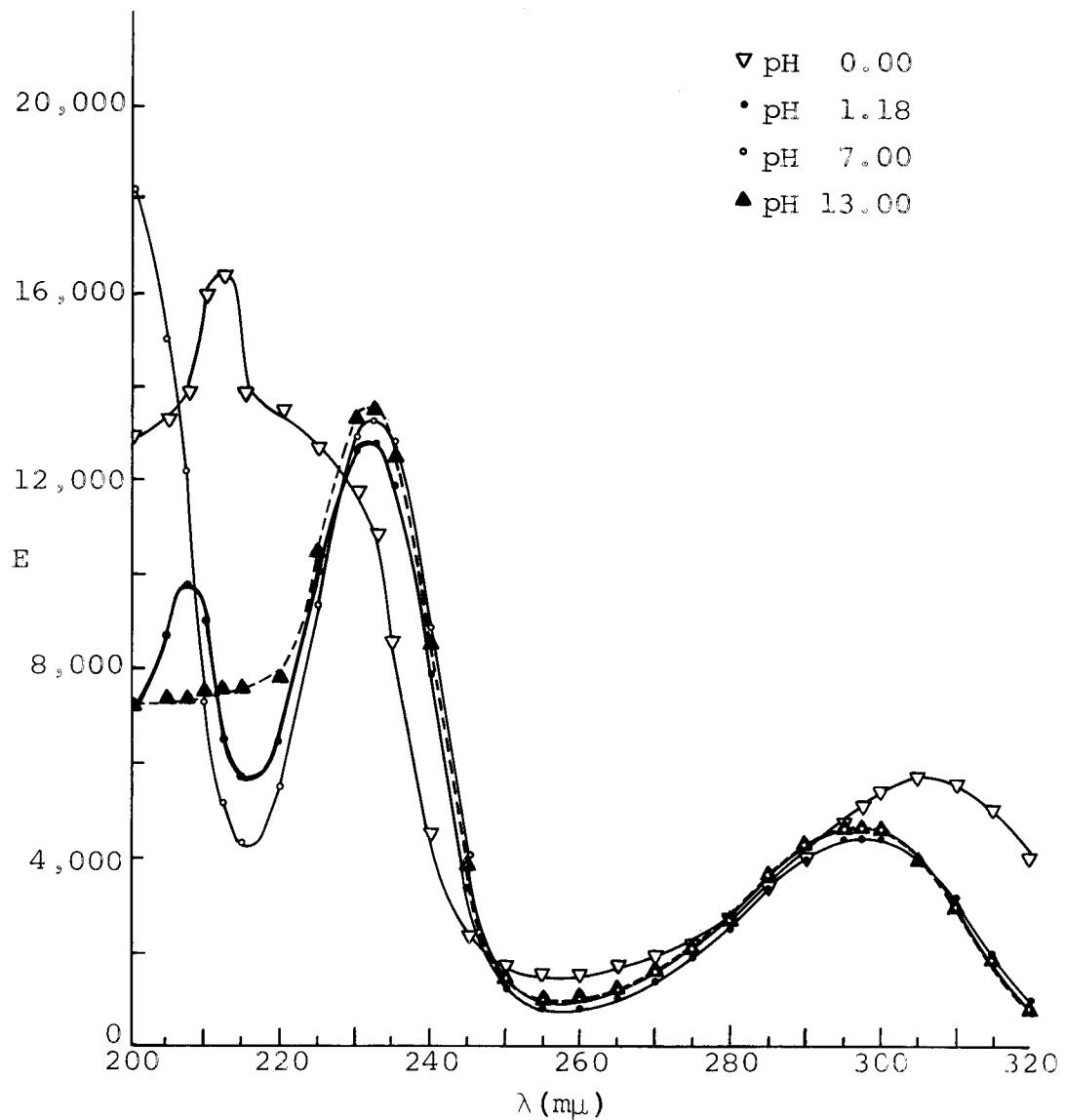


Figure 74. E versus λ of 2-Amino-4,6-Dichloropyrimidine by Method II.

Table LXXXII. Dissociation Constants of 2-Amino-4,6-Dimethylpyrimidine by Method I.

No.	pH	E at 218 m μ	E at 222 m μ	E at 225 m μ	E at 286 m μ	E at 295 m μ
1	0.57	10749	12101	11763	5048	6159
2	0.99	10628	12295	11378	5121	6159
3	2.00	10628	11957	11159	5092	6087
4	2.91	10628	12029	11353	5121	6063
5	3.35	10507	11860	11184	5048	5870
6	3.79	10266	11667	11159	5024	5604
7	4.32	9420	10942	11111	4831	4831
8	5.28	8575	10266	11087	4614	3913
9	6.04	8454	10121	10870	4565	3792
10	7.05	8213	10097	10870	4589	3986
11	8.10	8213	10097	10918	4589	3841
12	9.28	8213	10097	10894	4589	3841
13	9.95	8213	10024	10821	4565	3816
14	10.95	8575	10169	10966	4589	3792
15	12.00	8816	10435	11063	4589	3744
16	13.00	10386	11353	11643	4589	3744
17	14.00	17440	17029	15217	4565	3768

