

A SPECTROPHOTOMETRIC STUDY OF
ACID-BASE INDICATORS IN
LIQUID AMMONIA

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ABSTRACT

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by R. Dean Hill

The behavior of a weak acid in liquid ammonia can be described by an ionization step followed by a dissociation step:



The equilibrium constant for equation 1 was studied spectrophotometrically using indicators of the acid-base type. The dissociation reaction occurs to a negligible extent except in very dilute solutions. A method for the calculation of ionization constants from spectrophotometric data was devised for both indicators and other acidic or basic compounds which affect indicators. A low temperature cell was devised for spectrophotometric study of the ionization of such substances in the ultraviolet and visible region.

Five indicators were examined in detail. Absorption bands present in the visible and ultraviolet spectra were related to the molecular structure of each indicator. The extinction coefficient for each species was calculated. Four of the indicators studied were strong acids while the other was suitable for studying basic solutions. The indicators p-nitroacetanilide, 2,4-dinitroaniline, phenolphthalein, and thymol blue were found to have first ionization constants greater

than one in liquid ammonia. The effect of neutral salts upon these indicators was studied. The effect of temperature upon the phenolphthalein ionization was investigated in detail and ionization constants calculated for solutions of this indicator in the liquid range of ammonia.

A relationship between ammonium ion concentration and the absorbancy of phenolphthalein was found. This relationship enabled calculation of ionization constants of some weak acids. Thiourea, methylthiourea, and trimethylthiourea were found to be acidic in ammonia even though they are basic in water. Ionization constants for these substances are reported. Urea and methyl-substituted ureas have no effect on indicators which change color in acidic liquid ammonia, but they show a weakly basic reaction to thymol blue in its third ionization step. Urea does not affect tropeoline OO (which changes color in basic solution) and therefore urea probably is nearly neutral in ammonia.

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By

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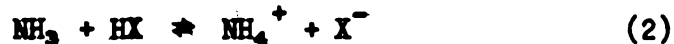
INTRODUCTION

Ammonia in the liquid state as an ionizing solvent and parent system of compounds has been extensively studied by many investigators (1, 2, 3, 4, 5, 6), usually in reference to its similarities to water. It is of interest to note that ammonia dissolves many ionic compounds (7, 8, 9, 10, 11) and as such has been utilized as a reaction medium for many substances which are obtainable by few other means. Ammonia as a parent solvent undergoes the autoionization:



The equilibrium constant for this reaction is reported to be 10^{-33} at -50°C (12). In the solvent system concept, ammonium compounds act as acids in ammonia and amides as bases (13).

Not only do ammonium compounds act as acids but any potential proton donor can undergo ammonolysis to produce ammonium ions:



Thus many substances which are weak acids, neutral compounds, or even basic substances in aqueous solution become acids in ammonia (14).

It has been shown that in solvents of medium dielectric constant, the coulombic force between ions is great enough to overcome the influence of the solvent and form ion pairs. Even higher aggregates form in liquid ammonia solutions more concentrated than about 10^{-3} molar (15).

This is a function of charge density of the ions as pointed out by Bjerrum (16)

$$\frac{1}{K_d} = \frac{4\pi N \frac{z_1 z_2 e^2}{1000 \text{ \AA} \cdot 2DkT}}{\quad}, \quad (3)$$

where K_d is the equilibrium constant of an ion pair dissociating into its ions, N is the Avagadro number, z_1 and z_2 are the charges on the respective ions, e is the electronic charge, D is the dielectric constant of the medium, k is the Boltzmann constant, T is the absolute temperature, and $\text{\AA}$ is the distance of closest approach of the ions. Bjerrum made the quite arbitrary definition that an ion pair is any two oppositely charged ions at a distance such that the electrostatic energy does not exceed $2kT$ (17). For water this distance is $3.57 \text{ \AA}$ at 25°C and for ammonia it is $9.24 \text{ \AA}$ at -77°C for a 1:1 electrolyte. Thus a substance which exists as an ionic species in the solid state is not completely dissociated in liquid ammonia. The number of unassociated ions in solution is then a function of cation-anion size and charge. Kraus, Hawes, and others have measured the conductances of many common electrolytes in ammonia and calculated dissociation constants of the order of magnitude of 10^{-4} (18, 19, 20, 21). This small value for K_d indicates that there is never a high concentration of solvated ions in ammonia except in very dilute solutions and that the solution chemistry of this solvent must take into consideration ion pairing.

In the consideration of any ionic equilibrium, the effect of ionic atmosphere must be taken into account. Debye and Hückel (22, 23) considered this in terms of Coulomb's law and the Boltzmann distribution law and observed that the true thermodynamic equilibrium constant of

a reaction must be stated in terms of activities and is related to concentrations by the activity coefficients. The expression in dilute solution for a given ionic activity coefficient is given by

$$-\log \gamma_1 = \frac{AZ_1^2 \sqrt{\mu}}{1 + B\dot{a} \sqrt{\mu}} \quad (4)$$

where Z_1 is the charge on the ion, γ_1 is the activity coefficient of that ion, A is a constant given by $1.82 \times 10^{-6} / (DT)^{3/2}$ and is equal to 0.509 at 25°C for water and 5.26 for ammonia at -77°C, B is $4.8 \times 10^9 / (DT)^{1/2}$, $\dot{a}$ is the distance of closest approach of ions, and μ is the ionic strength which is defined by

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \quad (5)$$

where C_i is the concentration of the ions. Equation 4 is valid for solutions up to 10^{-1} molar in high dielectric constant solvents and up to 10^{-3} molar in solvents of lower dielectric constant (24).

Since there is no experimental way to separate the positive and negative ion activity coefficients, equation 4 is used to express the mean activity coefficient, $\gamma_{\pm}$, which is defined by (25):

$$\log \gamma_{\pm} = \frac{m \log \gamma_+ + n \log \gamma_-}{m + n} \quad (6)$$

where $\gamma_{\pm}$ is the mean activity coefficient of a pair of oppositely charged ions of charge m and n . The effect of the ionic atmosphere on the nature of the solution for ion pairs is less well defined owing to the interaction of the coulombic forces between the ions involved. For a given ionic strength, the deviation from equation 4 in ammonia is greater than that in water. For ammonia however, the ion

association which occurs tends to offset this such that equation 4 remains valid as a first approximation in dilute solutions (26).

In ammonia as in other solvents, there is the possibility of a molecular species such as a weak acid undergoing an ionization step such that an ionization equilibrium is set up:



The ion pair formed can then participate in a dissociation equilibrium which is independent of the ionization step and can be described by:



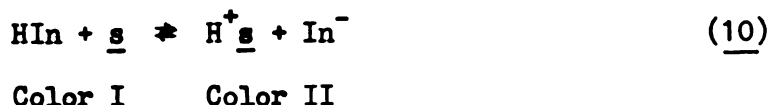
The overall equilibrium constant, $\underline{K}^*$, for the total reaction has been defined by Bruckenstein (27, 28) and Lagowski (29) as:

$$\underline{K}^* = \frac{\underline{K}_1}{1 + \underline{K}_1} \underline{K}_d \quad (9)$$

where $\underline{K}_1$ is the constant for the ionization equilibrium in equation 7 and $\underline{K}_d$ is the constant for the dissociation equilibrium in equation 8.

Owing to the greater basicity of ammonia compared to water, many weak acids in water are enhanced in acidity in ammonia; i.e. they undergo complete ionization though not complete dissociation. Nearly all acid-base indicators which are used in aqueous solution are themselves weak acids, usually one color in the molecular form and another color in the ionic form. Many of the familiar indicators dissolve in ammonia to form colored species, some of which are different from their aqueous counterparts (30). Neglecting ion pairs,

the equilibrium may be expressed in general as



where $\underline{s}$ is the solvent in question. The equilibrium constant for this reaction is:

$$K_{\text{HIn}} = \frac{a_{\text{H}^+ s} a_{\text{In}^-}}{a_{\text{HIn}} a_s} = \frac{[\text{H}^+ s][\text{In}^-]}{[\text{HIn}][s]} \cdot \frac{\gamma_{\text{H}^+ s} \gamma_{\text{In}^-}}{\gamma_{\text{HIn}} \gamma_s} \quad (11)$$

The absorption of the solution, i.e. the ratio of color I to color II is: determined primarily by the ratio of concentrations of [HIn] to [In⁻]. For water this becomes simply:

$$\text{pH} = \text{p}K'_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad (12)$$

where $\text{p}K'_{\text{HIn}}$ is defined by $\text{p}K_{\text{HIn}} + \log \frac{\gamma_{\text{In}^-}}{\gamma_{\text{HIn}}}$. In nonaqueous solvents where pH does not have the significance that it possesses in aqueous solution, the situation is more complex. Considering ion pairs in light of equations 10 and 11, the ratio of acid to anion indicator form is (31).

$$\sum \frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{HIn}] + [\text{H}^+ s \text{In}^-]}{[\text{In}^-]} \quad (13)$$

but no simple relationship exists between this ratio and hydrogen ion concentration. By appropriate choice of indicators and acid strength, Kolthoff and his students studied acid-base equilibria in acetic acid (32), acetonitrile (33), and dimethylsulfoxide (34).

Various indicators have been used in ammonia to follow neutralization

reactions (35) or to compare acid strengths (36) of some weak acids. The types of indicators which show reversible equilibria are the phthaleins represented by phenolphthalein (6), triphenylmethane as the sodium salt (37), azo and hydro compounds (38, 39), nitrophenols, and nitroanilines (40,41). It is of interest to note that sodium and potassium salts (42) of the various nitroanilines have been isolated. This gives some credence to the existence of a nitroaniline anion. Electrolysis of an ammonia solution of m-dinitrobenzene (43) has yielded hydrogen at the cathode. This evidence points to acid-base behavior for this type of indicator. Schattenstein (40) reported the colors (Table I) of several of these compounds in ammonia. Qualitatively observed colors of some other indicators of various types are listed in Table II (29).

Spectrophotometric studies of indicators in aqueous solution have become laboratory routine, but the difficulties involved in handling liquefied gases have been the subject of investigation for some time. Generally, the solution was placed in metal containers or sealed tubes and studied at room temperature (44). In low temperature studies, moisture condensation on cell windows has been prevented by several means. Cells have been protected by double windows with vacuum insulation or by a stream of dry gas (45, 46). A unique light-pipe cell using this property of polymethylmethacrylate has been utilized in the visible region by Lagowski (29). Modified polarimeter tubes have been used along with additional studies which mention no experimental details (47, 48, 49).

In aqueous solution, acid-base indicators are obviously affected by salts which undergo hydrolysis, and the effect of neutral salts

TABLE I

COLORS OF SOME SUBSTITUTED PHENOLS AND ANILINES IN AMMONIA (40)

Indicator	Neutral	Acid	Base
<u>m</u> -nitrophenol	orange	orange	cherry-red
<u>p</u> -nitrophenol	yellow	yellow	red
<u>o</u> -nitrophenol	yellow	yellow	yellow
2,5-dinitrophenol	red	red	precipitate
2,4-dinitrophenol	yellow	yellow	precipitate
2,4,6,-trinitrophenol	yellow	yellow	precipitate
<u>m</u> -nitroaniline	yellow	yellow	green
<u>p</u> -nitroaniline	yellow	yellow	orange
<u>o</u> -nitroaniline	yellow	yellow	red
2,4-dinitroaniline	red	red	---
2,4,6-trinitroaniline	orange	orange	precipitate
<u>p</u> -benzeneazoaniline	yellow	yellow	red
<u>p</u> -benzeneazodimethylaniline	yellow	yellow	violet
<u>p</u> -tolueneazodimethylaniline	yellow	yellow	violet

TABLE II

COLORS OF VARIOUS INDICATORS IN AMMONIA (30)

Indicator	Neutral	Acid	Base
methyl violet	colorless	orange-brown	green
thymol blue	blue	blue-green	blue-green
tropeoline OO	yellow	yellow	violet
methyl orange	yellow	yellow	red-brown
bromophenol blue	purple	purple	red-brown
alizarin red S	purple	purple	colorless
bromocresol purple	purple	purple	yellow
methyl red	yellow	yellow	red
bromothymol blue	blue	blue	yellow-green
neutral red	yellow	yellow	blue
turmeric	orange	red	yellow
phenolphthalein	pink	violet	colorless
alkali blue	red-orange	red-orange	yellow-green
alizarin yellow R	orange	yellow-orange	purple
methyl blue	red	red	blue-green
clayton yellow	red-orange	red-orange	blue-green
basic fuchsin	yellow	orange	blue
triphenylmethane	colorless	colorless	red
2,4-dinitrophenylhydrazine	green-yellow	green-yellow	purple
p-nitrophenylhydrazine	orange-yellow	orange-red	red
p-nitroacetanilide	colorless	yellow-green	yellow
o-nitroacetanilide	yellow	yellow	orange

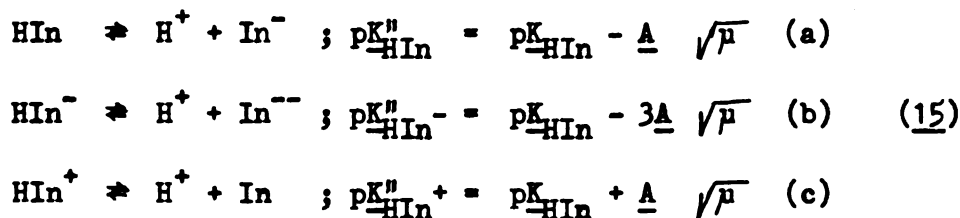
on these indicators has been the subject of investigation by several people (50, 51, 52, 53).

Since the equilibrium constant for an indicator acid (equation 11) involves activities, it can be seen that the concentrations of the colored forms will change as the activity coefficient ratio changes. Activity coefficients are directly related to the ionic atmosphere in the solvent--that is, to the ionic strength--as seen from equation 4. Hence, if the ionic strength of the solution changes, the color of the indicator also should change. This has been observed in water with several types of indicators in sodium chloride solutions (50).

Rearranging equation 12 and defining pK_{HIn}'' as $\log \frac{a_{\text{H}^+}}{a_{\text{HIn}}} - \log \frac{[\text{In}^-]}{[\text{HIn}]}$ gives:

$$pK_{\text{HIn}}'' = pK_{\text{HIn}} + \log \frac{\gamma_{\text{In}^-}}{\gamma_{\text{HIn}}} \quad (14)$$

Not only is this equation valid for uncharged acids, but it also applies to acids of the types HIn^- and HIn^+ . Then for the three cases, equation 14 can be combined with the Debye-Hückel limiting law (22) to give:



These equations are of the nature of first approximations in that the ions are considered point charges in a medium of uniform dielectric constant (51). They do, however, point out the effect that ionic strength has upon various types of indicators in water. Table III

TABLE III

SALT EFFECT CORRECTIONS FOR INDICATOR pK_a VALUES FOR
 AQUEOUS SOLUTIONS OF VARIOUS IONIC STRENGTHS* (50)

Indicator	Ionic Strength			
	<u>0.01</u>	<u>0.05</u>	<u>0.10</u>	<u>0.50</u>
methyl orange	0.02	0.04	0.04	0.04
methyl red	0.00	0.00	0.00	0.00
thymol blue [K_1]	0.00	0.00	0.00	0.00
thymol blue [K_2]	-0.04	-0.11	-0.16	-0.35
chlorphenol red	-0.02	-0.10	-0.15	-0.34
phenolphthalein	-0.02	-0.09	-0.14	-0.30
p-nitrophenol	-0.02	-0.03	-0.06	-0.22
triphenylcarbinol	---	0.08	0.17	---

*Tabulated corrections are $pK'' - pK_{HIn}$ values and are to be added to the observed pK_a . A negative correction indicates that the salt solution appears, from the indicator color, to be more basic than is actually the case.

shows a correlation between equations 15 and experimental data reported by Kolthoff (50). The nitrophenols are of the type found in equation 15a and show a negative salt effect. The sulfonephthaleins show the largest effect in accordance with 15b and triphenylcarbinol shows a positive effect as 15c predicts. The behavior of the indicators which show little or no effect have been explained by Klotz (52) in terms of the Debye-Hückel effective radius of ionic atmosphere. These indicators in their charged forms are zwitterions; hence if the ionic atmosphere is large enough to shield the charges from each other, the attraction between them can be neglected and the salt effect should be very small.

The effect of a change in temperature upon ionization constants of both indicator acids and nonindicator acids has been studied extensively in aqueous solution and reviewed by Everett and Wynne-Jones (54). The ionization constants of acids which are neutral molecules (e.g. acetic acid) or negatively charged (e.g. bicarbonate ion) rise with temperature up to a certain maximum, then fall as the temperature is increased further.

The main factor causing the fall in ionization with rising temperature is the effect of rising temperature on the dielectric constant of the medium, which is generally to decrease it. This is important in ionic dissociations where electric charges are separated, for the greater the dielectric constant, the easier it is to separate charges. In an acid-base reaction in which there is no separation of charge--e.g., in the ionization of positively charged acids--the dielectric constant is of minor importance and the equilibrium constants for such ionizations generally increase steadily with rising temperature (55, 56).

Of the various types of indicators, only a very few observations have been made concerning temperature effects in liquid ammonia, whereas the majority of such observations have been limited to aqueous solutions. Franklin (57) noted that neutral ammonia solutions of phenolphthalein are colorless at room temperature while Lagowski (29) observed the same indicator to be violet-colored with an absorption peak at 575 m μ at -77°C .

From the scanty information concerning temperature effects on various types of indicators in water, the following facts stand out.

The azo indicators show a considerable increase in ionization as the temperature rises. Such an indicator is of the positively charged acid type in which there is no separation of charge as the proton is released:



While it is true that the R group often contains a negatively charged group at the end opposite the amino group, this charge is quite far removed from the nitrogen atom and has little influence in restraining the removal of the proton (58).

In p-nitrophenol, where ionization of the phenolic group causes a separation of charges, ionization changes very little with temperature because of compensating effects. With increasing temperature, the dielectric constant falls and ionization decreases, whereas the increased thermal energy counters by increasing ionization. This effect takes place in only one temperature region which happens to be near room temperature for this type of indicator.

The phthaleins and sulfonephthaleins should be analogous, yet the

phthaleins show an appreciable change in ionization with temperature, probably owing to the fact that the effect of decreasing dielectric constant is greater than the strictly thermal effect upon the ionization constant.

EXPERIMENTAL

Spectrophotometry in liquid ammonia can be carried out either at room temperature in cells which will withstand the pressure exerted by ammonia (9.89 atmospheres at 25°C) (59), or in cooled cells maintained somewhere between the boiling point and freezing point of ammonia. Cells of this later design should be closed to the atmosphere as ammonia is hygroscopic and water changes the spectrum of many substances (60) dissolved in ammonia. The principal objection to the use of conventional cells is the formation of frost on the windows; hence some means must be devised for elimination of water from the cell faces.

Since absorption spectroscopy in ammonia is limited to the visible and ultraviolet parts of the spectrum due to strong absorption bands at 235 μ and at 1000 μ , (60) a cell can be constructed of standard borosilicate glass or some other material that is transparent to visible radiation for use in this region, or of silica for use in the ultraviolet and visible ranges of the spectrum.

ABSORPTION CELL

A low temperature spectrophotometer cell (Figures 1 and 2) was constructed around a commercial* cylindrical fused silica cell with optically flat windows and a path length of 10.000 mm. Two 7 mm inlet and outlet tubes were attached 180° apart. This cell (A) was suspended in a closed Pyrex tube by means of graded seals (B) and the

*American Instrument Co., Silver Springs, Maryland.

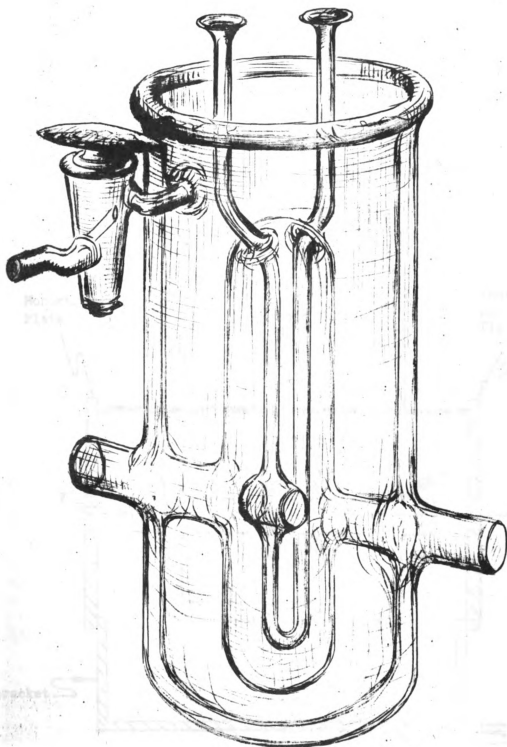


Figure 1. Low Temperature Spectrophotometric Cell

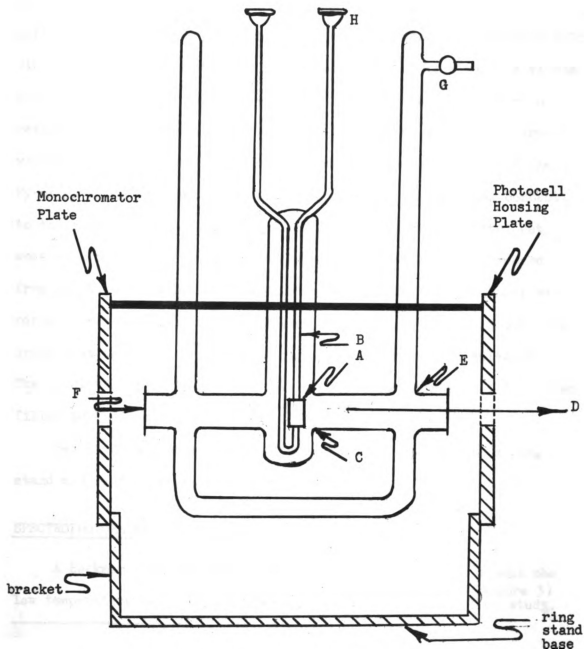


Figure 2. Low Temperature Spectrophotometric Cell (Schematic)

enclosing envelope was provided with two T-seals (C) at 180° along the light path (D). The resulting cross was fastened to the inside of a 90 mm Pyrex tube in such a manner that the light path did not go through Pyrex. The entire assembly was sealed inside a 105 mm tube to form a Dewar-type jacket. Two 16 mm tubes (E) were sealed to the outer wall of the flask in alignment with the light path. After these were cut off and ground square on a Carborundum wheel, two circular silica windows (F) 20 mm in diameter* were attached with black wax. A vacuum stopcock (G) enabled the Dewar-space to be evacuated. This design resulted in a total span of approximately 15 cm between the outermost windows. The cell is filled through tubes (H) extending out of the Pyrex envelope and beyond the top of the flask. These tubes connect to the ammonia line with ground glass ball joints and sockets, but were closed by an interconnecting U-tube when the cell was removed from the line. The space between the double walls and the envelope containing the silica cell could be filled with a cooling liquid. In order that the contents could be seen, the flask was not silvered. The total volume of the silica cell is less than five milliliters when filled to the level of the cooling bath.

Beaker clamps were used to attach the cell assembly to a ring stand modified as shown in Figure 2.

SPECTROPHOTOMETER

A Beckman Model DU spectrophotometer was modified to accept the low temperature cell and was used in all measurements in this study. (Figure 3)

*Quaracell Company Inc., New York

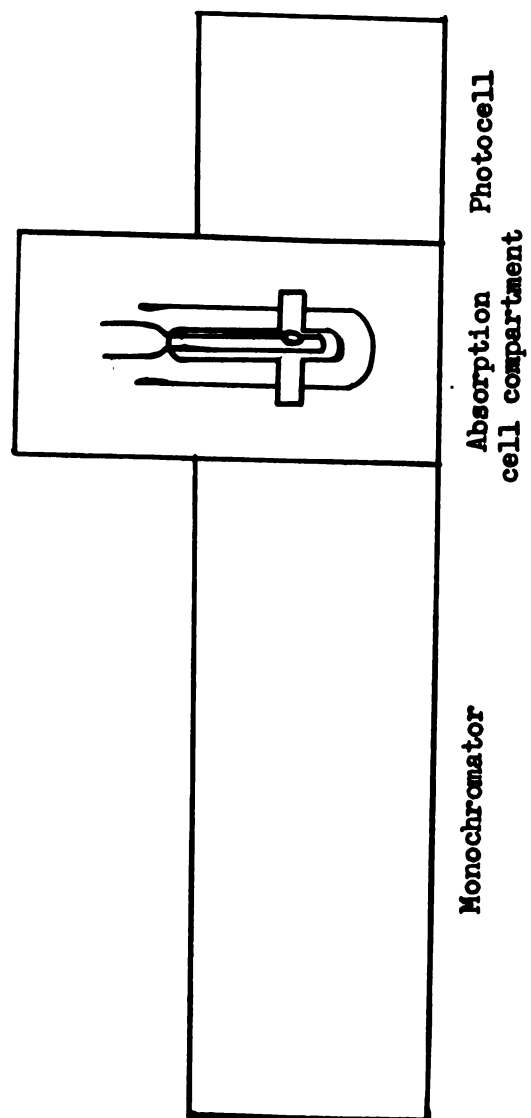


Figure 3. Spectrophotometer

The monochromator was separated from the photocell compartment and the conventional cell holder compartment was removed from the instrument. The ring stand containing the cell was visually aligned such that the light emitted from the monochromator slit passed through the cell and onto the photocell shutter. Longer bolts were constructed which passed through the photocell compartment, through the plates which were bolted on the ring stand, and fastened to the monochromator housing. For insulation purposes, Bakelite plates were placed between the monochromator housing and the ring stand plate as well as between the opposite ring stand plate and the photocell compartment. Dowel pins and holes insured reproducible positioning of the low temperature cell with respect to the monochromator and the photocell. A light-tight bag constructed of black poplin and rubberized cloth covered the cell during operation. Drawstrings were used to close the two side arms and the bottom. The ring stand, plates, insulating plates, etc., were painted black to eliminate any reflection of light.

A tungsten lamp was used in the region of the spectrum from 320 m μ to 1000 m μ and a violet filter was added for measurements from 320 to 400 m μ . For the 230 m μ to 350 m μ region ultraviolet radiation was obtained from a hydrogen lamp. An electronic power supply (Beckman Model No.23700) was used. This was set in position five when the tungsten lamp was used and in position seven with the hydrogen lamp. The monochromator slit widths used with these photomultiplier settings varied between 0.800 mm and 0.030 mm. To establish the thermal equilibrium necessary for reproducible instrument readings within an hour, the lamp housing was cooled by circulating tap water.

Since this instrument works on a single beam principle, it was necessary to fill the low temperature cell with pure liquid ammonia

and to determine the slit width opening for 100% transmittancy at each wavelength used. These values were recorded at constant sensitivity. Averages of three readings per wavelength were used as the slit width program. These readings were checked periodically and gave results within the precision of the instrument ($\pm 1\%$).

The effective path length of the cell was determined with a 0.1 M solution of cobalt ammonium sulfate in water according to a method given by Mellor (61). Pure water was employed to calibrate the slit width and then was replaced with the standard solution. The path length, $\underline{l}$, was found using Beer's law from the expression

$$\underline{l} = \frac{A_{(obs)}}{0.1742} \times 1.000 \quad (17)$$

where $A_{(obs)}$ is the observed absorbancy of the cobalt solution at 510 m μ and 0.1742 is the known absorbancy in a 1.000 cm cell. The effective path length was found to be a consistent value of 1.00 cm during this investigation.

Volumetric and Dilution Vessels

For preparing an ammonia solution of known concentration, a one liter volumetric flask (A) was modified by fastening two side arms (B) on the upper neck and joining a 24/40 ground glass joint (C) to the top (Figure 4). A three way stopcock (D) was placed on a long glass tube which reached to the bottom of the volumetric flask. With the tube in place, the volume of the flask was determined from the weight of water required to fill it to a reference mark. A weighed amount of solute was placed in the flask and ammonia condensed up to the mark

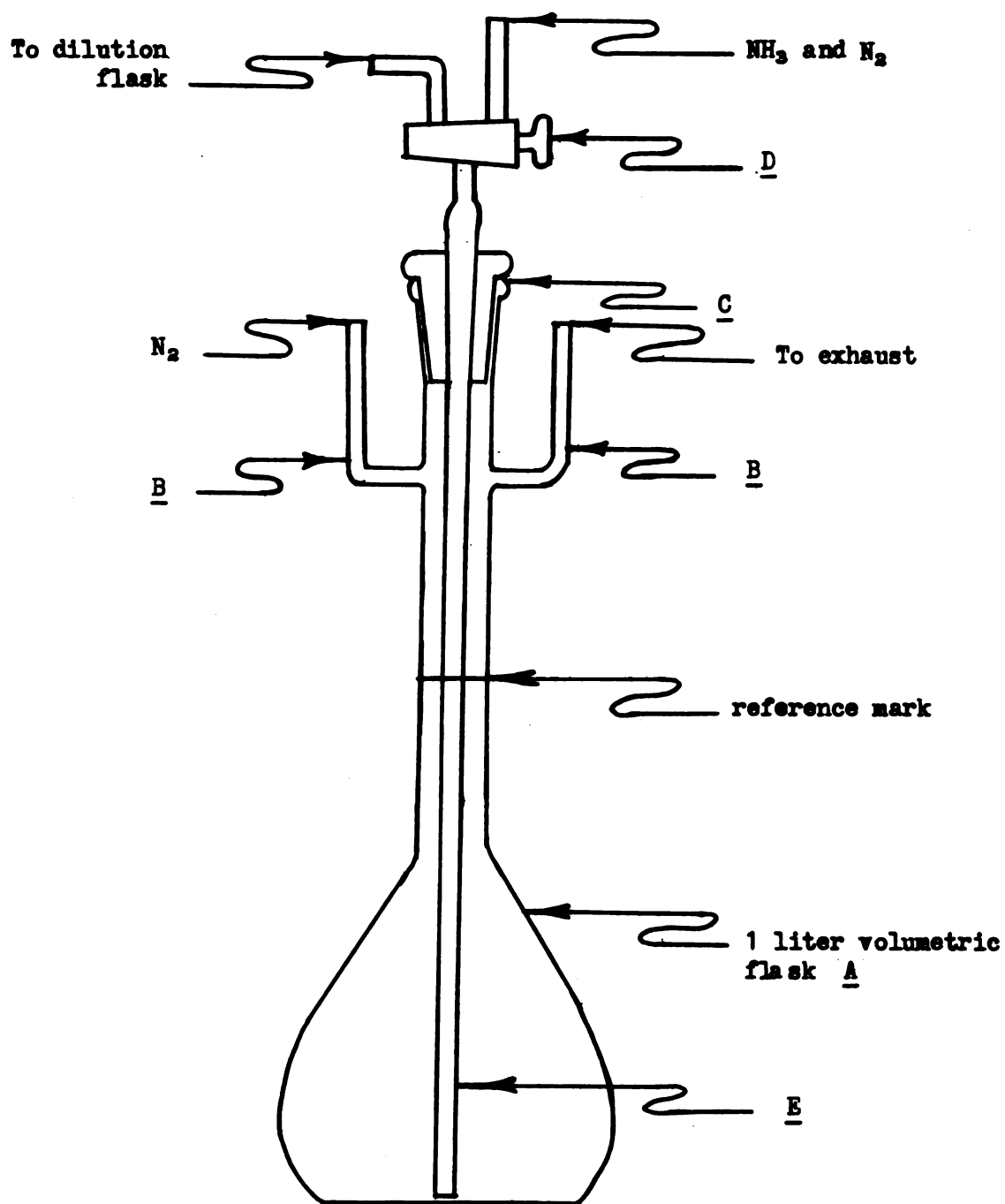


Figure 4. Volumetric Flask

by immersion of the entire vessel in a large Dewar flask filled with coolant. The resulting solution was essentially anhydrous as the inlet tube was not withdrawn and exposed to moisture present in the atmosphere.

Two dilution vessels similar to the one used by Lagowski (29) were used with slight modification. The first vessel consisted of two 200 ml round-bottom flasks connected at their necks such that a reference mark (A) was between them. A short section of a 50 ml graduated cylinder (B) was placed on the opposite end which acted as the neck of the vessel. A 2 1/4/40 standard taper ground glass joint (C) was placed on top and a 1 1/4/35 standard taper ground glass joint (D) holding an addition pistol was sealed on at an angle at the side of the neck. A 7 mm glass tube (E) was connected on the opposite side of the neck (Figure 5). The joint at the top of the flask accepted the upper piece (F) which carried a three-way stopcock as well as inlet and outlet tubes. The longest of the two tubes (G) extended to the bottom of the flask and was used to condense ammonia, introduce solution from the volumetric flask, withdraw solution to the spectrophotometer cell, and stir the solution by allowing dry nitrogen to pass through it. The shorter tube (H) extended only to the reference mark between the bulbs and was connected to the aspirator; through it solution could be withdrawn to the intermediate mark. Solid samples were introduced into the flask by means of the addition pistol (I). The other outlet was used as a vent to the exhaust manifold and also as a means of applying pressure to force solutions out of the flask.

The second vessel used was identical except that the bottom bulb had a volume of only 50 ml (Figure 6). The flask was used when a

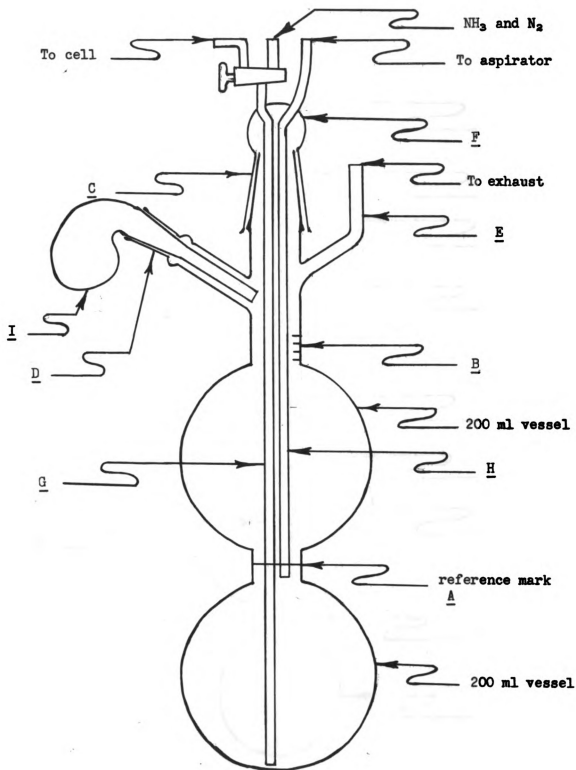


Figure 5. Dilution Flask

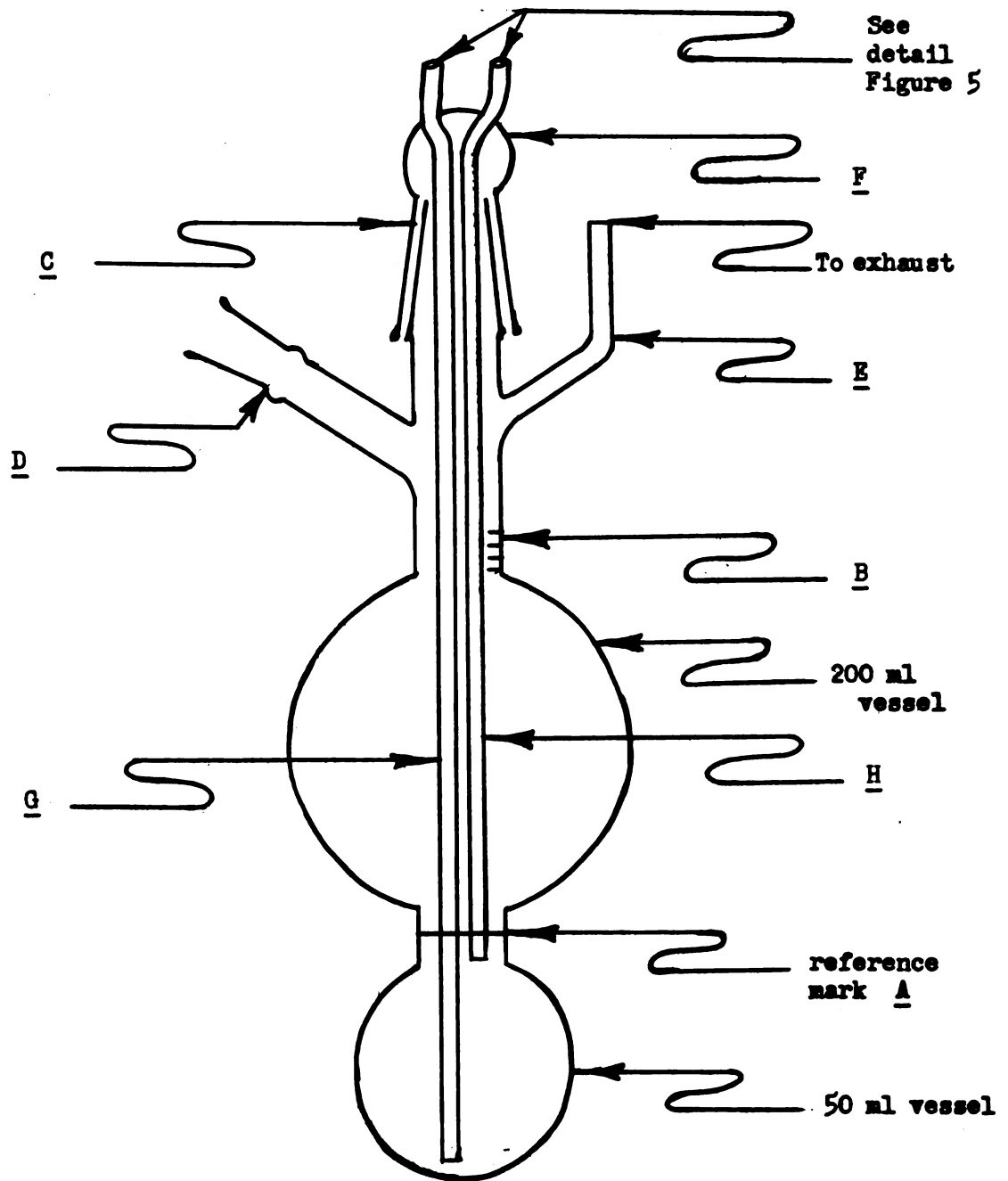


Figure 6. Dilution Flask

dilution factor greater than one-half was desired. These flasks were calibrated gravimetrically using distilled water with the glass tubing installed. By removing solution down to the middle reference marks, dilutions of approximately one-half and one-fifth could be made by addition of ammonia from the volumetric flask or by condensing ammonia to the proper reference mark on the neck. This method insured an essentially anhydrous system as the tubing did not have to be removed to make a measurement.

