SOLUBILITIES OF QUINOLINE, INDOLE, ACRIDINE, AND CARBAZOLE IN AQUEOUS ACIDIC SOLUTIONS

By

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PREFACE

In this research project the solubilities of four heterocyclic nitrogen compounds are measured in water, hydrochloric acid, and sulfuric acid at different temperatures. These nitrogen compounds are quinoline, indole, acridine, and carbazole. The following acidic solutions were considered: 0.02-N HCl, 0.2-N HCl, 0.02-N H_2SO_4, and 0.2-N H_2SO_4. The solubilities were measured at a temperature range of 20-60°C. The solubility data were used to predict the enthalpies of solutions and solubility parameters for the nitrogen compounds in water.

I wish to express my sincere gratitude and deep appreciation to my major adviser Dr. Mayis Seapan for his concern, help, and encouragement throughout my graduate work. I would also like to thank the School of Chemical Engineering of Oklahoma State University for providing me the opportunity, space, and supplies to conduct this research. My deep appreciation to the Embassy of Kuwait and Kuwait University for their financial and emotional support.

Finally, I wish to thank my parents and my wife for their love and encouragement throughout this study.

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CHAPTER I

INTRODUCTION

The heterocyclic nitrogen compounds of coal-derived liquids, shale oils, and other crude oils, have undesirable roles in industries dealing with such liquids and oils. These nitrogen compounds act as catalyst poisons and lead to deactivation of hydrotreatment catalysts. They also have a negative effect upon the performance of refinery catalysts. The high nitrogen content of these liquids reduces their utilization as fuel because the fuel bound nitrogen contributes to the formation of nitrogen oxides (NO_x) when these liquids are burned. Due to the toxic and mutagenic nature of these nitrogen compounds and their harmful effects on living creatures, their transport into the aquatic environment must be prevented.

These nitrogen compounds are usually removed from fuels by hydrotreatment, but they can also be removed by acid washing. The increased solubilities of these basic nitrogen compounds in acidic solutions is a potential method for their removal from coal-liquids and shale oils. However, previous studies on extractive upgrading of coal-derived liquids (1) showed the need for solubilities of the nitrogen compounds which are present in coal-derived liquids (CDL). The solubility data of the nitrogen compounds in aqueous solutions can also be important in water pollution control, in modeling natural water systems, and in petroleum research.

Solubilities of heterocyclic nitrogen compounds in water and in aqueous acidic solutions are not sufficiently available in the literature. Most of the solubility data reported in the literature are for the nitrogen compounds in organic solvents and for narrow ranges of temperature. Therefore, the objective of this project is to experimentally measure the solubilities of those nitrogen compounds that are present in high percentages in the CDL's, in water, and in aqueous solutions of hydrochloric and sulfuric acids. The compounds selected for the purpose of this work were quinoline (liquid), indole (solid), acridine (solid), and carbazole (solid). The solvents selected were water and solutions of 0.02-N HCl, 0.2-N HCl, 0.02-N H_2SO_4, and 0.2-N H_2SO_4.

These compounds are fairly insoluble in inorganic solvents; therefore, in order to measure their solubility, it is essential to use an analytical instrument which is sensitive to low concentrations of nitrogenous compounds. The experimental measurements of the solubilities of these nitrogen compounds in the solvents mentioned above were obtained by using an ultraviolet-visible (UV/vis) spectrophotometer. The solubilities were measured at different temperatures after keeping the samples in a constant temperature bath for more than 24 hours.

In this work the water solubility of quinoline has been measured at five temperatures in the range of 23.5-61°C. The solubility of acridine in water was measured at 10 different temperatures. The solubilities of the other two pure compounds (carbazole and indole) were measured in water and in 0.02-N HCl at three different temperatures each and the results are shown in tables and graphs in Chapter V. More solubility measurements for the hydrochlorides and sulfates of these four nitrogen compounds are shown in detail in Chapter V.

The experimental solubility data obtained in this work were used to determine the solubility parameters and the enthalpies of solutions for the four nitrogen compounds and their salts in water. These calculated values of solubility parameters (δ) and the enthalpies of solution (ΔH_s) are shown in Chapter VI along with the values obtained from the literature.

CHAPTER II

LITERATURE SURVEY

This chapter includes the following four sections: Nature of the Basic Nitrogen Compounds, Role and Effects of Nitrogen Compounds in Industry, Survey of Solubility Data, and Use of a UV/vis Spectrophotometer for Quantitative Analysis of N-Compounds.

Nature of the Basic Nitrogen Compounds

This section shows the nature of the basic nitrogen compounds and the percentages at which these compounds are found in coal-derived liquids and shale oils.

McKee, Ells, Goodwin, Gavin, Hamoi, George, Karrick, and Lyder (2) showed that when an oil shale is destructively distilled, the newly formed nitrogen compounds are distributed among the products of the distillation and appear in the form of ammonia and other basic compounds of nitrogen, mainly heterocyclic derivatives of the pyrrole (C_4H_5N) and pyridine (C_5H_5N) series. He showed that the shale oil contains varying amounts of nitrogen compounds in the form of basic tar of the pyridine and analogous series. The residual spent shale contains a considerable portion of the nitrogen, the chemical nature of which is not definitely known. The nitrogen contents of three samples of shale oils from the De Beque, Colorado shales are shown in Table I. This table shows that the nitrogen contents of distilled fractions increase as the boiling points of the fractions become higher.

TABLE I

PERCENT NITROGEN IN THE DISTILLED FRACTION (Ref. 3)

	Sample A	Sample B	Sample C
Percent Distilled	wt.% N	wt.% N	wt.% N
10	0.361	0.344	0.466
20	0.666	0.742	0.837
30	1.113	1.113	1.120
40	1.232	1.491	1.307
50	1.351	1.691	1.365
60	1.141	1.659	1.414
70	1.071	1.537	1.351
80	1.152	1.674	1.374
about 85	1.225	1.665	1.884
Crude Oil Used	1.500	1.855	1.605

Schiller (4) examined five liquid products from different pilot plants using column chromatography and combined gas chromatography-mass spectrometry (GC/MS). He found that the major compound types were quinolines, benzoquinolines, and carbazoles. The results of this GC/MS analysis are shown in Table II. This table indicates that the predominant compounds are quinolines, carbazoles, and benzoquinolines.

The nitrogen-containing compounds of interest were determined and classified into eight parent-compound groups. The eight parent compounds were acridine, carbazole, indole, quinoline, isoquinoline, aniline, pyridine, and pyrrole. However, in this project the solubility measurement will be limited to the first four compounds.

TABLE II

WEIGHT PERCENT OF SOME N-COMPOUNDS IN THE NITROGEN-RICH FRACTIONS OF FIVE SRC SOLVENTS (Ref. 4)

Compound Type	SRC Solvent Sample I	SRC Solvent Sample II	SRC-II Solvent Sample III	SRC Solvent Sample IV	CO-Steam Product
Pyridine, Aniline	0.0	2.2	3.9	7.9	1.0
Tetrahydroquinoline	1.8	5.2	8.3	5.0	1.9
Indoles	0.0	0.5	1.3	0.6	0.5
Quinolines	20.0	16.9	8.2	22.5	5.2
Carbazoles	19.7	10.5	10.5	6.9	7.0
Benzoquinolines	15.5	12.0	8.2	8.2	8.1
Naphthenobenzoquinolines	1.2	2.3	2.8	0.8	2.8
Azapyrene, Azafluoranthenes	1.1	2.0	3.5	1.3	1.8
Benzocarbazoles	3.5	2.0	1.4	0.7	3.8

Role and Effects of Nitrogen Compounds in Industry

Basic nitrogen compounds act as catalyst poisons by absorbing onto active acid sites of the catalyst, which leads to the deactivation of hydrotreatment catalysts.

It is well known that nitrogen compounds are present in fairly high levels in coal-derived liquids. The high nitrogen concentration reduces the utilization of these liquids as fuel. Lin and Holy (5) stated that coal liquids can be used as fuel by power generating plants or other industries that can scrub out the nitrogenous by-products. However, the refinement of coal-derived liquids is often not feasible because nitrogen has poisoning effects on refinery catalysts. Therefore, if coal-derived liquids are to become viable fuels for a variety of applications, it is necessary to reduce the nitrogen level substantially.

The increased solubility of basic nitrogen compounds in acidic solutions is a potential method for their removal from coal liquids. Several investigators have studied the removal of nitrogen compounds by acidic extraction. Some of these studies on the removal of nitrogen compounds by acidic solutions, particularly by sulfuric and hydrochloric acids are presented here. Lin and Holy (5) studied the extraction of the nitrogen compounds from a variety of coal-derived liquids by sulfuric acid solutions of 5-90% concentrations. Figure 1 shows that washing of an H-coal oil with sulfuric acid reduces its nitrogen content in all distillation fractions.

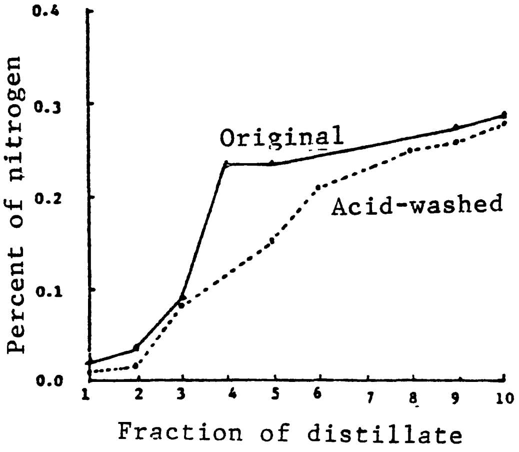


Figure 1. Acid Washing of H-Coal Light Distillate 400-650°F (Ref. 5)

Strachan, Field, and Fleming (6) have studied the solubility of o- and m-nitrotolene and hexafluoro-m-xylene in H_2O-H_2SO_4 mixtures. They have found that in all cases, as the H_2SO_4 content is raised, an initial salting out (a decrease in solubility) is followed by a steady and significant increase in solubility such that aromatics are over 100 times more soluble in 100% H_2SO_4 than in water. Their results are shown in Figure 2. In their study, the solubility determinations were made by a UV spectrophotometer.