$\lambda=218 \text{ m}\mu$, $x=8200$, $E=9600$, $y=10800$, $\text{pH}=4.25$, $\text{pK}_a=4.18$
 $x=8200$, $E=9500$, $y=10800$, $\text{pH}=12.60$, $\text{pK}_a=12.60$

$\lambda=222 \text{ m}\mu$, $x=10000$, $E=11000$, $y=12200$, $\text{pH}=4.20$, $\text{pK}_a=4.28$
 $x=10000$, $E=13000$, $y=16100$, $\text{pH}=13.55$, $\text{pK}_a=13.57$

$\lambda=225 \text{ m}\mu$, $x=10900$, $E=11100$, $y=11200$, $\text{pH}=4.60$, $\text{pK}_a=4.30$
 $x=10900$, $E=13000$, $y=15200$, $\text{pH}=13.50$, $\text{pK}_a=13.52$

$\lambda=286 \text{ m}\mu$, $x=4600$, $E=4800$, $y=5100$, $\text{pH}=4.30$, $\text{pK}_a=4.48$

$\lambda=295 \text{ m}\mu$, $x=3800$, $E=5000$, $y=6200$, $\text{pH}=4.20$, $\text{pK}_a=4.20$

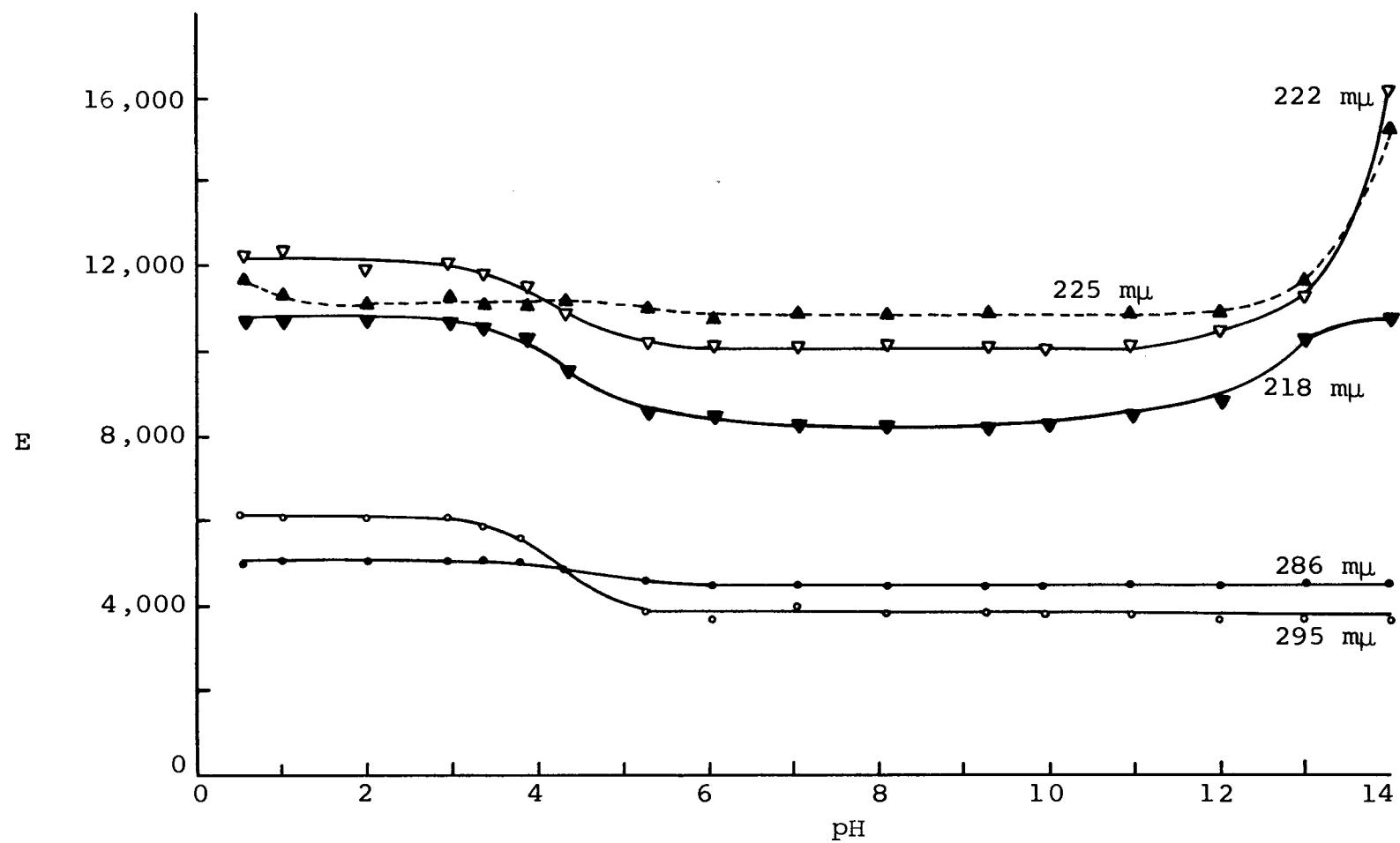


Figure 75. E versus pH of 2-Amino-4,6-Dimethylpyrimidine by Method I.