Thermostats

All measurements were carried out at constant temperatures with refrigerant baths of a suitable liquid cooled with Dry Ice. These mixtures maintained a given temperature when the Dry Ice was in excess. The cooling compartment built around the spectrophotometer cell was filled with the refrigerant mixture at all times. Because this cell was unsilvered, frost slowly formed on the outer walls of the vessel owing to radiant energy transfer, but any number of runs could be made with no appreciable change in temperature ($\pm 0.5^{\circ}\text{C}$). Using this system, frost did not appear either on the outer silica windows or on the windows of the inside cell itself.

The majority of the work was done at -77°C . This temperature was maintained with methyl Cellosolve (ethylene glycol monomethyl ether) as the heat transfer medium. For the other temperatures at which measurements were made, a series of organic liquids were used at their freezing points. These are listed in Table IV along with the temperature at which solid is in equilibrium with liquid.

TABLE IV

LIQUIDS USED FOR CONSTANT TEMPERATURE REFRIGERANTS ("Slush Baths")

<u>Liquid</u>	<u>Freezing Point, (°C)</u>
Ethylene dichloride	-35.6°C
Chlorobenzene	-45.2°C
Chloroform	-63.5°C
Methyl Cellosolve	-77.0°C

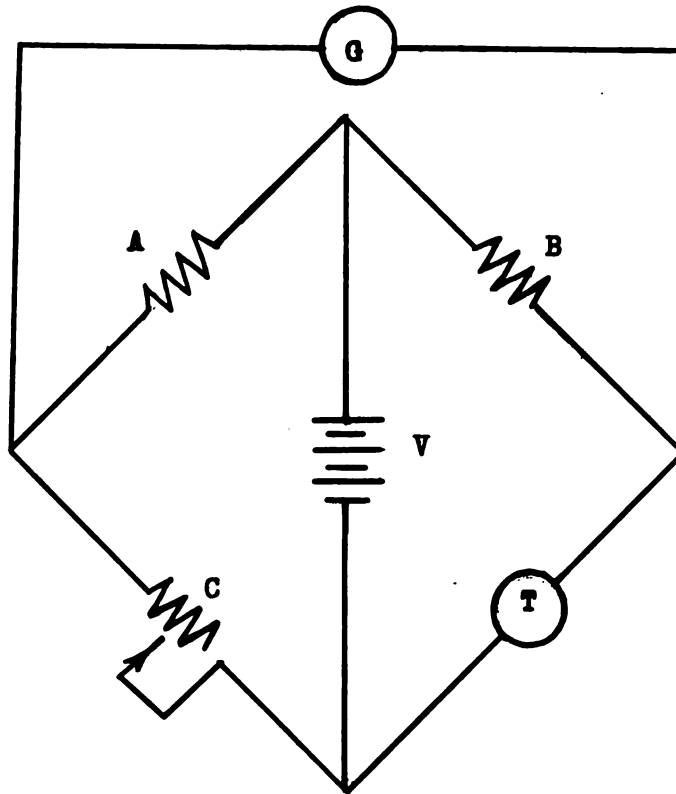
A typical constant temperature bath was made up by adding powdered Dry Ice to the liquid until a thick slurry was present in the refrigerant portion of the cell. Addition of excess Dry Ice to the liquids was not necessary and proved to be undesirable.

Temperature measurements were made by means of a temperature dependent resistor (thermistor)* which was inserted into a thermowell compartment which extended into the Pyrex envelope in proximity to the spectrophotometric cell. This well was sealed out of contact with the refrigerant by means of black wax. The thermistor was connected to a Wheatstone bridge as one leg of the resistance (Figure 7). The actual measurements were performed by balancing the two legs of the bridge to a null point by means of a ten-turn Helipot** resistor and recording the resistance needed to balance the bridge at a given temperature. The null point indicating device used was a Pye***

*Victory Engineering Corp., Union, N.J.

**Beckman Instruments, Inc., Fullerton, Calif.

***W. G. Pye Co., Cambridge, England.



- A = 1000 ohms
- B = 10,000 ohms
- C = Variable Resistor
- T = 5000 ohm Thermistor (VECO 35A3)
- G = Pye Optical Galvanometer
- V = Dry Cell Battery (6.0 volts)

Figure 7. Wheatstone Bridge

galvanometer. A 5000 ohm thermistor was found to have the correct resistance for temperatures between the boiling point and freezing point of ammonia. The thermistor was calibrated (Figure 8) by immersion in a liquid-solid slush bath of known temperature. When measurements were being made with the cell containing slush baths rather than excess Dry Ice, the variation in resistance was ± 55 ohms or $\pm 1.2^\circ\text{C}$.

Other cooling baths employed in condensation and transfer of the ammonia solutions were contained in large mouth Dewar flasks filled with Dry Ice-methyl Cellosolve mixture maintained at -77°C .

Ammonia System

The system used to handle the ammonia consisted of an inlet manifold and an exhaust manifold (Figure 9).

The inlet manifold was closed and evacuated by means of a stopcock U. Synthetic ammonia from a tank was introduced at B while dry nitrogen was connected at C. The open-ended manometer at A was used to determine the pressure of the inlet gases. Stopcock at E was usually in the off position such that D and F in the open position allowed the gases to pass through G, the drying chamber. This chamber was half filled with ammonia in which was dissolved sodium metal; it was cooled by a Cellosolve--Dry Ice mixture in a Dewar flask. The ammonia and nitrogen were passed through this solution at a steady rate which insured anhydrous conditions. Stopcock E was opened when the drying chamber entrance tube became clogged with sodium amide in the middle of a run. The valve at H was the outlet to the exhaust manifold. A stopcock at J was connected to the three way valve L,

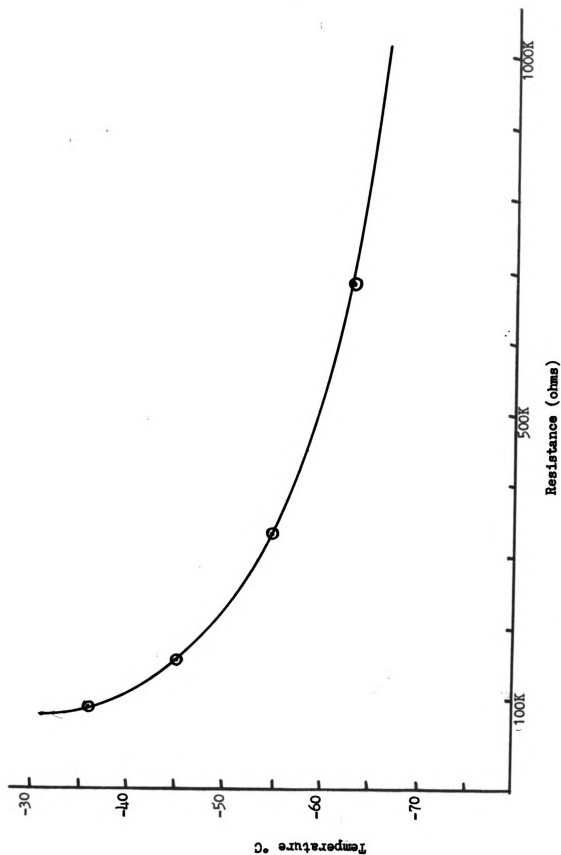


Figure 8. Thermistor Resistance Versus Temperature

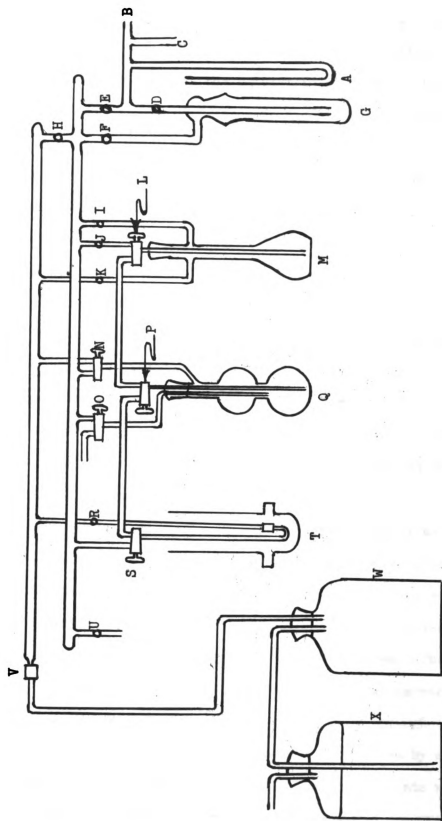


Figure 9. Ammonia Handling System

while I was connected to the upper neck tube on the flask. Stopcock K connected the exhaust manifold to the upper neck tube on flask M. Three-way stopcocks N, O, and P were connected to the dilution flask Q and were used in conjunction with the volumetric flask M and the spectrophotometer cell T. Valve P was connected to valve L by means of silicone rubber tubing* which maintains its elasticity at -77°C . The three-way stopcock at N was used as a gas inlet from the inlet manifold and also as an outlet to the exhaust manifold. Valve O connected the short tubing extending into the dilution flask to the aspirator for removing solution down to the reference mark between the bulbs. This stopcock was also used to introduce ammonia into the flask; the gas was condensed to the upper reference marks on the neck. Three-way stopcock S was used to introduce liquid ammonia from the dilution flask into the cell T, and also as an inlet to the manifold for the cell. Valve R was the cell exhaust connection. The one-way valve at V prevented water from backing up into the system if the internal pressure dropped below atmospheric pressure during condensation of the ammonia. Two large carboys, W and X, were used as traps for getting rid of excess ammonia and as ballast for the pressure in the system. The carboy X was filled with water and connected to W which contained the gas present in the system. Thus if the pressure decreased, the water would flow from X to W and not be forced into the ammonia system. The outlet from X was vented into a hood. The water in X also served as a "flow meter" to show how much nitrogen was being passed through the system. All flasks and vessels were connected to the system by means of Tygon or silicone rubber tubing and ground glass ball joints which alleviated any strain between the flasks and the manifold and prevented

*Dow Corning Corporation, Midland, Michigan

breakage. Flasks Q and M were cooled by Dewar vessels containing methyl Cellosolve--Dry Ice refrigerant.

Use of Vessels and Absorption Cell

The system described above made it possible to perform operations of condensing, stirring, diluting, filling, etc., in an essentially anhydrous system and to effect quantitative transfer of ammonia solution from one vessel to another. A typical run included making up a standard solution, dilution of this solution by a known amount, filling the spectrophotometer cell, and taking readings on the Beckman DU. These operations were carried out as follows.

The inlet manifold was sealed by closing the stopcocks and evacuating the system with an oil vacuum pump connected at U. Meanwhile a solution of sodium metal in ammonia was prepared in the drying chamber G by adding liquid ammonia from a siphon tank to sodium metal placed in the chamber. This solution was cooled in a Dewar flask and connected by means of ball and socket joints at D and F. The nitrogen valve was slowly opened after valve U was closed and D and F were opened. As nitrogen passed through the drying solution, H was opened and the system flushed with dry nitrogen. After the volumetric flask had been heated in a drying oven at 110°C for two hours, a weighed amount of solute was quickly introduced into this flask and the flask and contents were connected to the system at I, J, and K. Valve L was turned such that when K was opened, it allowed nitrogen to sweep through the flask. Valve H was closed; M was allowed to cool to room temperature while being flushed with nitrogen. The flask was then cooled to -77°C by surrounding it with a Dewar flask filled with

refrigerant. Ammonia from tank B was introduced and began to condense immediately. As the level of the liquid reached the reference mark, H was opened, the ammonia turned off, and the level checked. When this indicated one liter of solution, J was closed and L rotated to line up with P. In order to stir the solution and hasten equilibrium, nitrogen was bubbled through the solution at a vigorous rate. The dilution vessel Q was dried in an oven and attached at N, O, and P. It was cooled in the same manner as was flask M. Valve I was opened to nitrogen pressure which forced the solution from M through L and P into Q. As the reference mark was reached, H was opened and I was closed.

The solution in the dilution flask was used to fill the spectrophotometer cell in a like manner. With O off and N rotated, valve P was aligned with S to allow nitrogen pressure to force the liquid through T. When the cell was full, nitrogen pressure was released by opening H. With S and R closed, the cell was disconnected. The closed U-tube was placed over the opening and the entire assembly attached to the spectrophotometer.

Dilutions were carried out by aligning stopcock O with the aspirator connection which emptied the dilution vessel to the middle reference mark. Ammonia was condensed in the flask to the upper reference mark and nitrogen was bubbled through the solution to stir it. The dilution flask can be used in conjunction with the volumetric flask to change the concentration of one of the species in solution while concentrations of other solutes are held constant. Solute can be added to the dilution flask by means of the addition pistol.

The volume of the first dilution flask to the middle reference mark was 207.9 ml with the glass tubes installed. The upper reference

used gave a volume of 418.7 ml which resulted in a dilution factor of 0.496. The second dilution vessel had a volume of 54.90 ml when filled to the lower reference mark and a total volume of 258.0 ml. Its dilution factor was 0.211. Not only could pure ammonia be condensed in the dilution flask, but a known solution could be added to the mark from the volumetric flask as described above. Thus, all possible combinations of indicator, neutral salt, and ammonium salt concentrations could be varied or held constant with respect to each other.

Chemicals

Synthetic ammonia^{*} was used from two types of tanks. One was a siphon tube tank which delivered the liquid at the spout and was used in all synthetic work undertaken in this study when ammonia was used as a solvent. The other type was a regular gas delivery tank from which ammonia was distilled into the proper flask after passing through a sodium-ammonia drying solution.

Purified dry nitrogen^{**} was further dried in the same manner as the ammonia prior to use.

All inorganic salts employed were reagent grade, dried at 110°C for several days, and stored in desiccators containing Drierite or anhydrous magnesium perchlorate. Organic indicators were recrystallized from the appropriate solvents to constant melting points and stored in desiccators until used. Experimental details for preparation of other organic compounds used in this study are given in Appendix I.

^{*}Matheson, Inc., Joliet, Illinois.

^{**}General Dynamics Corporation.

Sodium Salt of Phenolphthalein

A reaction vessel for the preparation of alkali metal salts in ammonia was constructed by sealing a coarse porosity sintered glass frit to the bottom of a 300 ml three-necked flask. A stopcock was attached below the frit (Figure 10). A stirrer was fitted in the center neck along with an addition pistol and drying tube in the other two openings. One hundred milliliters of ammonia was introduced into this flask from a siphon tank. With the bottom stopcock closed, the ammonia remained above the glass frit. Phenolphthalein [4.5 grams ($1.4 \times 10^{-3} \text{M}$)] was dissolved and upon addition of 0.055 gram ($1.4 \times 10^{-3} \text{M}$) of sodium amide the red-purple color intensified. After a few minutes of stirring, the lower stopcock was opened into a 250 ml Erlenmeyer flask and the stirrer, drying tube, and pistol all were replaced with stoppers. As the ammonia evaporated, the pressure increase in the flask forced the solution to filter rapidly through the glass frit. Since the sodium salt is soluble in ammonia, the filtrate was evaporated to dryness in a stream of dry nitrogen and the salt recovered in quantitative yield (5.0 grams).

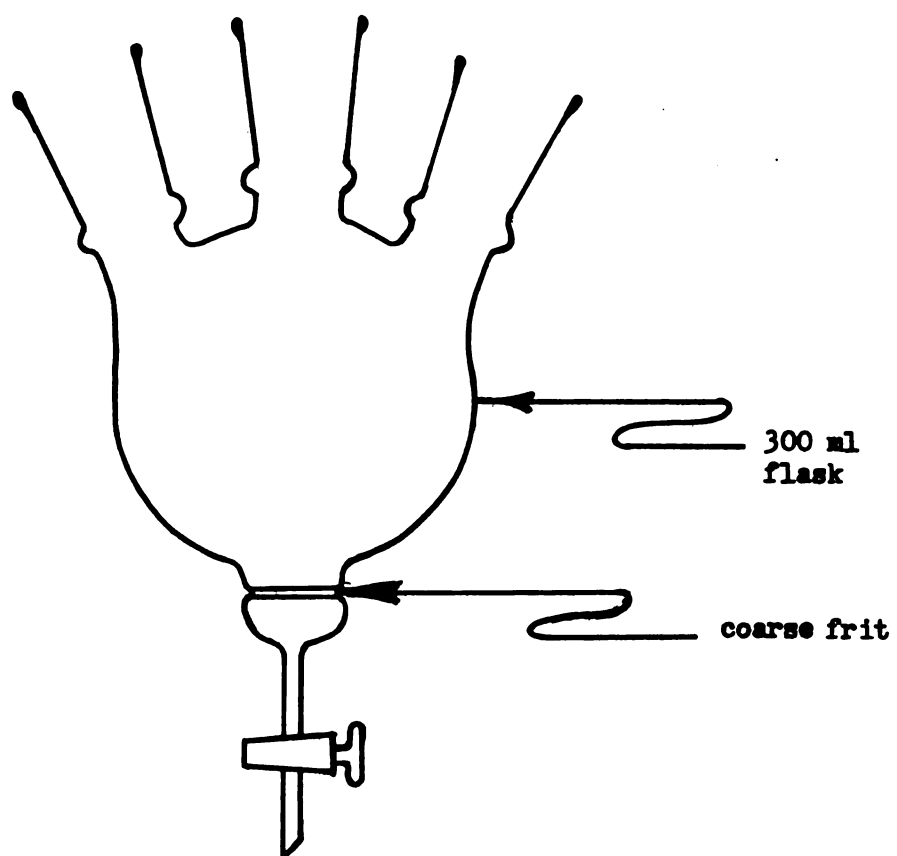
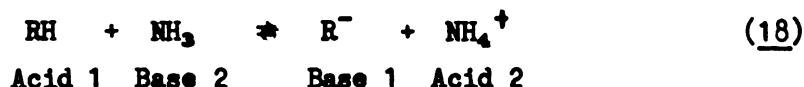


Figure 10. Filter Flask

RESULTS AND DISCUSSION

Introduction

Compounds which contain a labile hydrogen can act as acids toward ammonia even though they are bases in water:



If a color change occurs when Acid 1 becomes Base 1, the substance can be used as an indicator in ammonia. The concentration of Base 1 depends upon the equilibrium constant of equation 18, which in turn is dependent on the acidic nature of the compound and the basic nature of the solvent. For the general acid-base reaction



the ionization constant is

$$\underline{K}_1 = \frac{a_{\text{B}^-} \cdot a_{\text{Hs}^+}}{a_{\text{A}} \cdot a_{\text{s}}} = \underline{K}_{(\text{acidity})_{\text{A}}} \underline{K}_{(\text{basicity})_{\text{s}}} \quad (20)$$

where $\underline{K}_{(\text{acidity})}$ of any protonic acid (i.e. RH) is:

$$\underline{K}_{(\text{acidity})} = \frac{a_{\text{B}^-} \cdot a_{\text{H}^+}}{a_{\text{A}}} = \frac{1}{\underline{K}_{(\text{basicity})}} \quad (21)$$

Thus equation 20 shows the role of the basicity of the solvent in determining the ionization of an acidic compound. The extent to which

this compound ionizes is then a measure of its acid strength. Because of the difficulties in evaluating the constants $\underline{K}_{(\text{acidity})}$ and $\underline{K}_{(\text{basicity})}$ present in equation 20, indirect methods must be used to evaluate acid strengths. If the ionization constants of two acids A_1 and A_2 are compared in ammonia, then from equation 20:

$$\frac{(\underline{K}_1)_1}{(\underline{K}_1)_2} = \frac{\underline{K}_{(\text{acidity})A_1}}{\underline{K}_{(\text{acidity})A_2}} \quad (22)$$

where the basicity of the solvent cancels out. Comparison of two acids in one solvent therefore should give the same ratio of $(\underline{K}_1)_1$ to $(\underline{K}_1)_2$ as in any other solvent.

Equation 20 does not describe completely the acid-base equilibrium as there is not only the ionization of the species to consider but its dissociation also. These steps can be represented by two separate equilibria:



where equation 23 is the ionization step and equation 24 is the dissociation step. In solvents of high dielectric constant the dissociation step may be essentially complete, but in ammonia with its dielectric constant of about 23, the distinction is important.

Because no further ionization can occur when an ionic crystal dissolves, dissociation is the only dissolution reaction which ionic substances undergo. Dissociation in solutions of many ionic compounds

has been studied conductometrically (3, 15), and K_d has been found to have an approximately constant value of 10^{-4} for one-one electrolytes. Hence in ammonia ion pairs predominate except in very dilute solutions of the order of $10^{-3}M$ or less. Higher aggregates such as ion triplets and quadruplets also exist (62), but only at greater concentrations than those encountered in this study. Conductivity--like electromotive force measurements--cannot be used to obtain ionization constants of acids because it does not distinguish between ion pairs and molecules.

The intrinsic acidity of a compound can be determined by its ionization constant and can be compared with other compounds in this respect. Many organic compounds which act as indicators in aqueous solutions also form colored solutions in ammonia. Since these indicators are acids in water, their acidity is enhanced when dissolved in ammonia. Thus most indicators show little or no change in going from acid to neutral ammonia solutions while many more display a change from neutral to basic solution. Several of the more promising indicators, i.e. ones showing a definite acid to neutral change, are listed in Table V together with their color changes.

Of the various experimental methods available for studying solutions, absorption spectroscopy seems to be best suited for investigating indicator systems. Indicator color changes afford easy

TABLE V

INDICATOR COLOR CHANGES IN AMMONIA

Indicator	Acid	Neutral	Base
p-Nitroacetanilide	colorless	yellow	yellow
2,4-Dinitroaniline	orange	red	yellow
Phenolphthalein	pink	purple	colorless
Thymol Blue	blue	blue-green	blue-green
Tropeoline OO	yellow	yellow	purple

access to very useful data; the molecular form of the indicator acid absorbs at a wavelength different from the ionized form, and spectrophotometric measurements permit calculation of ionization constants.

There are several things to consider in applying this method to ammonia. Even though the effects of solvation upon the electronic energy levels of a molecule are not well known, it has been assumed that the extinction coefficient of an ionic species in a solvent such as ammonia is the same whether the ions exist as ion pairs or as discrete ions. If Beer's Law is valid, the expression for the absorbancy due to a given indicator anion at a single wavelength for unit path length is

$$\underline{A} = \epsilon \underline{C}_1 + \epsilon \underline{C}_2 \quad (25)$$

where $\underline{A}$ is the absorbancy, ϵ is the molar extinction coefficient (assumed to be the same for associated and dissociated ions), $\underline{C}_1$ is the concentration of indicator anion pairs, and $\underline{C}_2$ is the concentration

of dissociated anions. Factoring equation 25 gives:

$$\underline{A} = \epsilon(\underline{C}_1 + \underline{C}_2) \quad (26)$$

Solving for the total concentration ($\underline{C}_1 + \underline{C}_2$) gives the expression used to calculate anion concentrations:

$$(\underline{C}_1 + \underline{C}_2) = \frac{\underline{A}}{\epsilon} \quad (27)$$

Equation 27 assumes the spectrum of ion pairs to be the same as that of free ions; that is, the spectral contribution of free (dissociated) solvated ions cannot be distinguished from the ion pair absorption.

Ammonia is so basic that even very weak proton donors are converted to ammonium ions, the strongest acid species that can exist in liquid ammonia solution. This phenomenon is illustrated by acetic acid, a weak acid in water but a strong (i.e., completely ionized) acid in ammonia.

The indicator acids studied in this research were found to have first ionization constants greater than one. These indicators, therefore, are strong acids in liquid ammonia.

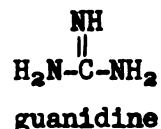
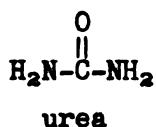
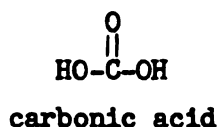
The color changes of acid-base indicators in liquid ammonia do not have the same significance as in aqueous solutions. In water the ratio of acid form to base form is directly related to the activity of the hydrogen ion. When a pH measurement is made in aqueous solution, the difference between the value of an experimental parameter in unknown and reference solutions is attributed entirely to a change in activity of the hydrogen ion. The activity is assumed to be

unaltered by exchange of one anion for another.

In water, these assumptions are valid as first approximations, but when applied to ammonia, the effect of ion pairing must be considered. Hydrogen ion activity cannot be measured directly as all experimental methods give mean activity rather than the activity of a single ion. Since Fuoss and Kraus (15) have demonstrated experimentally that dissociation constants are of the order of 10^{-4} for salts in ammonia, and since they have shown that dissociation constants vary with the anion present, it follows that a correlation of the type made in aqueous solution is not valid in ammonia. In liquid ammonia no single relationship holds between the concentration or activity of the ammonium ion and the ratio (r) of indicator anion to molecular indicator. This investigation shows that plots of the logarithm r versus the logarithm of the ammonium ion concentration do not give straight lines (Figures 11 through 14). These figures also show that the functions are highly dependent on the nature of the anion present.

Weak Acids

According to the Franklin concept (6) of the nitrogen system of compounds, guanidine is the analog of carbonic acid while urea is the mixed aquo-ammono compound.



Carbonic acid is a weak acid in water, urea is weakly basic, and guanidine is a strong base in this medium. In ammonia, on the other hand, it has been postulated that both urea and guanidine are weak

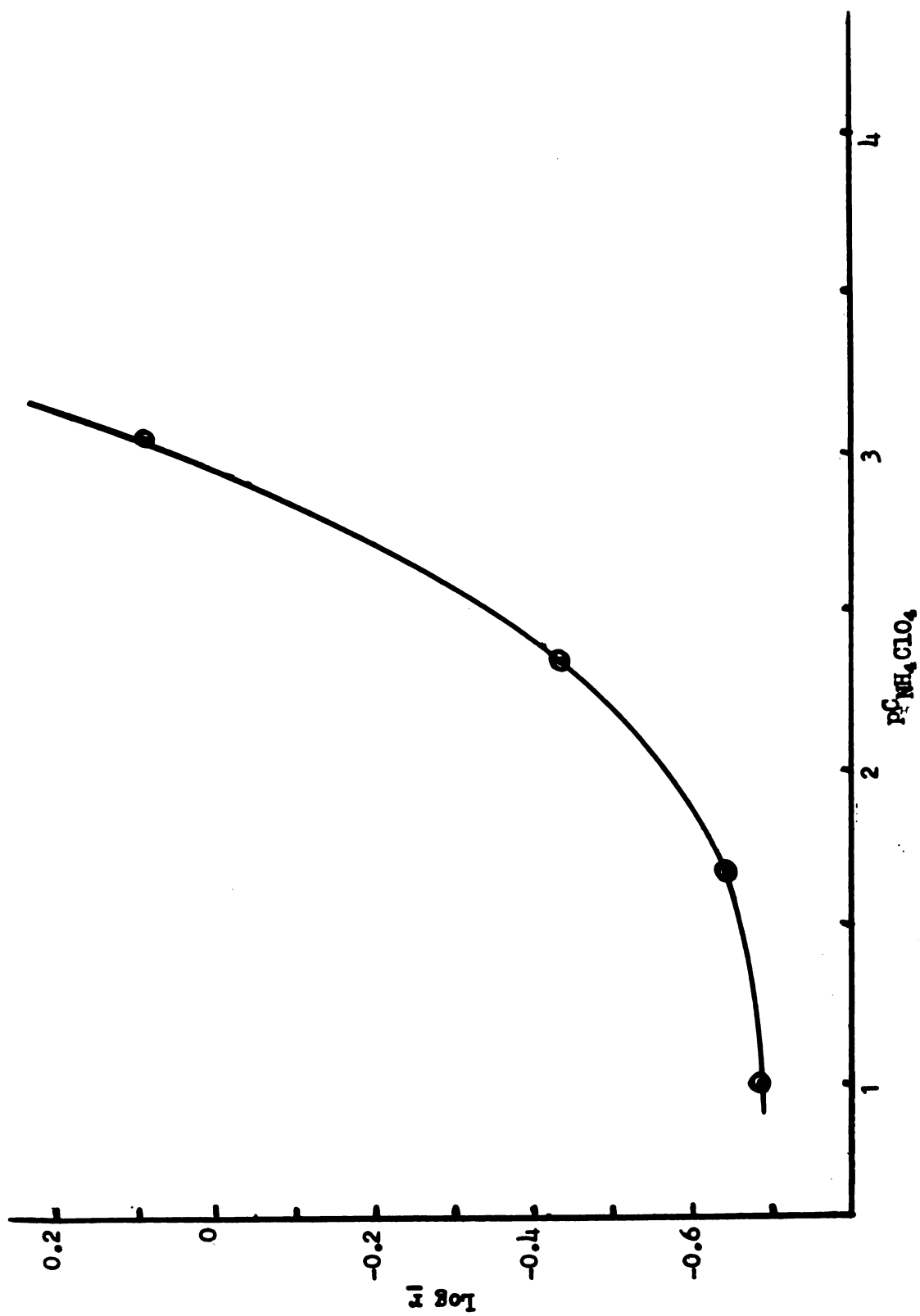


Figure 11. Log of Concentration of Ammonium Perchlorate Versus $\log r$ of Phenolphthalein

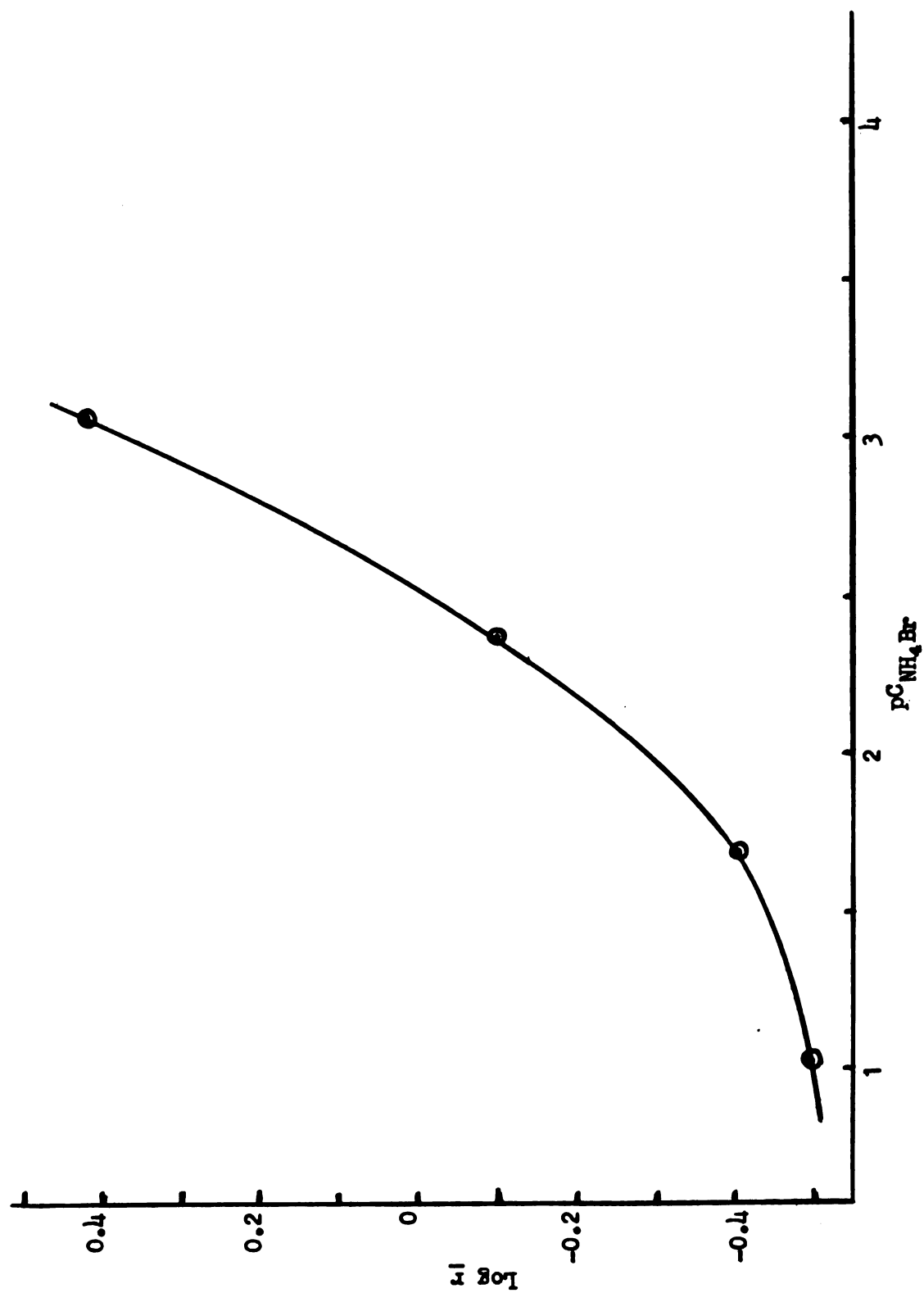


Figure 12. Log of Concentration of Ammonium Bromide Versus $\text{Log } r$ of Phenolphthalein