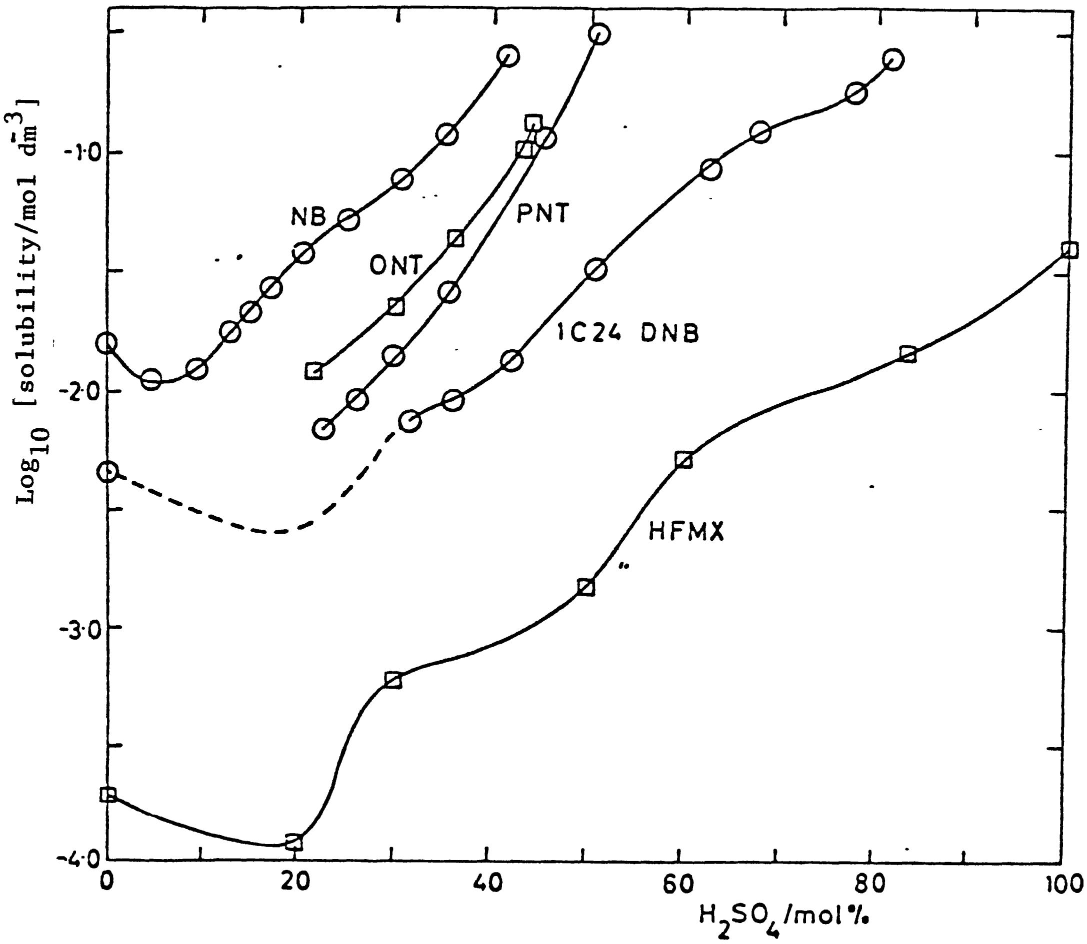


Figure 2. Solubility Versus mol% H_2SO_4

Hydrocarbon mixtures are often contacted with aqueous sulfuric acid in both oil refining and other industrial processes. The solubility behavior of different hydrocarbons in acidic solutions is therefore of considerable importance.

Moore, Sutton, Turrill, Long, Johnson, and Hettinger (7) used acidic solutions of about 40% to extract nitrogen compounds in a shale oil upgrading process known as EXTRACTACRACKING. Cooney, Beal, and Hazlett (8) have studied the stability of two types of shale-diesel fuel marine (DFM). They have found that the high concentration of N-compounds and also the presence of certain types of N-compounds lead to less stable shale-DFM. They have stated that nitrogen-containing aromatics (e.g., pyrroles, pyridines, quinolines, and indoles) are often intimately involved in the reactions leading to deposition of insoluble sediments and gums in both petroleum and shale-derived fuels. They have also shown the results of extraction of these N-compounds by using 0.2 N hydrochloric acid solution.

Schneider, Hollstein, and Janoski (9) have used dry hydrogen chloride to remove basic nitrogen compounds from a coal liquid.

Solubility Data

In this section the water solubilities of some heterocyclic nitrogen compounds will be reviewed. The solubilities of quinoline, indole, acridine, and carbazole in water and other solvents will be discussed in more detail. The physical properties of these four compounds are shown in Appendix A.

Katritzky (10) discussed the solubility of heterocyclic compounds in water and in organic solvents. While water is the most important solvent, and the solubility usually increases with temperature, the temperature coefficient of the solubility can have very different values according to the type of the solute. For example, the N-heteroatom compound with a π-electron deficiency is more water soluble than the corresponding hydrocarbons because of the ability of the spare electron pair on the nitrogen atom to form hydrogen bonds with the solvent. This explains why pyridine is completely miscible with water in contrast to benzene. The fusion of a benzene and pyridine ring to give quinoline involves an increase in the solubility of quinoline over that of benzene or naphthalene, and a decrease compared with that of pyridine.

Katritzky (10) added that further substitution of nitrogen atoms into the naphthalene ring can lead to the high water solubility being regained, as can be seen from the solubilities in water at 20°C shown in Table III.

TABLE III

WATER SOLUBILITY OF SOME N-COMPOUNDS
AT 20°C (Ref. 10)

Compound	State	Solubility in 1 part in
Benzene	Liquid	660.0
Naphthalene	Solid	40,000.0
Pyridine	Liquid	miscible
Quinoline	Liquid	150.0
Isoquinoline	Liquid	220.0
Acridine	Solid	20,000.0
Pyridazine	Liquid	miscible
Pyrimidine	Solid	<1
Pyrazine	Solid	0.6
Quinoxaline	Solid	1.5
Pteridine	Solid	7.0

Individual solubilities and physical properties of quinoline, acridine, indole, and carbazole will be presented here.

Quinoline

According to vonOettingen (13) quinoline is a colorless, strongly refracting liquid of pungent odor, turning dark in contact with the air. It boils at 238°C to 239°C and has a specific gravity of 1.095 at 20°C. The free base is not easily soluble in water, but it is readily soluble in alcohol, ether, and benzene; with equimolecular parts of acids, it forms salts. While the hydrochloride is hygroscopic, the tartrate is well defined, and at the same time, easily soluble in water. Simple physical properties of quinoline are given in Table XXIII in Appendix A.

The solubility of quinoline in water at different temperatures is shown in Table IV.

Albert (14) reviewed the solubility data of quinoline in water and concluded that the most commonly used laboratory reference books give 6 g per 100 ml. at 20°C or simply 0.06 kg/m^3. Albert (14) made an accurate determination of solubility of quinoline in water and found that the solubility at 20°C is 0.65% w/v, or 1 part in 153, or simply 6.5 kg/m^3.

Although the most commonly used preparative separation procedures make use of the differing solubilities of quinoline salts, the data published about the solubilities of these salts of quinoline are very few. In principle, the salts used in separation procedures are phosphates and sulfates of quinoline, isoquinoline, and quinaldine (12). According to Jones (12), the solubility of quinoline phosphate in water is 155 kg/m^3 at 20°C. This value is much less than that of isoquinoline phosphate, so

TABLE IV

SOLUBILITY OF QUINOLINE IN WATER

Temperature, °C	Solubility (kg/m^3)	Ref. Page
20.0	6.4	10(179)
10.0	8.4	12(20)
15.5	8.6	12(20)
19.1	9.1	12(20)
23.5	9.4	12(20)
29.7	9.7	12(20)
36.0	10.0	12(20)
43.5	10.4	12(20)
52.0	10.7	12(20)
60.0	11.1	12(20)
66.0	11.5	12(20)
73.0	12.0	12(20)
20.0	6.5	14(252)
20.0	6.4	15
30.0	6.8	15
40.0	7.2	15
50.0	7.7	15
60.0	8.2	15
20.0	0.67*	16
25.2	0.63*	17
30.3	0.75*	17

* The original values given in references (16) and (17) at temperatures of 20.0, 25.2, and 30.3°C are 0.067, 0.0627, and 0.0753 wt.% respectively. These values are apparently one order of magnitude less than the other solubility data, which seem to be due to an error in the original publication.

that recrystallization provides a method of purification. But the acid sulfate of quinoline is 2-3 times as soluble as isoquinoline sulfate in ethanol, and crystallization has been used to separate them.

Since in this project ultraviolet spectroscopy is used to measure the solubilities, the absorption spectra of different compounds will be presented here.

Figures 3-5 show the ultraviolet absorption spetra of quinoline in different solvents as given in the literature. Figures 3 and 4 show the spectra of quinoline in cyclohexane, and Figure 5 shows the spectrum of quinoline in isooctane. The effect of the solvent on the shape and magnitude of the spectra can be seen by comparing curve Number 5 in Figure 4 and curve Number 1 in Figure 5.

The spectrum of the quinolinium ion has been determined in hydrochloric and sulfuric acid. The spectrum in aqueous hydrochloric acid is shown in Figure 6. This figure shows the effect of the proton (H^+ ion from the HCl acid) on the shape of the quinoline spectrum. The coordinate in Figure 6 represents Log ε where ε is the molar extinction coefficient with the concentration units in gmole/lit.

An examination of the literature shows that there is no study on the quinolinium hydrochloride or quinolinium sulfate from the standpoint of their solubilities and UV absorption spectra.