Table LXXXIII. Dissociation Constants of 2-Amino-4,6-Dimethylpyrimidine by Method II.

λ (m μ)	E at	E at	pH 7.03		pH 1.3	
	pH 1.00	pH 4.00	E	pK _a	E	pK _a
200	10060	8333	6099	-	7971	-
205	6763	5254	3973	3.93	8442	-
210	6184	5254	4481	3.92	8998	-
215	8877	7597	6522	3.92	9543	-
220	11703	10386	9287	3.92	11123	-
222	12017	10930	10085	3.89	11473	-
225	11353	10990	10749	3.82	11510	-
230	7488	8756	9843	3.93	9843	3.93
235	2959	4952	6643	3.93	6401	3.86
240	833	2041	3007	3.90	2838	3.82
245	531	930	1220	3.86	1196	3.83
250	543	797	978	3.85	990	3.88
255	664	990	1208	3.83	1220	3.85
260	894	1341	1643	3.83	1667	3.86
265	1280	1812	2198	3.86	2210	3.88
270	1896	2476	2874	3.84	2899	3.86
275	2754	3261	3575	3.79	3611	3.84
280	3744	4046	4227	3.78	4227	3.78
285	4831	4698	4577	3.96	4541	-
286	4976	4771	4589	3.95	4541	-
290	5676	4988	4420	3.91	4384	3.94
295	6135	4771	3756	3.87	3684	3.90
300	5918	4094	2717	3.88	2657	3.90
305	5012	3068	1594	3.88	1546	3.89
310	3502	1884	700	3.86	652	3.88
315	1872	906	217	3.85	205	3.86
320	688	314	48	3.85	48	3.85

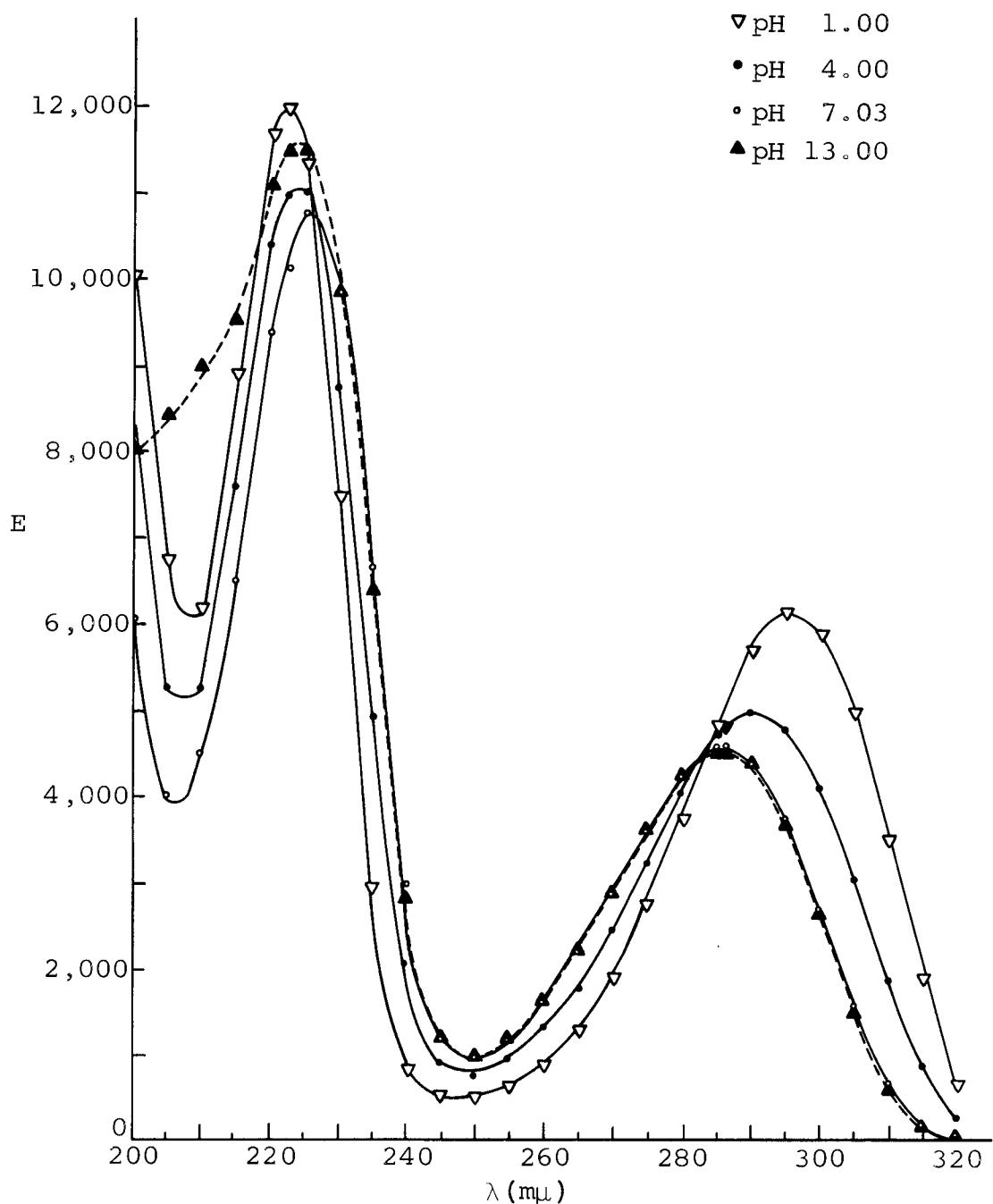


Figure 76. E versus λ of 2-Amino-4,6-Dimethylpyrimidine by Method II.