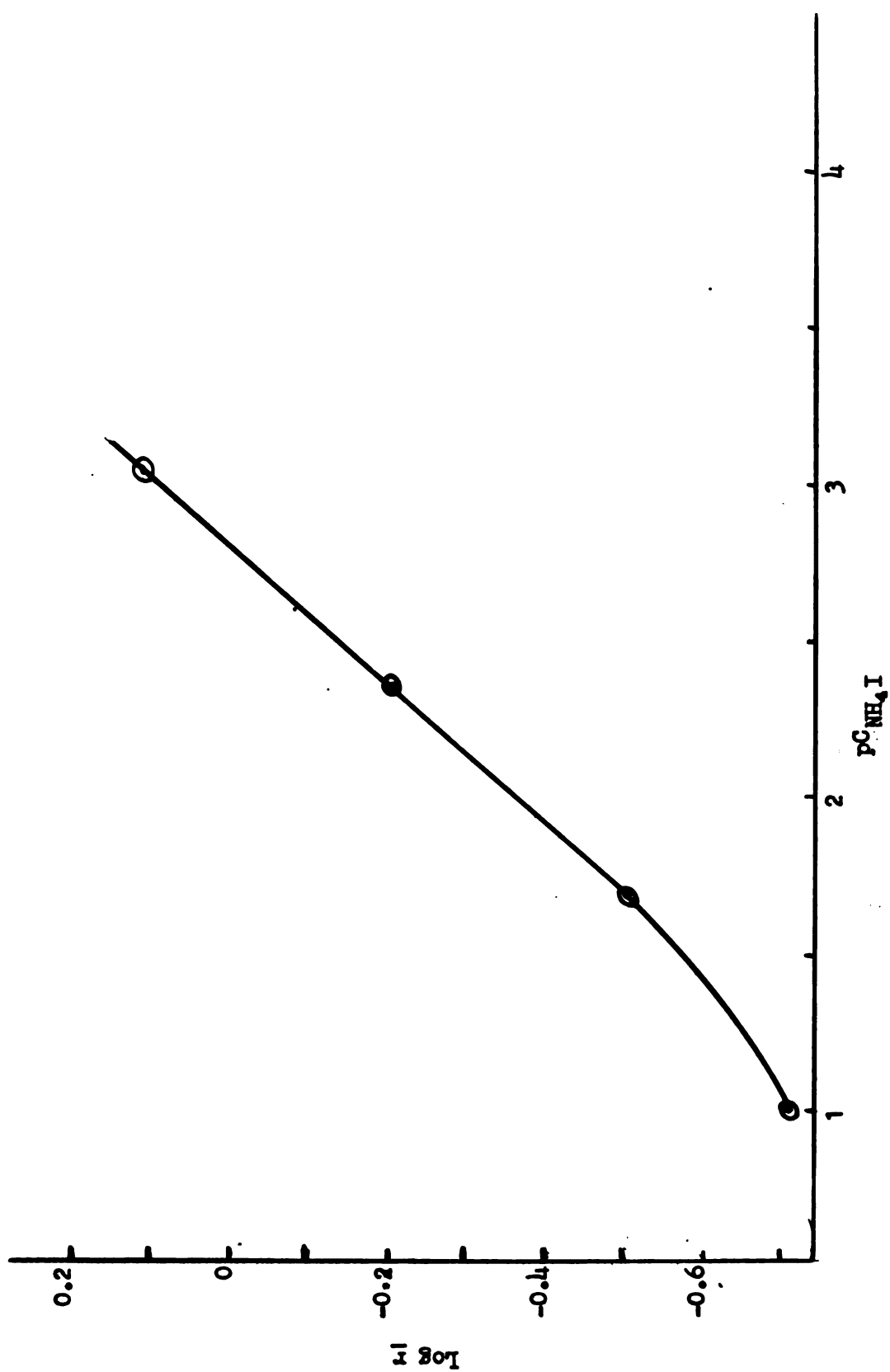


Figure 13. Log of Concentration of Ammonium Iodide Versus Log r of Phenolphthalein

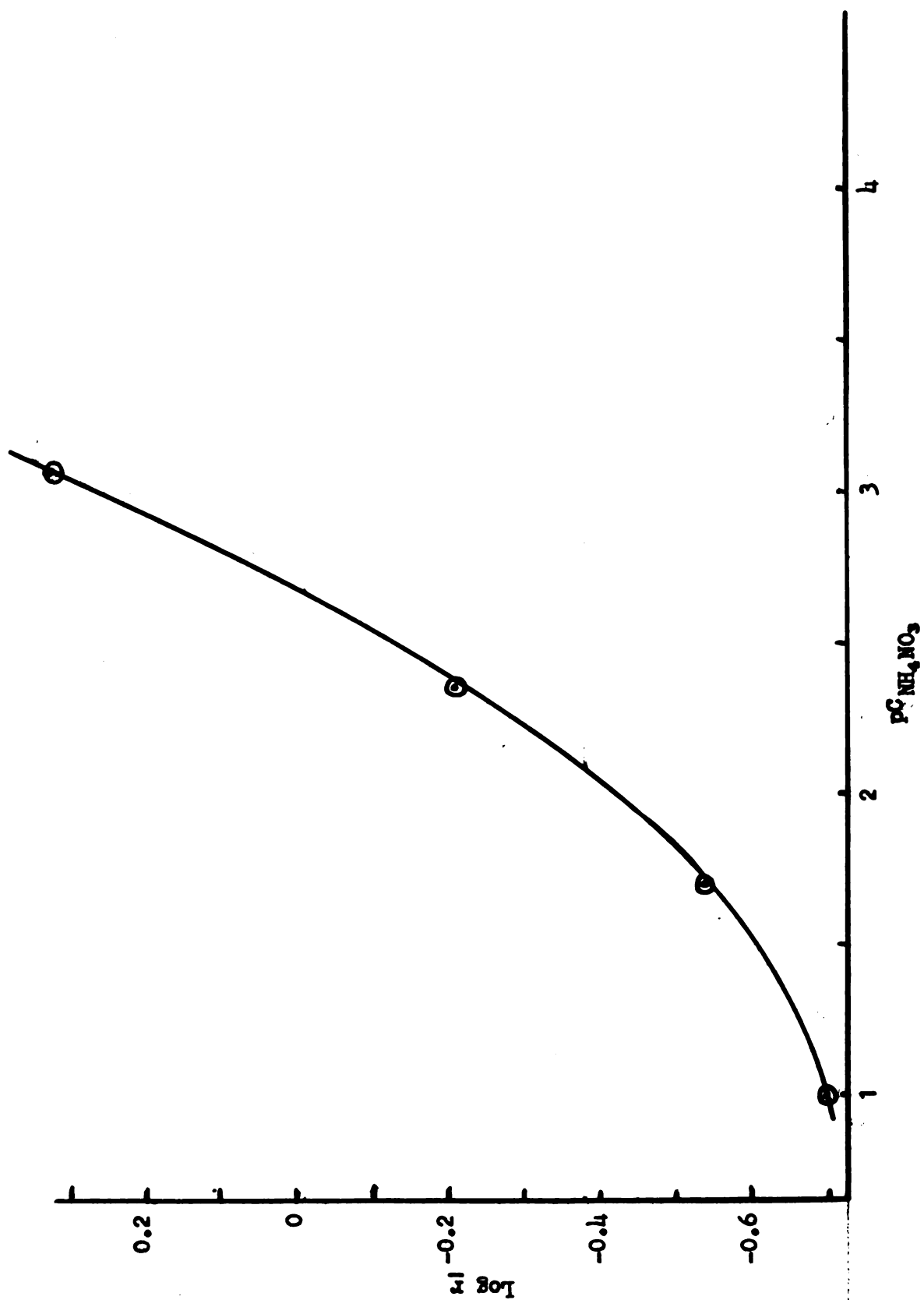


Figure 14. Log of Concentration of Ammonium Nitrate Versus $\text{Log } r$ of Phenolphthalein

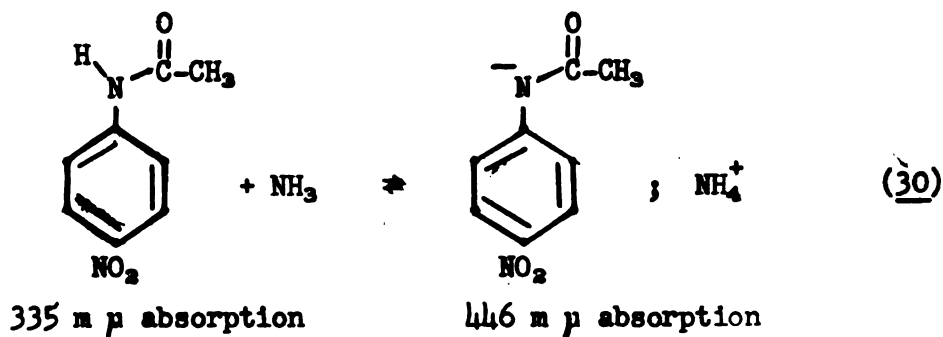
acids, and indeed from the structure of these compounds, amphiprotic behavior might reasonably be expected:



where R is the $H_2N-\overset{\overset{O}{\parallel}}{C}-$ or $H_2N-\overset{\overset{NH}{\parallel}}{C}-$ group. Evidence of the acidity of these two compounds in ammonia is that: (1) potassium salts can be prepared using potassium amide in ammonia, and (2) hydrogen is evolved when elemental potassium is used in the same reaction (64, 65).

The spectra of urea and methylsubstituted ureas in water show an absorption band in the far ultraviolet which shifts to longer wavelengths as the number of methyl groups substituted for hydrogens is increased (Figure 15). Because ammonia absorption bands occur in the region where these compounds absorb, direct spectrophotometric study of these compounds in solution is blocked. Indicators therefore have been used to investigate the acid-base properties of substituted ureas.

In a preliminary study, several indicators were selected on the basis of the difference in color which they display in acid and neutral ammonia solution. The simplest of these indicators is p-nitroacetanilide. Its yellow-green color in pure liquid ammonia is greatly intensified by the addition of potassium amide. p-Nitroacetanilide contains one acidic hydrogen atom in the molecule and presumably reacts with ammonia according to equation 18:



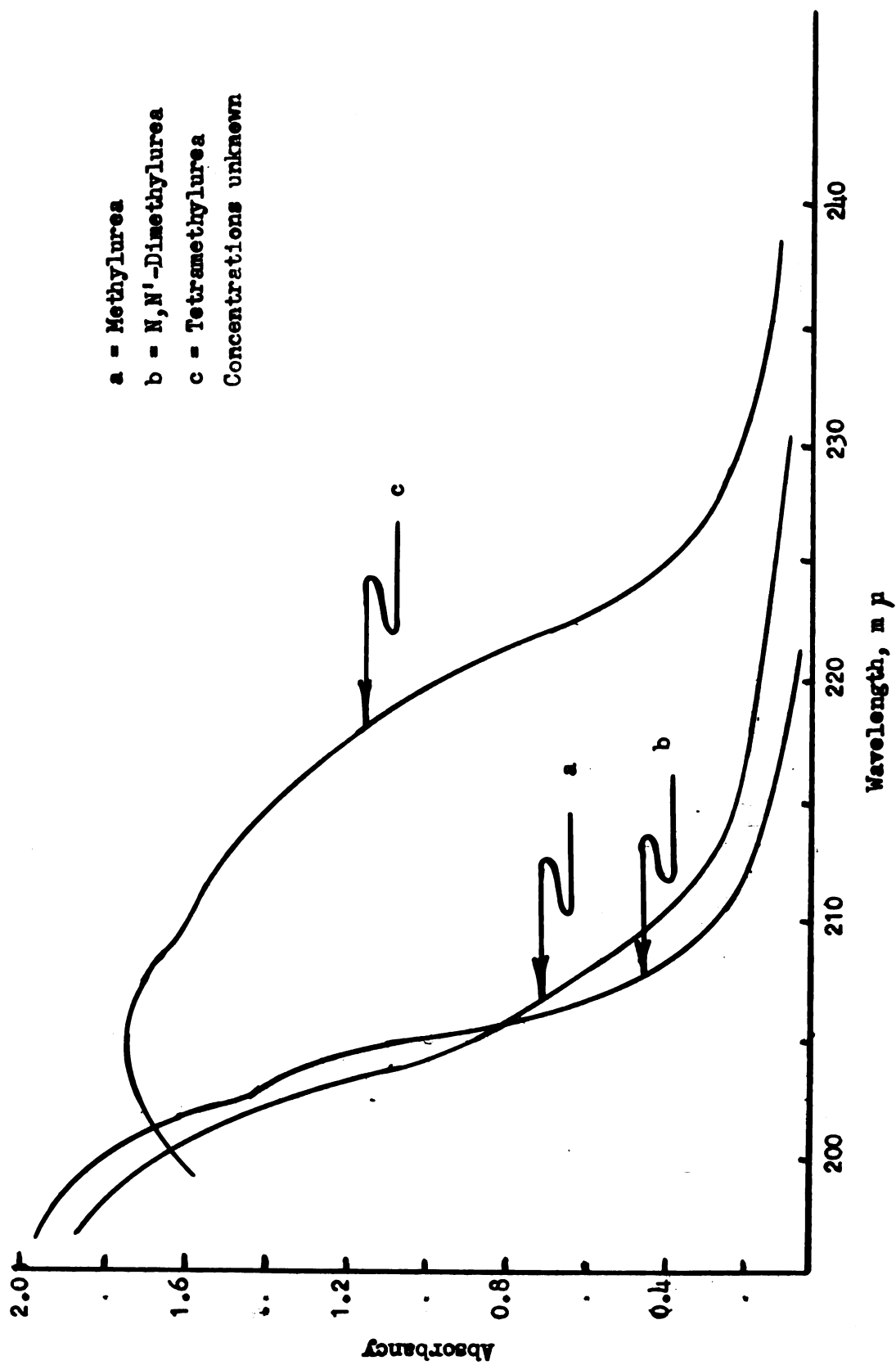


Figure 15. Absorption Spectra of Some Methylsubstituted Ureas in Water

The ultraviolet and visible spectrum of this indicator (Figure 16) shows bands at 335 m μ and 446 m μ which are attributed to the molecular acid species and the ammonium ion pair respectively. Ammonium perchlorate added to the solution depresses the band at 446 m μ and increases the 335 m μ band as would be expected from the equilibrium indicated in equation 12. (Figures 17 through 19). K_1 for this reaction was calculated (Table VI) by the method described in Appendix II and found to be 17. Such a large value of the equilibrium constant is not surprising in a medium as basic as ammonia where acidity is enhanced and ionization is extensive.

The extinction coefficients (Table VI) for molecular and ionized p-nitroacetanilide were calculated by the method described in Appendix II; the greater value for the molecular form explains why the absorption bands approach the same size even though the equilibrium favors the ammonium-anion pair.

By analogy to the behavior of phenols in water solutions, p-nitroacetanilide should have a rather large salt effect and this is observed. (Figure 20). This can be explained in terms of the thermodynamic equilibrium constant. The ionization constant for an indicator acid is

$$K_1 = \frac{[H^+; In^-]}{[HIn]} \cdot \frac{\gamma_{H^+; In^-}}{\gamma_{HIn}} \quad (31)$$

or

$$K_1 = K_1' \frac{\gamma_{H^+; In^-}}{\gamma_{HIn}} \quad (32)$$

where K_1' is the concentration ratio. If the ionic atmosphere changes--as by addition of a neutral salt--the activity coefficient factor in

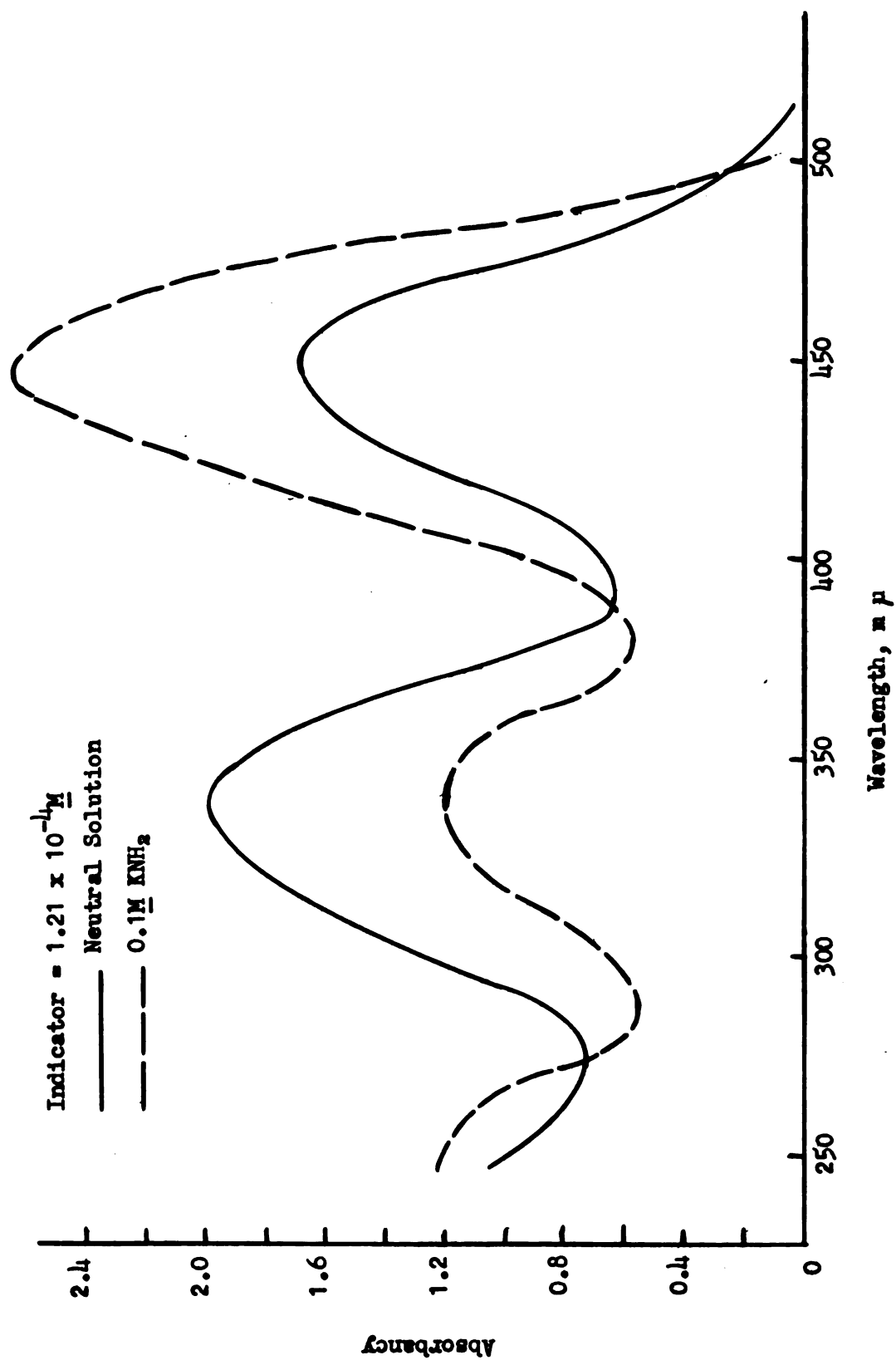


Figure 16. Absorption Spectra of p-Nitroacetanilide in Ammonia

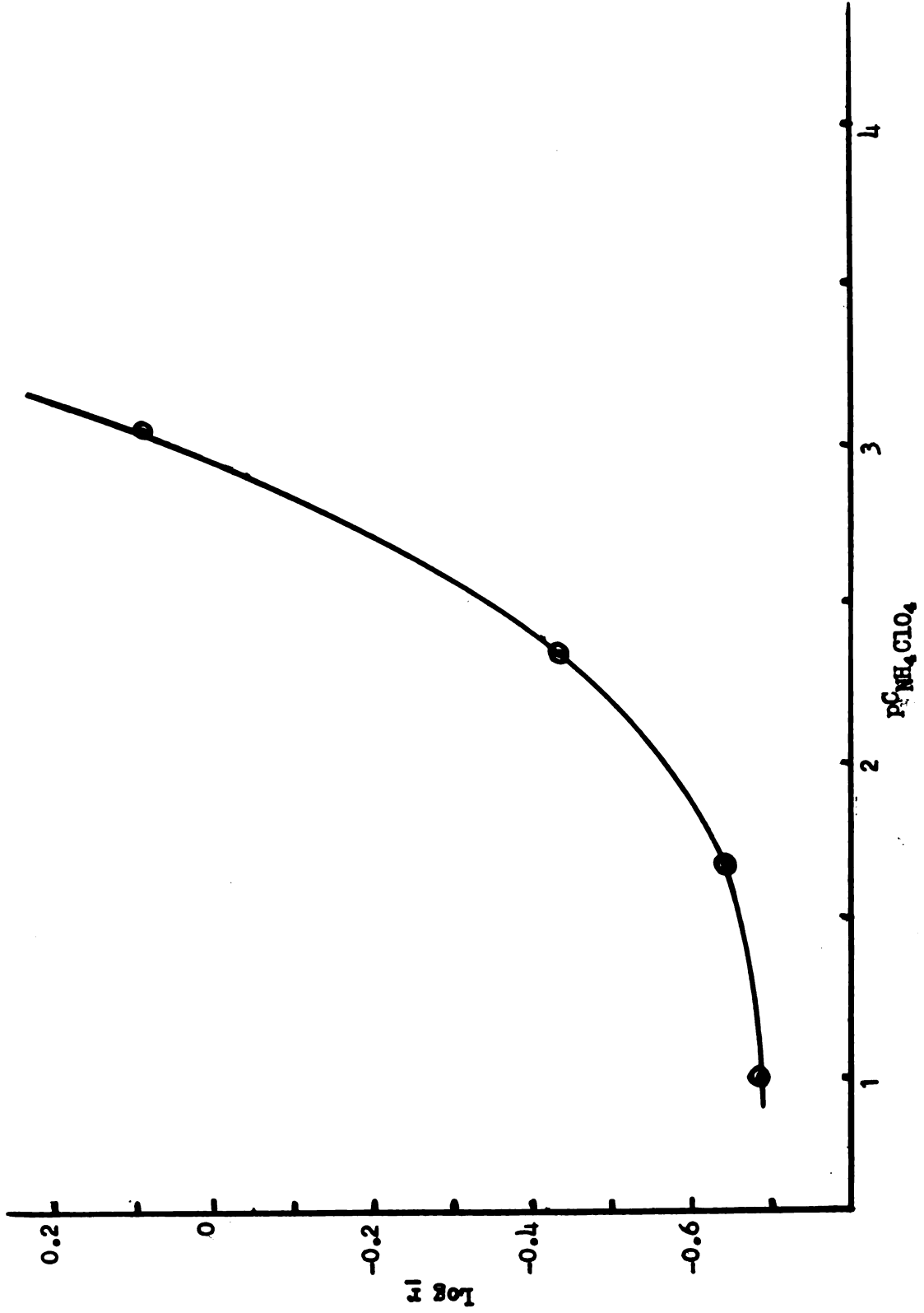


Figure 11. Log of Concentration of Ammonium Perchlorate Versus $\log r$ of Phenolphthalein

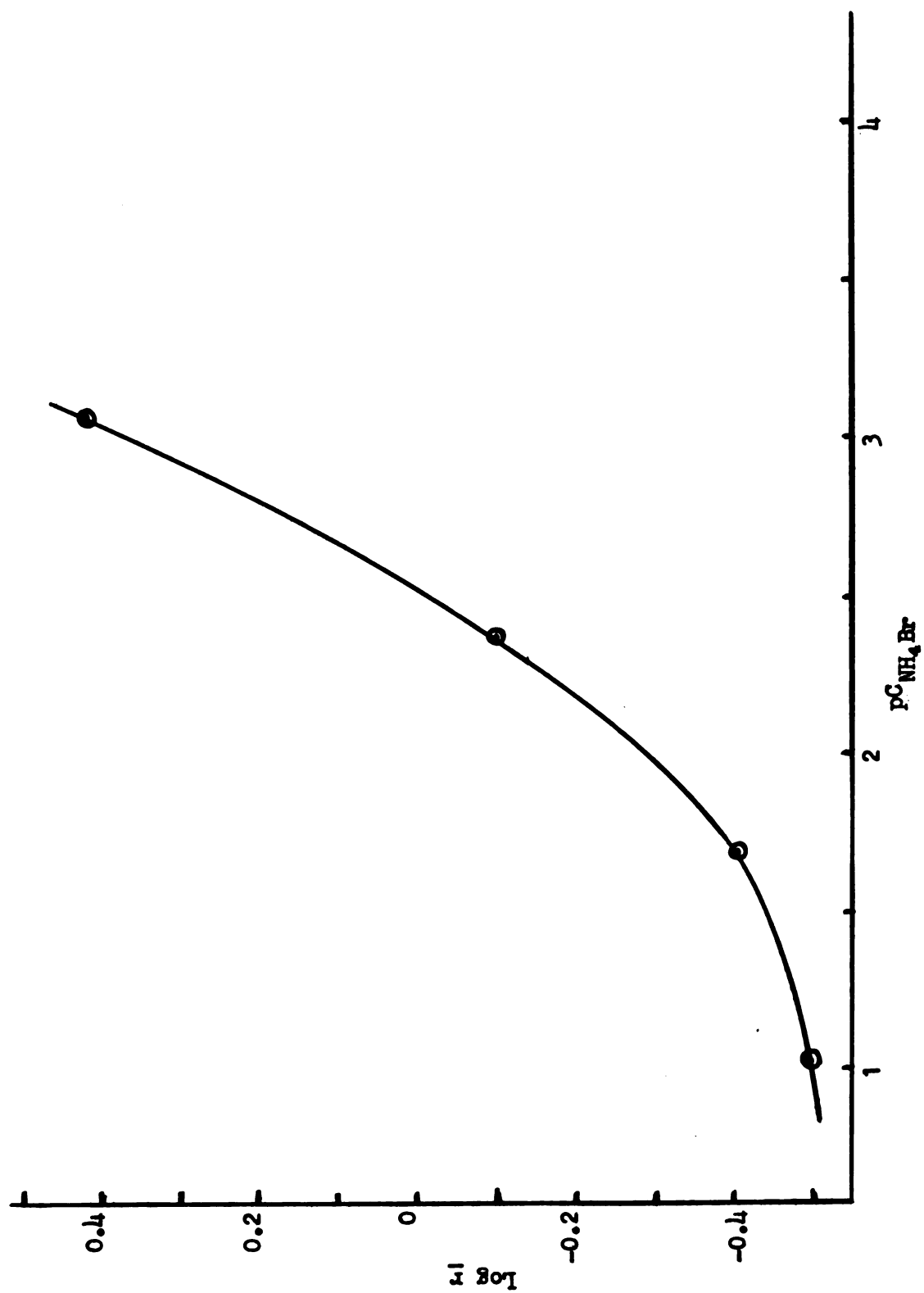


Figure 12. Log of Concentration of Ammonium Bromide Versus $\text{Log } r$ of Phenolphthalein

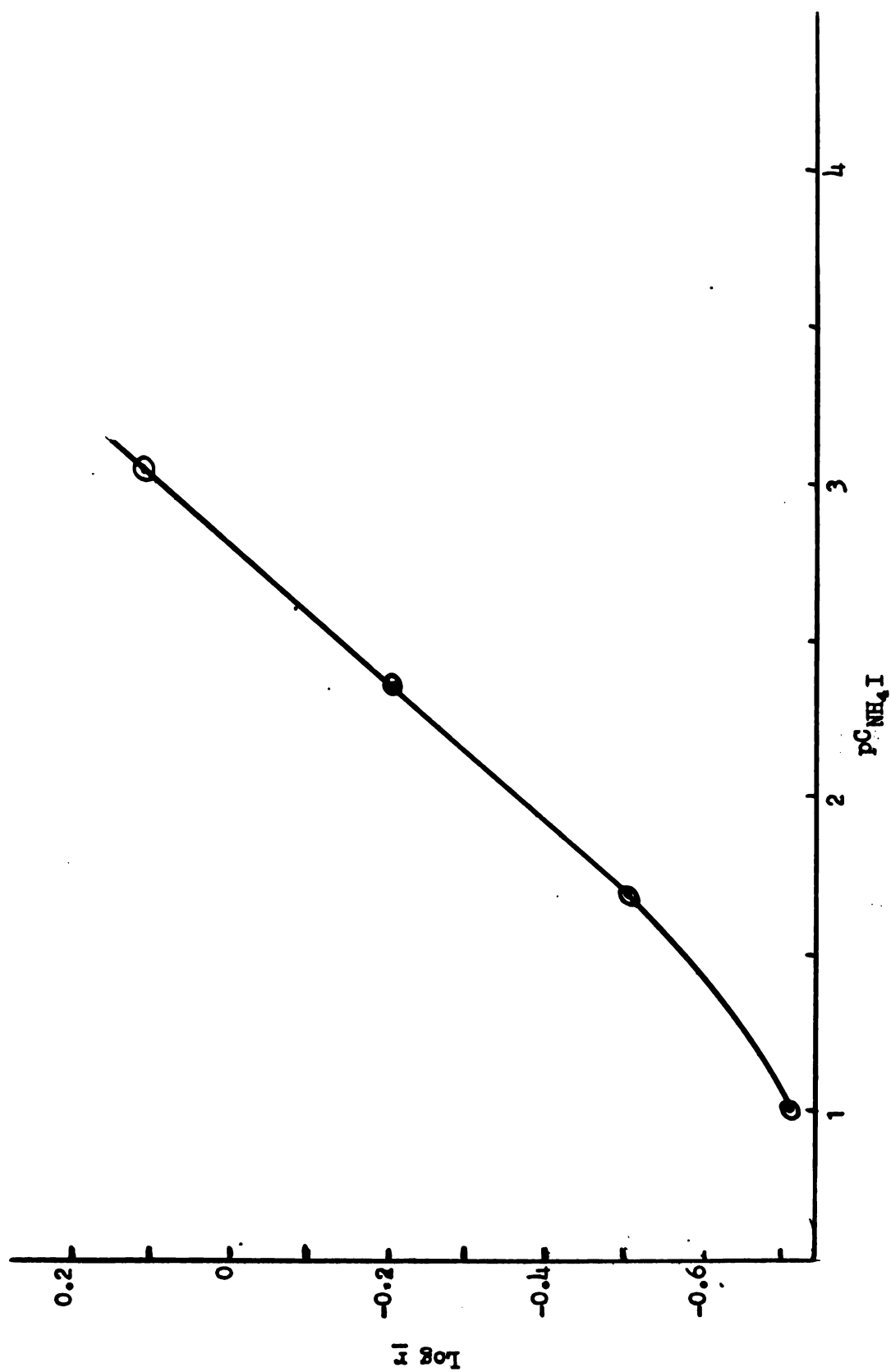


Figure 13. Log of Concentration of Ammonium Iodide Versus $\text{Log } r$ of Phenolphthalein

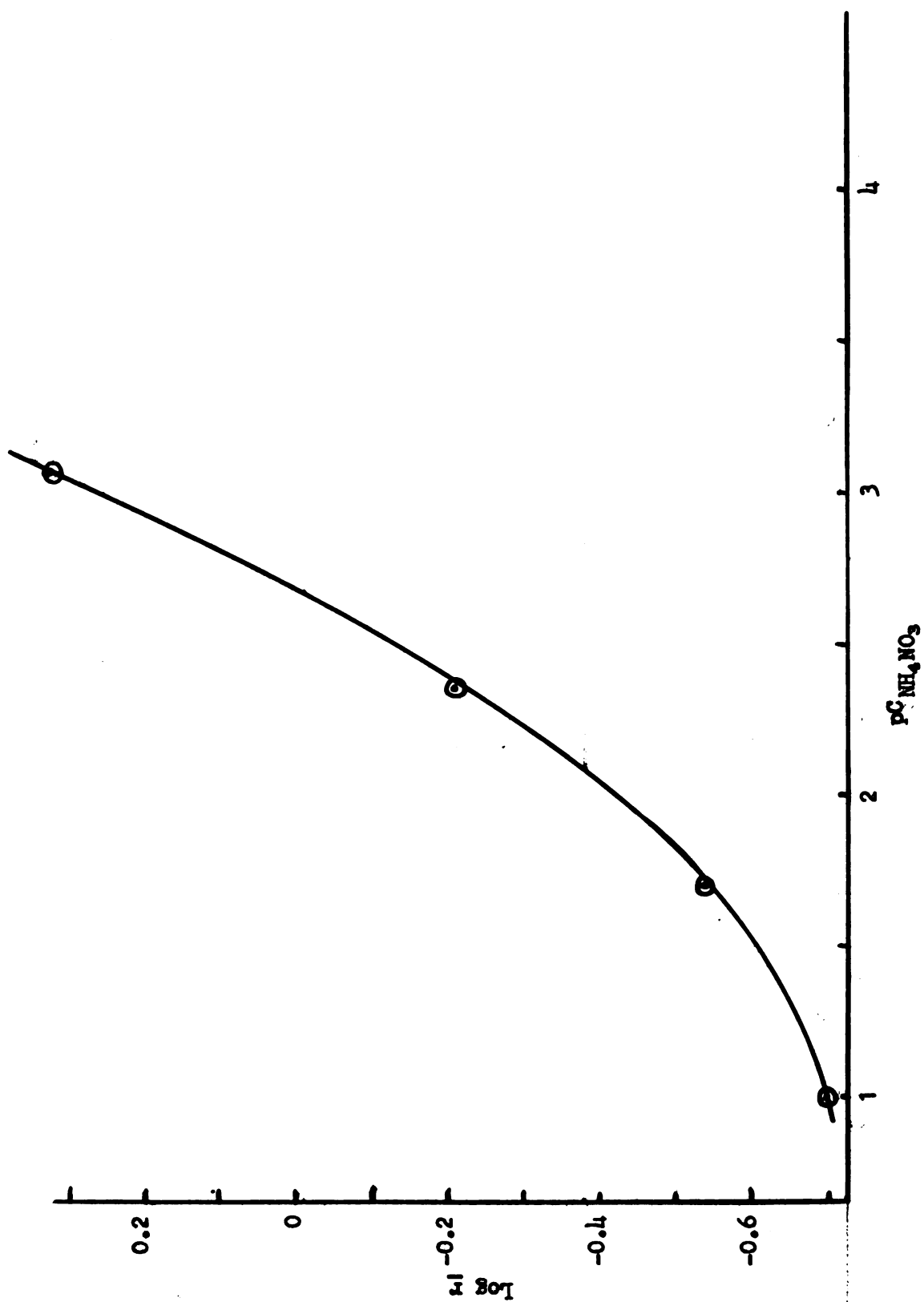


Figure 14. Log of Concentration of Ammonium Nitrate Versus $\text{Log } r$ of Phenolphthalein

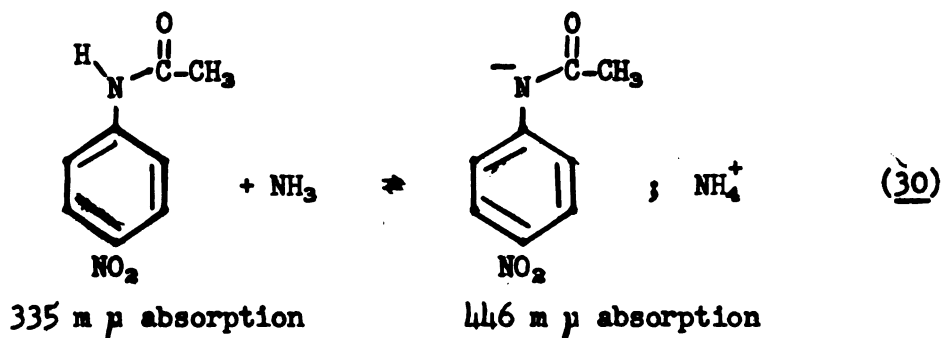
acids, and indeed from the structure of these compounds, amphiprotic behavior might reasonably be expected:



where R is the $\text{H}_2\text{N}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-$ or $\text{H}_2\text{N}-\overset{\text{NH}}{\underset{\parallel}{\text{C}}}-$ group. Evidence of the acidity of these two compounds in ammonia is that: (1) potassium salts can be prepared using potassium amide in ammonia, and (2) hydrogen is evolved when elemental potassium is used in the same reaction (64, 65).

The spectra of urea and methylsubstituted ureas in water show an absorption band in the far ultraviolet which shifts to longer wavelengths as the number of methyl groups substituted for hydrogens is increased (Figure 15). Because ammonia absorption bands occur in the region where these compounds absorb, direct spectrophotometric study of these compounds in solution is blocked. Indicators therefore have been used to investigate the acid-base properties of substituted ureas.