Acridine

According to Albert (20), acridine is a cream-colored, somewhat volatile solid, melting at 111°C. It is sparingly soluble in water and readily soluble in practically all organic solvents, generally with an intense violet fluorescence. Acridine and its derivatives have several

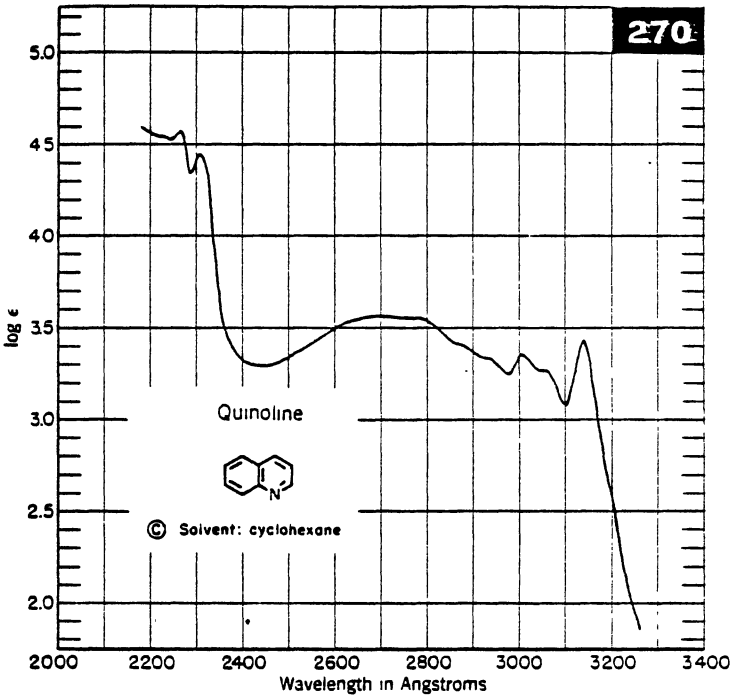
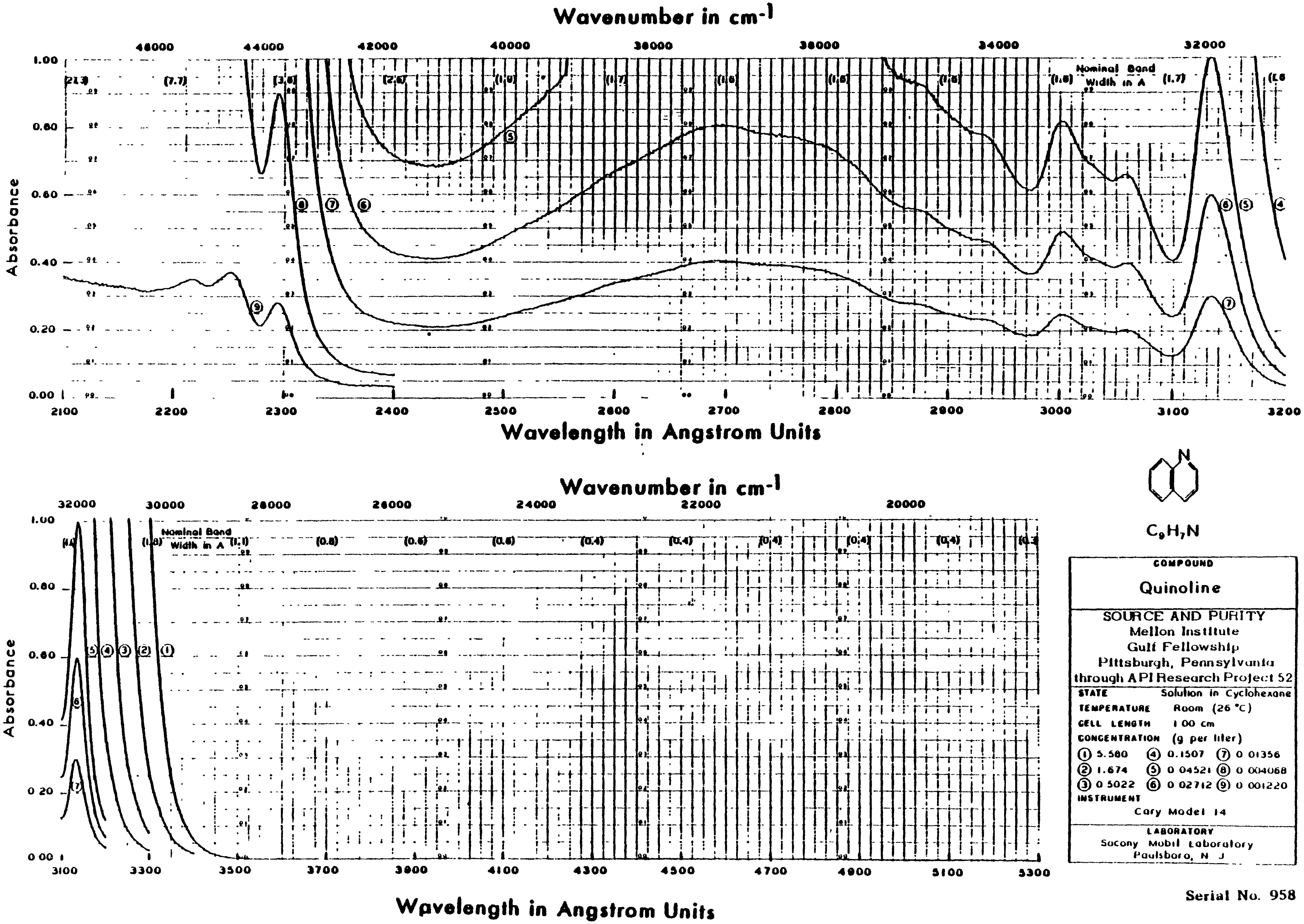


Figure 3. UV Spectrum of Quinoline in Cyclohexane (Ref. 18)



C_9H_7N

COMPOUND

Quinoline

SOURCE AND PURITY
Mellon Institute
Gulf Fellowship
Pittsburgh, Pennsylvania
through API Research Project 52

STATE Solution in Cyclohexane
TEMPERATURE Room (26 °C)
CELL LENGTH 1 00 cm
CONCENTRATION (g per liter)

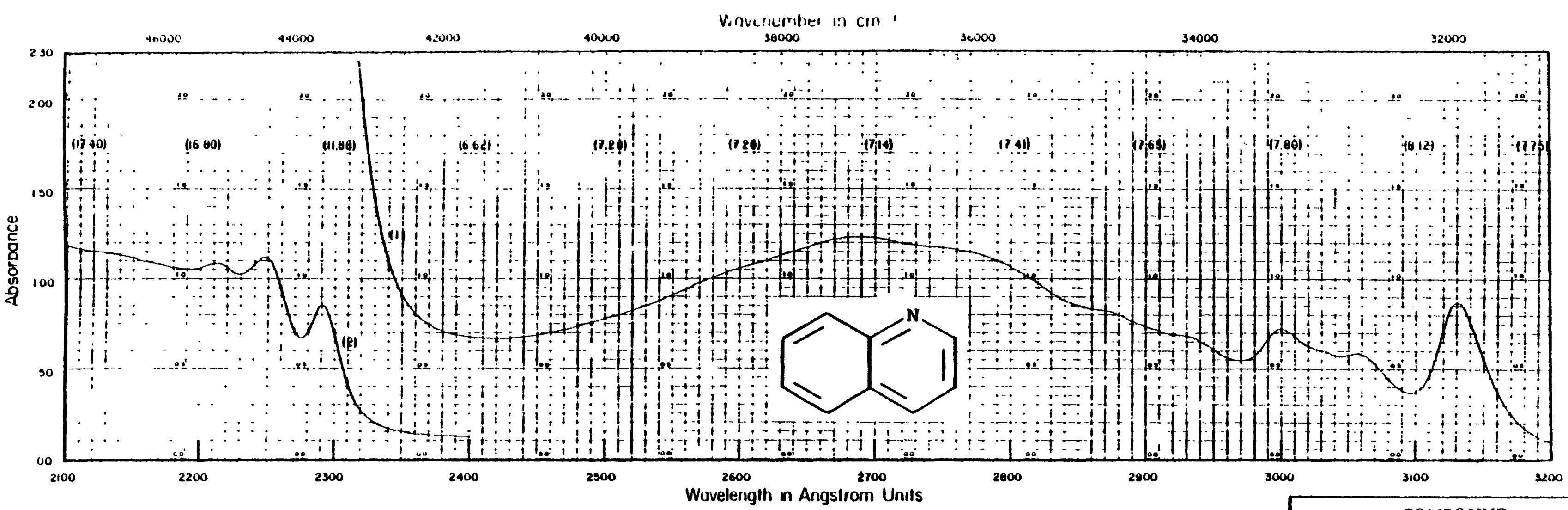
① 5.580 ④ 0.1507 ⑦ 0 01356
② 1.674 ⑤ 0 04521 ⑧ 0 004068
③ 0 5022 ⑥ 0 02712 ⑨ 0 001220

INSTRUMENT
Cary Model 14

LABORATORY
Socony Mobil Laboratory
Paulsboro, N J

Serial No. 958

Figure 4. UV Spectrum of Quinoline in Cyclohexane (Ref. 19)



COMPOUND
Quinoline
C_9H_7N

SOURCE AND PURITY
API Research Project 52b
U. S. Bureau of Mines
Laramie, Wyoming
99.9 mole percent (Estimated)

STATE: Solution in isooctane
TEMPERATURE: Room
CELL LENGTH: 1 cm
CONCENTRATION: Grams per liter
(1) 0.04264
(2) 0.00426

INSTRUMENT Cary Model 11

LABORATORY
Bureau of Mines
Laramie Petroleum Research Center
Laramie, Wyoming

Figure 5. UV Spectrum of Quinoline in Isooctane (Ref. 19)

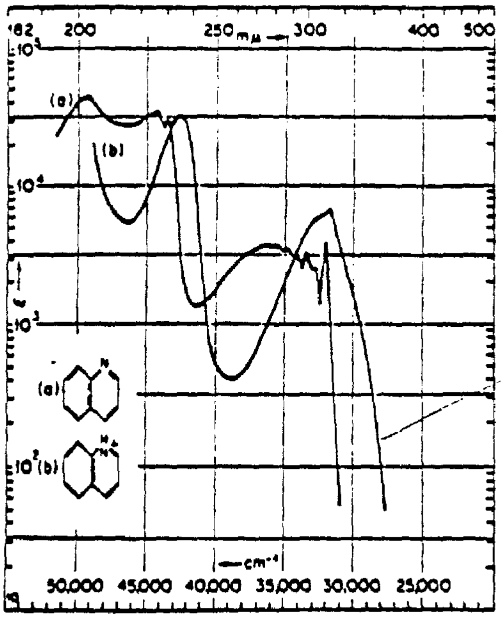


Figure 6. Ultraviolet Spectrum of Quinoline (Ref. 12)

properties in common with their anthracene analogues (such as ultraviolet spectra and fluorescence), but in other properties they often resemble the corresponding quinolines. The properties of acridine can be modified to an extraordinary extent by appropriate substitution, for example, the degree of basic strength and also the color can be varied at will throughout a wide range.

The physical properties of acridine are shown in Table XXIV in Appendix A.

Elderfield (21) mentioned that acridine is a moderately weak base (pKa = 5.6), very slightly stronger than aniline, pyridine, and quinoline, which have the pKa values 4.7, 5.2, and 4.9 respectively.

The solubility data of acridine in various solvents are less available than that of quinoline. In Table V, some of the solubility data of acridine in different solvents are shown.