Table LXXXIV. Dissociation Constants of 2-Amino-4-Methylpyrimidine by Method I.

No.	pH	E at 224 m μ	E at 288 m μ	E at 299 m μ
1	0.50	13283	3947	4724
2	0.86	13333	3972	4699
3	1.66	13396	3997	4662
4	2.37	13183	3922	4599
5	2.75	13145	3910	4474
6	3.37	12895	3922	3985
7	4.34	11717	3734	3133
8	4.75	12143	3860	3108
9	5.40	12130	3885	3070
10	6.27	12105	3860	3020
11	6.99	12180	3872	2995
12	8.13	12068	3860	3008
13	9.14	12030	3860	3020
14	10.15	12118	3872	3008
15	10.90	12694	3860	3008
16	12.00	12644	3847	2970
17	13.00	13095	3872	3008
18	14.00	17920	3847	3008

$\lambda=224 \text{ m}\mu$, $x=12800$, $E=12000$, $y=13400$, $\text{pH}=3.60$, $\text{pK}_a=3.47$
 $x=13000$, $E=15300$, $y=17900$, $\text{pH}=13.80$, $\text{pK}_a=13.85$

$\lambda=288 \text{ m}\mu$, pK_a undeterminable

$\lambda=299 \text{ m}\mu$, $x=3000$, $E=3900$, $y=4700$, $\text{pH}=3.50$, $\text{pK}_a=3.45$

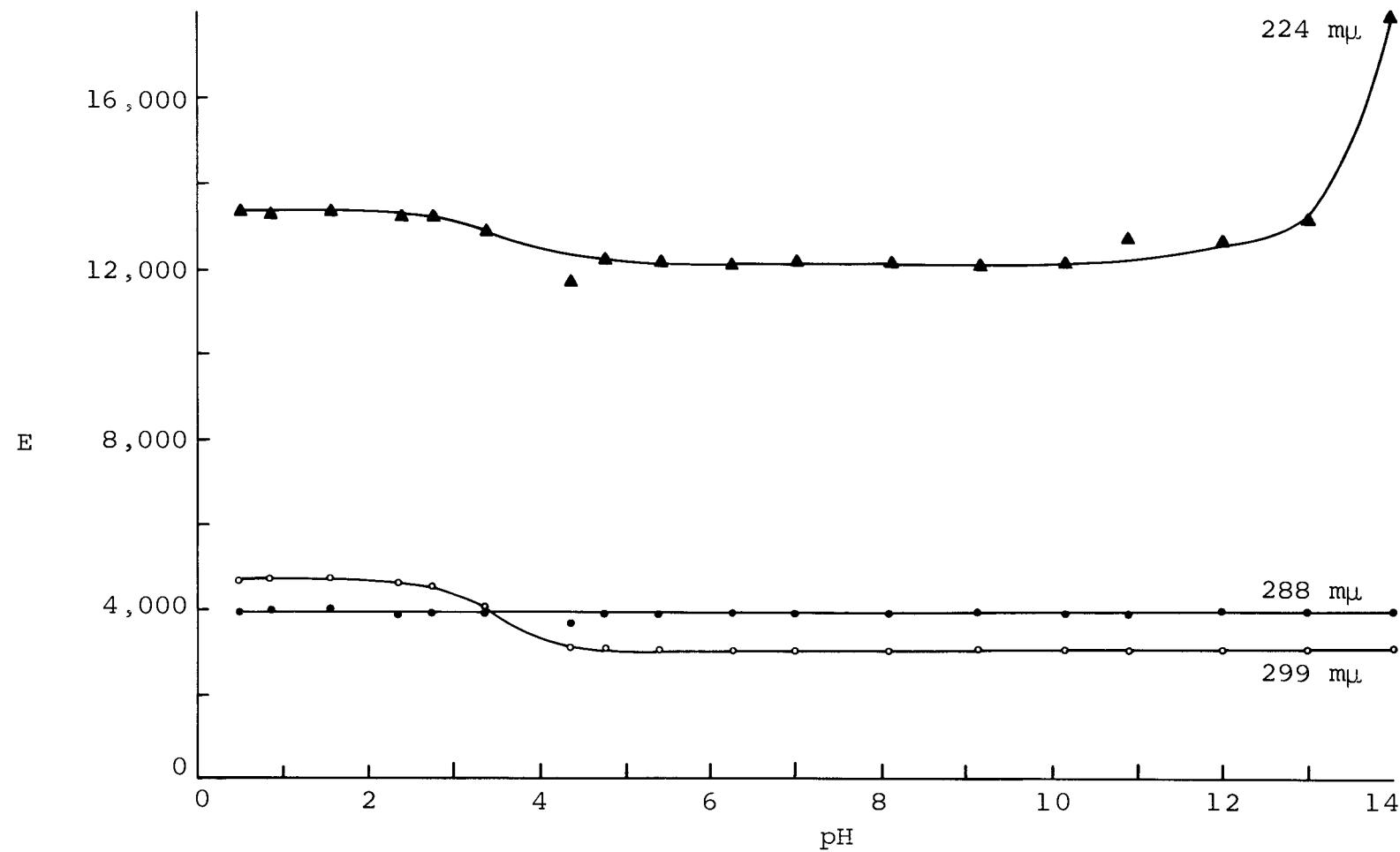


Figure 77. E versus pH of 2-Amino-4-Methylpyrimidine by Method I.