In a preliminary study, several indicators were selected on the basis of the difference in color which they display in acid and neutral ammonia solution. The simplest of these indicators is p-nitroacetanilide. Its yellow-green color in pure liquid ammonia is greatly intensified by the addition of potassium amide. p-Nitroacetanilide contains one acidic hydrogen atom in the molecule and presumably reacts with ammonia according to equation 18:



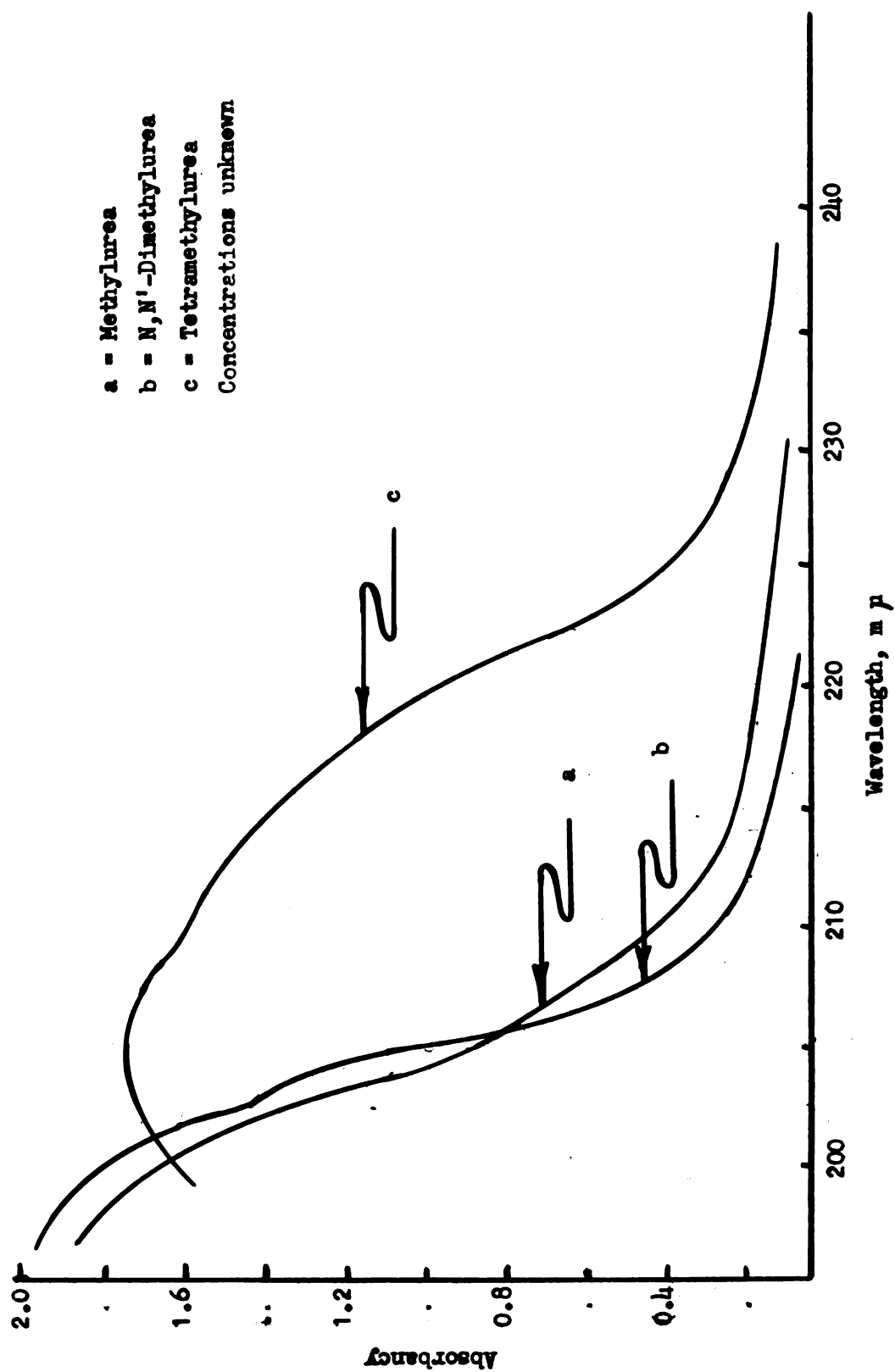


Figure 15. Absorption Spectra of Some Methylsubstituted Ureas in Water

The ultraviolet and visible spectrum of this indicator (Figure 16) shows bands at 335 m μ and 446 m μ which are attributed to the molecular acid species and the ammonium ion pair respectively. Ammonium perchlorate added to the solution depresses the band at 446 m μ and increases the 335 m μ band as would be expected from the equilibrium indicated in equation 12. (Figures 17 through 19). K_1 for this reaction was calculated (Table VI) by the method described in Appendix II and found to be 17. Such a large value of the equilibrium constant is not surprising in a medium as basic as ammonia where acidity is enhanced and ionization is extensive.

The extinction coefficients (Table VI) for molecular and ionized p-nitroacetanilide were calculated by the method described in Appendix II; the greater value for the molecular form explains why the absorption bands approach the same size even though the equilibrium favors the ammonium-anion pair.

By analogy to the behavior of phenols in water solutions, p-nitroacetanilide should have a rather large salt effect and this is observed. (Figure 20). This can be explained in terms of the thermodynamic equilibrium constant. The ionization constant for an indicator acid is

$$K_1 = \frac{[H^+; In^-]}{[HIn]} \cdot \frac{\gamma_{H^+; In^-}}{\gamma_{HIn}} \quad (31)$$

or

$$K_1 = K_1' \frac{\gamma_{H^+; In^-}}{\gamma_{HIn}} \quad (32)$$

where K_1' is the concentration ratio. If the ionic atmosphere changes--as by addition of a neutral salt--the activity coefficient factor in

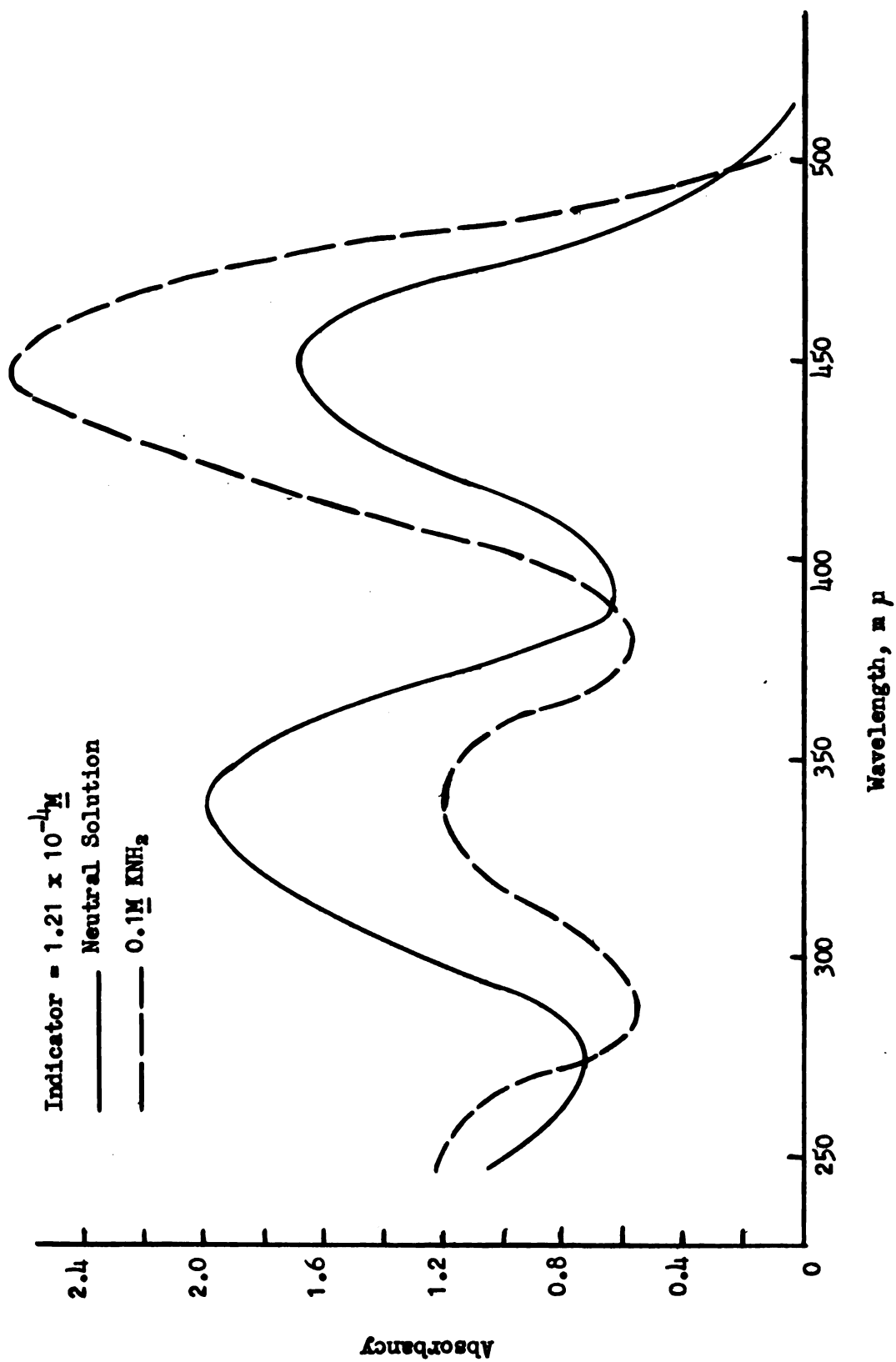


Figure 16. Absorption Spectra of p-Nitroacetanilide in Ammonia

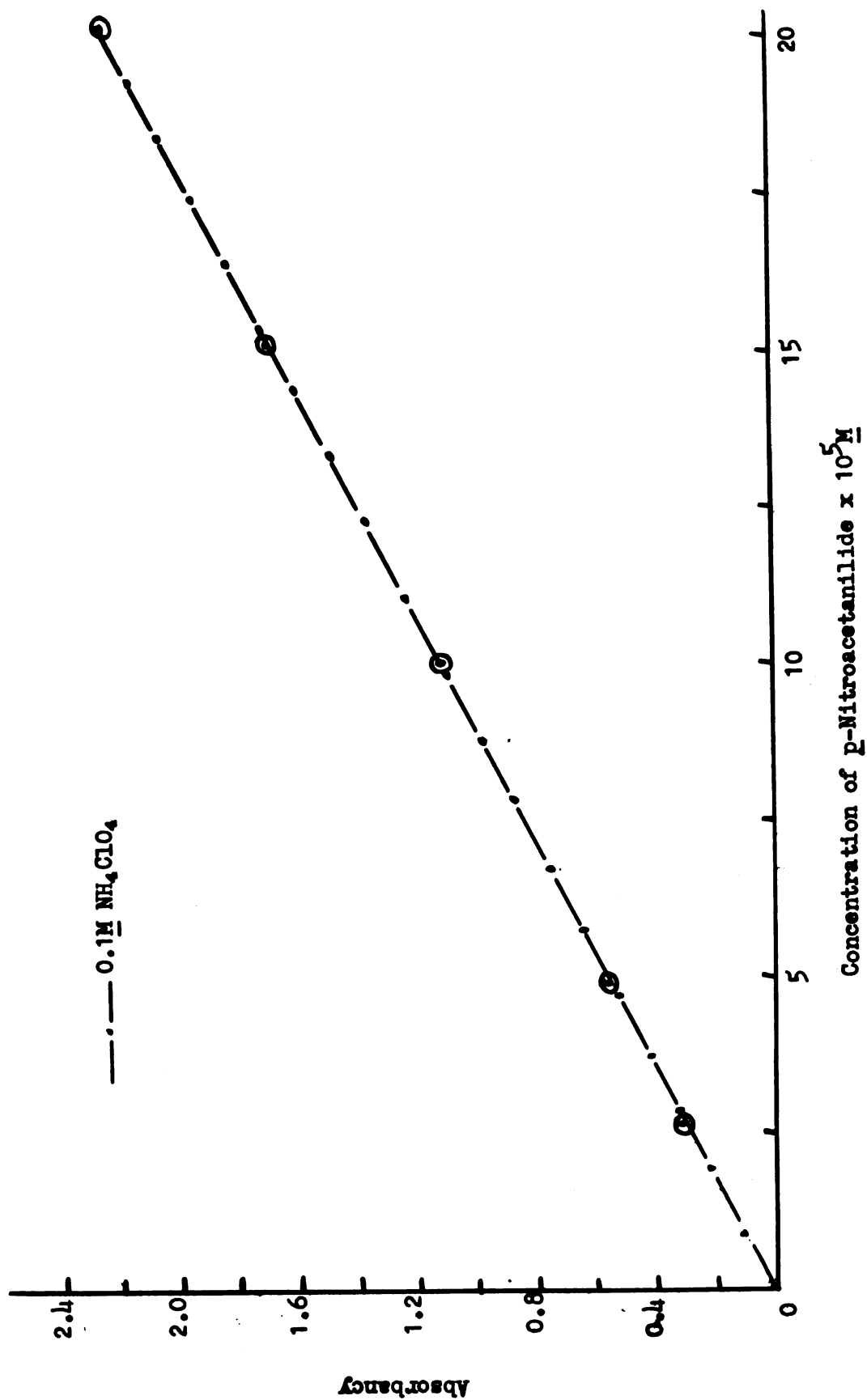


Figure 17. Absorbance Versus Concentration of p-Nitroacetanilide at 335 m μ

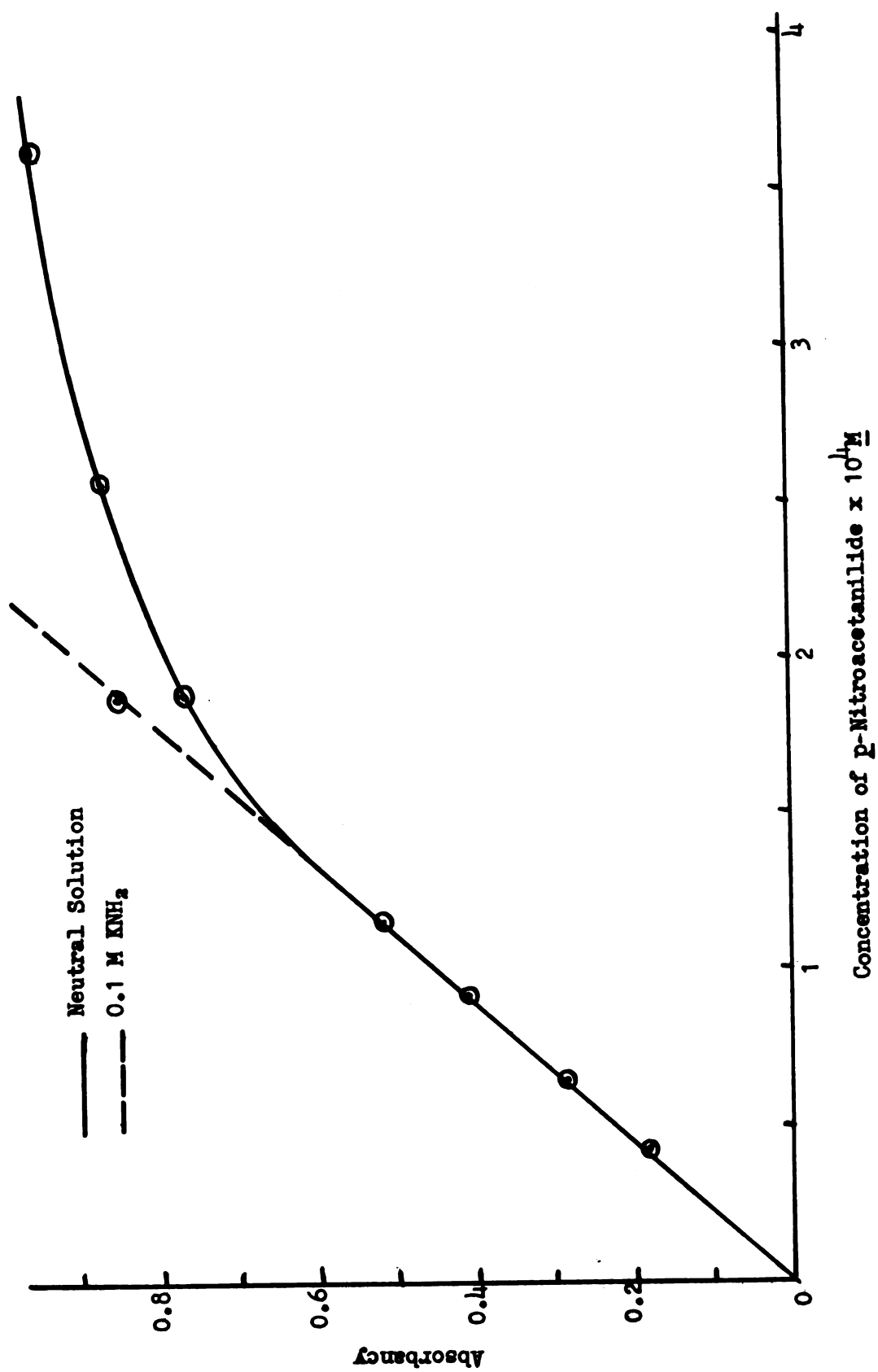


Figure 18. Absorbance Versus Concentration of p-Nitroacetanilide at 446 m μ

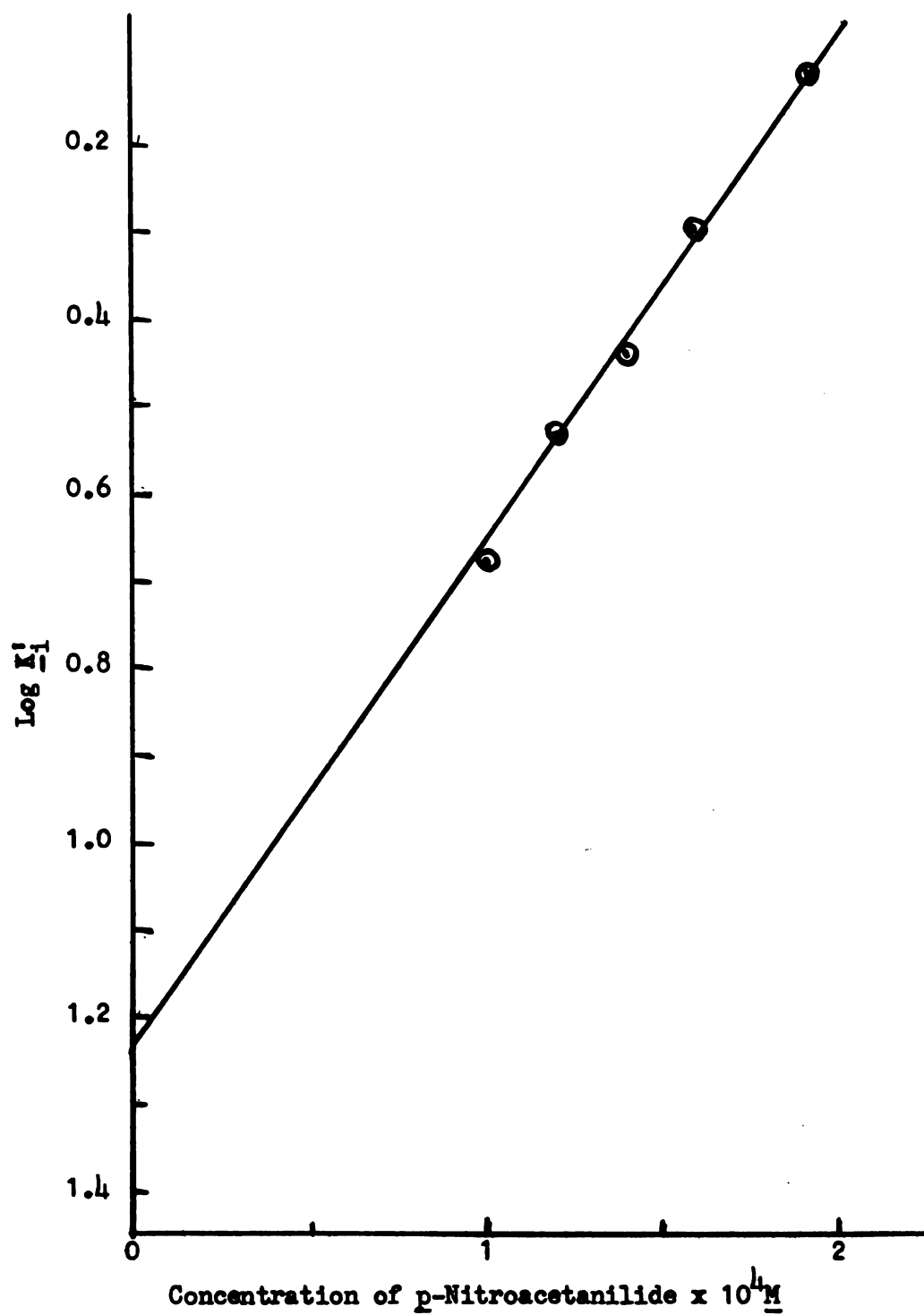


Figure 19. Log of K'_1 Versus Concentration of p-Nitroacetanilide at 44.6 m μ

TABLE VI

IONIZATION CONSTANTS AND EXTINCTION COEFFICIENTS FOR
VARIOUS INDICATORS IN AMMONIA AT -77°C

Indicator	Ionization Constant		Extinction Coefficient	
	Step	K_1		Wavelength m μ
p-Nitroacetanilide	K_1	17.0	1.07×10^4	335
			4.25×10^3	446
2,4-Dinitroacetanilide	K_1	1.59	1.80×10^4	385
	K_2	8.3×10^{-3}	1.55×10^4	535
Phenolphthalein	K_1	∞	5.86×10^4	575
	K_2	24.0		
Thymol Blue	K_1	∞	1.56×10^4	301
	K_2	0.42	1.25×10^4	390
	K_3	4.26×10^{-3}	7.60×10^5	620
Tropaeoline 00			6.67×10^4	276
			3.05×10^5	460
			1.57×10^5	590

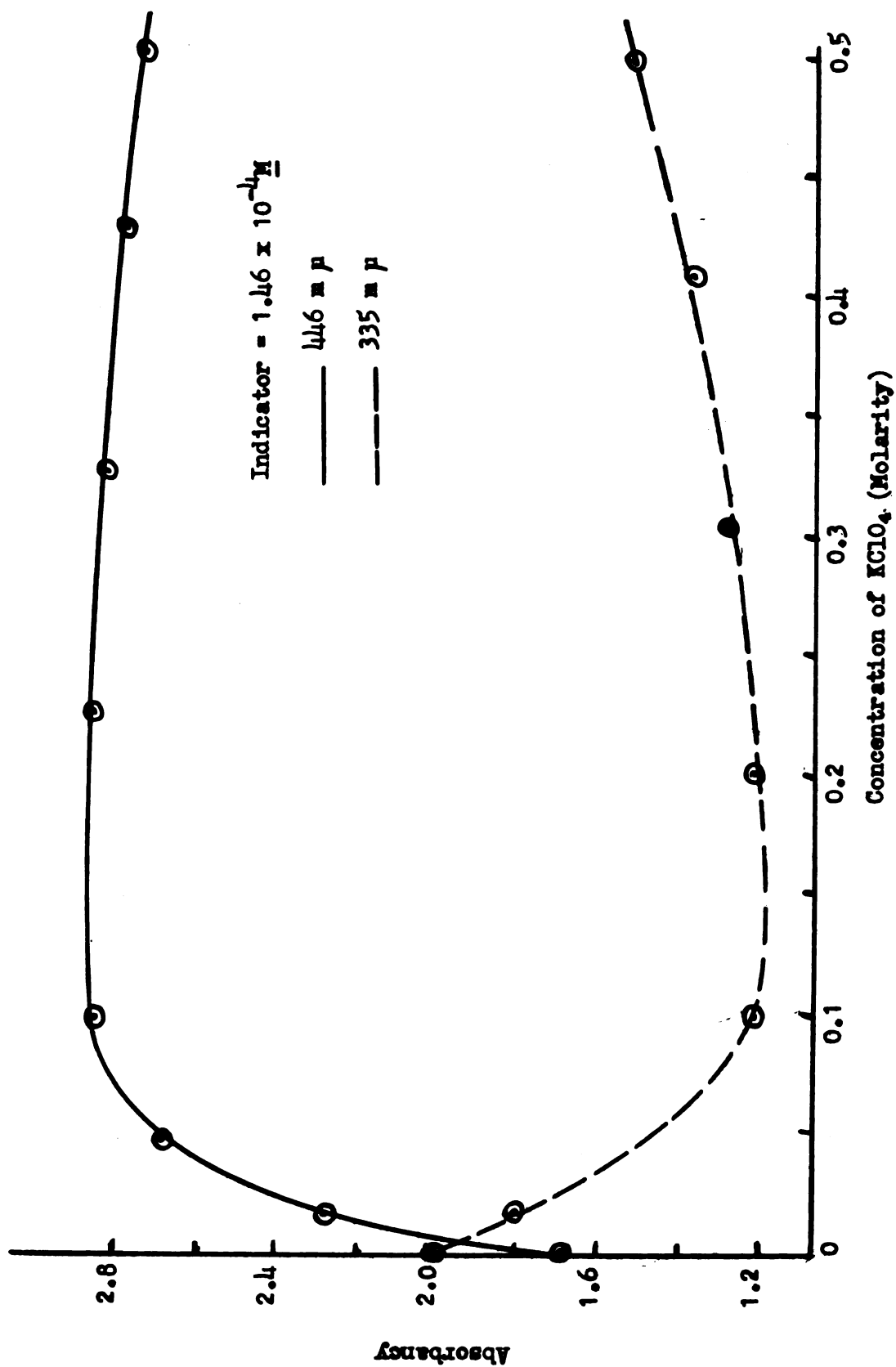


Figure 20. Absorbance of p-Nitroacetanilide Versus Concentration of Potassium Perchlorate

equation 32 decreases. As a result, K_1' must increase in order to maintain the equilibrium constant. The ionization of the indicator therefore increases; thus the concentration of ammonium ion pairs and free ions increases while the concentration of unionized acid decreases. The reaction can be pictured as one in which each ion or ion pair in the solution is surrounded by an ionic atmosphere arising in the following manner.

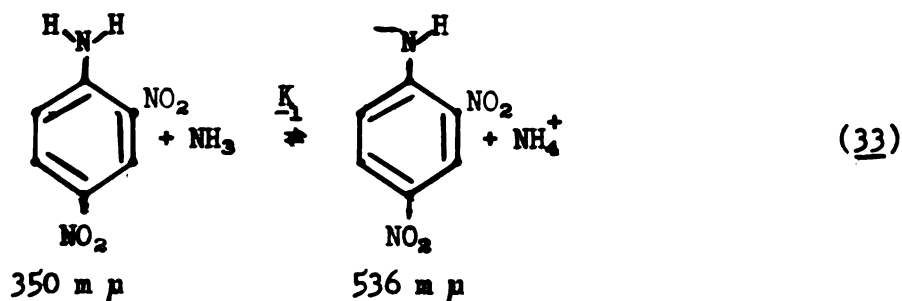
Consider a small volume element surrounding an indicator ion at a given point in the solvent. This volume element should have a net positive or negative charge, depending on the charge character of the central ion, and the probability of finding ions of opposite charge in the space surrounding a given ion is greater than the probability of finding ions of the same sign. Charge density in the ionic atmosphere decreases outward from the central ion and the net charge of the entire atmosphere is equal in magnitude but opposite in sign to the charge of the ion (65).

The ionic atmosphere is changed by addition of neutral salts. As the neutral salt density increases around an ammonium ion--indicator anion pair, it becomes increasingly favorable for dissociation to take place. Then in order for the equilibrium governing the indicator acid to be maintained, ionization of the acid molecule must increase and the absorbancy in turn changes. At the same time the charge density of the ionic atmosphere becomes greater in the solution and the potential

energy needed to separate charges becomes less. Thus, the same effect is achieved as results from increasing the dielectric constant of the solvent. At about 0.1M neutral salt, the absorbancy of p-nitroacetanilide at 446 m μ goes through a maximum and then begins to decrease at higher concentrations. At salt concentrations above those at which the Debye-Hückel expression (equation 4) no longer holds (i.e. above approximately 0.1M), the activity coefficients increase after passing through a minimum. Hence K_1' must then decrease. At these concentrations, the Onsager extension (24) must be applied in order to be in agreement with the observed data.

2,4-Dinitroaniline, an ammono analog of phenol, has more than one replaceable hydrogen. The monoalkali metal salts of this compound have been prepared (43) but the dialkali metal salts have not been isolated.

A neutral ammonia solution of 2,4-dinitroaniline is red, an acidic solution is orange, and a basic solution is yellow. The spectrum of a neutral solution of this indicator shows bands at 385 m μ and 536 m μ . The tailing off of the 385 m μ band into the visible region along with the decrease of the 536 m μ band upon addition of an ammonium compound results in the observed orange color in acidic medium (Figure 21). Also a new band arises in acidic solution at 350 m μ which masks the 385 m μ band above 0.02M in ammonium ion. The 385 m μ band persists in basic solution and may be attributed to the doubly-charged anion. The reactions which dinitroaniline are believed to undergo, together with the band assignments, are:



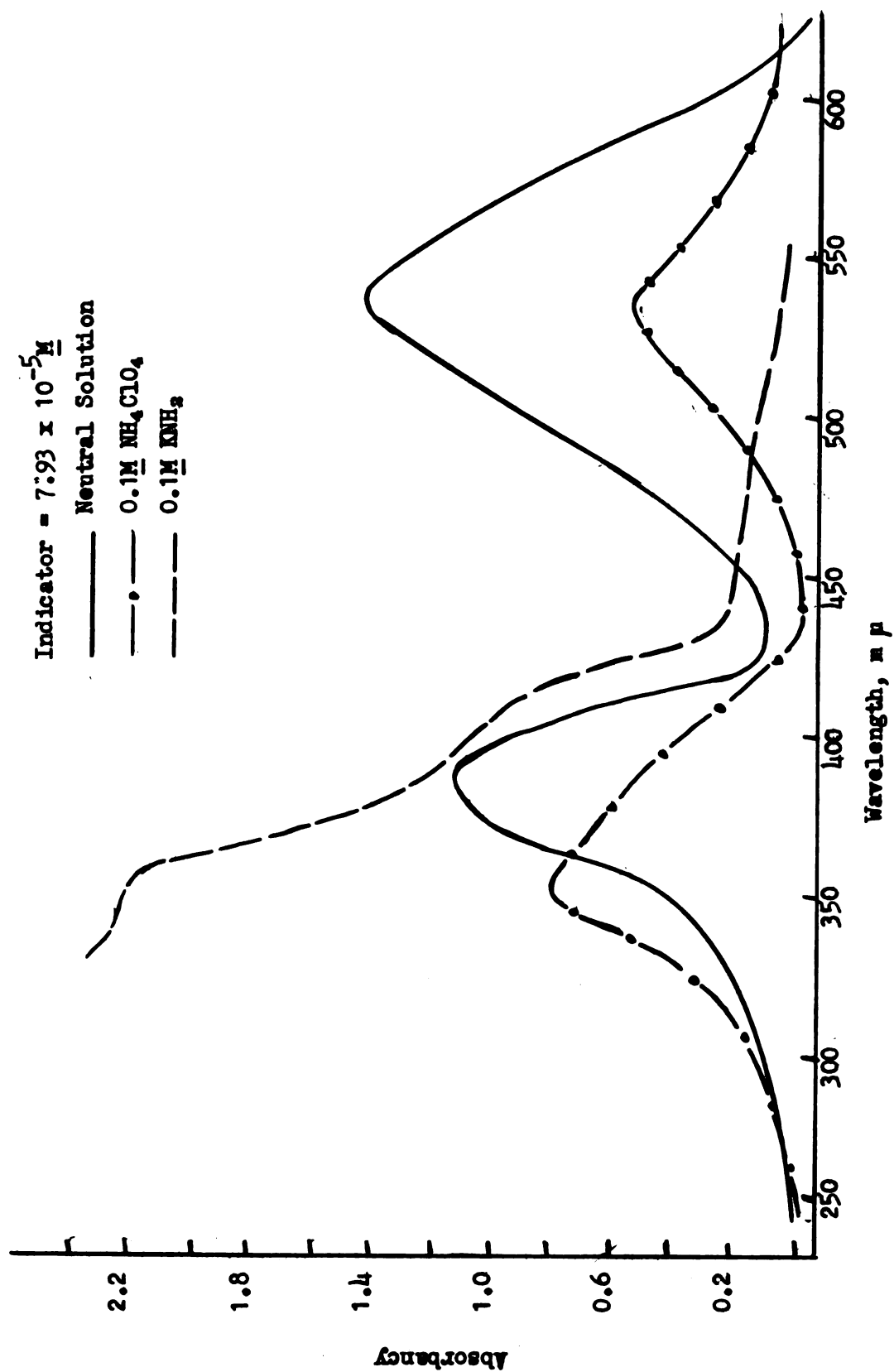
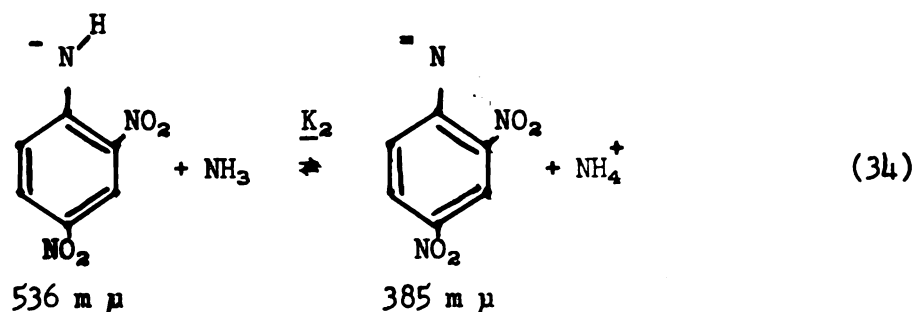


Figure 21. Absorption Spectra of 2,4-Dinitroaniline in Ammonia



The extinction coefficients for these species and the ionization constants for these reactions were calculated by the method of Appendix II from data of Figures 22-25. Results are reported in Table VI (page 54). K_1 for equation 33 shows that dinitroaniline is a strong acid and is largely converted to its red anion by the basic solvent. The small value of the equilibrium constant for the second ionization step (8.3×10^{-3}) and the fact that the extinction coefficients are nearly the same lends support to the absorption band assignments.

The salt effect upon 2,4-dinitroaniline is quite marked (Figure 26) as is expected. Because the ionic strength of the solution affects the absorbancy of this indicator, the total ion concentration (as a summation of concentrations of both ion pairs and solvated ions) was kept constant. Thus any change in the absorbancy was due to ammonium ions (Figure 27). In these solutions of constant ionic concentration, it was assumed as a first approximation that the dissociation constants of potassium salts are the same as the dissociation constants of the ammonium salts owing to the similarities of the cation sizes and charges. This assumption is supported by the conductivity work of Fuoss and Kraus (15).