TABLE V

SOLUBILITY OF ACRIDINE IN DIFFERENT SOLVENTS (Ref. 22)

Solvent	T,°C	Solubility (wt.%)
Enthanol	25	14.0
Benzene	25	17.0
Diethylether	25	6.0
Water	25	0.005(32 mg. lit^{-1})

Albert (20) reported some solubility data for acridine in different solvents. He stated that:

> One gram of acridine is soluble in less than 1 ml. of boiling benzene or alcohol, in 5 ml. of benzene at 20°C, in 6 ml. of alcohol at 20°C, in 16 ml. of ether at 20°C, and 1.8 ml. of boiling cyclohexane. It is sparingly soluble in light petroleum. The solubility in water is about 1 in 20,000, and it is not much greater in boiling water. It is slightly soluble in liquid ammonia and liquid sulfur dioxide.

He also mentioned some salts and complexes of acridine, which are shown in Table VI.

Albert (20) mentioned several ways for the detection and determination of acridine. He said that traces of acridine can be detected by the characteristic fluorescence of neutral molecule and of ion also by the pH of the change of fluorescence from violet to green in water, corresponding to the pKa = 5.6. Acridine has also been detected as the perchlorate, as the silico-tungstate, or by precipitation reactions and crystal shape. The acridine content of coal-tar has been determined by extraction with sodium bisulphite.

The ultraviolet absorption spectra of acridine in two solvents are shown in Figures 7 and 8.

Albert (20) also stated that although the large peak (about 390 nm) of acridine extends slightly further into the visible range than does the leading edge of anthracene (about 380 nm), the two spectra are extraordinarily similar. Figure 7 shows the spectra of acridine in two aqueous solutions at two different pH values. Figure 8 shows the spectrum of acridine in 95% ethanol. Again, these figures show the effect of the pH of the solution and the type of solvent on the shape and magnitude of the spectra.

TABLE VI

THE SALTS AND COMPLEXES OF ACRIDINE
(Ref. 20)

Bisulphate ($C_{13}H_9N + H_2SO_4$)	Obtained by adding alcohol to a solution of acridine in strong sulfuric acid and washing the yellow crystals with alcohol.
Dichromate ($C_{13}H_9N + 0.5\ H_2Cr_2O_7$)	Orange crystals, sparingly soluble in water. From these, the base is readily regenerated with warm ammonia solution.
Hydrochloride ($C_{13}H_9N + HCl + 1.5\ H_2O$)	Lemon-yellow crystals, readily soluble in water with a yellow color, and a green fluorescence which is evident only on dilution. This salt becomes anhydrous, and can be dried to constant weight, at 120°C. It is easily salted out of aqueous solution by chloride ions. Other hydrates are known.
Nitrate ($C_{13}H_9N + HNO_3$)	Yellow crystals from water, anhydrous or + $2H_2O$ depending on the temperature softening at 180°C, and melting sharply at 186°C, with foaming.
Perchlorate ($C_{13}H_9N + HClO_4$)	Yellow crystals from glacial acetic acid or carbon tetrachloride, m.p. 238°C (decomp.).
Periodide ($C_{13}H_9N + HI + I_2$)	Brown crystals from alcohol.
Picrate ($C_{13}H_9N + C_6H_3O_7N_3$)	Yellow needles from alcohol, m.p. about 208° (decomp.); sparingly soluble in water. Alcohol dissolves 0.04%; benzene 0.01%.
Sulphate ($C_{13}H_9N + 0.5\ H_2SO_4$)	Yellow crystals soluble easily in hot water but with difficulty in alcohol.
Tartrate	Useful for purification of acridine.
Aurichloride ($C_{13}H_9N + HAuCl_4$)	Yellow and insoluble in water.

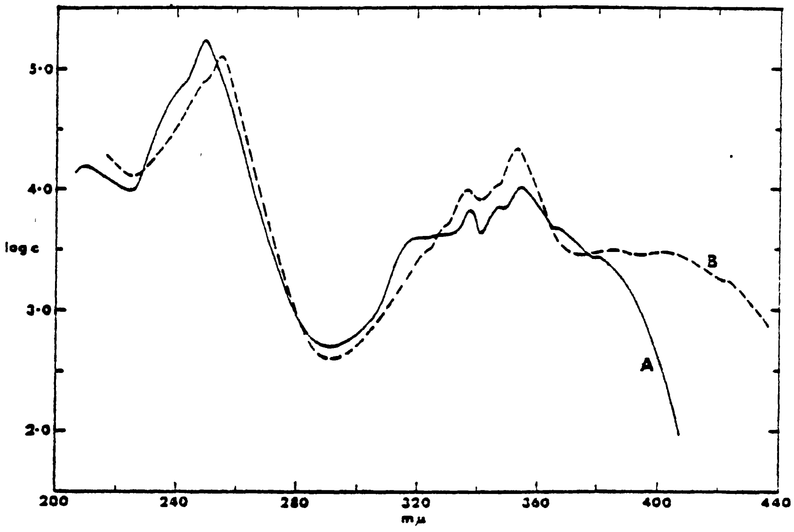


Figure 7. UV Spectra for Acridine
A. Neutral species in water, pH=8
B. Cation in water, pH=3 (Ref. 16)

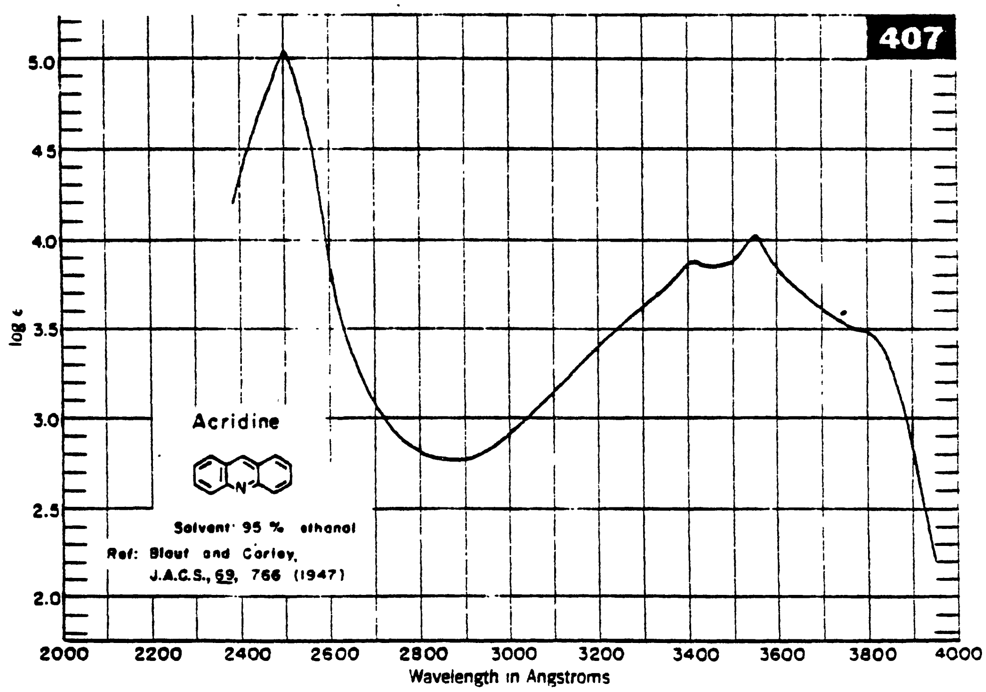


Figure 8. UV Spectrum of Acridine (Ref. 18)

Indole

There is less information available about the physical and chemical properties of Indole. However, Houlihan (23) reported a melting point of 52-54°C and a boiling point of 254°C. He also stated that the low melting point and moderate polarity of indole afford good solubility in a wide range of solvents including petroleum, ether, benzene, chloroform, and alcohol. Indole has a slight solubility in water at 20°C which is 1 part by wt. in 540 (10) and (23), but good solubility in boiling water. Reference (11) gives the solubility of indole in water at 20°C as 0.0204 g in 100 g H_2O. The solubility data of indole in other solvents can be found in reference (17).

The ultraviolet absorption spectra of indole derivatives are highly characteristic and sensitive to changes in substitution on the indole nucleus. They are therefore important in the identification of indole structures. Two ultraviolet absorption spectra of indole in two solvents will be shown below. Figure 9 shows the spectra of indole in cyclohexane and Figure 10 shows the UV spectra of indole in isooctane as reported by API research project 44.

Carbazole

The physical properties as well as the safety and health hazards of both carbazole and indole are shown in Appendix A.

The solubility of carbazole in water at 20°C is given in reference (10) as 1 part by wt. in 60,000. The solubility data of carbazole in other solvents can be found in reference (21).

The UV spectra of carbazole in ethanol and in methanol are shown in Figures 11 and 12 respectively.