Table LXXXV. Dissociation Constants of 2-Amino-4-Methylpyrimidine by Method II.

λ (m μ)	E at	E at	pH 7.00		pH 13	
	pH 1.12	pH 3.37	E	pK _a	E	pK _a
200	17447	7519	4894	-	9085	-
205	8723	5865	4149	-	11596	-
210	7362	6454	5532	3.38	15319	-
215	10426	9524	8298	3.50	14511	-
220	13234	12406	11170	3.54	11234	3.52
224	12872	12531	12234	3.31	11702	3.76
225	12447	12155	12340	-	11766	3.49
230	6851	8459	10191	3.40	10106	3.38
235	1915	3321	6064	3.66	6064	3.66
240	340	1128	2234	3.52	2234	3.52
245	234	589	851	3.24	638	-
250	319	627	745	-	702	-
255	426	789	1064	3.27	936	-
260	638	1053	1383	3.27	1341	3.21
265	936	1404	1851	3.35	1809	3.31
270	1362	1867	2340	3.34	2340	3.34
275	1915	2406	2979	3.41	2894	3.37
280	2596	3070	3511	3.34	3447	3.27
285	3340	3634	3872	3.28	3809	-
288	3702	3922	3936	-	3915	-
290	3936	4010	3936	-	3894	-
295	4404	4160	3617	-	3532	-
299	4489	3985	3085	3.62	3085	3.62
300	4511	3922	2957	3.58	2872	3.62
305	4128	3358	2106	3.58	2064	3.60
310	3383	2506	1234	3.53	1213	3.54
315	2489	1654	553	3.49	532	3.50
320	1298	890	170	3.62	149	3.63