The spectrum of phenolphthalein in ammonia is characterized by a single absorption band at $575 \text{ m } \mu$ (Figure 28) and is similar to the spectrum obtained from this indicator in basic water solution which has

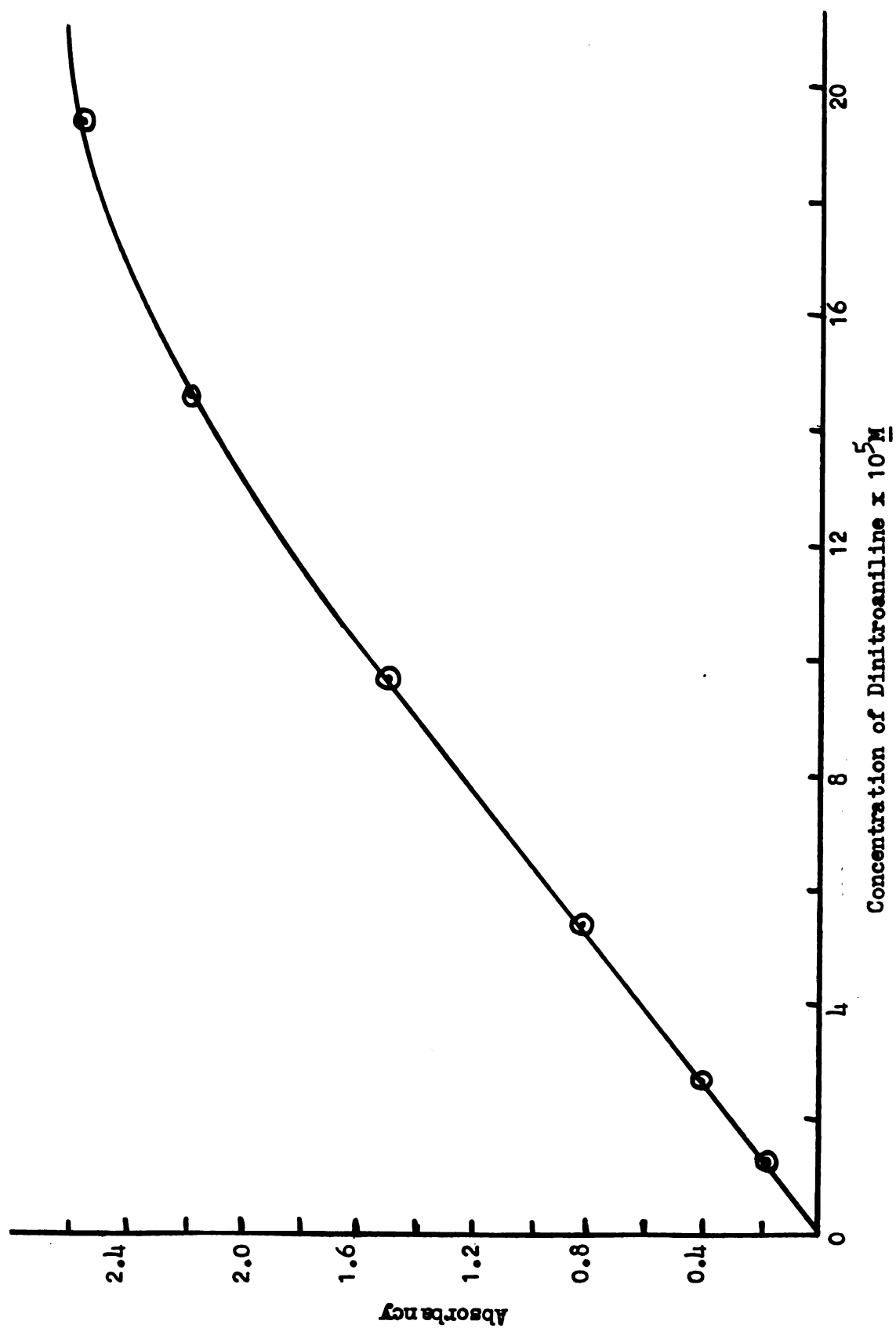


Figure 22 . Absorbance Versus Concentration of Dinitroaniline at 536 m μ

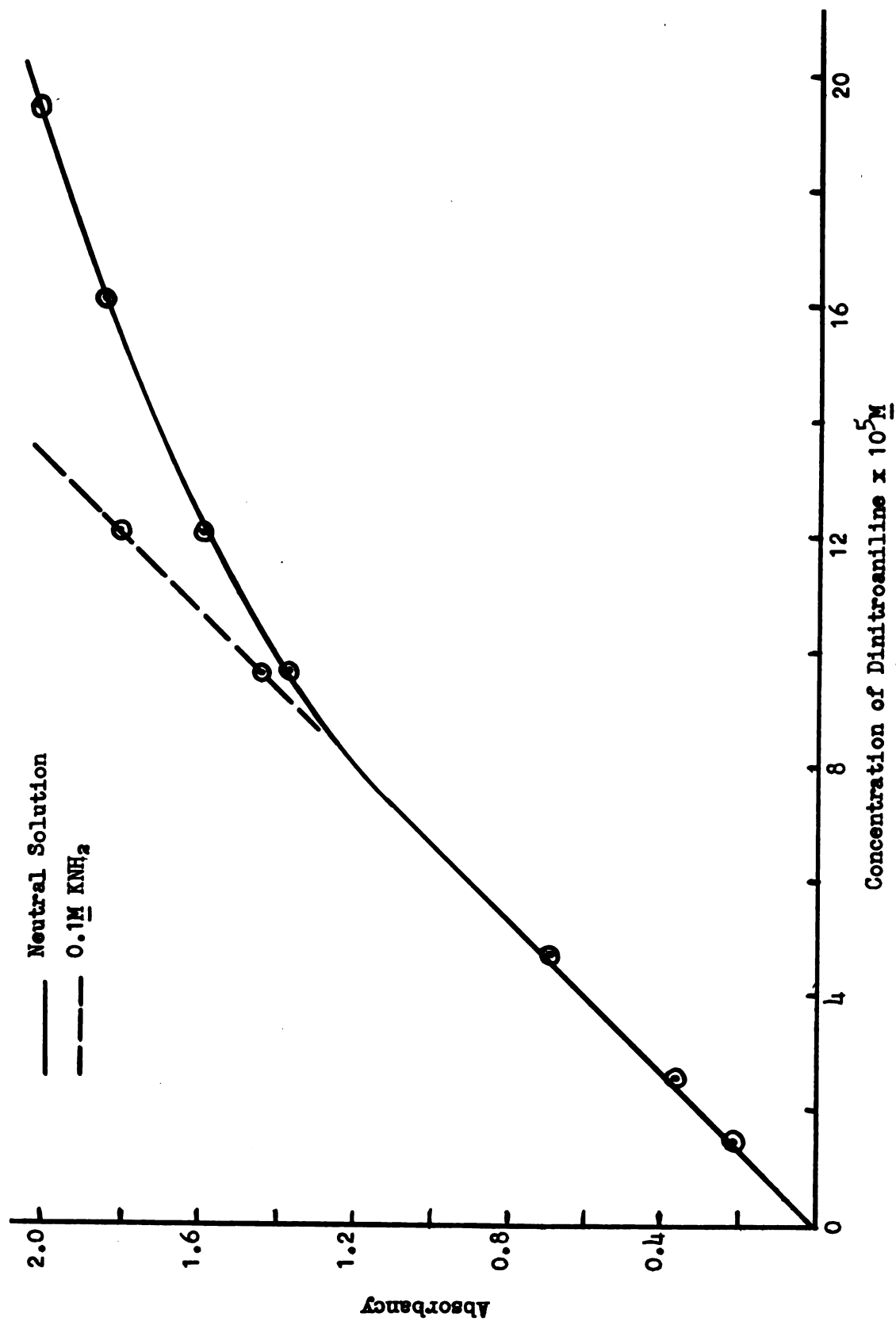


Figure 23. Absorbance Versus Concentration of Dinitroaniline at 385 m μ

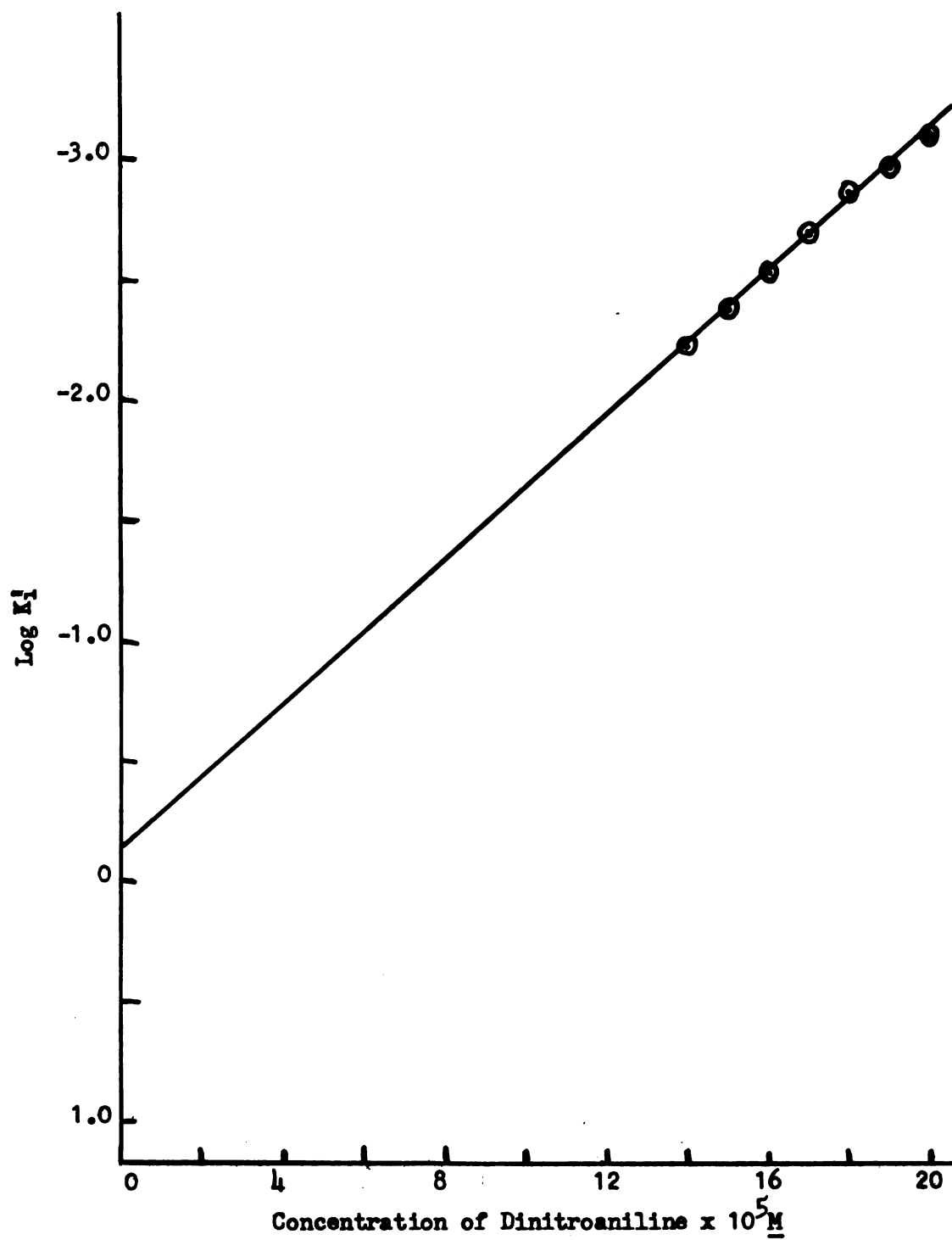


Figure 24. $\text{Log } K'_1$ Versus Concentration of Dinitroaniline at 536 m μ

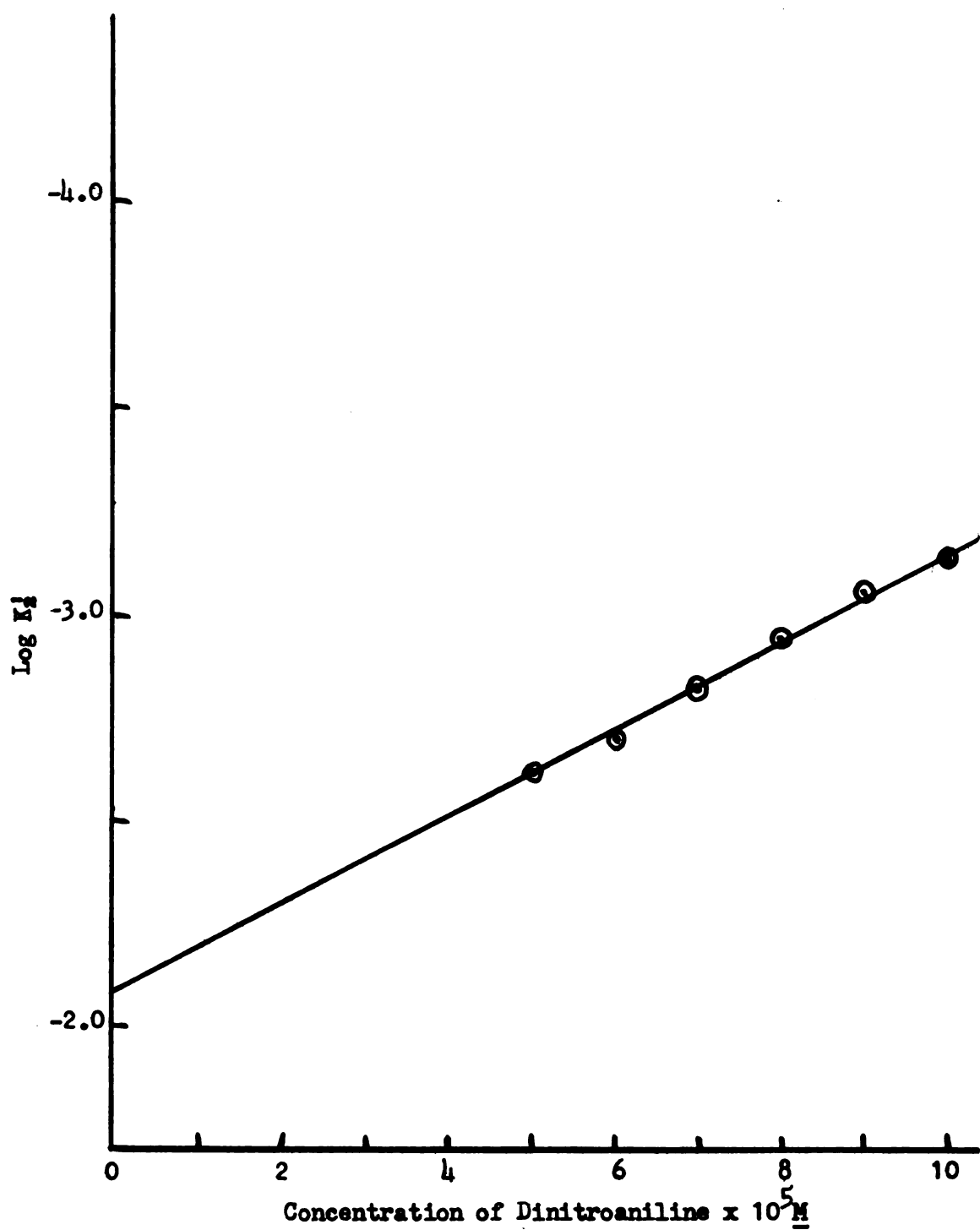


Figure 25. $\text{Log } K'_2$ Versus Concentration of Dinitroaniline at 385 m μ .

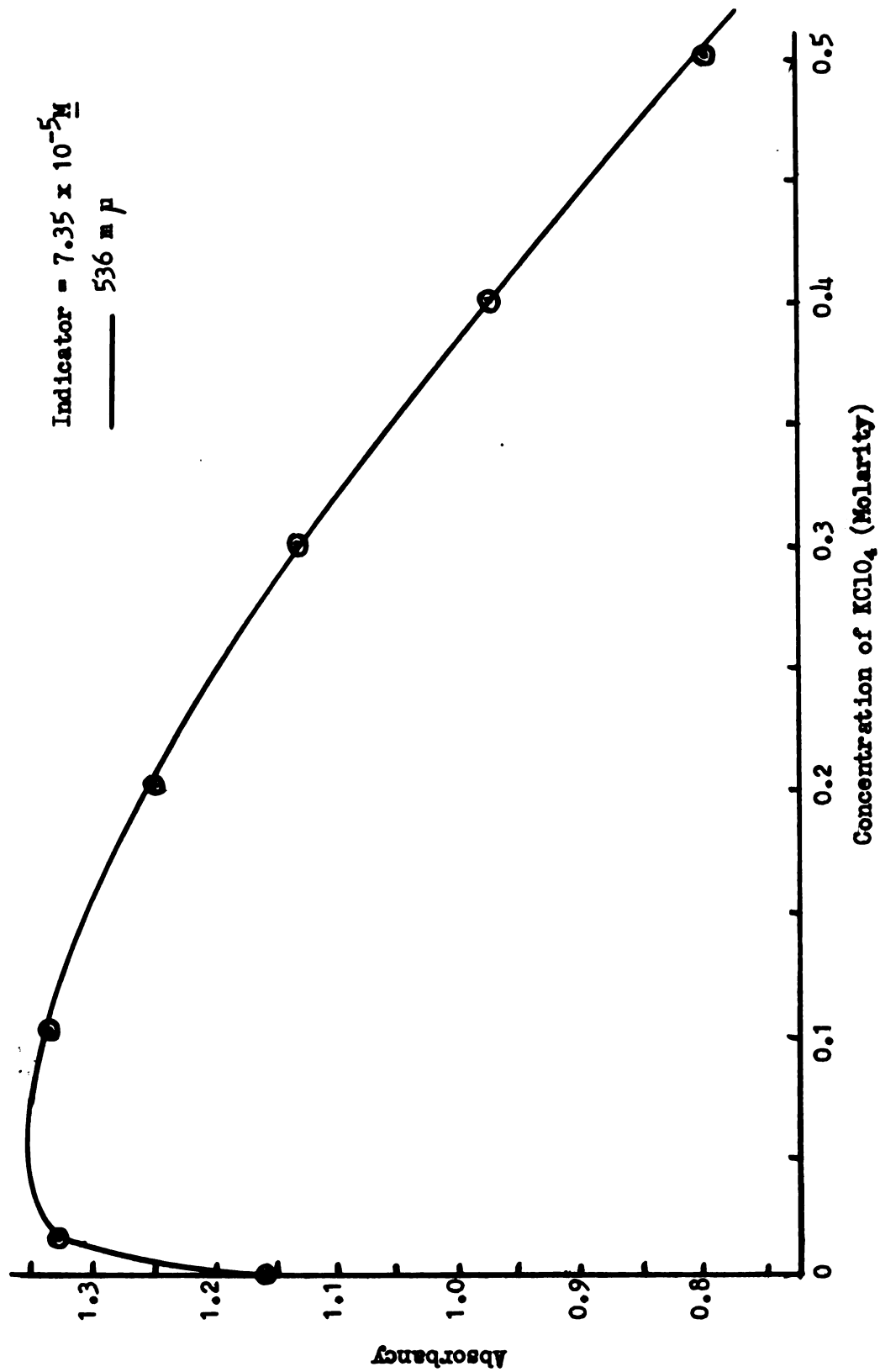


Figure 26. Absorbance of Dinitroaniline Versus Concentration of Potassium Perchlorate

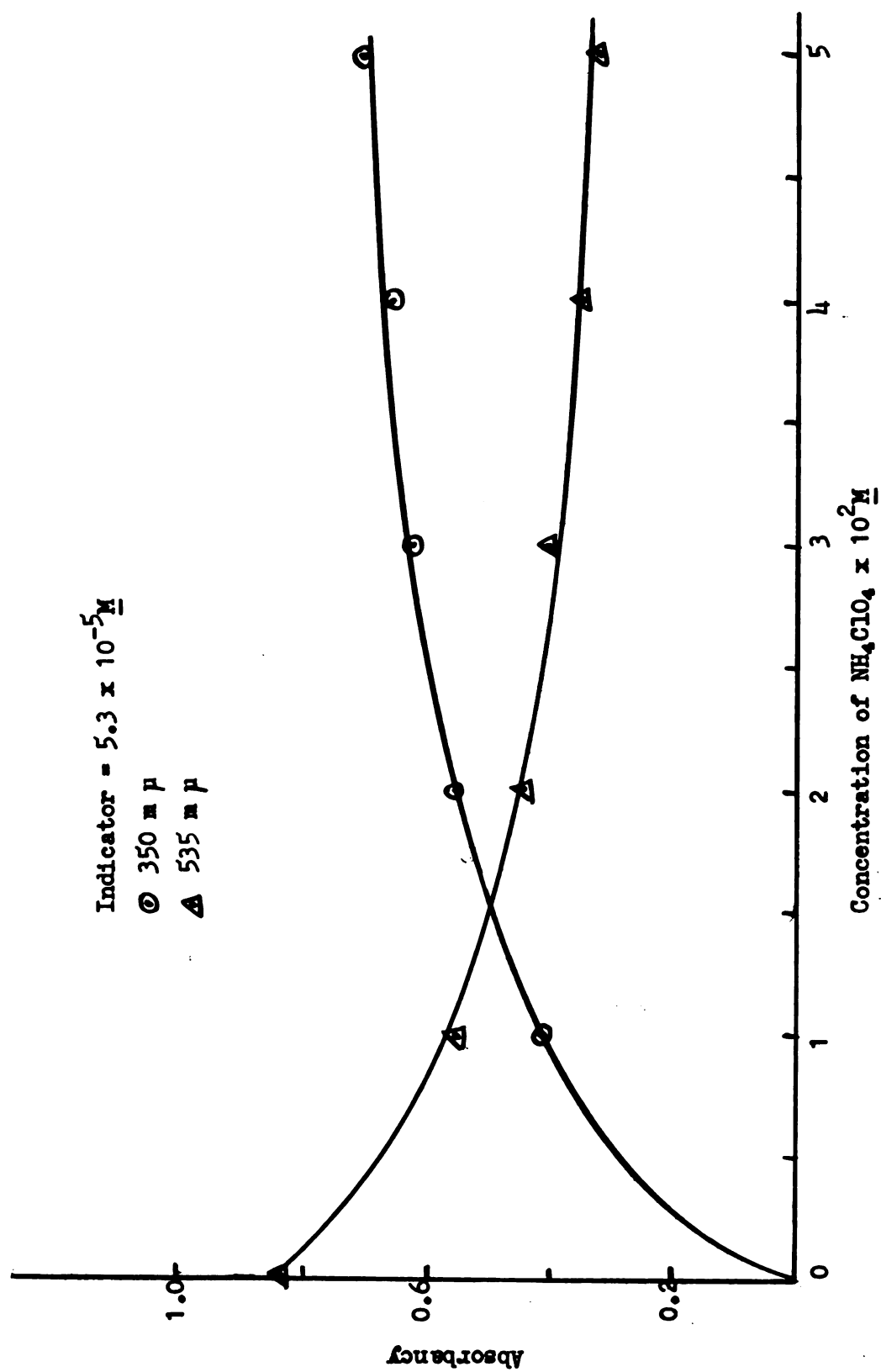


Figure 27. Absorbance of Dinitroaniline Versus Ammonium Perchlorate at Constant Ionic Concentration

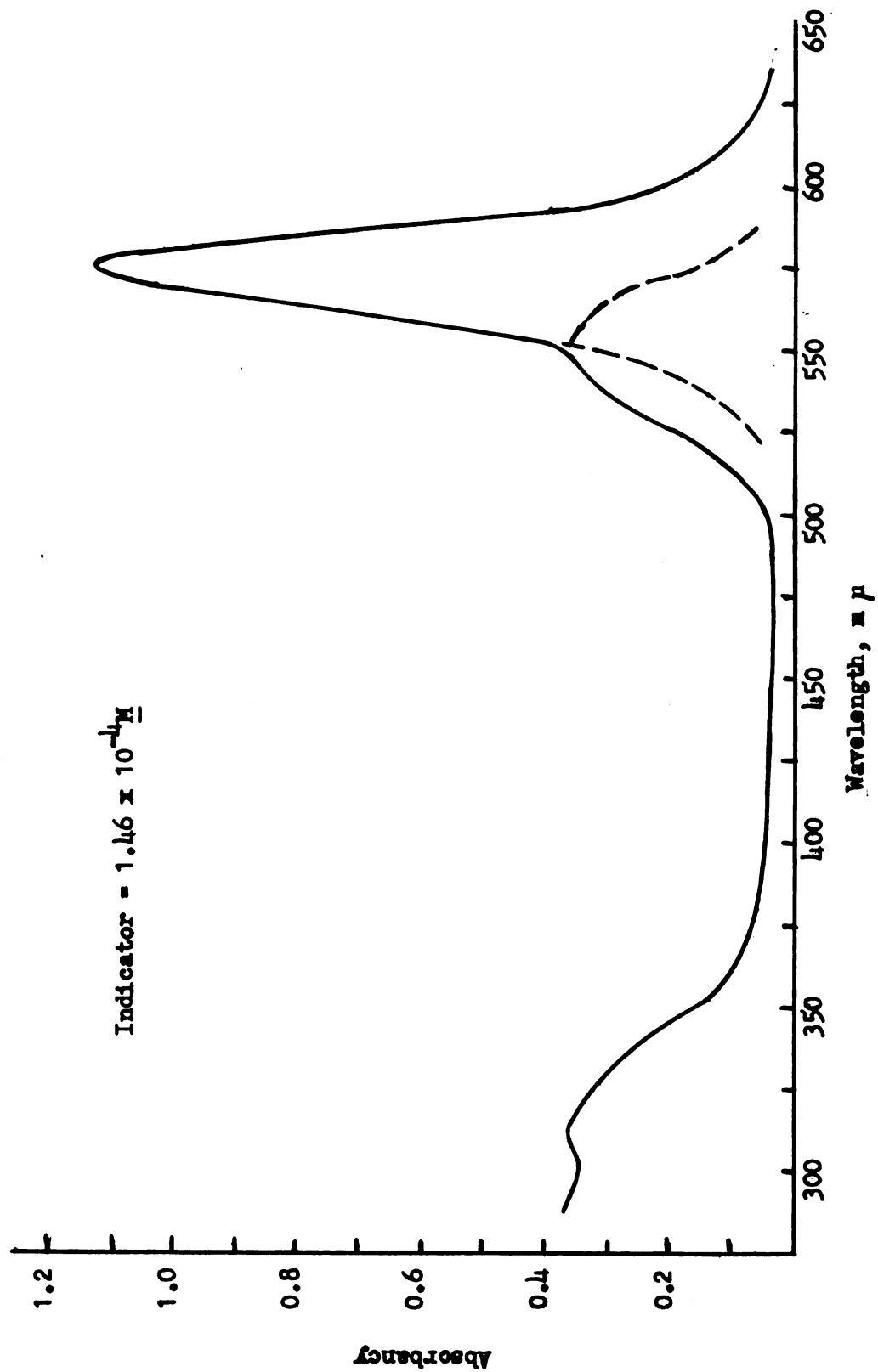
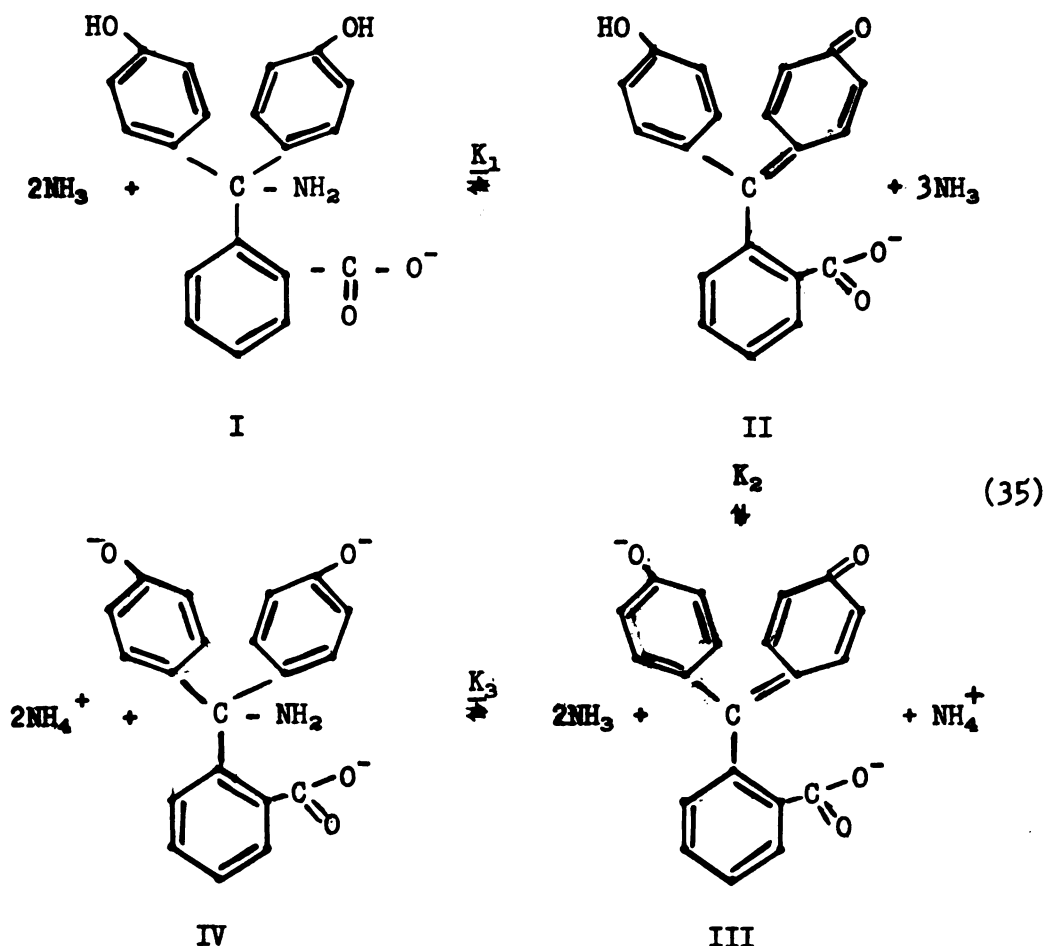


Figure 28. Absorption Spectrum of Phenolphthalein in Ammonia

a single band at 560 m μ (Figure 29). The shift resulting from solvent change can be explained in terms of the structure of the molecule.

The indicator acid, obtained from stock in the lactone form, undergoes ring opening in the presence of base to yield a carbinol form in water or an amide form in aqueous ammonia. It is proposed that phenolphthalein in anhydrous ammonia exists as the amide form (I) in equilibrium with structures II, III, and IV:



The formation of I apparently proceeds as rapidly as solution occurs and the immediate formation of II gives the solution its characteristic purple color. As base (i.e. potassium amide) is added, the color intensifies. A shift to III is indicated since it has a higher

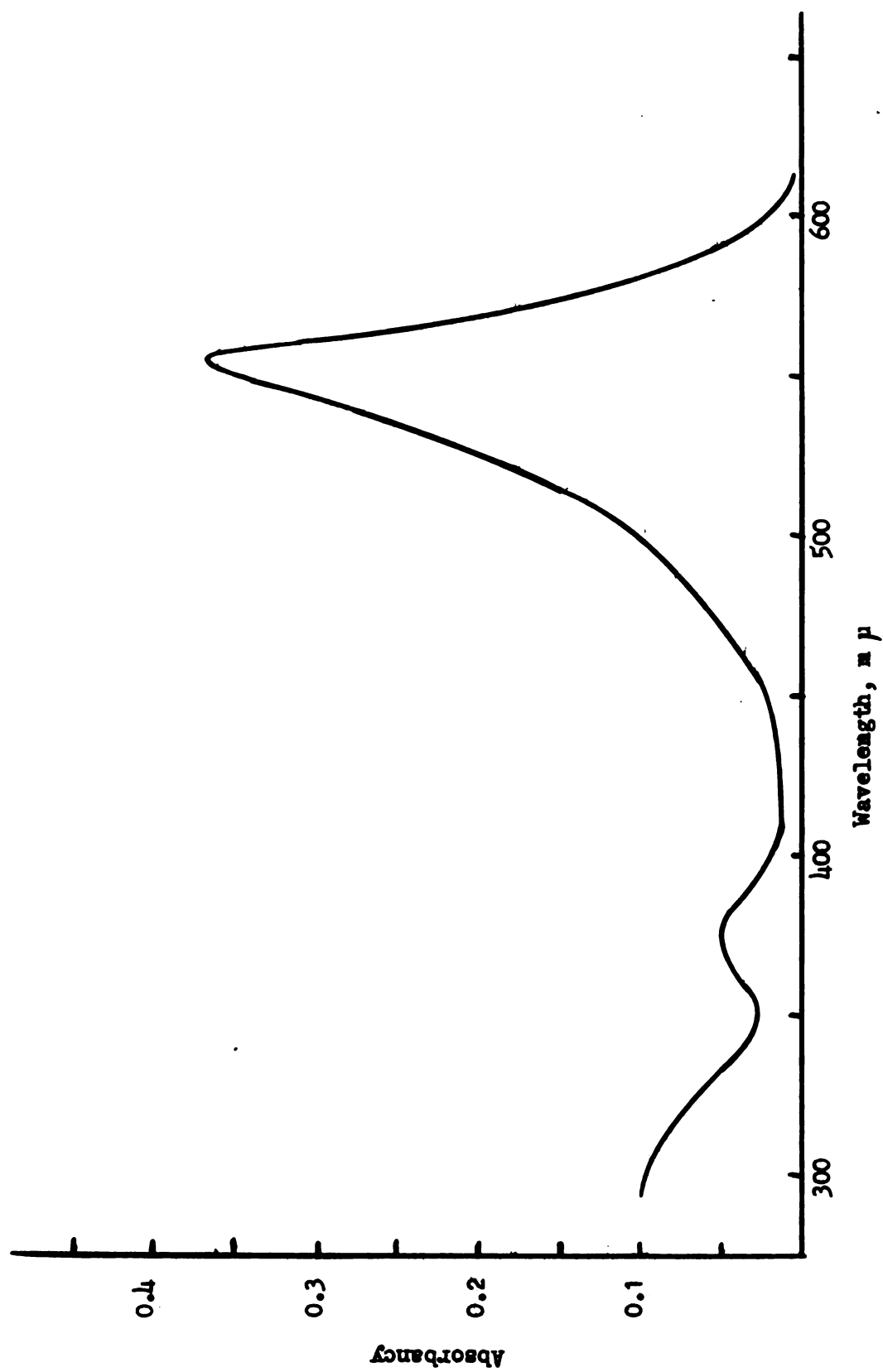


Figure 29. Absorption Spectrum of Phenolphthalein in Aqueous Ammonia

extinction coefficient than II. As the addition of base is increased, the solution turns colorless as IV is formed. With the addition of ammonium ion to the neutral purple solution, the color turns light pink but never disappears entirely. Since absorption bands are by nature symmetrical (66), presumably there are two bands present in this region (dotted lines, Figure 28). The small hump observed at the lower wavelength of the large absorption band can be attributed tentatively to form II which may well have a smaller extinction coefficient than form III because of its electronic structure. The extinction coefficient for the 575 m μ band (Figures 30-32) calculated by the method in Appendix II is 5.86×10^4 , which is in good agreement with 7.7×10^4 calculated by Lagowski (29) using a different method. Franklin observed (57) ammonia solutions of phenolphthalein to be colorless at room temperature, whereas this study shows that ammonia solutions of this indicator have a distinctive purple color at -77°C . As the temperature is raised, the color gradually changes to a light pink at the boiling point of ammonia, and as the solution is allowed to warm to room temperature in sealed tubes, the color disappears completely. The loss of color occurs in the vicinity of -10°C , the exact temperature depending upon the concentration of indicator present. If the first reaction in equation 35 represents the equilibrium in question, it can be seen that increasing the temperature should shift the position of equilibrium to the left in the following manner. Since there is no separation of charge in this reaction, the equilibrium constant should be little affected by temperature. On the other hand, if this process consists of two steps, the equilibrium constant should vary with temperature, as was found to be the case (Figures 33-35, Table VII). Presumably the equilibrium measured spectrophotometrically is that represented by K_2 in

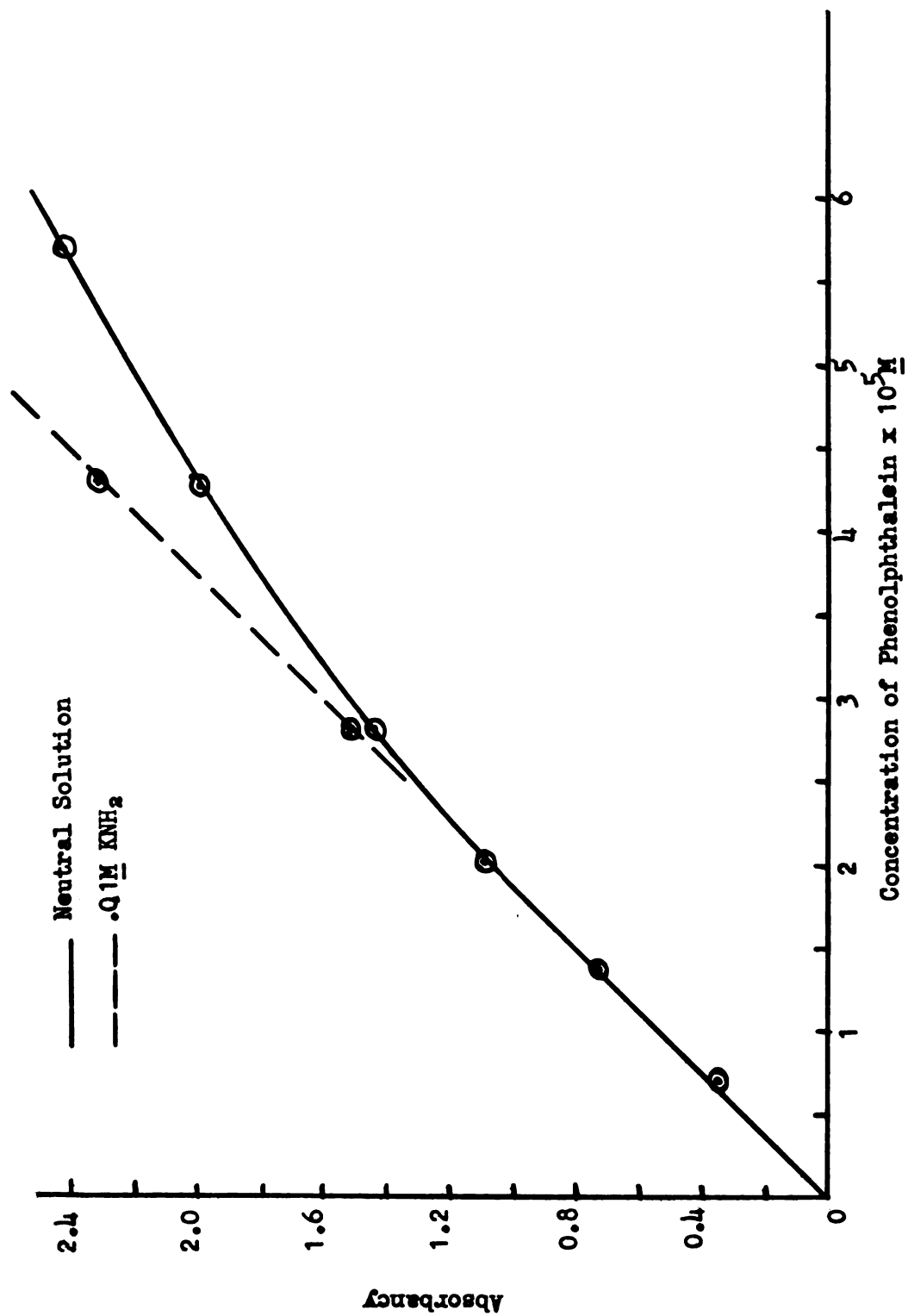


Figure 30. Absorbance Versus Concentration of Phenolphthalein at 575 m μ and -77°C