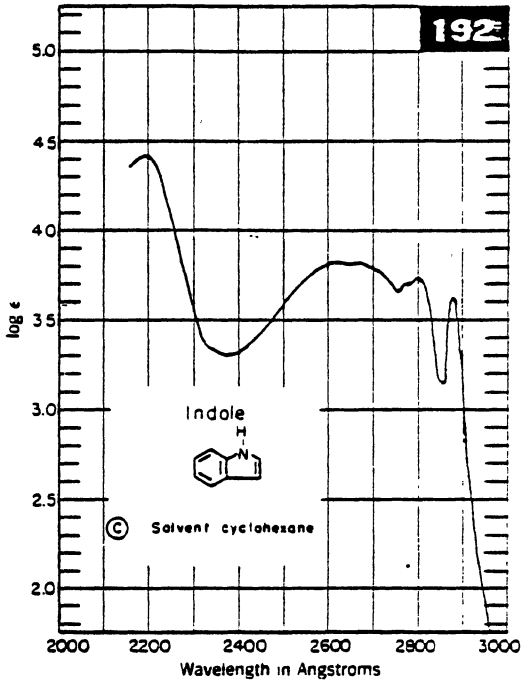
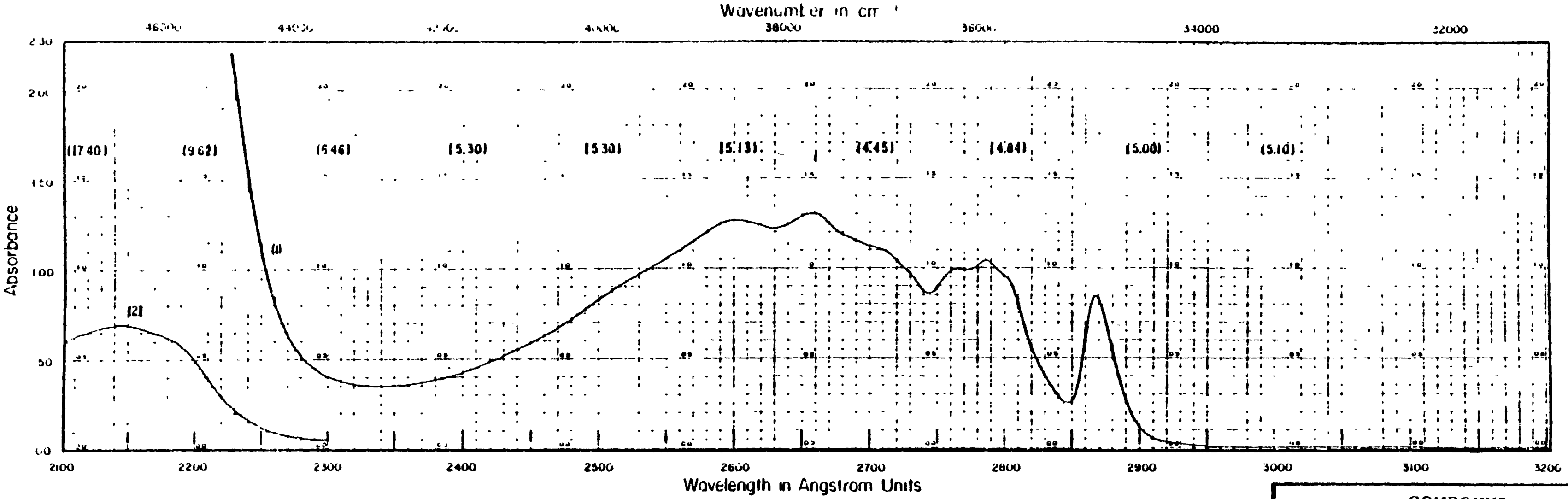


Figure 9. UV Spectrum of Indole in Cyclohexane (Ref. 18)



COMPOUND
Indole
C_8H_7N

SOURCE AND PURITY
API Research Project 52b
Bureau of Mines
Laramie, Wyoming
99.9 mole percent (Estimated)

STATE: Solution in Isooctane
TEMPERATURE: Room
CELL LENGTH: 1.0 cm
CONCENTRATION: Grams per liter
(1) 0.025
(2) 0.0025

INSTRUMENT: Cary Model 11

LABORATORY
Bureau of Mines
Laramie Petroleum Research Center
Laramie, Wyoming

Figure 10. UV Spectrum of Indole in Isooctane (Ref. 19)

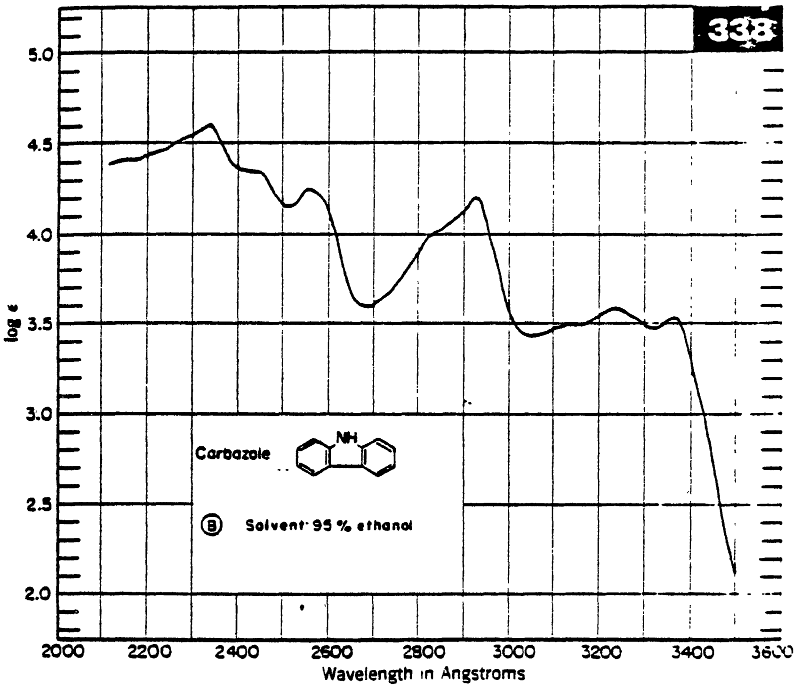
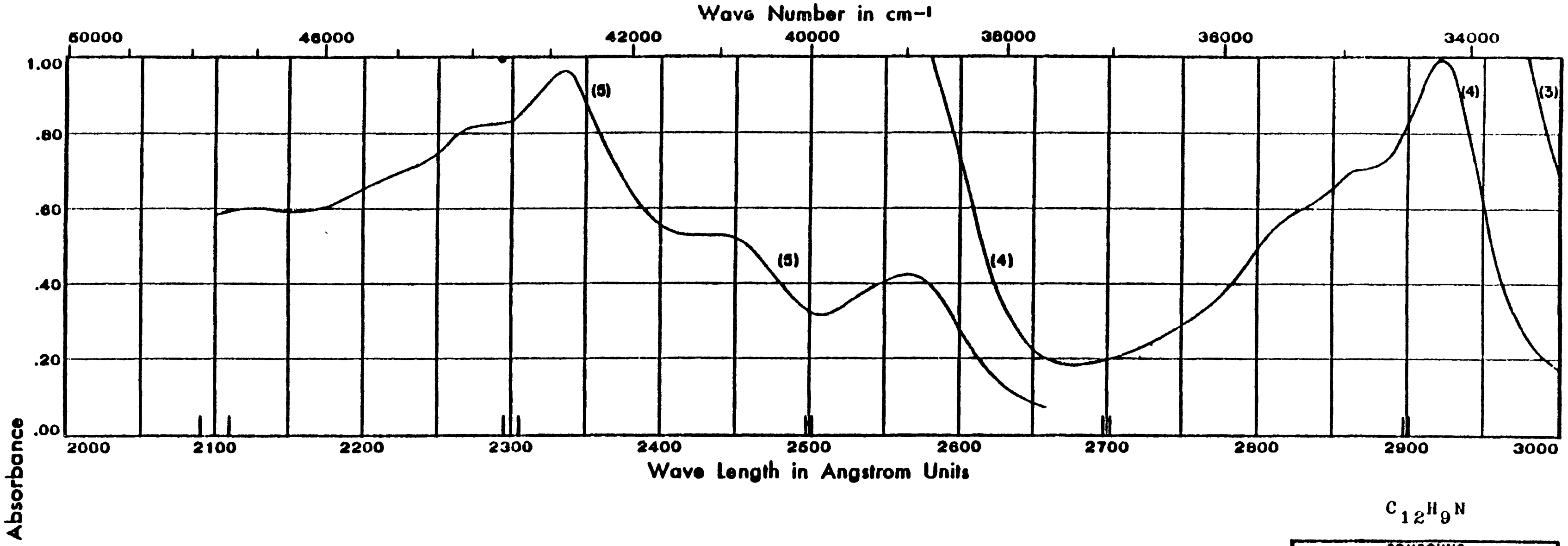


Figure 11. UV Spectrum for Carbazole in Ethanol (Ref. 18)



$C_{12}H_9N$

COMPOUND
Carbazole
Spec. No 3-122

SOURCE AND PURITY
Shell Development Co
M.P. 244.3-246.1°C

STATE Solution in Methanol
TEMPERATURE 25°C
CELL LENGTH 1.00cm

CONCENTRATION (g per liter)
(1) 1.01
(2) 0.101
(3) 0.0104
(4) 0.0101
(5) 0.00404

LABORATORY
Shell Development Co

Figure 12. UV Spectrum of Carbazole in Methanole (Ref. 19)

Use of a UV/vis Spectrophotometry for Quantitative Analysis of N-Compounds

This section reviews some of the investigations done on the UV/vis spectrophotometry and the procedures followed to use this technique to measure the solubility of coal-derived products. The reasons for selecting a UV/vis spectrophotometer in this project are also discussed.

Howell and Hargls (24) mentioned some methods of analysis. They stated that despite the development of many competitive analytical techniques, spectrophotometry continues to be very popular. The inherent ease and simplicity of the spectrophotometric method coupled with the availability of inexpensive, reliable, and now automated instruments are undoubtedly important reasons for this popularity.

Bartle, Collin, Stadelhofer, and Zander (25) reviewed the recent developments in the analysis of coal-derived products and mentioned the importance of UV/vis absorption spectrophotometry in these analysis. They stated that UV/vis absorption spectrophotometry is suitable for the detection and quantitative determination of certain constituents of coal-tar fractions provided that the fraction is not too complex.

Willie May (26) discussed some of the methods used for measurement of the aqueous solubility of aromatic hydrocarbons. One of these methods is the UV spectrophotometer. The procedure he mentioned in using the UV spectrophotometer to study the temperature dependency of the aqueous solubility of Polycyclic Aromatic Hydrocarbons (PAH) is as follows: Saturated solutions were prepared by adding 20g of each solid to a 250 cm^3 glass-stoppered flask containing distilled water. The flasks were suspended in an open water bath and shaken gently for one to three weeks between measurements. Temperature control was maintained to within

± 0.5°C. Samples of the solutions for measurement were withdrawn with pipets through glass wool plugs and emptied into volumetric flasks containing measured amounts of cyclohexane for extraction of the aqueous solutions. The volume of cyclohexane was chosen so that the measured signal fell in the range between 0.5 and 1.5 absorbance units.

Albert (14) used the following procedure to measure the solubility of quinoline in water at 20°C: Quinoline (9.1 g) was dissolved in hot water (8 cm^3), cooled, and the milky emulsion left for 18 hours in a thermostat at 20°C ± 0.02. The aqueous layer was decantd and centrifuged. A sample (5 cm^3) was diluted 800-fold with 0.1 N-hydrochloric acid and the density of the quinolinium cation peak at 313 nm was found to be 0.401.

The UV/vis spectrophotometer has been selected for the solubility measurement in this project for the following reasons: The sensitivity and precision of the UV/vis photometry in detecting low concentrations (ppm), the linearity of the absorbance intensity with the concentration of the solution, all the nitrogen compounds which will be studied in this project can absorb light in the UV/vis range (200-400 nm), all the solvents which will be used in this project have no interference with the UV spectra of the compounds, and finally, the systems of concern in this study are not multicomponent systems and hence no separation is needed.