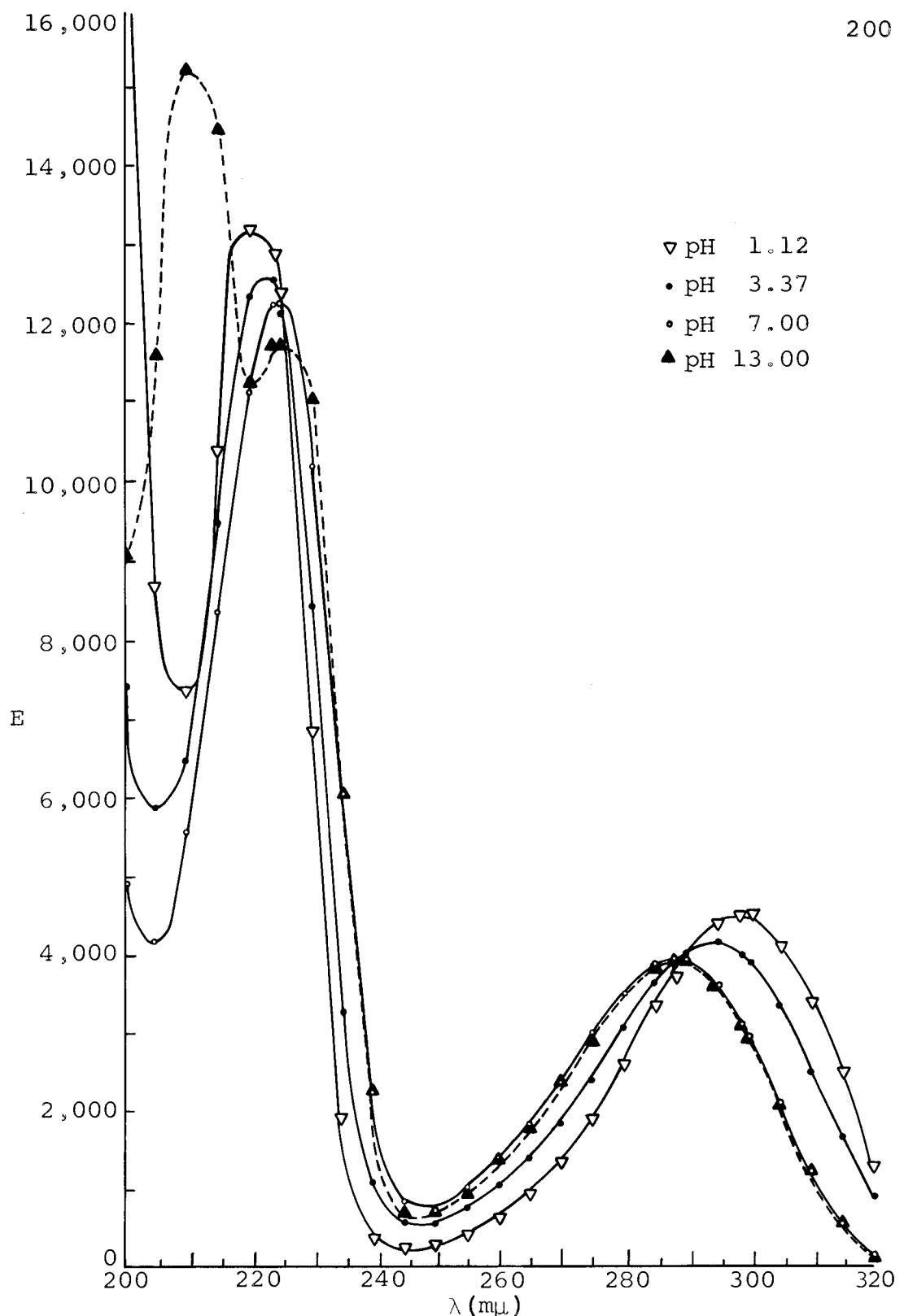


Figure 78. E versus λ of 2-Amino-4-Methylpyrimidine by Method II.

Table LXXXVI. Dissociation Constants of 4,5,6-Triaminopyrimidine by Method I.

No.	pH	E at 210 m μ	E at 215 m μ	E at 277 m μ
1	0.10	12207	14463	2314
2	0.61	11426	13335	2893
3	0.92	10414	11976	3587
4	1.32	9546	10790	4194
5	1.52	9199	10500	4339
6	1.80	9199	10327	4542
7	2.21	9083	10211	4599
8	2.62	9228	10240	4628
9	3.00	9112	10182	4628
10	3.54	9112	10153	4599
11	4.05	9119	10240	4570
12	4.55	9922	10616	4628
13	5.02	10443	10790	4570
14	5.56	12265	11831	4542
15	6.05	13827	12583	4397
16	6.54	15331	13538	4455
17	7.01	15736	13596	4455
18	7.40	16025	13740	4426
19	7.97	15997	13885	4455
20	8.57	15620	13596	4426
21	8.99	15620	13827	4426
22	9.57	16025	13856	4426
23	9.99	16054	13596	4455
24	10.58	15823	13827	4455
25	10.92	15968	13596	4455
26	11.50	15794	13596	4397
27	12.00	15910	13306	4397
28	12.50	15476	13306	4368
29	13.00	11947	11686	4397
30	13.50	8562	8707	4397
31	14.00	5438	5612	4397

Table LXXXVI. (Continued)

$\lambda=210 \text{ m}\mu$, $x= 9100$, $E=10600$, $y=12200$, $pH= 0.85$, $pK_a= 0.88$
 $x= 9100$, $E=12500$, $y=16000$, $pH= 5.65$, $pK_a= 5.66$
 $x= 5400$, $E=10500$, $y=15800$, $pH=13.25$, $pK_a=13.27$

$\lambda=215 \text{ m}\mu$, $x=10100$, $E=12300$, $y=14600$, $pH= 0.85$, $pK_a= 0.87$
 $x=10100$, $E=12000$, $y=13750$, $pH= 5.70$, $pK_a= 5.66$
 $x= 5600$, $E= 9700$, $y=13750$, $pH=13.40$, $pK_a=13.39$

$\lambda=277 \text{ m}\mu$, $x= 2200$, $E= 3400$, $y= 4650$, $pH= 0.85$, $pK_a= 0.87$