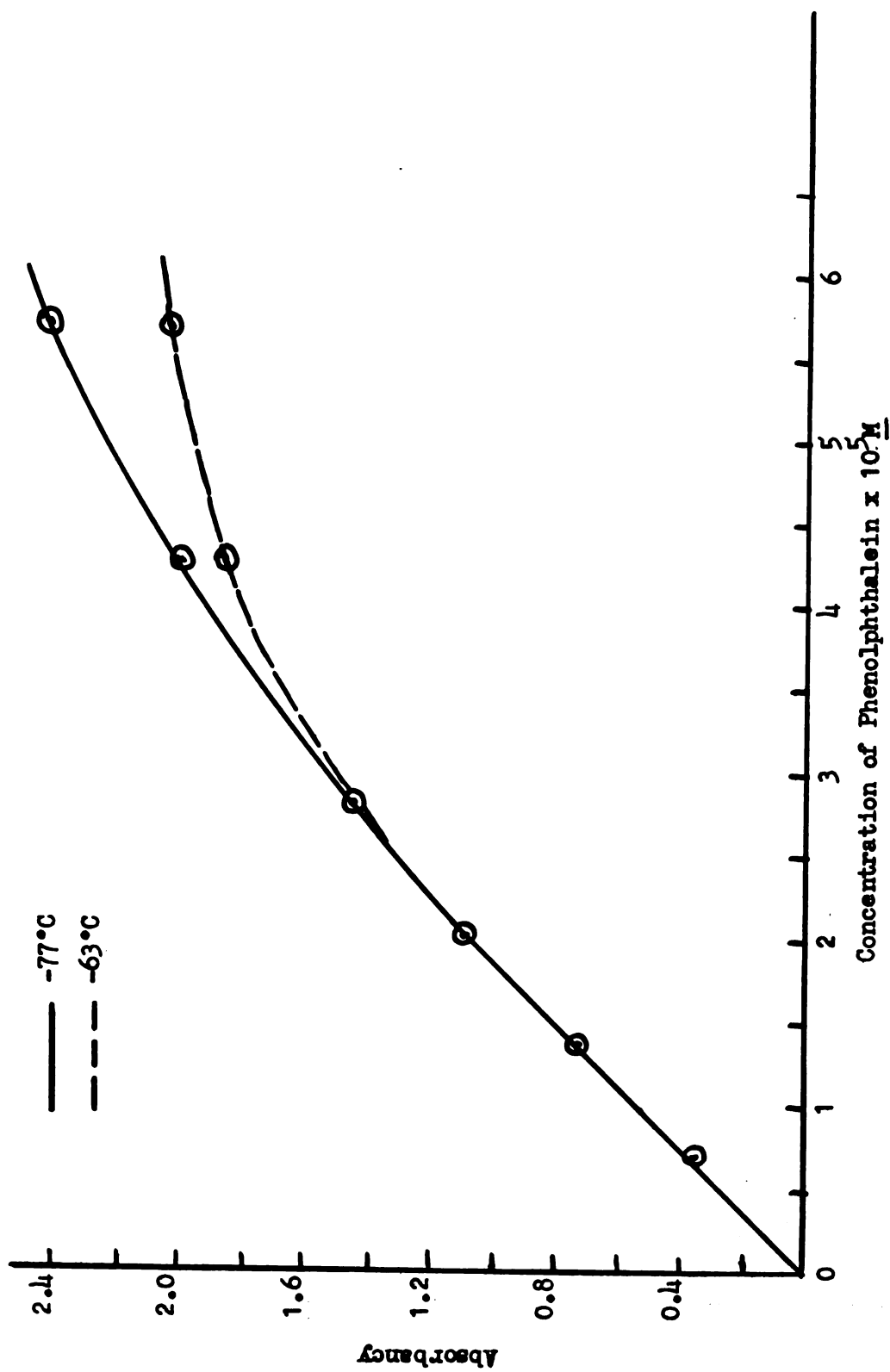


Figure 31. Absorbance Versus Concentration of Phenolphthalein at 575 m μ

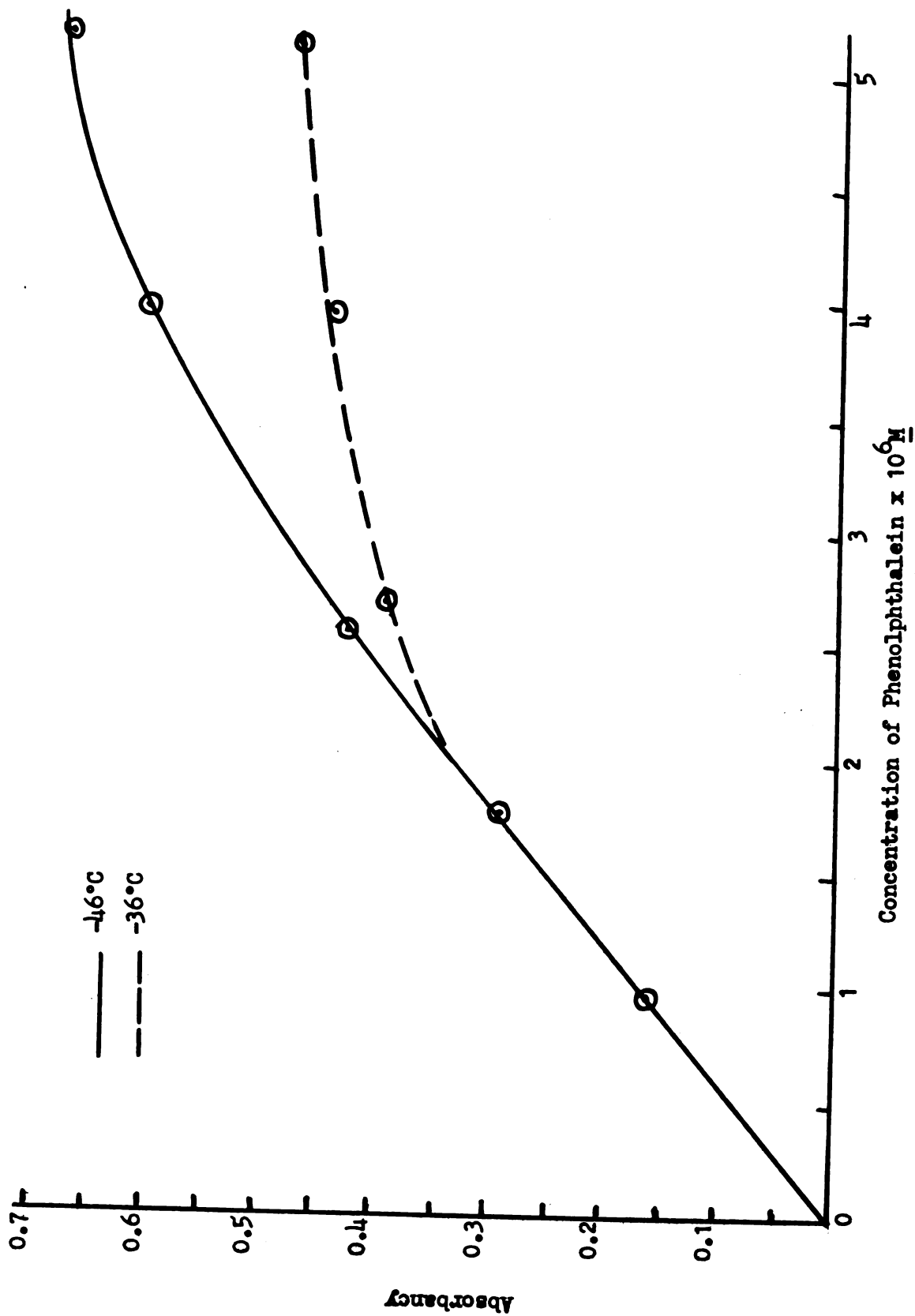


Figure 32. Absorbance Versus Concentration of Phenolphthalein at 575 m μ

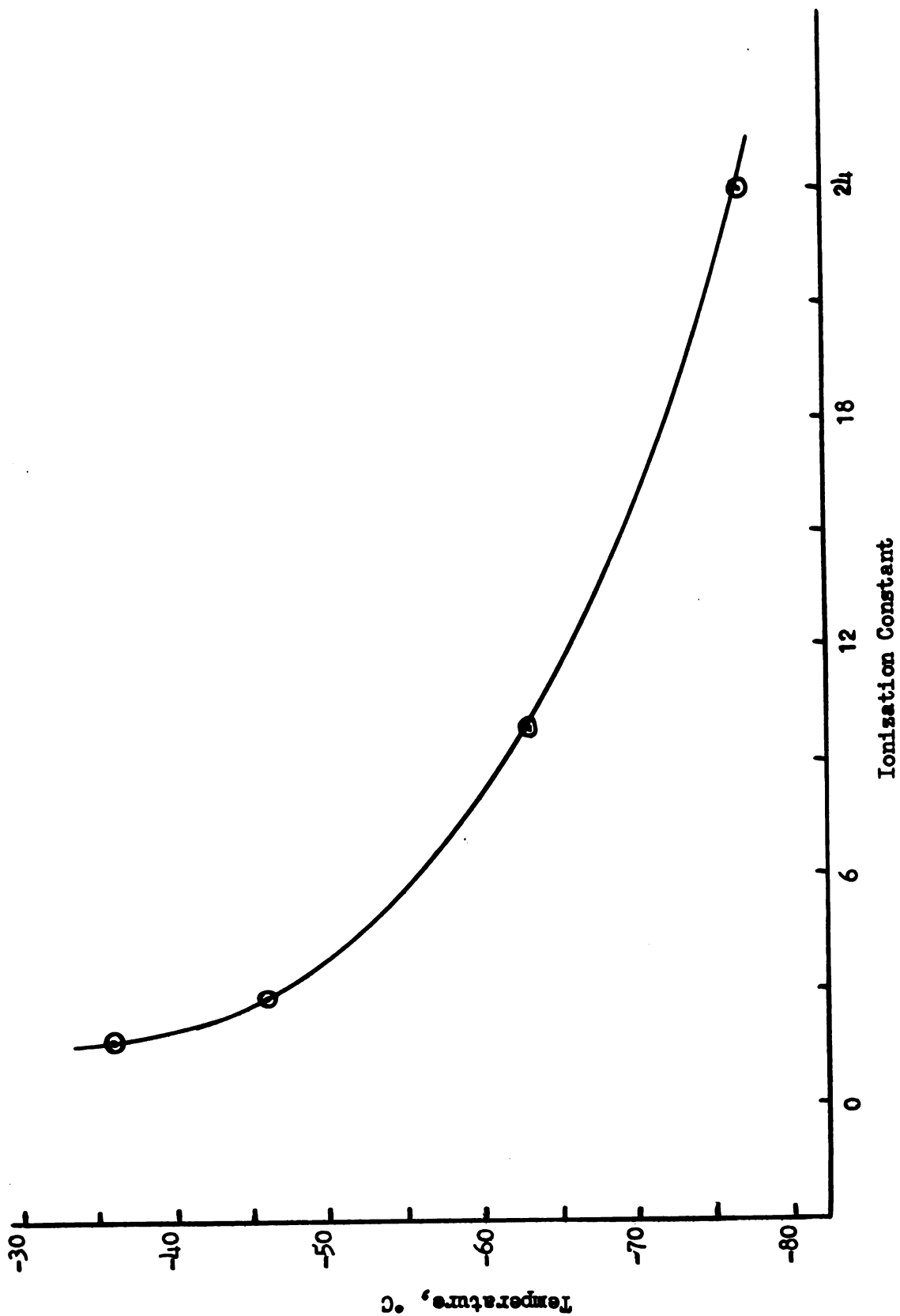


Figure 33. The Constant K_a Versus Temperature for Phenolphthalein

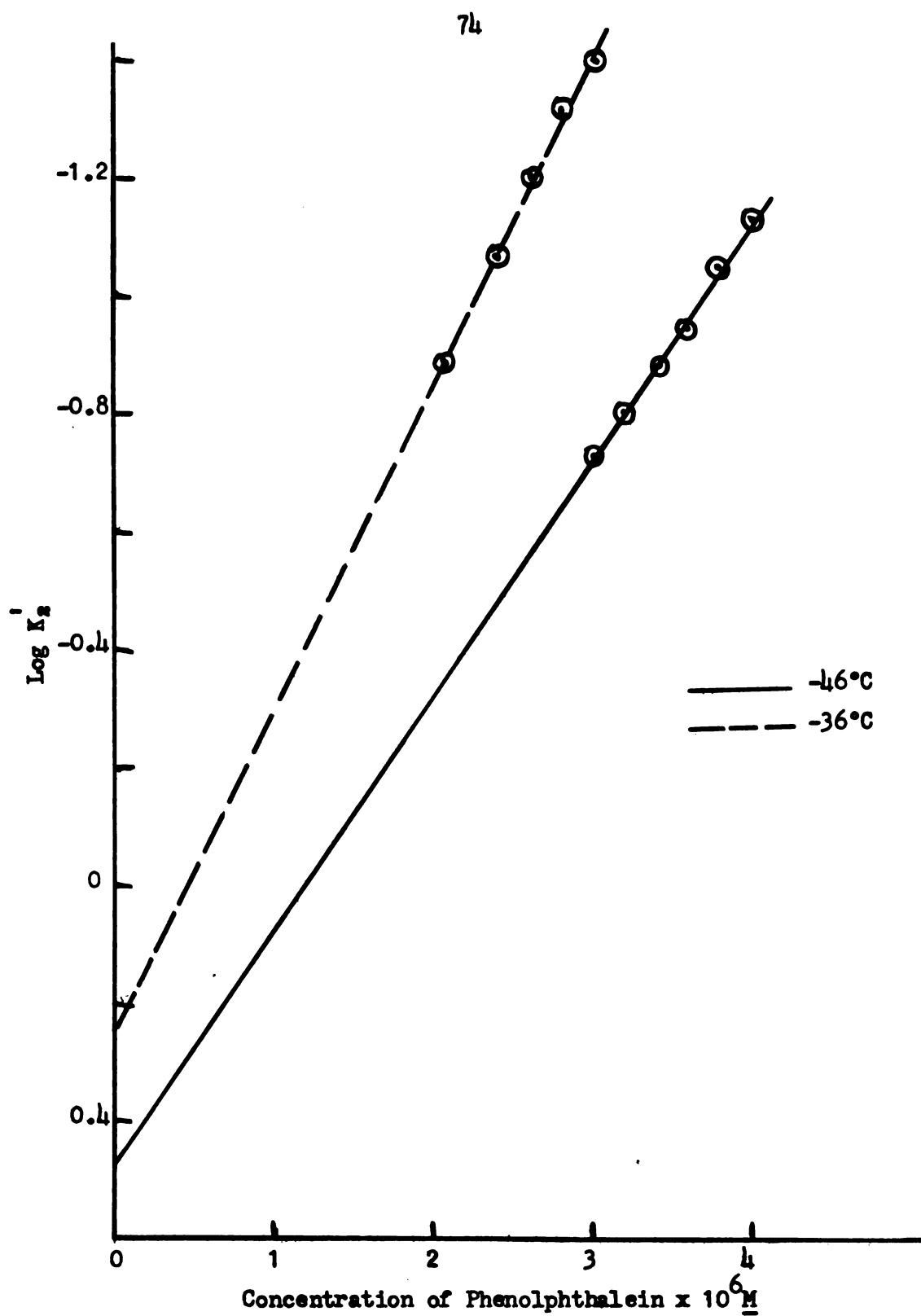


Figure 34. Log K_2' Versus Concentration of Phenolphthalein at 575 m μ .

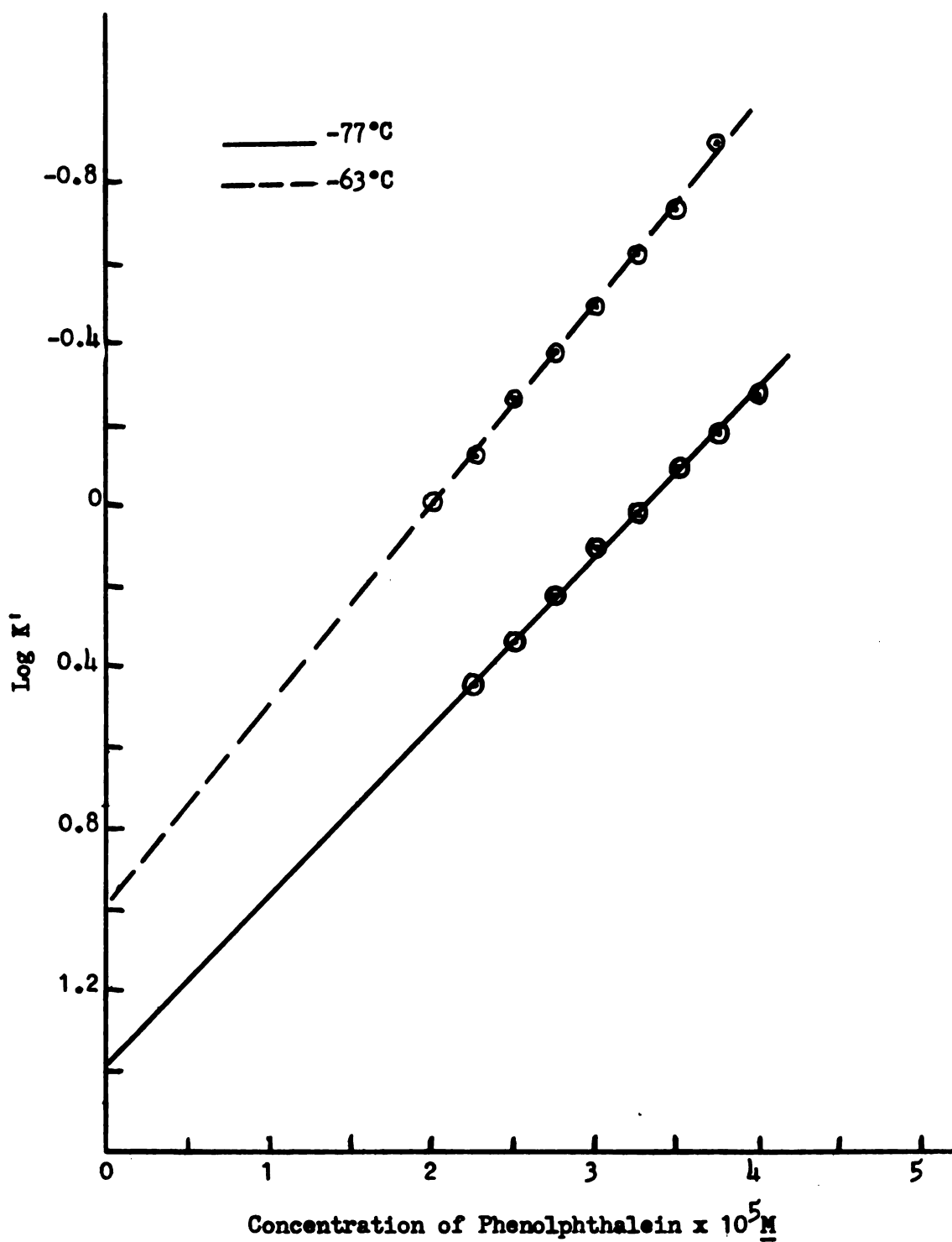


Figure 35. Log K' Versus Concentration of Phenolphthalein
at 575 m μ

TABLE VII

IONIZATION CONSTANTS OF PHENOLPHTHALEIN AT VARIOUS TEMPERATURES

Temperature °C	Log K_2	K_2
-36	0.225	1.69
-46	0.470	2.95
-63	0.991	9.80
-77	1.380	24.0

equation 35. As the temperature is raised, form III is converted to II and the equilibrium represented by K_1 is in turn shifted to the left, resulting in production of a colorless species.

The salt effect upon phthalein indicators is quite pronounced in water solution (58) and this is also observed with phenolphthalein in ammonia. As seen in Figure 36 and 37, the effect of the neutral salts depends upon the anion more than the cation. This is attributed to the greater polarizability of the anion and its subsequent effect upon ion pairing and dissociation constants.

The indicators so far discussed change color in acidic solutions. Such indicators can be used to measure the acid strengths of compounds which contain an ammonium ion or produce an ammonium ion by solvolysis. Even though thiourea and its methyl-substituted derivatives are bases in water, these compounds are acids in liquid ammonia and ammonolyze to form ammonium ions.

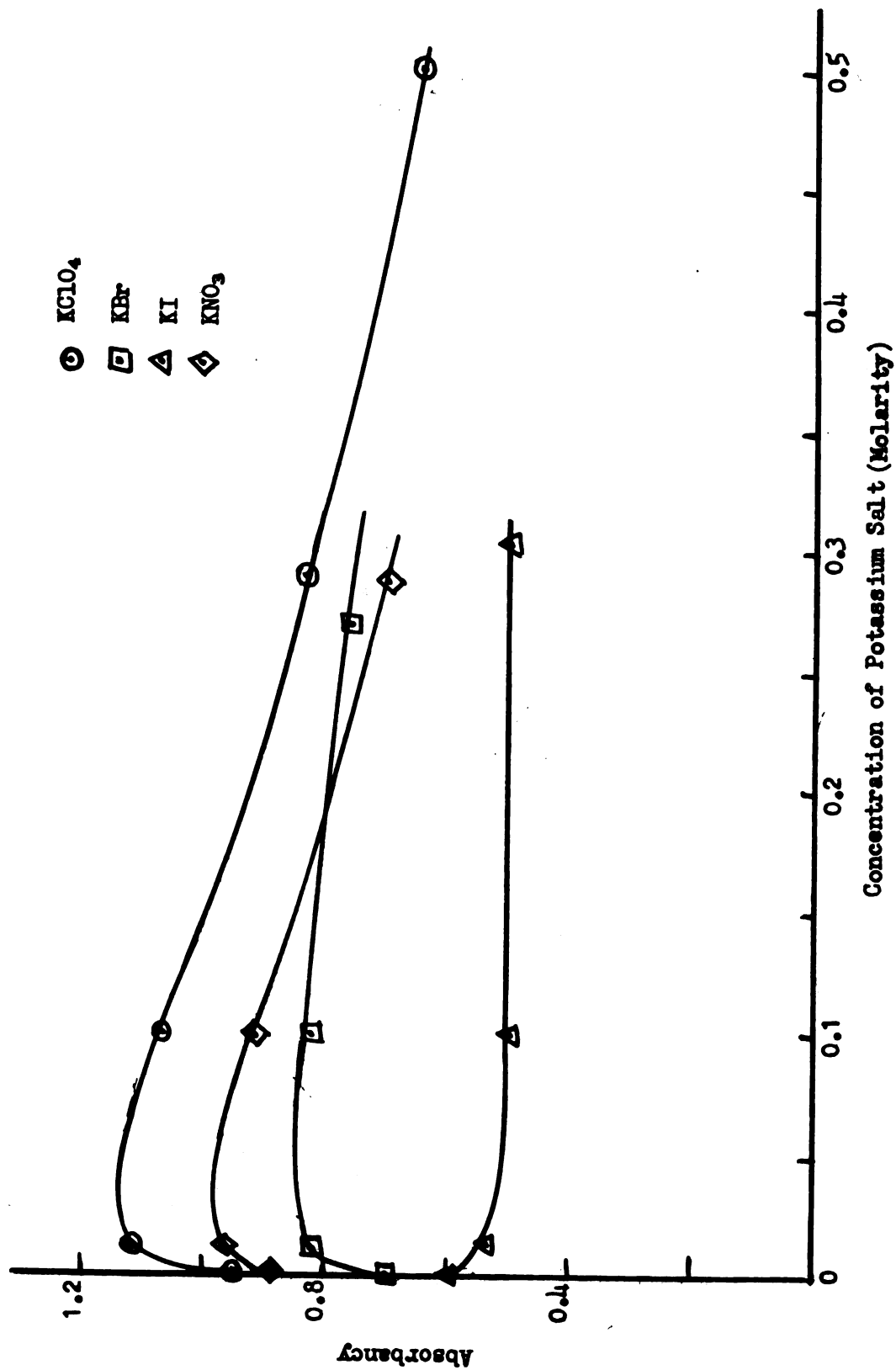


Figure 36. Absorbance of Phenolphthalein Versus Concentration of Potassium Salts

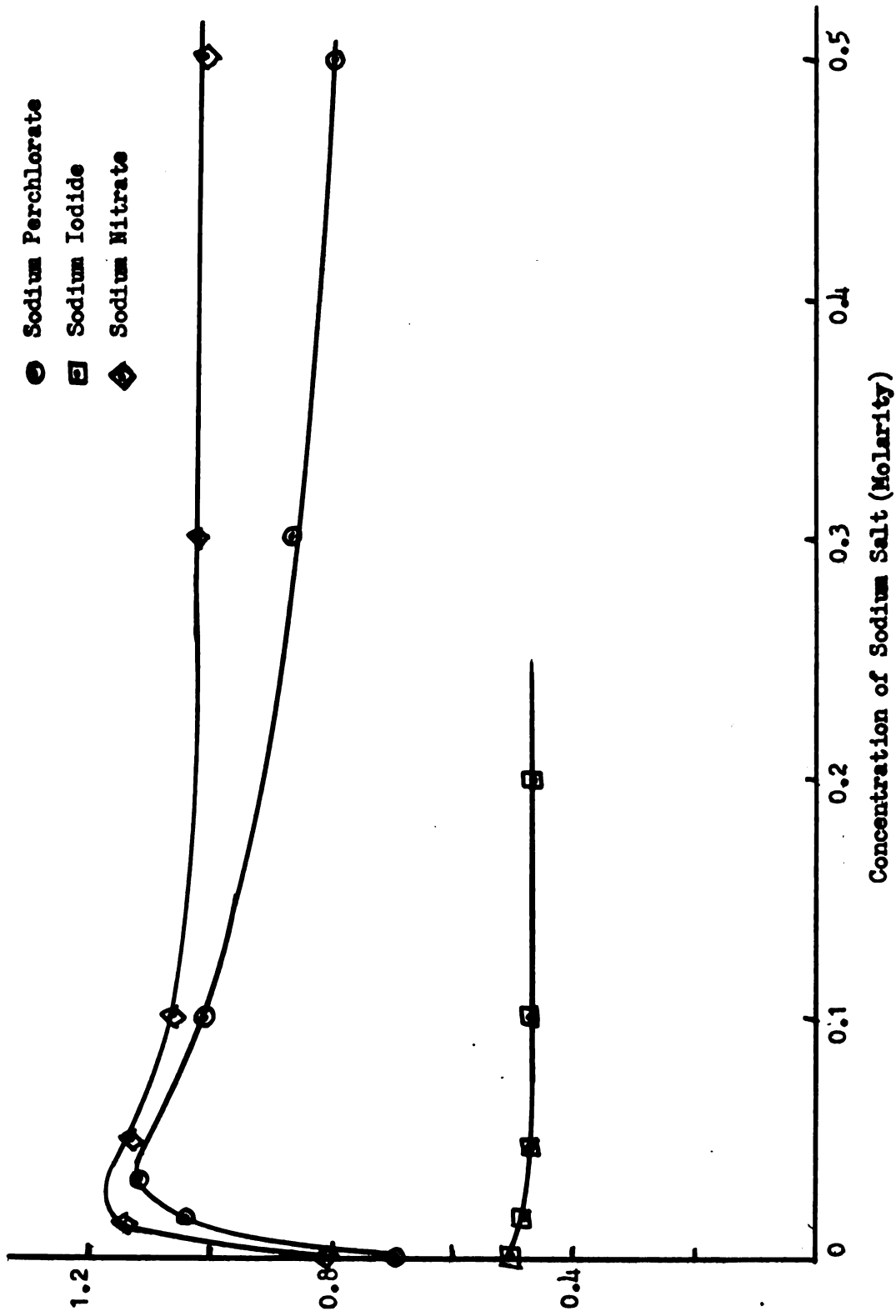


Figure 37. Absorbance of Phenolphthalein Versus Concentration of Some Sodium Salts at 575 m μ

The reaction of thiourea in ammonia was investigated by examining its effect upon phenolphthalein (Figure 38). It was observed that thiourea reacts as an acid by lightening the color of the indicator solution. Measurements of the absorbancy of phenolphthalein in various concentrations of thiourea (Figure 38) allowed calculation of K_i' by the method of Appendix II. A plot of $\log K_i'$ versus concentration extrapolated to infinite dilution (Figure 39) gave the ionization constant for thiourea. Since the value obtained is 7.1×10^{-3} , thiourea can be considered to be a weak acid which presumably reacts as:



Substitution of methyl groups for hydrogens in thiourea should decrease the acid strength; this is shown to be true by the ionization constants which were obtained in a similar way for some methyl-substituted thioureas (Table VIII).

TABLE VIII

IONIZATION CONSTANTS OF SOME THIOUREAS

Compound	$\log K_i$	$K_i (x 10^3)$
Thiourea	-2.15	7.1
Methylthiourea	-2.42	3.8
Trimethylthiourea	-3.25	0.18

Methylthiourea is slightly less acidic than thiourea and trimethylthiourea even less acidic. Trimethylthiourea still affects the indicator

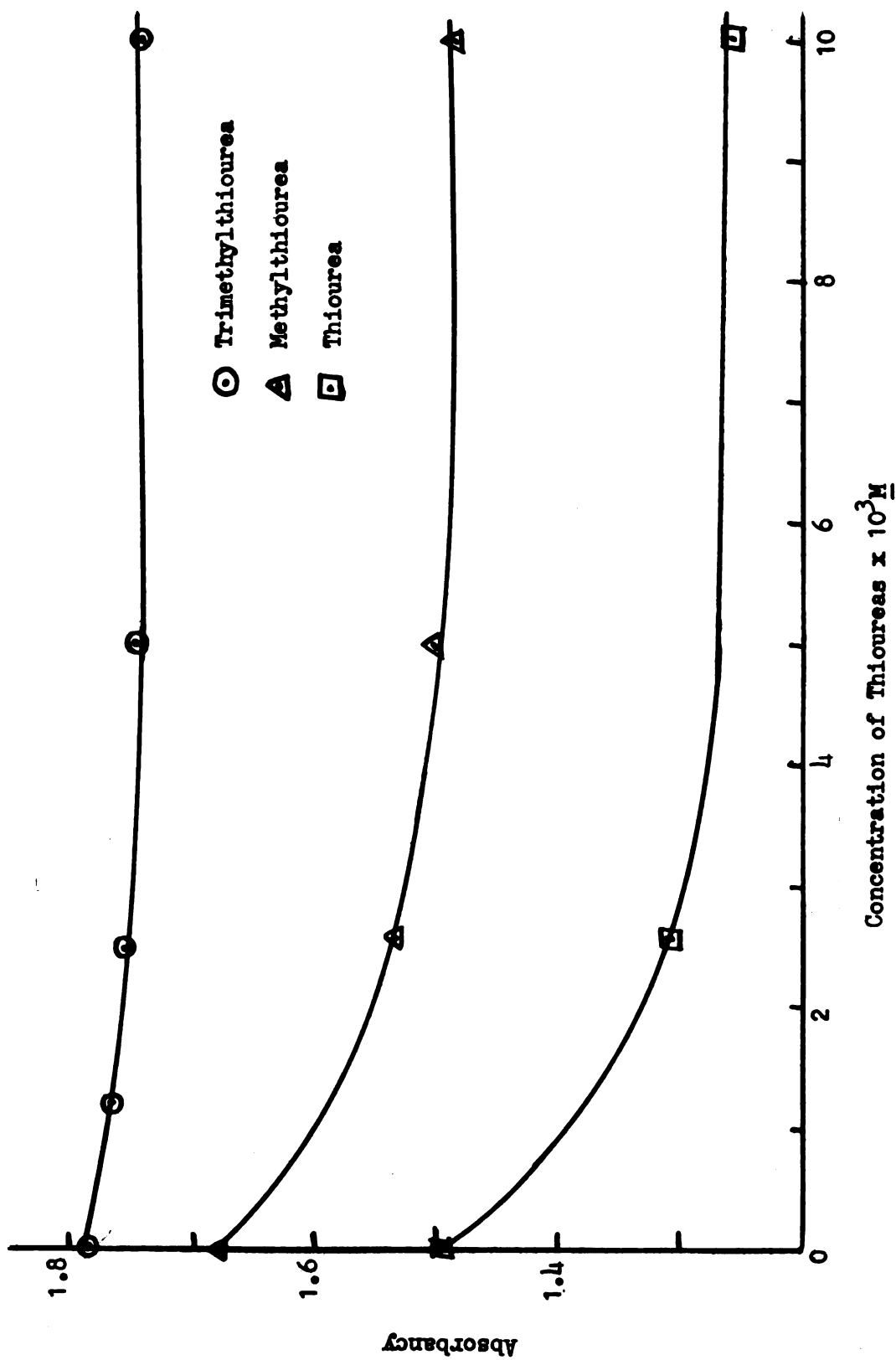


Figure 38. Absorbance of Phenolphthalein Versus Concentration of Some Thioureas at Constant Potassium Iodide Concentration

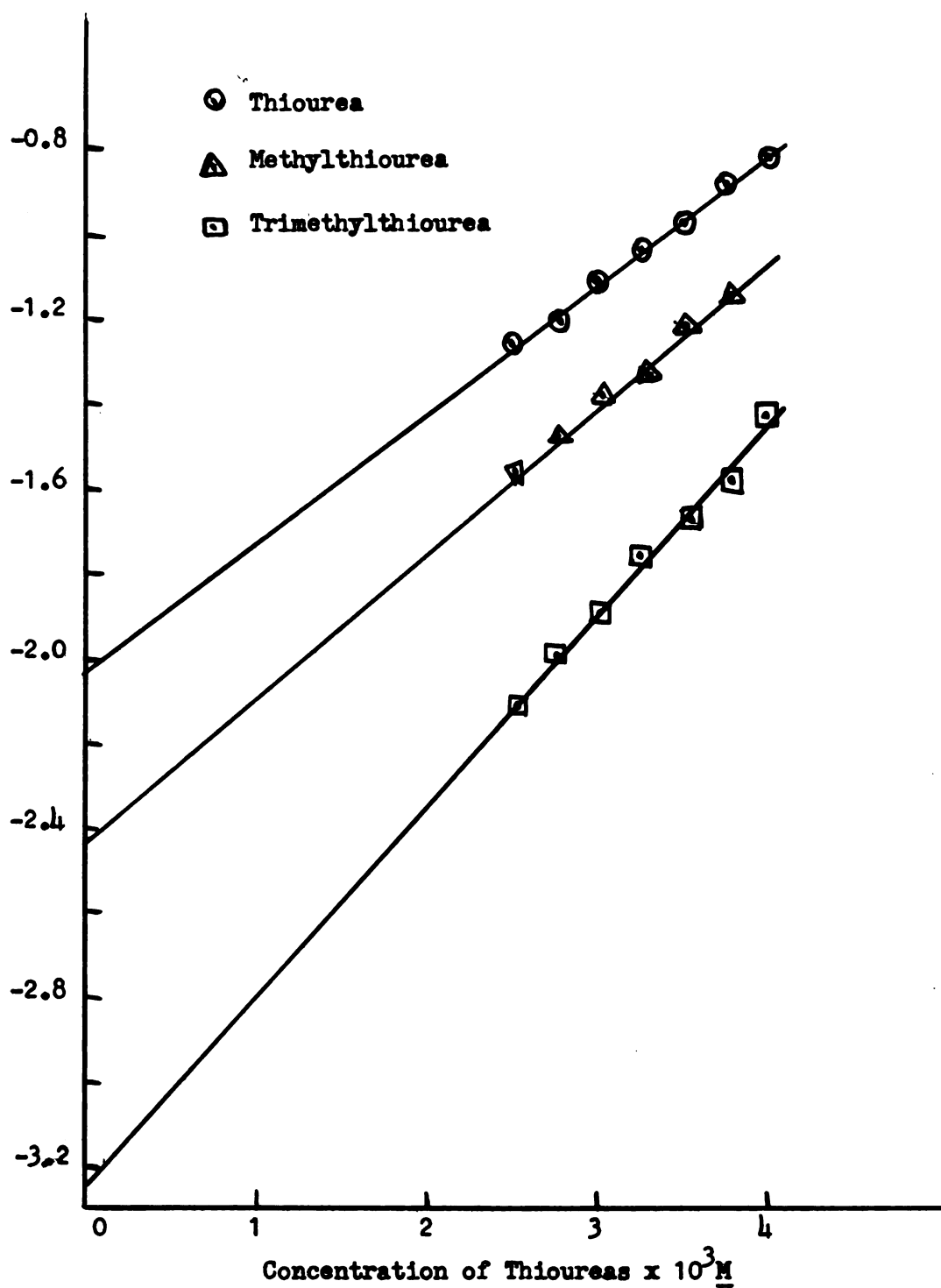


Figure 39. Log K_1 Versus Concentration of Some Thioureas

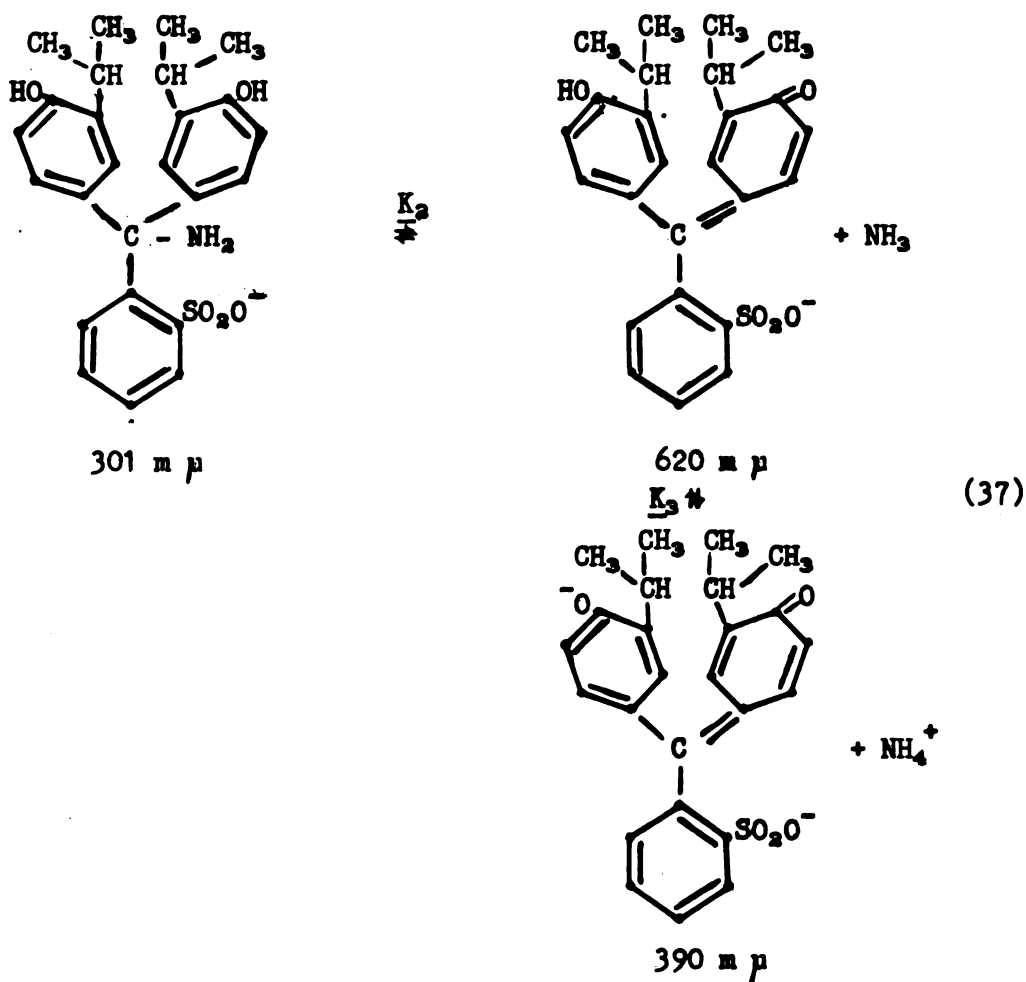
sufficiently to permit calculation of its ionization constant.