CHAPTER III

THERMODYNAMICS OF SOLUBILITY

In this chapter theoretical aspects of the solubility of liquids and solids in liquid solvents will be discussed. The solubility of gases in liquids is not within the scope of this work and hence will not be considered. This chapter will be divided into three sections. The first discusses the theoretical and semiempirical equations used for the calculation of solubility. Next, the parameters needed in the solubility equations and the procedures for predicting these parameters will be discussed, and last, some correlations found in the literature which correlate the solubility with other properties of the solutes will be described.

Solubility Equations

Theoretical Equations

Hildebrand and Scott (27) present a comprehensive discussion of ideal and nonideal solutions, solubility of liquids in liquids, solubility of solids in liquids, and other related subjects. For the ideal solubility of liquids in liquids they derived the following equation:

$$RT_c = \frac{2x_1x_2v_1^2v_2^2}{(x_1v_1 + x_2v_2)^3}(\delta_1 - \delta_2)^2 \qquad [1]$$

and for the nonideal solubility of liquids in liquids they give the following equation:

$$\ln x_2 = - \frac{V_2\phi_1^2}{RT} (\delta_1 - \delta_2)^2 \qquad [2]$$

where R = the ideal gas constant = 1.987 cal/g mole. K

T_c = the critical temperature of solute, K

x_1 = the mole fraction of solvent

x_2 = mole fraction of solute

v_1 = molal volume of solvent, cm^3/mole

v_2 = molal volume of solute, cm^3/mole

δ_1 = solubility parameter of solvent, $(cal/cm^3)^{\frac{1}{2}}$

δ_2 = solubility parameter of solute, $(cal/cm^3)^{\frac{1}{2}}$

ϕ_2 = the volume fraction of solvent

($\phi_1 \equiv 1.0$ for dilute solutions)

For the nonideal solubility of solids in liquids they presented the following equation:

$$\log \frac{x_2^i}{x_2} = \frac{V_2\phi_1^2(\delta_1 - \delta_2)^2}{4.575\ T} \qquad [3]$$

where x_2^i = the ideal mole fraction of solute

T = absolute temperature, K

and x_2, v_2, δ_1, δ_2, and ϕ_1 are as defined for equations [1] and [2].

For the case of solid solutes well below their melting points, Hildebrand and Scott (27) present the following equation:

$$RT \ln \frac{x_2^i}{x_2} = B\, x_1^2 \qquad [4]$$

where B = a constant

x_1 = mole fraction of solvent

and x_2^i, and x_2 are as defined for equation [3].

According to Hildebrand and Scott (27) the ideal mole fraction of solute (x_2^i) used in equation [3] and [4] can be replaced by the relative activity of the solute (a_2^s). This relative activity (a_2^s) can be calculated from the following expression:

$$\log a_2^s = \frac{-\Delta H_m^F}{4.575}\left(\frac{T_m - T}{T.T_m}\right) + \frac{\Delta C_p}{4.575}\left(\frac{T_m - T}{T.T_m}\right) - \frac{\Delta C_p}{1.985}\log\frac{T_m}{T} \qquad [5]$$

where, $\Delta C_p = C_p^l - C_p^s$, and ΔH_m is the heat of fusion at the melting point, T_m. Derivation of equation [5] in addition to other procedures for evaluation of a_2^s will be discussed in more detail in the next section.

Hildebrand and Scott (27) also stated that a convenient quantitative check on equation [3] at a single temperature can be made by inserting the experimental solubilities, molal volumes, and solubility parameters for different solvents, and observing the degree of uniformity of the solubility parameter of the solute (δ_2).

Shinoda (28) presents a general equation for solubility, and derived the solubility equation for special cases of liquids and solids in liquids. The general form is:

$$RT \ln \frac{f_2}{f_2^o} = RT \ln a_2 \simeq RT \ln x_2 + V_2\phi_1^2(\delta_1 - \delta_2)^2 \qquad [6]$$

where, f_2^o = fugacity of component 2 in the pure liquid state

f_2 = fugacity of component 2 in the solution.

For the solubility of liquids in liquids and for the case of small solubility of solvent (component 1) in solute (component 2) the following expression is given:

$$\ln a_2 \simeq 0 \simeq \ln x_2 + \frac{V_2\phi_1^2(\delta_1^2(\delta_1 - \delta_2)^2}{RT} \qquad [7]$$

where, a_2 = relative activity of component 2 (solute) and x_2, v_2, ϕ_1, and δ's are as defined for equation [1].

And for the case of solubility of solids in liquids the following expression is given:

$$\ln \frac{P_2^s}{P_2^o} \simeq \ln a_2 \simeq \ln x_2 + \frac{V_2\phi_1^2(\delta_1 - \delta_2)^2}{RT} \qquad [8]$$

where P_2^s = vapor pressure of solid

P_2^o = vapor pressure of supercooled liquid.

Semiempirical Equations

The estimation method presented here was proposed and evaluated by Gemehling, Anderson, and Prausnitz (29). If the heat of fusion, ΔH_F, the melting point, T_m, and the activity coefficient (as a function of composition), γ_1, are known or can be estimated, then the solubility of the solid solute, x_1 (in mole fraction) can be predicted. The estimation of solubility from estimated activity coefficients is a fairly recent development. Solubility data are more frequently used to obtain activity coefficients. The activity coefficient, γ, is a measure of the nonideal behavior of a chemical in solution. The approach, based upon theoretical consideration, has been made possible by recent advances in the estimation of activity coefficient from structural information alone, as will be discussed in the next section.

The solubility equation of solid solutes in liquids is given as:

$$\ln \gamma_1 x_1 = \frac{\Delta H_F}{RT}\left(\frac{T}{T_m} - 1\right) \qquad [9]$$

Equation [9] may be simplified if one assumes that the change in γ_1 with x_1 may be described by the two-suffix Margules equation. The modified form then will be:

$$\ln x_1 + (1-x_1)^2 \ln \gamma_1^\infty = \frac{\Delta H_F}{RT}\left(\frac{T}{T_m} - 1\right) \qquad [10]$$

where, γ_1^∞ is the infinite dilution activity coefficient for the solute. The estimation procedure may be even further simplified if x_1 is less than 0.01 the factor $(1-x_1)$ then approaches unity and we may write:

$$\ln x_1 = \frac{\Delta H_F}{RT}\left(\frac{T}{T_m} - 1\right) - \ln \gamma_1^\infty \qquad [11]$$

The procedure for calculating γ_1^∞ will be discussed in the next section.

According to Grain (30) the method of estimating γ_1^∞ from the structural information is still being developed and because the use of activity coefficients to estimate solubility has been little studied, the range of applicability and accuracy of the overall method have not been established.

Evaluation of Parameters Needed
for the Solubility Equation

Evaluation of Solubility Parameters (δ)

The solubility parameter of a solute in a solvent can be estimated by different methods. Hildebrand and Scott (27) mentioned seven methods for the estimation of the solubility parameter δ. Only four of these methods will be discussed and the other three will be briefly mentioned.

Method 1: Estimation of δ from Heats of Vaporization

The solubility parameter δ is defined as:

$$\delta = (- E/V^{1})^{\frac{1}{2}} \qquad [12]$$

where, -E is the energy of vaporization to the gas phase at zero pressure, and V^1 is the molal volume of the liquid. Therefore, at low vapor pressures where the vapor in equilibrium with the liquid is essentially ideal, we can replace -E by ΔE, and that in turn by ΔH^v - RT to get:

$$\delta \simeq \left(\frac{\Delta H^{v} - RT}{V^{1}}\right)^{\frac{1}{2}} \qquad [13]$$

Method 2: Estimation from Hildebrand Rule

For many substances no heats of vaporization are known. For such cases, it is possible to estimate the heat of vaporization from the boiling point, provided the liquid is nonpolar (or nearly so) by the aid of the Hildebrand Rule. This empirical formula is given here:

$$\Delta H_{298}^{v} \text{ (cal/gmole)} = -2950 + 23.7\ T_b + 0.020\ T_b^2 \qquad [14]$$

or

$$\Delta H_{v}^{b} \text{ (cal/gmole)} = 17.0\ T_b + 0.009\ T_b^2 \qquad [15]$$

where T_b is the normal boiling point in K.

Method 3: Estimation from Equations of State and Critical Constant

The solubility parameter may also be estimated from:

$$\delta = 1.25\ P_c^{1/2} \qquad [16]$$

The constant 1.25 has been empirically obtained.

P_c = critical pressure, atm.
δ = solubility parameter, $(\text{cal/cm}^3)^{1/2}$

Method 4: Estimation from Solubility Data

The solubility parameters of a solute are obtained from measurements of the solubility in a number of solvents whose δ-values are known. Then the average of these values is taken to represent δ_2 of the solute in any solvent.

The other three methods are based on the utilization of internal pressure, surface tension, and optical data. Numerical values of the solubility parameters for many elements and compounds are given in references 27 and 31.

Evaluation of Relative Activity (a)

Hildebrand and Scott (27) stated that in dealing with the solubility of solids, we need to calculate the activity of the solid referred to the pure supercooled liquid, $a_1^s = f_2^s/f_1^o$. The equation

$$\frac{d \ln a_1^s}{dT} = \frac{H_1^l - H_1^s}{RT^2} = \frac{\Delta H_1^f}{RT^2} \qquad [17]$$

can be integrated under the assumption that the heat of fusion ΔH^f, is constant, giving

$$\ln a^s = - \frac{\Delta H^f}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad [18]$$

where T_m = melting point temperature, K.

When the molal heat capacities of the liquid and solid forms of solute, C_p^l and C_p^s, are known, it is better to consider the variation of ΔH^f with temperature,

$$\frac{d\ (H^l - H^s)}{dT} = C_p^l - C_p^s = \Delta C_p^f \qquad [19]$$

for which we obtain

$$\Delta H^f = \Delta H_m^f - \Delta C_p\ (T_m - T) \qquad [20]$$

where ΔH_m^f is the heat of fusion at the melting point.