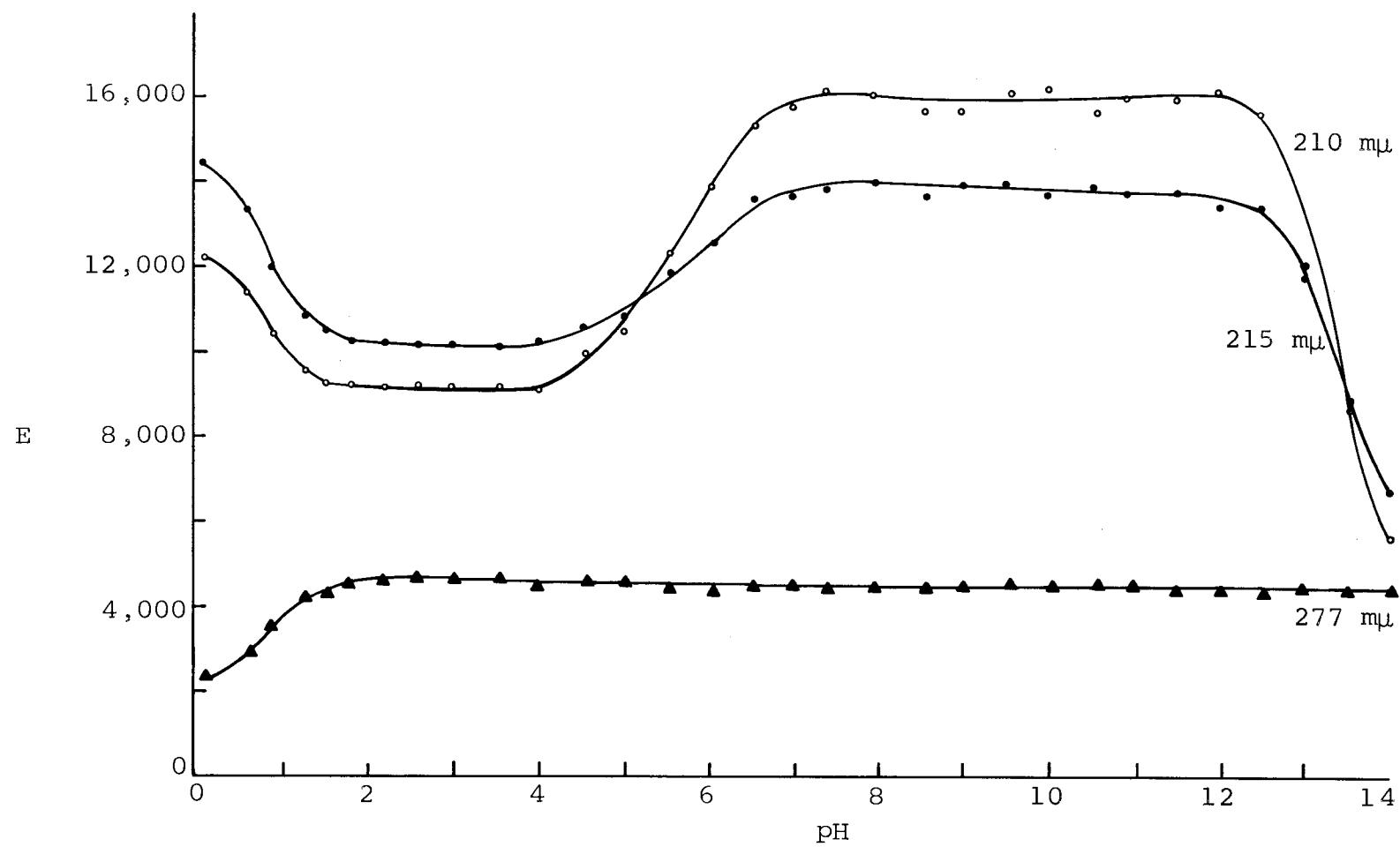


Figure 79. E versus pH of 4,5,6-Triaminopyrimidine by Method I.

Table LXXXVII. Dissociation Constants of 4,5,6-Triaminopyrimidine by Method II.

λ (m μ)	E at pH 1.02	E at pH 5.80	pH 7.01		pH 13	
			E	pK _a	E	pK _a
200	9835	9546	10153	-	10963	-
205	9314	11860	13885	5.70	11137	-
210	10182	13248	15649	5.69	11426	-
215	11542	12439	13653	5.93	11281	-
220	9835	8389	8100	-	6943	5.80
225	4339	3760	3789	-	3182	5.80
230	1331	1591	1996	5.99	1793	5.69
235	781	1099	1504	5.90	1475	5.87
240	839	1157	1562	5.90	1591	5.93
245	1041	1273	1736	-	1793	-
250	1475	1591	2025	-	2112	-
255	2112	1938	2430	-	2459	-
260	2893	2546	2893	-	3008	-
265	3616	3211	3471	-	3529	-
270	3905	3905	4050	-	4108	-
275	3905	4455	4397	-	4426	-
277	3905	4484	4397	-	4397	-
280	3905	4484	4310	-	4310	-
285	3876	4194	3732	-	3616	-
290	3789	3558	2661	-	2546	-
295	3442	2748	1620	-	1446	-
300	2922	1996	839	5.90	694	5.95
305	2343	1446	405	5.86	289	5.91
310	1736	1012	174	5.86	87	5.91
315	1157	579	58	5.75	0	5.80
320	579	289	29	5.75	0	5.80