In the determination of the acid strengths of these weak acids, it had to be considered that neutral salts have effects on the indicator of the same order of magnitude as the weak acids and also that plots of the logarithm of r versus the negative logarithm of the ammonium ion concentration ($pC_{NH_4^+}$) do not give straight lines for all anions (Figures 11 to 14). In the investigation of these weak acids, potassium iodide was used in constant concentration because the plot of pC_{NH_4I} versus the logarithm of r approached a straight line in the concentration range used. Any ammonium ion produced by solvolysis would react toward phenolphthalein as ammonium iodide owing to the large excess of iodide ion present. Potassium iodide was present in large enough excess in all cases to give a constant salt effect.

Weak Bases

Because ammonia is strongly basic, solute acidity is enhanced and the majority of bases in liquid ammonia are weak. Indicators which are useful in studying basic solutes exhibit different colors in neutral and basic solutions. For spectrophotometric study of base strengths in ammonia, two approaches were used. In the first, a polyprotic acid indicator was chosen and one of the latter steps in its ionization was used as the indicator reaction with bases. This method is especially advantageous where very weak bases are concerned as their effect upon strongly acidic indicators is negligible. The second method was to choose an indicator which changes color on the basic side of neutrality in ammonia and whose ionization constant can be found in terms of the amide ion concentration.

The indicator thymol blue (thymol sulfonephthalein) is of the first type mentioned above. It has, in addition to the sulfonic acid group, two replaceable hydrogens which comprise the second and third ionization steps. The sulfonic acid group is such a strong acid that in ammonia it is completely ionized. The measurable ionization steps are:



Solutions of this indicator in ammonia are blue in an acidic medium and a blue-green color in both neutral and base. It has absorption bands at 301 m μ , 390 m μ , and 620 m μ (Figure 40). In acid solution the band at 390 m μ decreases in intensity, giving the solution its characteristic blue color owing to the 620 m μ band. As the solution becomes more basic, the 390 m μ band increases, giving the blue-green color as the yellow component is increased in intensity

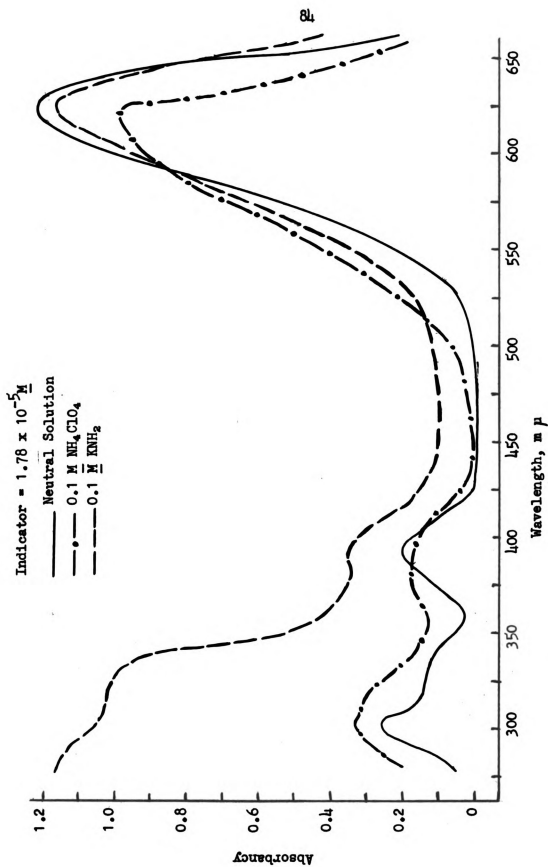


Figure 40. Absorption Spectra of Thymol Blue in Ammonia

(Figures 41 and 43). The band at 301 m μ follows Beer's Law (Figure 42) at all concentrations measured and is assigned to the species formed by the loss of the sulfonic acid proton. The 390 m μ band is assigned to the structure resulting from ionization K_3 in equation 37 (loss of the third proton). Spectrophotometric measurement of this band should give the data needed to calculate ionization constants of weak bases. The ionization constants and extinction coefficients for the species in equation 37 are listed in Table VI (page 54) and were determined by the method of Appendix II from the data of Figures 44 and 45.

Tropeoline OO (the sodium salt of diphenylaminoazobenzene-p-sulfonic acid) is an indicator which has a different absorption band in basic solution from that in acidic or neutral solution. The spectrum of a neutral solution of tropeoline OO has two absorption bands at 276 m μ and 460 m μ (Figures 46-48). The latter band is responsible for the intense yellow color observed for this indicator in neutral ammonia solution. Acidic solutions yield the same spectrum as the neutral solution, as would be expected for azo type indicators in such a basic medium. In aqueous solution the acid form of an azo dye is protonated on the nitrogen--nitrogen (azo linkage) giving quinonediimine structure, while in basic solution the color is due to the azo structure itself. The color shown in neutral ammonia is the same as in aqueous base. The deep violet color of amide solutions of this indicator is attributed to a different reaction from those found in aqueous solution. Schattenstein (41) postulated that the color change arises from addition of the amide ion to the azo linkage:

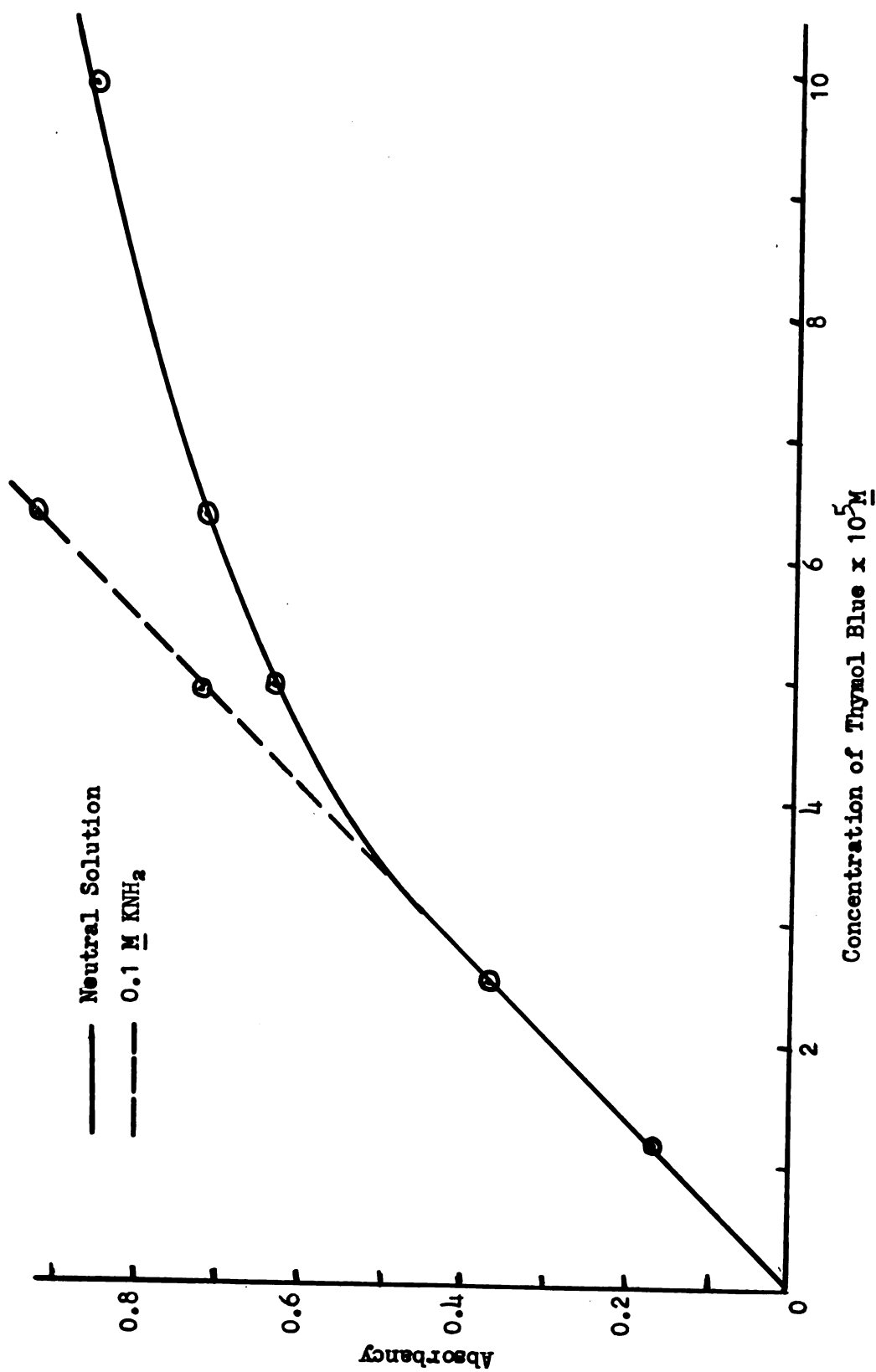


Figure 41. Absorbance Versus Concentration of Thymol Blue at 390 $m\mu$

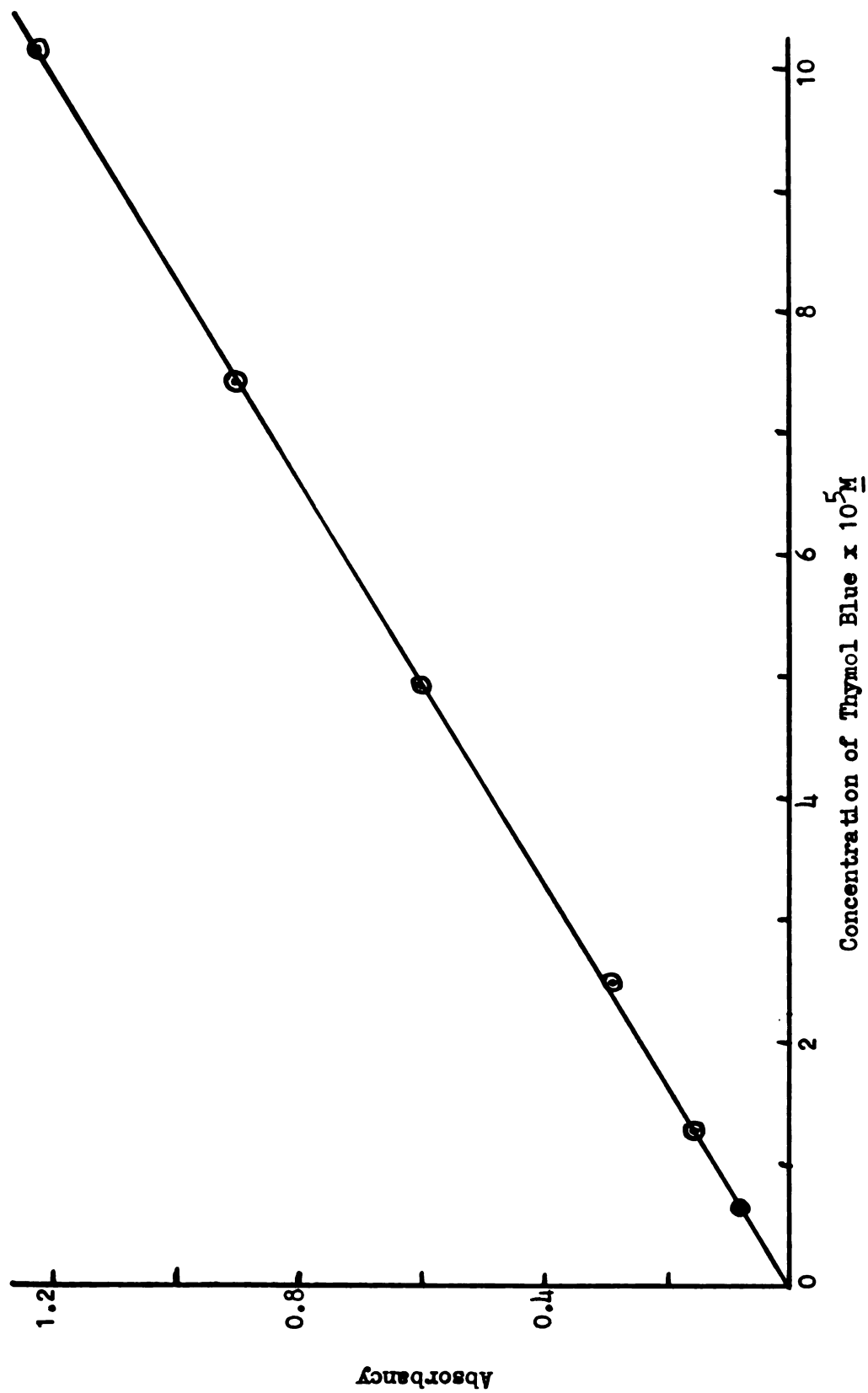


Figure 42. Absorbance Versus Concentration of Thymol Blue at 301 m μ

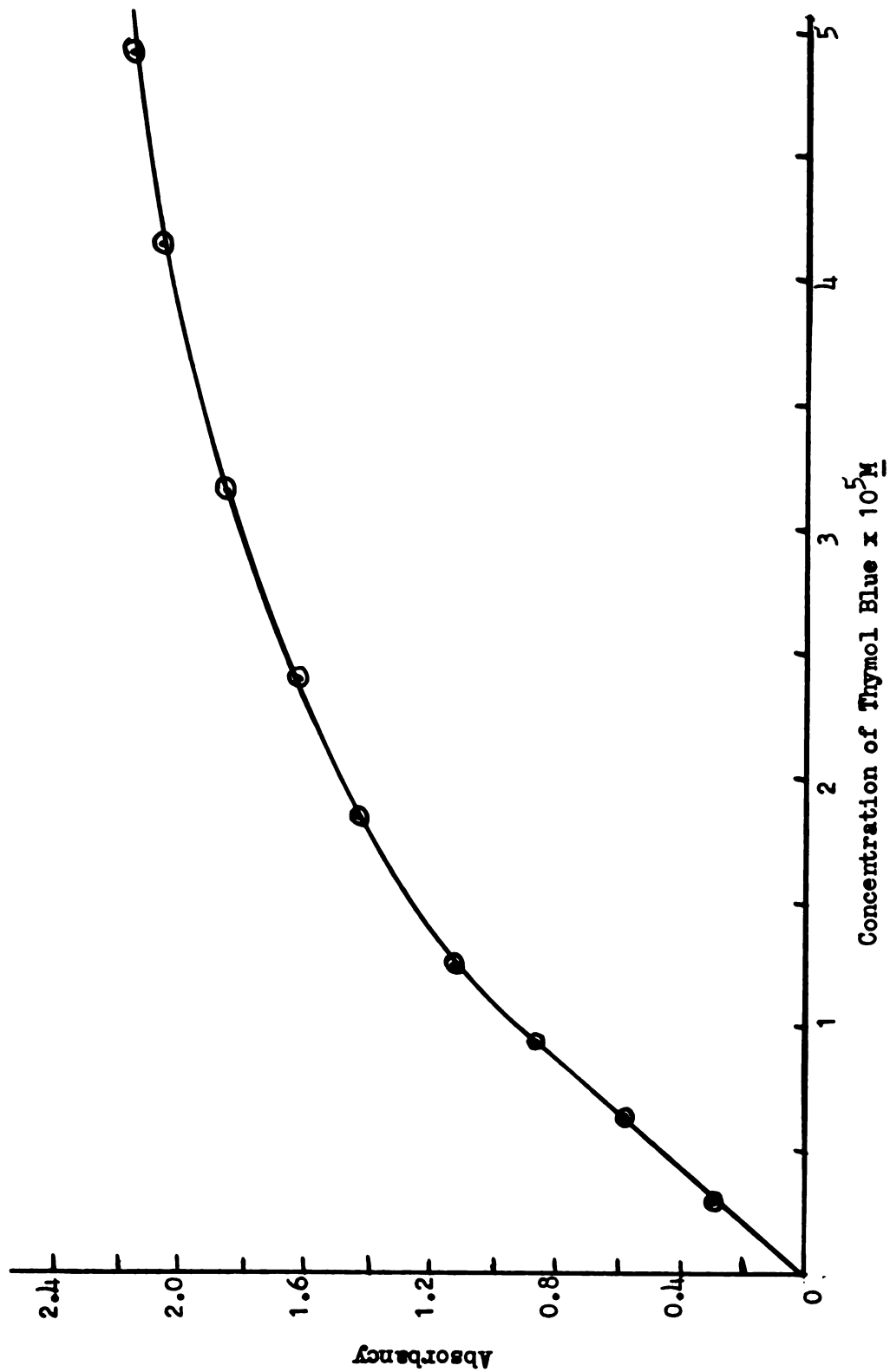


Figure 43. Absorbance Versus Concentration of Thymol Blue at $620 \text{ m}\mu$

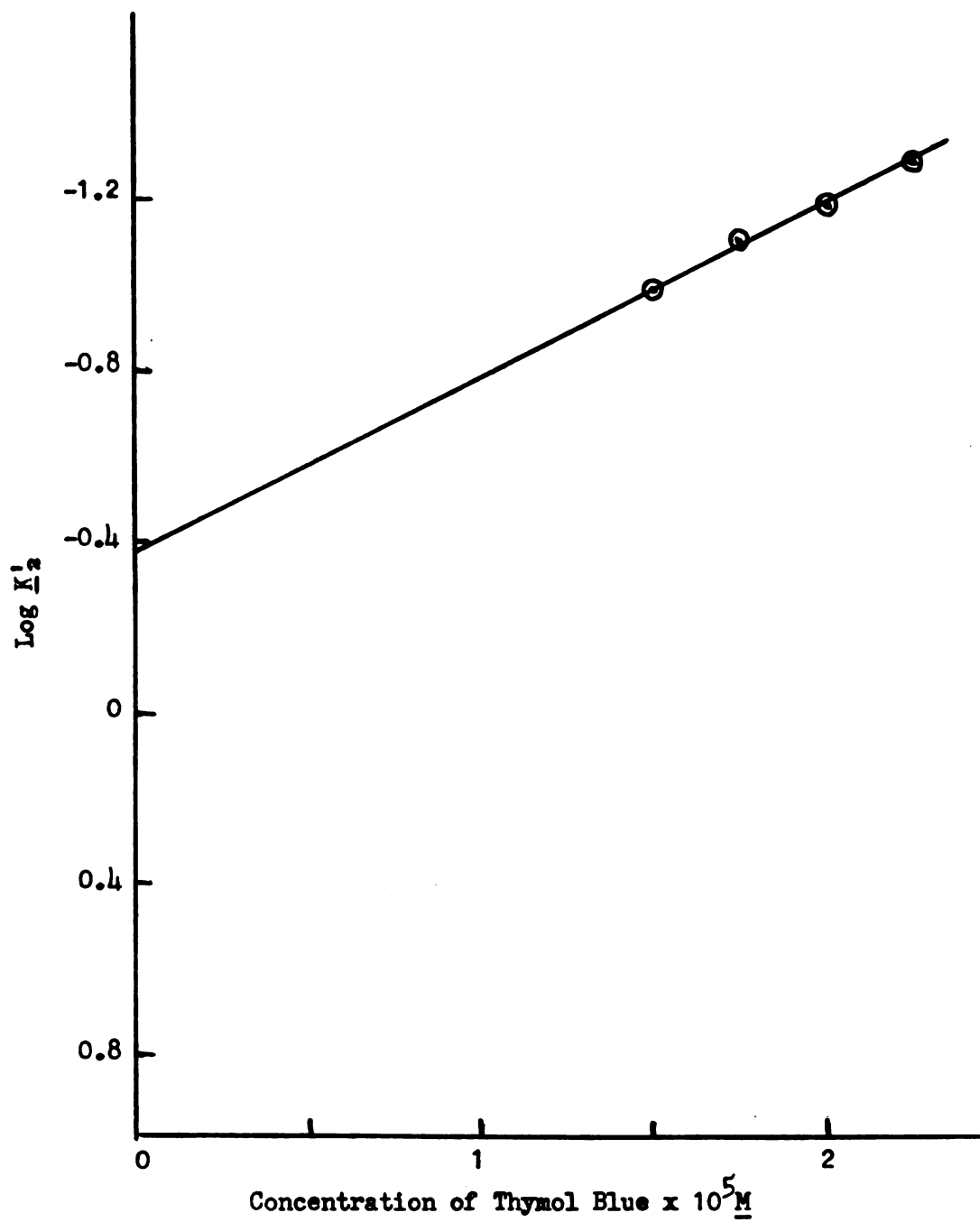


Figure 44. $\text{Log } K'_2$ Versus Concentration of Thymol Blue at 620 m μ

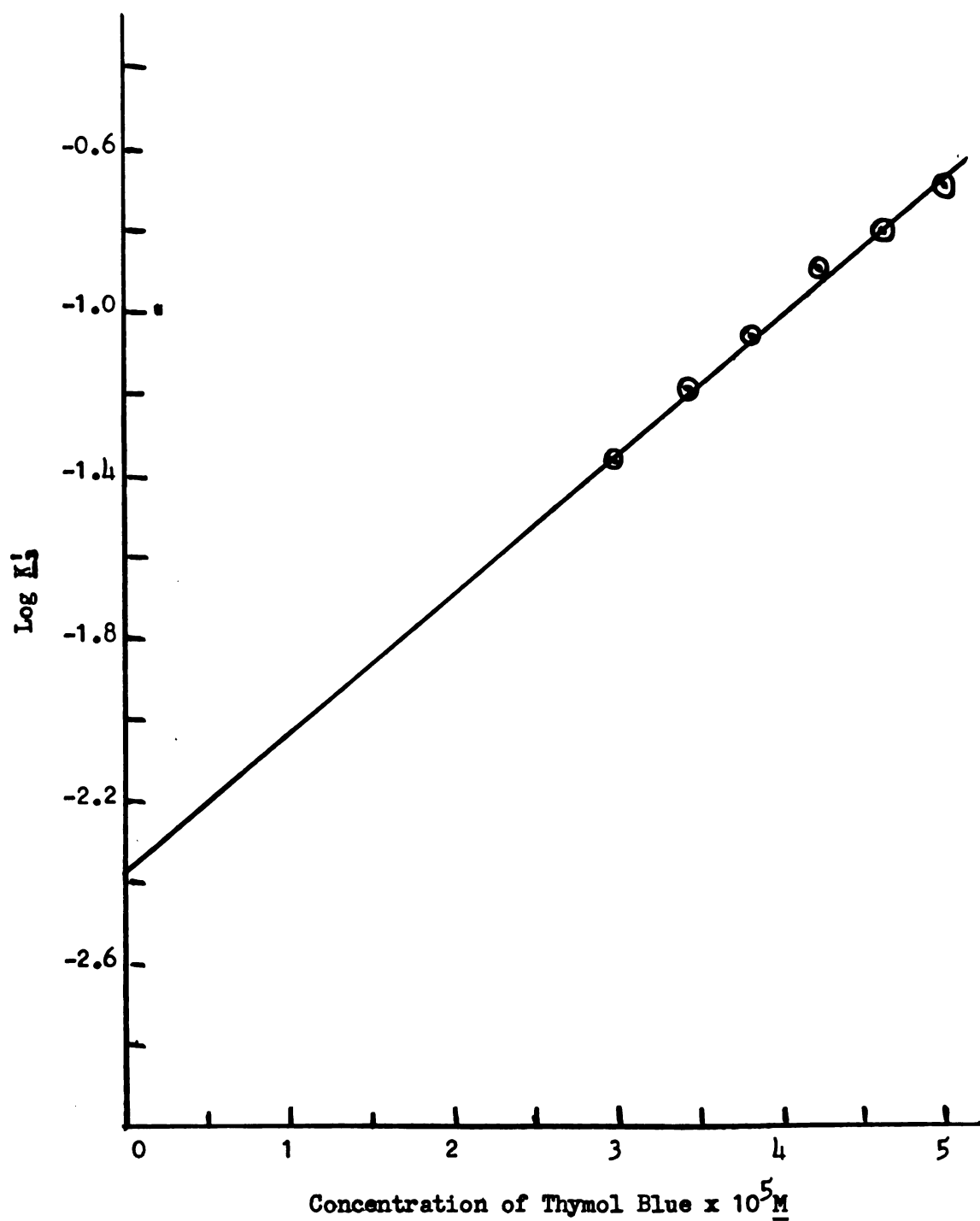


Figure 45. $\text{Log } K'$ Versus Concentration of Thymol Blue at 390 m μ

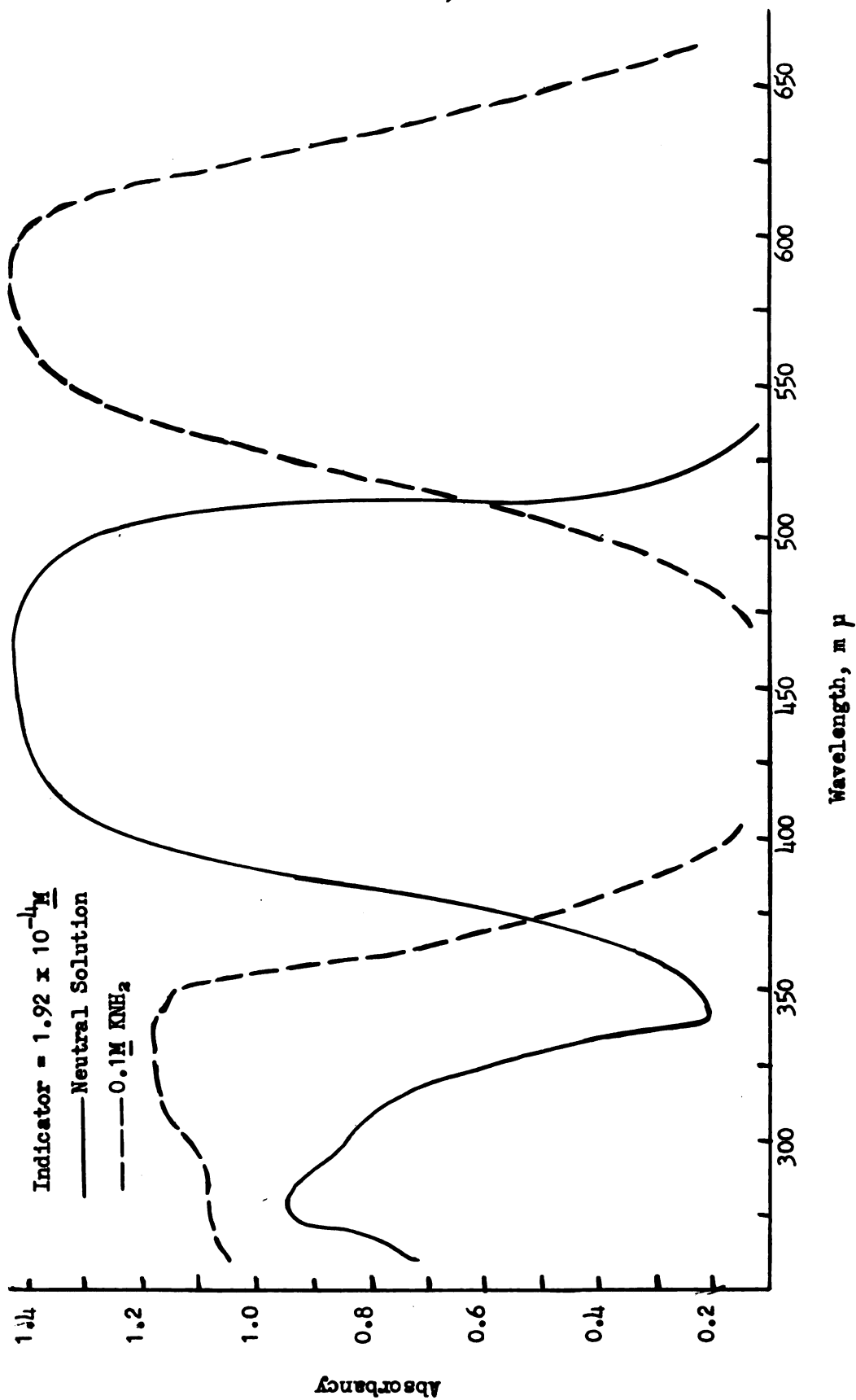


Figure 46. Absorption Spectra of Tropaeoline OO in Ammonia

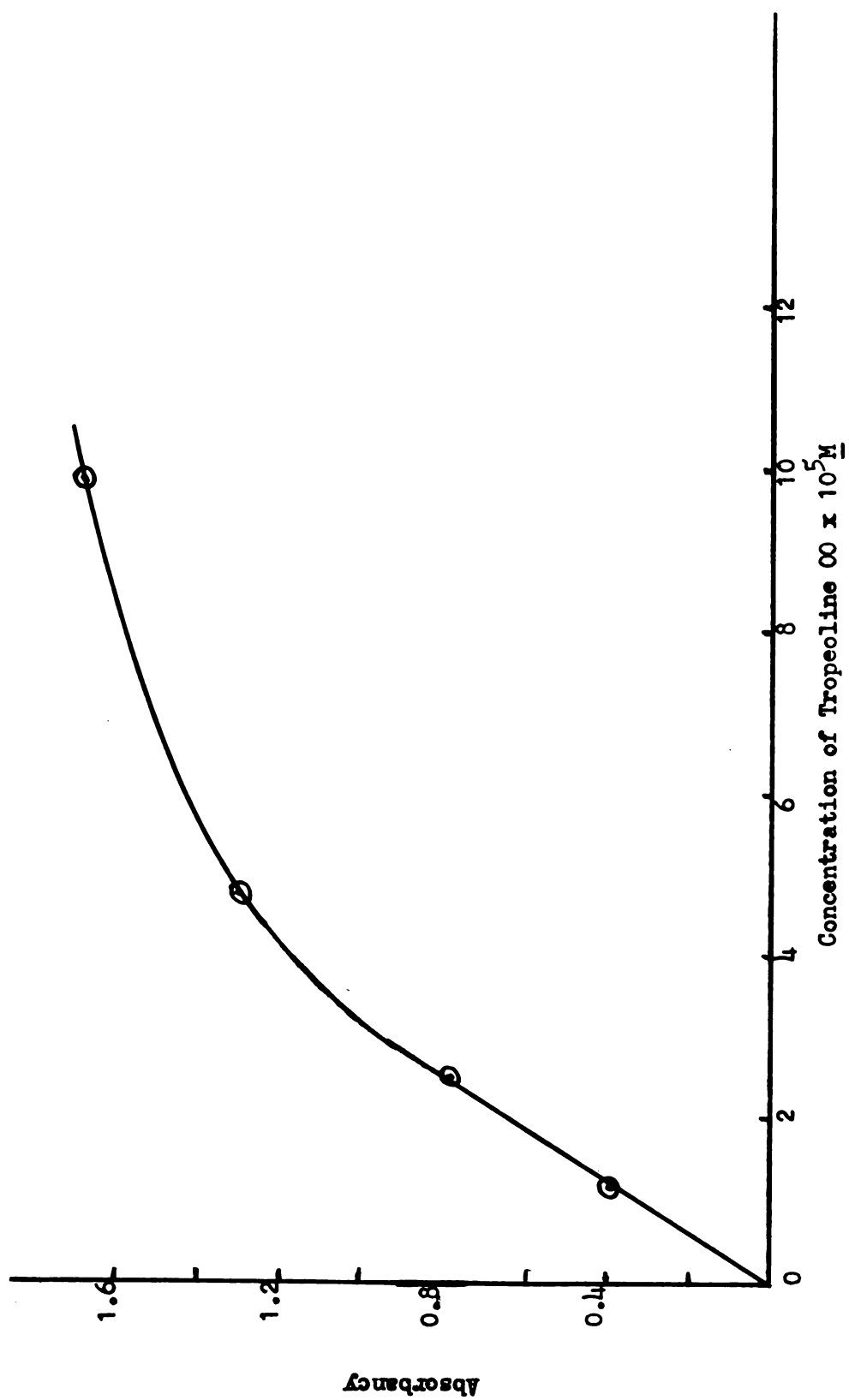


Figure 47. Absorbance Versus Concentration of Tropeoline OO at 460 m μ

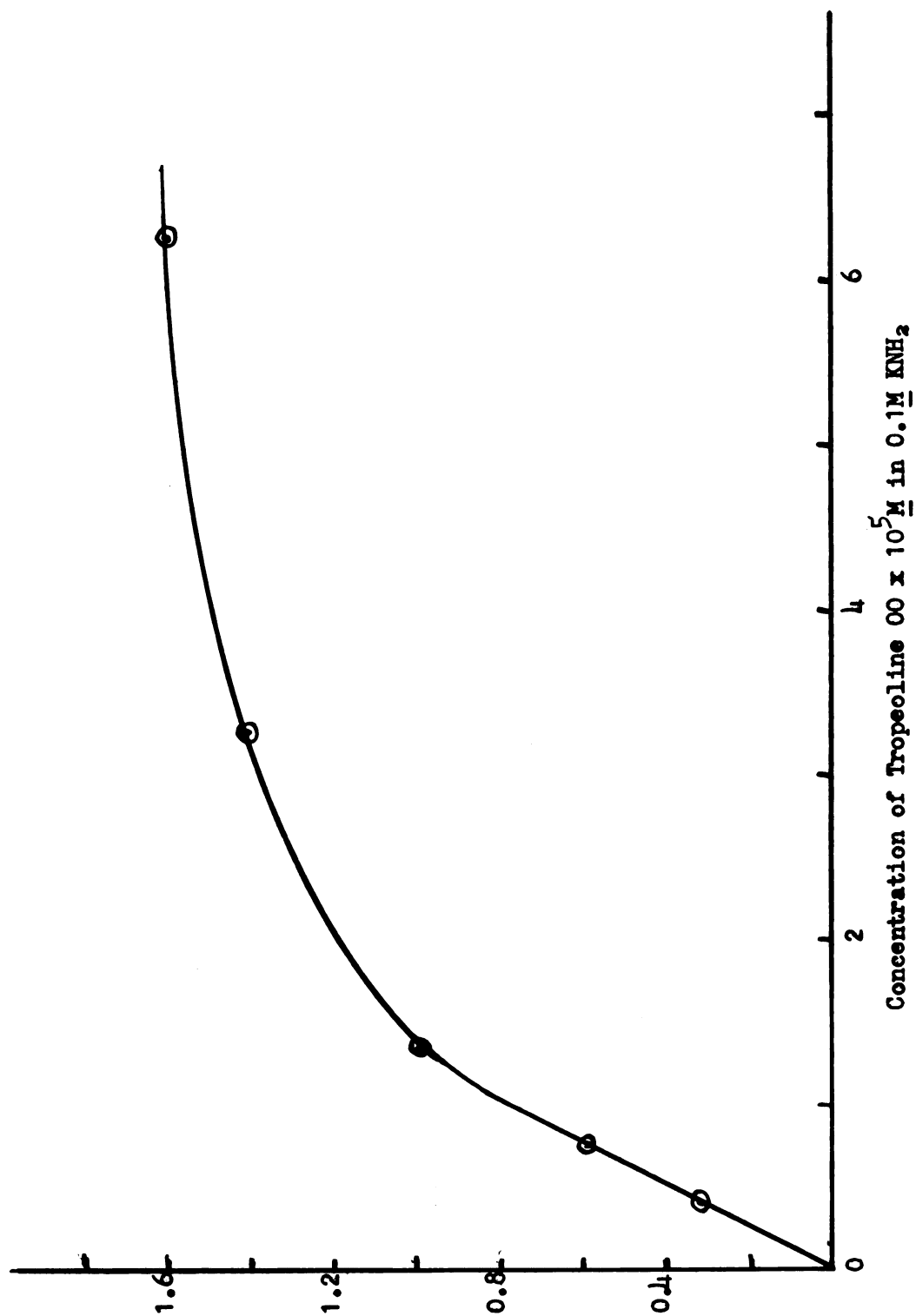
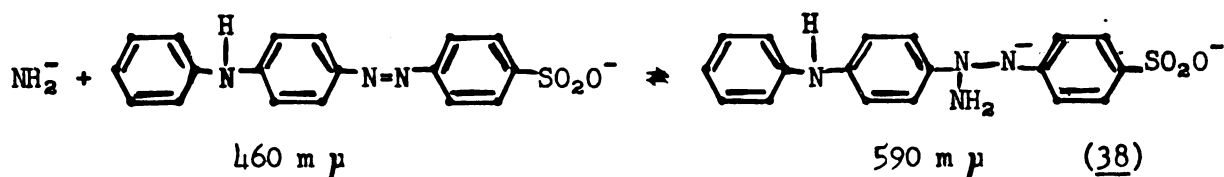


Figure 48. Absorbance Versus Concentration of Tropeoline OO at 590 m μ



The band at 590 m μ is present only in basic solution and is thus assigned to the structure in equation 38. From basic to acidic solution (i.e., on addition of an ammonium compound), a very sharp color change from purple to yellow occurs. All other indicators studied showed a gradual transition from one color to the other. Figure 49 shows a steep slope at the transition point of tropeoline OO for both bands. The salt effect upon azo indicators is in general negligibly small and this was observed for tropeoline OO. A reasonable explanation lies in the fact that the azo ion is quite large and could well be of approximately the same size as the ionic atmosphere, thus minimizing the salt effect.