Substituting equation [20] into equation [17] and integrating we get:

$$\ln a^s = \frac{-\Delta H_m^f}{R} \left(\frac{T_m - T}{T_m T}\right) + \frac{\Delta C_p}{R} \left(\frac{T_m - T}{T}\right) - \frac{\Delta C_p}{R} \ln \frac{T_m}{T} \qquad [21]$$

Now, if we substitute for R = 1.987 cal/gmole K we obtain the same relation as given by equation [5]

$$\log a^s = \frac{-\Delta H_m^f}{4.575}\left(\frac{T_m - T}{T_m T}\right) + \frac{\Delta C_p}{4.575}\left(\frac{T_m - T}{T_m T}\right) - \frac{\Delta C_p}{1.987}\log\frac{T_m}{T} \qquad [5]$$

Shinoda (28) considered the first term of equation [5] and reported the following equation for the relative activity of solids:

$$\ln a^s = \frac{-\Delta H^f}{R}\left(\frac{T_m - T}{T_m T}\right) \qquad [22]$$

Estimation of the Infinite Dilution Activity Coefficient

This method requires a knowledge of the molecular structure. As introduced by Pierotti, Deal, and Derr (32) the technique relates γ_1^∞ to the molecular structures of the solute and solvent molecules through an equation that contains the number of carbon atoms for both species. The general form is:

$$\log \gamma_1^\infty = A_{1,2} + B_2\frac{N_1}{N_2} + \frac{C_1}{N_1} + D(N_1 - N_2)^2 + \frac{F_2}{N_2} \qquad [23]$$

where subscript 1 refers to solute and 2 to solvent, and

$A_{1,2}$ = coefficient which depends on nature of solute and solvent functional group

B_2 = coefficient which depends only on nature of solvent functional group

D = coefficient independent of solute or solvent functional groups

F_2 = coefficient which essentially depends only on nature of solvent functional group

N_1 N_2 = number of carbon atoms in solute and solvent respectively.

Grain (30) listed a table for these constants along with some modification on the general form (equation 23) for homologous series of solutes and solvents. The closest structures in this table to the nitrogen compounds are those of the n-alkylbenzene in water. Therefore if we use the modified form of equation [23] for the n-alkylbenzene and the correction factors given in a table in reference (29), then the infinite activity coefficient for the solid compounds can be estimated from the following expression:

$$\log \gamma_1^{\infty} = A_{1,2} + B_2(N_1 - 6) + C_1 \left(\frac{1}{N_1 - 4}\right) \qquad [25]$$

At 25°C Grain (30) gives the following values for the constants:

$A_{1,2} = 3.554$

$B_2 = 0.622$

and $C_1 = 0.466$

Correlations of Solubility With Other Parameters

Almgren, Marts, Grieser, Powell, and Thomas (33) show a linear correlation between the logarithm of the solubility in water of aromatic hydrocarbons and their normal boiling points. Their plot of the logarithm of the water solubility of a variety of aromatic hydrocarbons as a function of their normal boiling point is shown in Figure 13. A linear least-squares analysis of this plot is given by the following formula:

$$\log S = 0.0138\ T_b + 0.76 \qquad [25]$$

with a correlation coefficient of 0.97.

S = solubility in mole/dm^3

T_b = normal boiling point in °C.

May (26) discussed the temperature dependency of the water solubility of some aromatic hydrocarbons and the calculation of ΔH_s from solubility data. He showed the following formula for calculating ΔH_s from the solubility data:

$$\frac{d(\ln S)}{d(\frac{1}{T})} = \frac{-\Delta H_s}{R} \qquad [26]$$

where T is the absolute temperature, R is the ideal gas constant, and S is the molar solubility at T. Values of ΔH_s at 298 K can be calculated from equation [27] which is a least-squares fit of the integrated form of equation [26].

$$\ln S = \frac{-\Delta H_s}{RT} + b \qquad [9]$$

where b is a constant.

May (26) has also showed some correlations of solubility with molecular parameters. The aqueous solubility of aromatic hydrocarbons has been shown to be related to carbon number, molar volume, and molecular length. These parameters along with molar solubility (expressed as In S) of the compounds are shown by tables and graphs in reference (26).

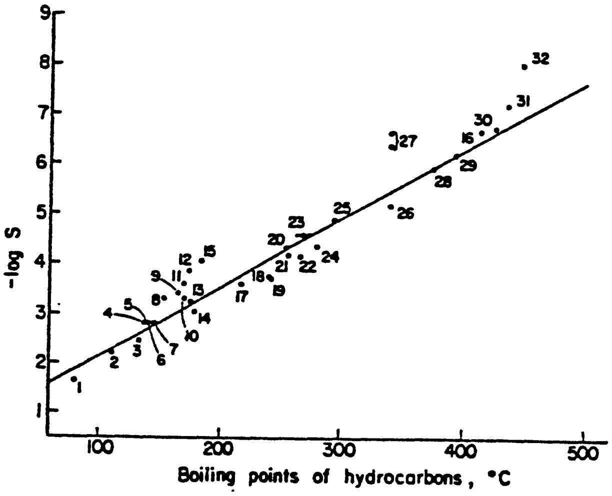


Figure 13. The logarithm of the solubility in water of aromatic hydrocarbons at 25°C, as a function of their normal boiling points (Ref. 33).

(1) benzene
(2) toluene
(3) chlorobenzene
(4) ethylbenzene
(5) p-xylene
(6) m-xylene
(7) O-xylene
(8) isopropylenzene
(9) 1, 3, 5-trimethylbenzene
(10) 1, 2, 4-trimethylbenzene
(11) tert-butylbenzene
(12) sec-butylbenzene
(13) 1, 4-dichlorobenene
(14) indane
(15) n-butylbenzene
(16) 1, 2-benzofluorene
(17) naphthalene
(18) 2-methylnaphthalene
(19) 1-methylnaphthalene
(20) biphenyl
(21) 1-ethylnaphthalene
(22) 1, 4-dimethylnaphthalene
(23) acenaphthalene
(24) 1-bromonaphthalene(at 21°C)
(25) fluorene
(26) phenanthrene
(27) anthracene
(28) fluoranthrene
(29) pyrene
(30) triphenylene
(31) 1, 2-benzan-thracene
(32) chrysene

CHAPTER IV

APPARATUS AND EXPERIMENTAL PROCEDURE

Apparatus

The experimental apparatus used in this project consisted of a constant temperature bath and a UV/vis spectrophotometer.

The constant temperature bath is a precision scientific constant temperature circulating system model TS-66600-4. A built-in cooling coil is provided and the low end of the temperature range is governed by the coolant used. The maximum rated temperature is 210°F. As a result of the adjustable Micro-Set Thermoregulator used, a control sensitivity of ± 0.02°F may be expected over the entire range. Minor modification has been made to this unit by replacing the bath top with a plexiglass top. This plexiglass top has a wider opening, and hence three 100 ml volumetric flasks can be put in the bath at the same time to let the samples reach equilibrium with the constant temperature of the bath.

The sensitivity of this bath in controlling the temperature (± 0.01°C) is an important reason for selecting this unit.

The ultraviolet/visible spectrophotometer is a Perkin Elmer Lambda 3A UV/vis spectrophotometer. It is a double beam, ratio recording, UV/vis spectrophotometer with a microprocessor electronics. It has a wavelength range of 190-750 nm and a wavelength accuracy of ± 0.5 nm. The ease in using this instrument, the ability in detecting very small concentrations (ppm), and the accuracy in the wavelength and absorbance readings are the main reasons for selecting this instrument. A Perkin Elmer model 561, chart recorder was also used with this UV/vis spectrophotometer to record the UV spectra of the compounds.

Chemicals:

The compounds and solvents used in this project are:

Quinoline - reagent grade, Fisher Scientific Company product,

Acridine - Kodack product,

Carbazole - Kodack product,

Indole - 99% purity from Alfa product.

Hydrochlorid Acid: Two solutions with different concentrations were used: (a) concentrated (37.7%) HCl solution, a product of Backer Analyzed Reagent, and (b) 1.0 N solution, a product of Fisher Scientific Company. The latter was used to prepare 0.02 N and 0.2 N-HCl solutions.

Sulfuric Acid: Again two solutions of H_2SO_4 were used: (a) concentrated (96.3%) H_2SO_4 solution, a product of Backer Analyzed Reagent, and (b) 1.0 N-solution, a product of Fisher Scientific Company which was used to prepare 0.02-N and 0.2-N H_2SO_4 solutions.

Experimental Procedure

The procedure followed in this experiment can be divided into two parts: (A) the procedure used to measure the solubility of the pure nitrogen compounds in different acidic solutions, and (B) the procedure used to measure the solubility of the salts of these nitrogen compounds in different acidic solutions.

Procedure for the Pure Nitrogen Compounds

The procedure used to measure the solubility of the pure nitrogen compounds in different acid solutions is as follows:

(1) The constant temperature bath was set on the desired temperature and allowed to reach equilibrium.

(2) A 100 ml. volumetric flask is filled to about 2/3 with the solvent, either water or acidic solutions of HCl or H_2SO_4. An excess amount of the nitrogen compound is dissolved in the solvent until saturation where some nitrogen compound remains undissolved in the bottom of the flask. The flask is then shaken well and kept in the bath for about 48 hours, during which time the flask was shaken two to three more times.

(3) After 48 hours a few cubic centimeters (ranging from 2-5 cm^3) of clear solution is pipetted from the clear solution layer of the top of the mixture.

(4) This sample of the saturated compound is then diluted by the same solvent by 800-10^4 fold.

(5) Diluted solution is then analyzed in the UV/vis spectrophotometer and its absorption intensity is measured.

Procedure for the Salts of the Nitrogen Compounds

The procedure used to measure the solubility of the hydrochlorides and sulfates of the nitrogen compounds in different acidic solutions is as follows:

(1) 5-10 grams of the pure nitrogen compound is reacted with

sufficient amounts of concentrated hydrochloric or sulfuric acids in a beaker to produce the hydrochloride or sulfate of the nitrogen compound respectively.

(2) The product of this reaction, which is hydrochloride or sulfate, is filtered and washed with distilled water thoroughly 3-5 times and is washed with the same solvent to be dissolved in for two more times.

(3) This nitrogen compound salt is then left until it drys and the same procedure used for pure nitrogen compound is followed.

The calibration curves used in the determination of solubility were obtained by preparing standard solution with known concentrations and read by the UV/vis spectrophotometer. These solutions were prepared as follows:

(1) 35-100 mg. of the N-compound or its salt is weighed and dissolved in 1 liter of the solvent. (Note: In the case of carbazole 10 mg. is weighed and dissolved in 2 liters of solvent.)

(2) More diluted solution is then prepared from this 1 liter solution by adding proper amounts of solvent. The final concentration of these solutions ranged from 0.1-3.0 mg/lit.