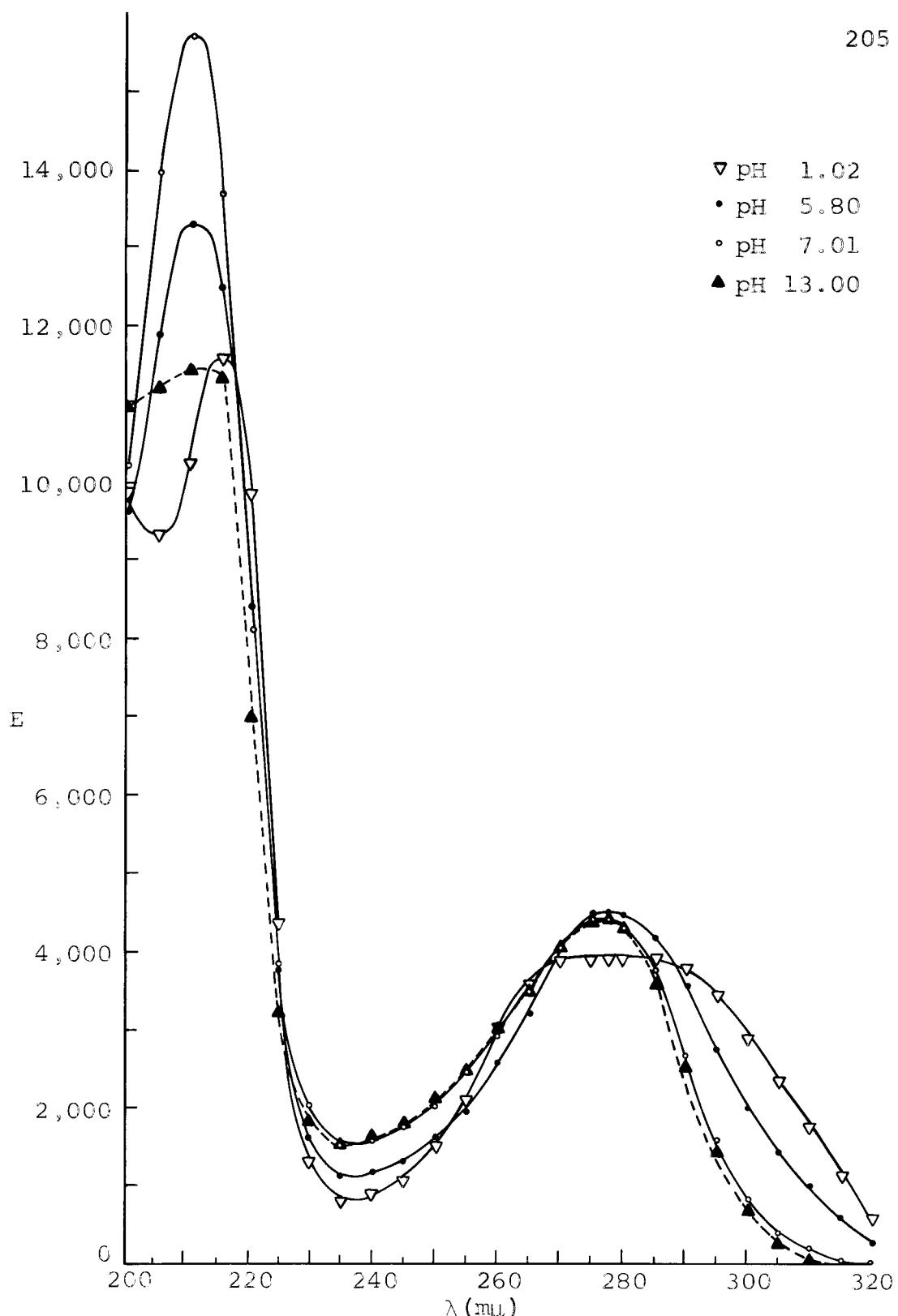


Figure 80. E versus λ of 4,5,6-Triaminopyrimidine by Method II.

SUMMARY

Ultraviolet spectroscopic methods lend themselves only for the determination of those dissociation constants which are the consequence of changes within a chromophoric group.

In the case of compounds having a single active site conjugated with or inherent in the chromophoric group (see Table IV) the dissociation constants as determined by Methods I and II are in fair agreement with those determined by other methods. However, Method II may yield dissociation constants which are suspect with compounds belonging to this group.

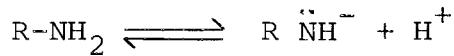
An accurate determination of dissociation constant by Method II can only be made when the extinction coefficients of the protonated and deprotonated forms of the compound involved in the given dissociation are known. In the case of compounds having more than a single dissociation constant, this would involve the accurate determination of the extinction coefficients of intermediate ions (single protonated, double protonated, etc.) in the absence of other absorbing forms. For this reason, Method II can only be reasonably reliable in the measurement of those compounds having not more than one constant, provided the extinction coefficient of intermediate ion can be determined and the difference in the

magnitude of the two constants is such as to make this possible. This limits the usefulness of the procedure almost entirely to compound having single reactive site in the chromophore.

The compounds involved in these studies fell into two groups, (a) those in which the $\lambda_{\text{max.}}$ remained constant while extinction coefficients changed with pH, and (b) those in which both extinction coefficients and $\lambda_{\text{max.}}$ changed with pH. In general, those compounds in group (a) were in much better agreement with known literature data of dissociation constants than those of group (b).

The most accurate determination using Method I depends on the choice of λ to be used in making the extinction coefficient -pH profile. This choice can best be made after taking this profile in ten $\text{m}\mu$ intervals over the entire ultraviolet spectrum, as illustrated in the case of p-aminobenzoic acid.

In a number of instances dissociation constants were found for reactions which are best explained on the hypothesis that a proton has been abstracted from an amino substituent.



The frequency of these observations indicates that some change in structure of the chromophoric group must be taking place in the alkaline solution.

The failure to get good agreement of dissociation constants for compounds having three or more active sites associated with chromophoric group, as measured by Method I and other methods, indicates the limitations of these methods.

In general, the dissociation constants as determined by Method I at different regions of the usable spectra are in fair agreement. However, deviations up to almost one order of magnitude have been observed in certain instances.

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APPENDIX

ABBREVIATIONS

b = broad peak

C = conductivity method

P = potentiometric method

S = spectroscopic method

sh = shoulder of the peak

sm = small peak

T = titration method

$pK_a - pH\ 7$ = pK_a calculated from E at pH 1, pH 7,
and intermediate pH

$pK_a - pH\ 13$ = pK_a calculated from E at pH 1, pH 13,
and the same intermediate pH

pK_a refers to dissociation constant of the
protonated form of the organic base