Urea does not react with the indicators which have been found useful for determination of the strengths of weak acids (phenolphthalein, 2,4-dinitroaniline, and p-nitroacetanilide). Urea does, however, react as a neutral or basic compound toward them. It was observed by Lagowski (29) that urea and several other compounds postulated as weak acids in ammonia have no effect upon phenolphthalein. On the other hand, the effect of urea upon thymol blue is as a very weak base (Figure 50). Urea does not affect tropeoline OO, however, and consequently its acid strength must be very close to that of a neutral ammonia solution. Though potassium salts of urea have been prepared (64), these reactions were done in potassium amide solution which is a considerably stronger base than ammonia. The sodium salt of urea can be

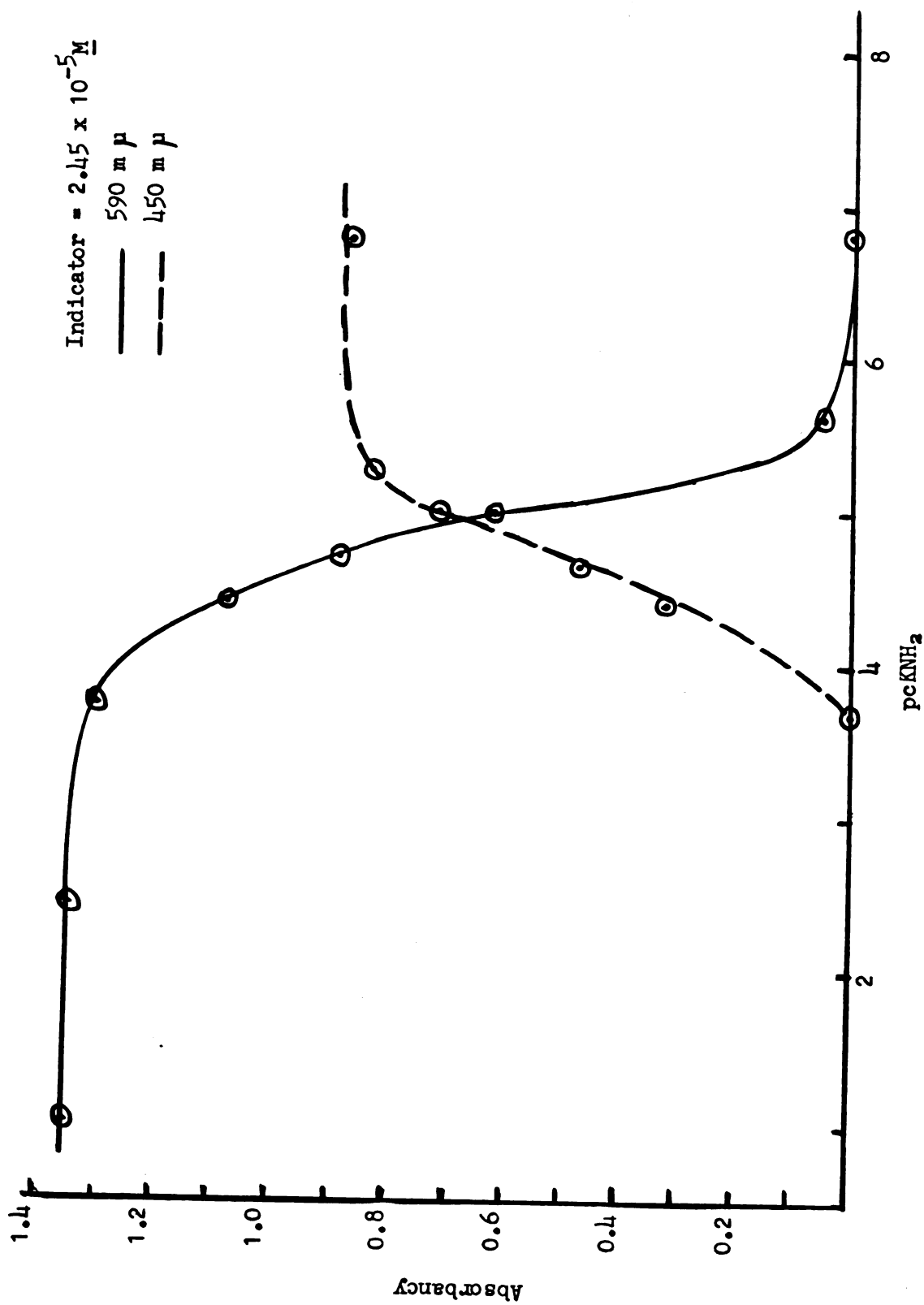


Figure 49. Absorbance of Tropeoline OO Versus Log of Potassium Amide Concentration

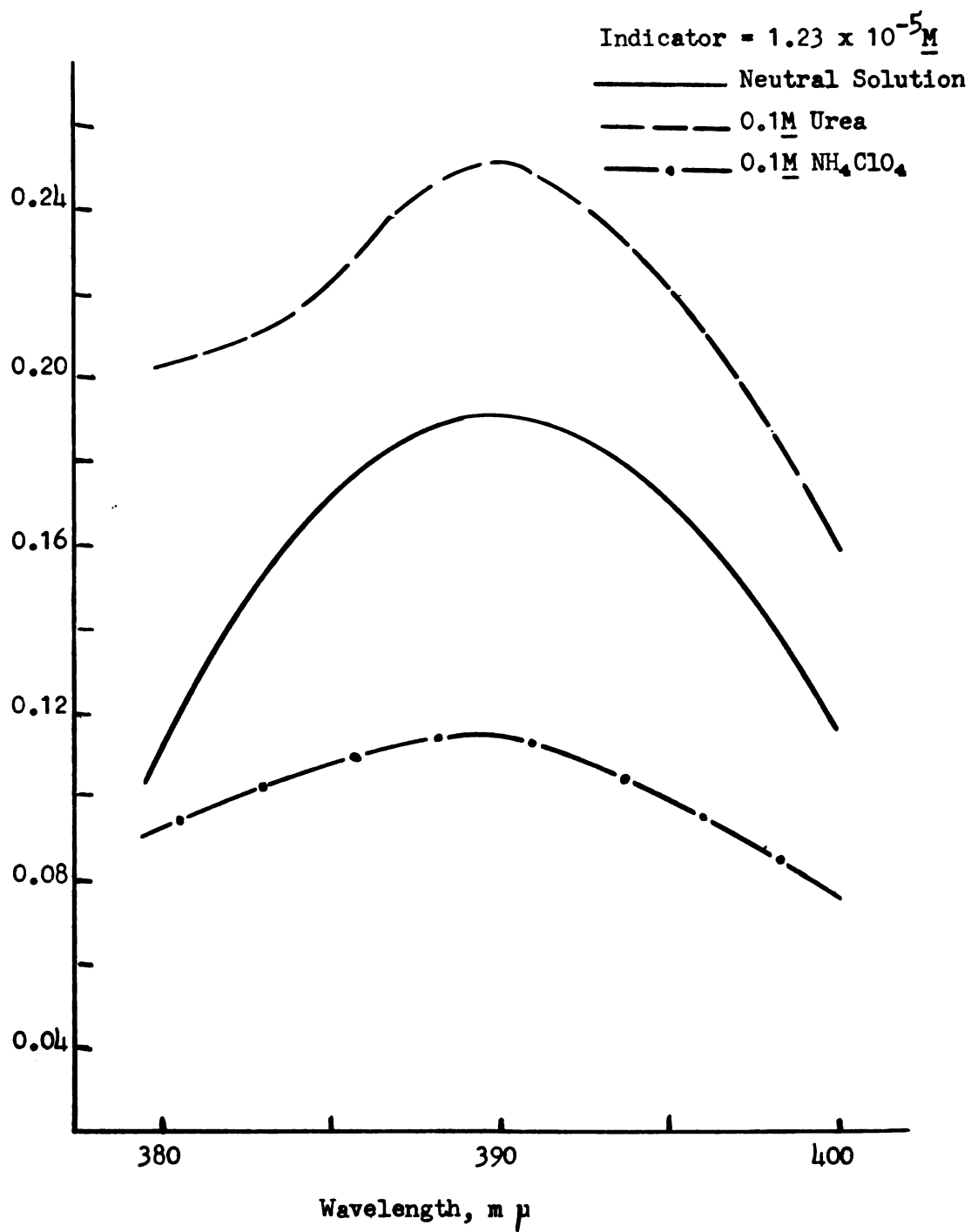
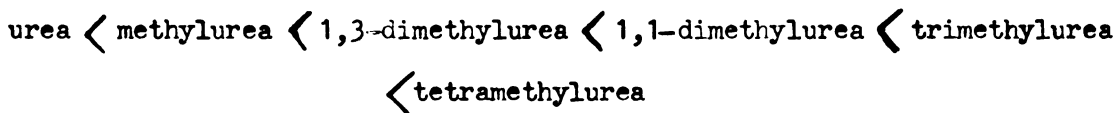


Figure 50. Absorption Spectra of Thymol Blue in the Presence of Urea at 390 mμ

prepared but it has only been obtained using elemental sodium (63).

These data can be reconciled if urea is considered to be an amphiprotic substance as shown in equations 28 and 29(p.47). The species present in neutral ammonia could be that represented in equation 29, which would affect a basic indicator such as thymol blue but not tropeoline OO. Also in the presence of a stronger base such as amide ion, urea could react in the manner indicated in equation 28. The effect of substituting methyl groups for hydrogens in urea should increase the base strength, although the magnitude observed is not as great as would be predicted from their structures. The order of base strength is:



which is in agreement with that observed by Anderson (69) who used potentiometric titrations in acetonitrile to determine relative base strengths.

There is disagreement as to the position of protonation in urea when it acts as a base in aqueous solution. It is not certain whether hydrogen resides on the nitrogen atom (67) or the oxygen atom (68). On the other hand there seems to be general agreement in the case of thiourea that the nitrogen is protonated. In water, thiourea is a weaker base (or stronger acid) than urea. The observation of this study is that the same order prevails in liquid ammonia, but thiourea acts as a weak but measurable acid while urea is very nearly a neutral species and indeed may be basic.

Ultraviolet spectra in basic liquid ammonia solutions are blocked because of the absorption of the amide ion (Figure 51).

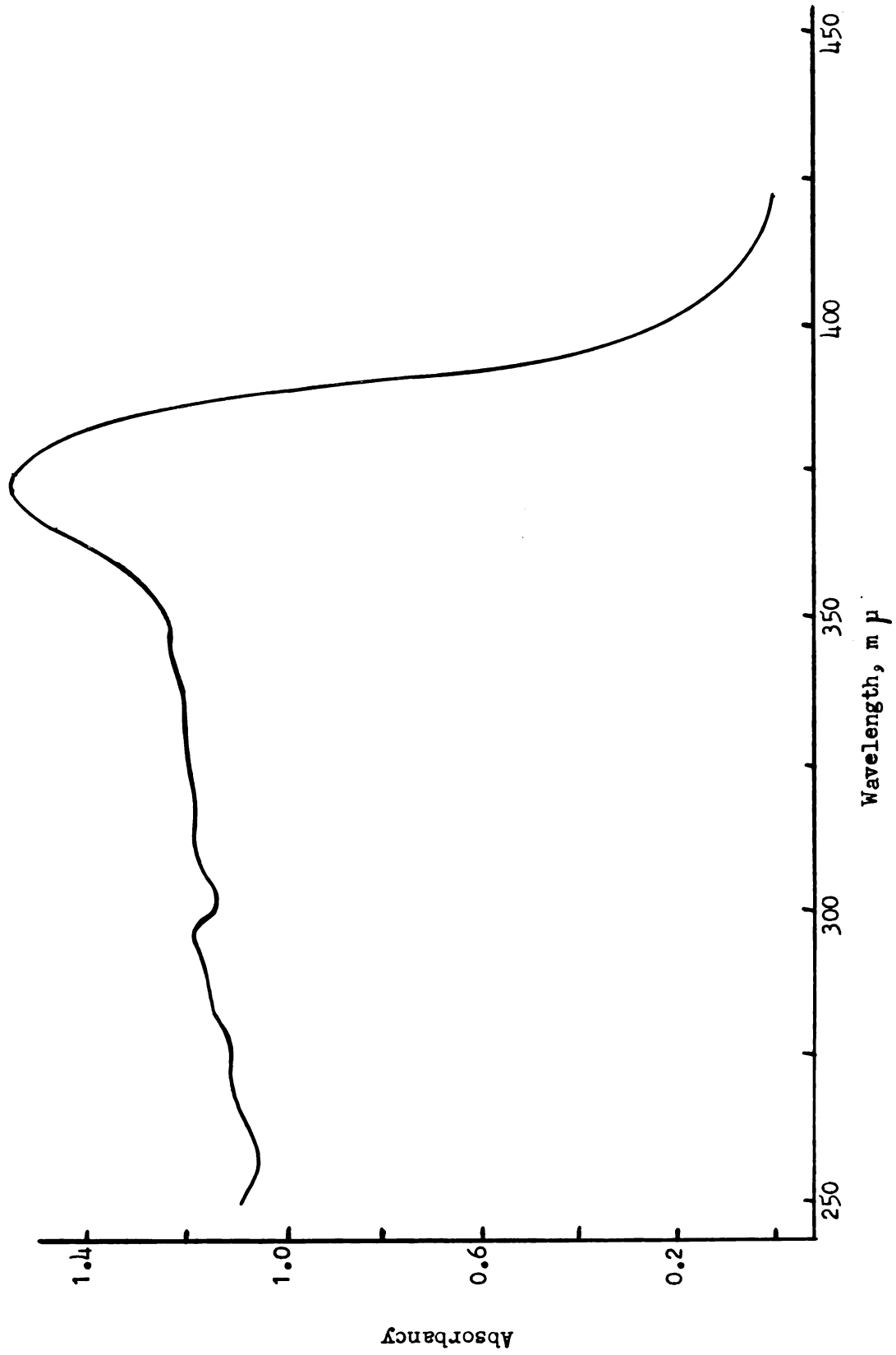


Figure 51. Absorption Spectrum of Potassium Amide in Ammonia

SUMMARY

A method was devised for studying the absorption spectra of solutions in liquid ammonia in the ultraviolet and visible regions of the spectrum by means of a low temperature cell. Five indicators were studied in detail. *p*-Nitroacetanilide, 2,4-dinitroaniline, phenolphthalein, and thymol blue were found to have first ionization constants greater than one, which is expected in view of the acidic character of these indicators. Assignments were made correlating molecular structure with the absorption bands, and extinction coefficients for the structures were calculated. The effects of ammonium ion and amide ion were investigated and also the effects of neutral salts upon the absorbancy of the indicators were defined. The change in color with increasing temperature for phenolphthalein was measured and ionization constants calculated for various temperatures in the liquid range of ammonia.

The acidic indicators were used to determine the relative acidity of some thioureas which were found to be weak acids in ammonia as opposed to their basic nature in water. Ionization constants for the thioureas were found to be of the order of 10^{-3} .

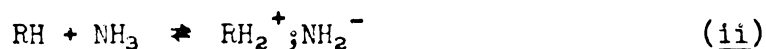
Tropeoline OO was studied as a basic indicator and defined in terms of its structure and absorption band assignments. Extinction coefficients were calculated for the species present at each peak.

Urea had no effect upon the more acidic indicators but showed a basic reaction toward thymol blue in its third ionization step. Investigation of urea using tropeoline OO indicated urea to be a neutral or weakly basic compound.

APPENDIX I

PREPARATION AND PURIFICATION OF METHYLSUBSTITUTED UREAS AND THIOUREAS

Urea and thiourea have labile hydrogen atoms as well as a basic site in their molecules and can thus react in an amphiprotic manner:



The extent of ionization is a function of the nature of the molecular species and varies with a change in molecular structure. Substitution of methyl groups for hydrogens in urea and thiourea provides a series of compounds with which this trend may be studied. A series of methylsubstituted ureas and thioureas was synthesized and purified.

Urea

Urea obtained from stock (Eastman, yellow label), being very soluble in water, was precipitated from dilute nitric acid solution as the nitrate. After filtering, the precipitate was redissolved in boiling water to form a saturated solution and allowed to cool slowly. The long needles of urea nitrate obtained were air dried and the melting point determined to be 148-151°C (reported 152°C). After two recrystallizations, the reported melting point was obtained.

To recover urea from this compound, a method according to Wurtz (70) was employed. Barium carbonate was added in excess to urea nitrate in water and the solution was evaporated to dryness. The solid was extracted with hot absolute alcohol in which urea is

appreciably soluble but in which barium nitrate is insoluble. Pure urea was obtained by evaporation of the alcohol. The melting point determined was 130-131°C (reported m. p. 132.7°C).

Urea was recrystallized directly from absolute alcohol giving a melting point of 132-132.5°C.

Methylurea

The general method of Wurtz (70) was used to synthesize this compound. It involves the isomerization of salts of substituted amines with cyanic acid to give the substituted urea. In this case methylamine sulfate in aqueous solution was allowed to react with the calculated amount of potassium cyanate. The mixture was evaporated on a steam bath under water aspiration until a dry residue was obtained. This was extracted with hot absolute alcohol, the solution filtered, and the filtrate evaporated to obtain methylurea in 60% yield.

Methylurea was purified by the nitrate precipitation method discussed for urea. The melting point of methylurea so obtained was 97-100°C (reported 101°C).

A different method was used to obtain methylurea of higher yield and greater purity. This involves the rearrangement of nitrourea according to Davis and Blanchard (71). Nitrourea was prepared by letting urea nitrate rearrange in the presence of concentrated sulfuric acid at 0°C. The mixture was poured over ice, filtered, and recrystallized immediately from ethyl alcohol. The nitrourea thus obtained was allowed to react with methylamine in water. The solution was warmed to initiate the reaction and cooled to moderate the reaction once under way. The product was obtained upon evaporation of the solvent and recrystallized from acetone, from which stout needles were obtained in 85% yield; m. p. 102°C.

N,N-Dimethylurea

The unsymmetrical dimethylurea was prepared by use of the method of Leuckart (72). Dimethylamine sulfate was allowed to react with potassium cyanate and evaporated to dryness. Extraction with hot alcohol and cooling gave the product in 50% yield, with a melting point of 175-180°C (reported 182°C). The method of Davis and Blanchard (71) used in preparing methylurea was used also. Nitrourea was allowed to react with dimethylamine in water. Upon evaporation of the solvent and recrystallization of the residue from alcohol, the product was obtained in 88% yield; m. p. 182°C.

N,N'-Dimethylurea

The reaction between methylisocyanate and methylamine results in good yields of symmetrical dimethylurea. Methylisocyanate was obtained by reaction of p-methyltoluenesulfonate with potassium cyanate. These were heated at 80°C in the presence of sodium carbonate and methylisocyanate distilled at 42°C. This was also obtained by means of an azide rearrangement reaction (73). Sodium azide was mixed with acetylchloride and heated to 60°C. The methylisocyanate was distilled into anhydrous diethyl ether.

The methylisocyanate in ether was added to an ether solution of methylamine with stirring and cooling. The ether was allowed to evaporate and the residue allowed to cool from boiling benzene, whereupon large needles crystallized out. After two recrystallizations from benzene, the substance melted at 105-106°C (reported 106°C).

Trimethylurea

A method (74) similar to that used for symmetrical dimethylurea was used to prepare this compound. Methylisocyanate was prepared in ether and allowed to react with dimethylamine; cooling and stirring were used. The compound crystallized and a quantitative recovery was made upon evaporation of the solvent. The product was sublimed under vacuum and crystallized in long needles in the receiver. The melting point was 75-76°C (reported 75.5°C).

Tetramethylurea

Tetramethylurea was obtained from John Deere Chemical Company, Pryor, Oklahoma. It was distilled in the absence of moisture to obtain the water-white liquid boiling at 175-177°C. The refractive index was 1.4473. Reported boiling point 176°C at 760 mm Hg; refractive index 1.4488.

Thiourea

The impure compound obtained from stock (Eastman, yellow label) was recrystallized twice from 95% ethanol. The melting point was 180-182°C (reported 182°C).

Methylthiourea

The reaction between methylisothiocyanate and ammonia (75) results in high purity methylthiourea. One recrystallization from absolute alcohol gave a melting point of 117-119°C (reported 118-119°C).

Trimethylthiourea

The same reaction used for preparation of methylthiourea (75)

was modified by allowing methylisothiocyanate to react with dimethylamine in absolute alcohol for 24 hours at reflux temperature. As the reaction mixture cooled, trimethylthiourea crystallized. The melting point obtained was 75-78°C (reported 78°C).

APPENDIX II

SPECTROPHOTOMETRIC DETERMINATION OF IONIZATION CONSTANTS OF INDICATOR ACIDS

When an acid, HA, is dissolved in liquid ammonia, the following equilibria are established:



Equation i represents the ionization step or formation of ion pairs while equation ii represents the equilibrium between the ion pair and its ions. The first equilibrium is a function of the relative acid-base strength of the solute acid and the solvent, while the second equilibrium is largely dependent upon the dielectric constant of the solvent. The equilibrium constant for this dissociation is fairly constant for a large number of compounds in ammonia, i.e., approximately 10^{-4} (15).

If the molecular species, HA, absorbs radiation at a different wavelength from the species A^- , and further if the wavelength of the absorption band is the same for the anion A^- as for the ion pair $\text{NH}_4^+; \text{A}^-$, then the equilibrium constant, K_1 (ionization constant for reaction i) can be calculated.

In the quantitative spectrophotometric determination of absorbing species, the Beer-Lambert Law is used. One form of this states:

$$A = \epsilon cl \quad (\text{iii})$$

where A is the absorbancy, ϵ is the molar extinction coefficient for the species in question, c is the actual concentration, and l is the path length of monochromatic radiation. If equation iii is differentiated with respect to concentration, the following is obtained:

$$\frac{dA}{dc} = \epsilon l \quad (\text{iv})$$

Using unit light path for l and plotting the change of absorbancy with change in concentration, a straight line having slope ϵ is obtained if Beer's Law is obeyed. If acid HA is a weak acid, then as the concentration increases, the deviation from a straight line and from Beer's Law becomes greater. Neglecting the second equilibrium (equation ii), an ionization constant, K_1 , can be formulated:

$$K_1 = \frac{a_{NH_4^+} a_{A^-}}{a_{HA} a_{NH_3}} \quad (\text{v})$$

Since the spectrophotometer measures concentration, K_1 can be expressed in these terms:

$$K_1 = \frac{[NH_4^+][A^-]}{[HA][NH_3]} \cdot \frac{\gamma_{NH_4^+} \gamma_{A^-}}{\gamma_{HA} \gamma_{NH_3}} \quad (\text{vi})$$

Another constant, K'_1 , is defined for the concentration ratio of anion to acid

$$K'_1 = \frac{[NH_4^+][A^-]}{[HA]} \quad (\text{vii})$$

where K'_1 includes the activity of the solvent. At infinite dilution

the activity coefficients equal one and $\underline{K}'_1$ becomes equal to $\underline{K}_1$:

$$\underline{K}_1 = \underline{K}'_1 = \frac{[\text{NH}_4^+; \text{A}^-]}{[\text{HA}]} \quad (\text{viii})$$

The calculation of anion and molecular acid concentrations can be accomplished if the extinction coefficient of the anion is known. The extinction coefficients can be found from the slope of the straight part of the curve which results from a plot of A versus concentration. This assumes that at low concentrations the indicator exists in its anionic form. As the curved portion of this line is approached, various values of anion and molecular concentrations can be found by graphical methods. Upon substitution into equation vii, values for $\underline{K}'_1$ can be found. A plot of the logarithm of $\underline{K}'_1$ versus concentration of acid, HA, gives a straight line with the intercept at infinite dilution which gives a value for $\underline{K}_1$.

APPENDIX III

ABSORPTION SPECTRA DATA FOR VARIOUS INDICATORS IN LIQUID AMMONIA

p-Nitroacetanilide ($1.21 \times 10^{-4} M$)

<u>Wavelength</u>	<u>Absorbancy</u>	
	<u>Neutral</u>	<u>Base</u>
<u>m μ</u>		
250	1.063	1.191
255	1.014	1.194
260	0.922	1.106
265	0.804	0.958
270	0.764	0.836
275	0.694	0.683
280	0.720	0.594
285	0.720	0.594
290	0.888	0.551
295	1.053	0.606
300	1.200	0.658
310	1.573	0.847
320	1.850	1.063
330	1.939	1.161
340	1.979	1.211
350	1.857	1.100
360	1.564	0.955
370	2.031	0.938
380	2.013	0.892
390	0.879	0.571
400	0.664	0.965
410	1.062	1.368
420	1.440	1.841
430	1.832	2.337
440	2.174	2.568
450	2.275	2.602
460	2.119	2.468
470	1.816	2.055
480	1.115	1.377
490	0.552	0.625
500	0.192	0.188

Tropeoline OO ($1.92 \times 10^{-4} M$)

<u>Wavelength</u>	<u>Absorbancy</u>	
	<u>Neutral</u>	<u>Base</u>
250	0.810	1.071
255	0.730	1.049
260	0.720	1.052
265	0.790	1.058
270	0.870	1.074
275	0.950	1.081
280	0.940	1.087
285	0.930	1.094
290	0.900	1.095
295	0.870	1.085
300	0.840	1.106
305	0.820	1.119
310	0.790	1.148
315	0.725	1.152
320	0.650	1.161
325	0.525	1.162
330	0.420	1.167
335	0.295	1.179
340	0.190	1.180
345	0.155	1.173
350	0.220	1.128
355	0.245	1.020
360	0.290	0.790
365	0.380	0.610
370	0.500	0.485
375	0.600	0.355
380	0.740	0.265
385	0.930	0.225
390	1.073	0.190
395	1.194	0.150
400	1.272	0.120
410	1.362	0.110
420	1.382	0.075
430	1.401	0.070
440	1.403	0.075
450	1.404	0.075
460	1.421	0.095
470	1.409	0.125
480	1.410	0.190
490	1.345	0.300
500	1.000	0.440
510	0.540	0.610
520	0.210	0.830
530	0.080	1.059
540	0.025	1.222
550	0.010	1.333

Tropeoline 00 Continued

<u>Wavelength</u>	<u>Absorbancy</u>	
<u>m μ</u>	<u>Neutral</u>	<u>Base</u>
560	0	1.390
570	0.005	1.418
580	0.025	1.442
590	0.030	1.443
600	0	1.414
610	0	1.305
620	0	1.127
630	0	0.910
640	0	0.630
650	0	0.410

Phenolphthalein ($1.46 \times 10^{-4} M$)

<u>Wavelength</u>	<u>Absorbancy</u>	
	<u>Neutral</u>	<u>Acid</u>
250	0.302	1.118
255	0.280	1.215
260	0.285	1.230
265	0.270	1.136
270	0.288	1.027
275	0.316	0.855
280	0.313	0.760
285	0.345	0.700
290	0.365	0.680
295	0.342	0.650
300	0.330	0.620
310	0.352	0.565
320	0.316	0.470
330	0.295	0.415
340	0.245	0.390
350	0.140	0.360
360	0	0.230
370	0	0.200
380	0	0.185
390	0	0.156
400	0	0.142
410	0	0.136
420	0	0
430	0	0
440	0	0
450	0	0
460	0	0
470	0	0
480	0	0
490	0	0
500	0.015	0.155
510	0.070	0.162
520	0.121	0.155
530	0.237	0.155
540	0.294	0.152
550	0.365	0.184
560	0.660	0.208
570	1.085	0.220
575	1.125	0.238
580	0.960	0.230
590	0.490	0.222
600	0.196	0.195
625	0.036	0
650	0.028	0

2,4-Dinitroaniline ($7.93 \times 10^{-5} \text{M}$)

<u>Wavelength</u>	<u>Absorbancy</u>		
	<u>Neutral</u>	<u>Acid</u>	<u>Base</u>
250	0.018	0.015	--
260	0.021	0.021	--
270	0.023	0.022	--
280	0.225	0.020	--
290	0.020	0.042	--
300	0.015	0.070	--
310	0.098	0.150	--
320	0.097	0.320	--
330	0.150	0.410	2.310
340	0.208	0.640	2.285
350	0.293	0.775	2.222
360	0.691	0.750	2.143
370	0.930	0.660	1.722
380	1.06	0.550	1.345
385	1.14	0.530	1.237
390	1.11	0.520	1.780
400	0.900	0.344	1.081
410	0.664	0.198	0.941
420	0.146	0.110	0.620
430	0.080	0	0.240
440	0.110	0	0.220
450	0.157	0	0.210
460	0.322	0	0.205
470	0.391	0	0.202
480	0.526	0.111	0.140
490	0.688	0.143	0.120
500	0.854	0.244	0.105
520	1.180	0.290	0.095
535	1.405	0.530	--
540	1.361	0.305	0.012
560	1.040	0.220	0
580	0.681	0.210	0
600	0.281	0.200	0
625	0.013	0.010	0
650	0	0	0

Thymol Blue ($1.78 \times 10^{-5} \text{M}$)

<u>Wavelength</u>	<u>Absorbancy</u>		
	<u>Acid</u>	<u>Neutral</u>	<u>Base</u>
250	0.175	0	1.184
255	0.125	0	1.160
260	0.110	0	1.158
265	0.120	0	1.159
270	0.140	0	1.167
275	0.165	0.010	1.159
280	0.200	0.070	1.157
285	0.250	0.125	1.138
290	0.285	0.180	1.095
295	0.300	0.215	1.063
301	0.325	0.250	1.040
305	0.315	0.220	1.031
310	0.305	0.180	1.028
315	0.290	0.145	1.030
320	0.275	0.155	1.038
325	0.240	0.150	1.021
330	0.205	0.140	0.980
335	0.180	0.125	0.890
340	0.170	0.105	0.780
345	0.145	0.080	0.660
350	0.140	0.060	0.540
355	0.140	0.040	0.480
360	0.140	0.030	0.400
365	0.155	0.035	0.385
370	0.170	0.075	0.375
375	0.160	0.070	0.345
380	0.165	0.090	0.340
385	0.170	0.155	0.350
390	0.180	0.200	0.355
395	0.170	0.140	0.350
400	0.135	0.095	0.315
410	0.125	0.110	0.230
420	0.065	0.035	0.155
430	0.010	0	0.120
440	0	0	0.095
450	0.010	0	0.085
460	0.015	0	0.080
470	0.010	0	0.085
480	0.040	0	0.100
490	0.070	0	0.090
500	0.075	0	0.105
510	0.125	0	0.110
520	0.175	0.020	0.125
530	0.260	0.070	0.220
540	0.325	0.135	0.270

Thymol Blue Continued

<u>Wavelength</u>	<u>Absorbancy</u>		
	<u>Acid</u>	<u>Neutral</u>	<u>Base</u>
550	0.440	0.225	0.340
560	0.530	0.360	0.430
570	0.640	0.520	0.560
580	0.750	0.670	0.700
590	0.850	0.810	0.760
600	0.930	1.006	0.950
610	0.960	1.148	1.082
620	0.980	1.211	1.174
630	0.740	1.198	1.171
640	0.470	0.975	0.990
650	0.270	0.620	0.680

Potassium Amide (0.1M)

<u>Wavelength</u>	<u>Absorbancy</u>
250	1.087
255	1.067
260	1.072
265	1.081
270	1.091
275	1.090
280	1.108
285	1.114
290	1.122
295	1.132
300	1.128
305	1.125
310	1.149
315	1.160
320	1.163
325	1.171
330	1.177
335	1.183
340	1.198
345	1.218
350	1.219
355	1.388
360	1.438
365	1.444
370	1.456
375	1.431
380	1.385
385	1.085
390	0.660
395	0.355
400	0.215
410	0.085
420	0.055

APPENDIX IV

SUGGESTIONS FOR FURTHER STUDY

1. The relative base strengths of urea, thiourea, and guanidine in water are:



The order of urea and thiourea are the same in ammonia with thiourea displaying acidic character while urea is very weakly basic. Guanidine should then be more basic than urea in ammonia and this could be studied by use of basic indicators of the azo type such as tropeoline OO.

2. When an ammonia solution of m-dinitrobenzene is electrolyzed, hydrogen is evolved at the cathode (43) and the nitro group is reduced. This suggests formation of an ammonium compound and use as an acid-base indicator. It was observed during the course of this study that trinitrobenzene also forms highly colored solutions and further study of it is recommended.

3. The ion product of water can be determined directly by spectrophotometric means, while in ammonia the value of 10^{-33} for its ion product was determined by electrochemical means. Because ion pairing is extensive in ammonia, a spectrophotometric determination of the ion product may be more valid as this method measures concentrations and not activities.

4. When a liquid ammonia solution of 2,4-dinitroaniline in a sealed tube was warmed from -77°C to room temperature, the deep red

color became orange. Upon cooling, a red compound precipitated and redissolved upon standing. Since evaporation of ammonia solutions of 2,4-dinitroaniline always gives a yellow compound, perhaps the red precipitate could be the ammonium salt of dinitroaniline. The spectrophotometric study of temperature effects on this is recommended.

5. The indicator tropeoline OO has a very sharp color change from acidic to basic solution (or vice versa) in ammonia. This could be used in acid-base titrations in ammonia as a visual indicator to show the equivalence point of a neutralization reaction. Other azo dyes may have this property, and because the salt effect is negligible for this indicator, investigation is warranted.

6. In the two-step equilibria established in ammonia by addition of a molecular solute, the ionization step is more dependent upon the nature of the solute than upon the solvent. Since this is the equilibrium which can be studied spectrophotometrically, a look at some indicators in other solvents such as pyridine or amine-type solvents and a comparison of acidities should lead to a fundamental characteristic of acids and bases.

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