CHAPTER V

EXPERIMENTAL RESULTS

Experimental measurements of the solubility of four nitrogen compounds and their hydrochlorides and sulfates in different acidic solutions have been carried out. Solubility of quinoline in water at five different temperatures are shown in Table VII and plotted in Figure 14. The solubility of quinolinium hydrochloride in water, 0.02-N HCl and 0.2-N HCl at 23.5°C are shown in Table VIII. Table IX shows the solubility of quinolinium sulfate in water, 0.02-N H_2SO_4 and 0.2-N H_2SO_4 at 23.5°C.

The solubility of acridine in water has been measured at different temperatures in the range of 19-61°C. Acridine was washed four to five times with distilled water before dissolving in solvent in order to remove any possible soluble impurities existing in the sample. These experimental measurements, in form of average solubilities, are shown in Table X. A plot of these measurements is also shown in Figure 15 which is a least-squares fit of these data points.

The solubilities of acridinium hydrochloride in water, 0.02-N HCl and 0.2-N HCl have been measured at three different temperatures. The solubility of pure acridine in these solutions has been calculated from the solubility values of the hydrochloride as discussed in Appendix D. Table XI and Figure 16 show the experimentally measured solubilities

TABLE VII

SOLUBILITY OF QUINOLINE IN WATER

Temperature, °C	Average Solubility, kg/m^3	Standard Deviation
23.5	6.6	0.24
35.0	7.3	0.40
45.0	7.7	0.05
50.0	8.1	0.36
60.0	8.4	0.80

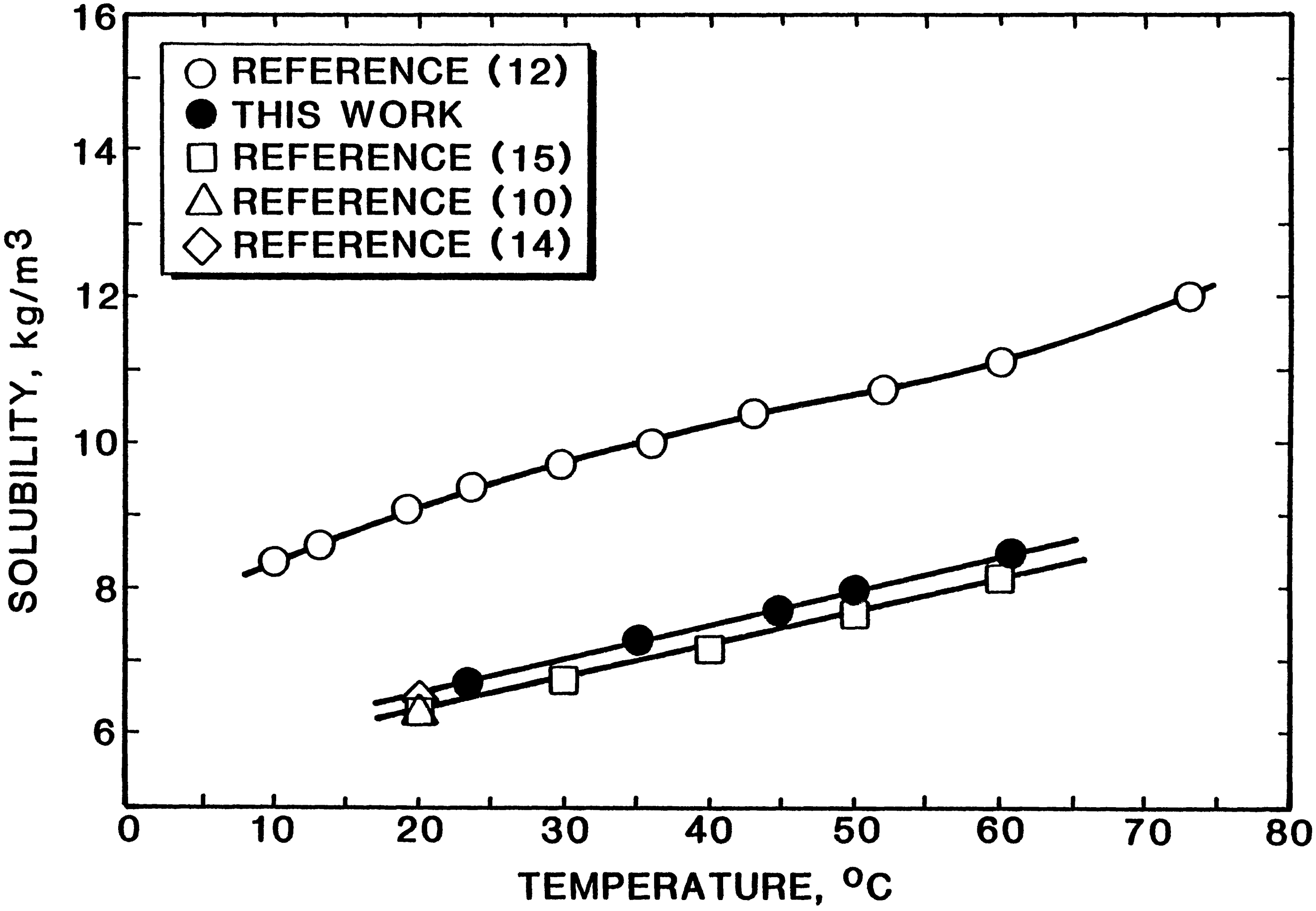


Figure 14. Solubility of Quinoline in Water

TABLE VIII

SOLUBILITY OF QUINOLINIUM HYDROCHLORIDE

Temperature, °C	Solvent	Solubility, kg/m^3
23.5	Water	700
23.5	0.02 N HCl	very solubile
23.5	0.2 N HCl	very soluble

TABLE IX

SOLUBILITY OF QUINOLINIUM SULFATE

Temperature, °C	Solvent	Solubility, kg/m^3
23.5	Water	500
23.5	0.02 N H_2SO_4	very soluble
23.5	0.2 N H_2SO_4	very soluble

TABLE X

SOLUBILITY OF ACRIDINE IN WATER

Temperature, °C	Average Solubility kg/m^3	Standard Deviation
19.0	0.1362	0.0134
20.0	0.1495	0.0535
23.0	0.1420	0.0020
25.0	0.2120	0.0080
30.0	0.2350	0.0070
40.0	0.3294	0.0007
41.0	0.2925	0.0276
45.0	0.3292	0.0233
48.0	0.2940	0.0390
61.0	0.5540	0.0180

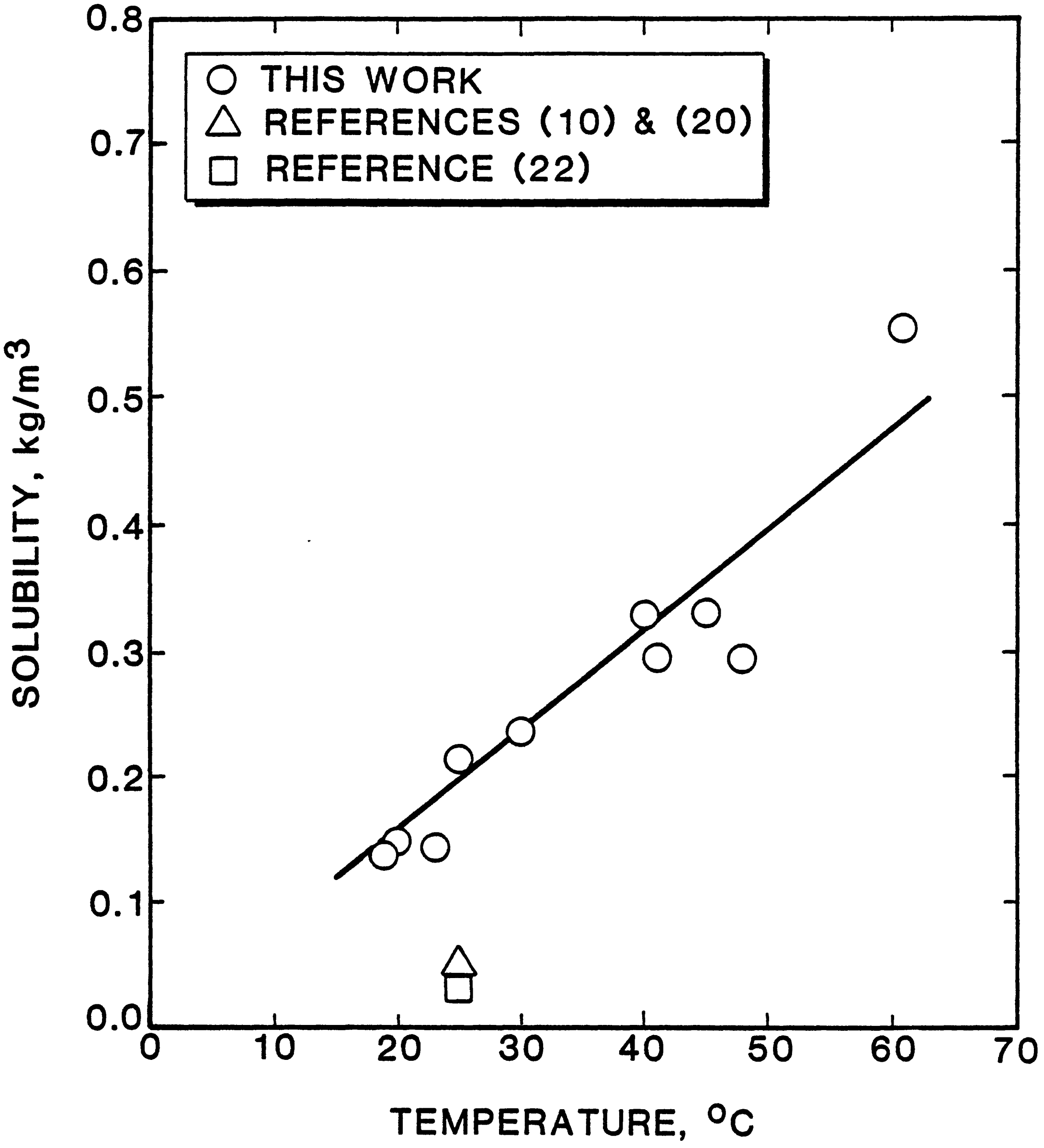


Figure 15. Solubility of Acridine in Water

TABLE XI

SOLUBILITY OF ACRIDINIUM HYDROCHLORIDE

Solvent	Temperature °C	Solubility of Acridinium Hydrochloride, kg/m ^{3}	Standard Deviation	Solubility of Acridine, kg/m ^{3}	Standard Deviation
Water	21.5	7.696	3.74	5.899	2.867
	25.0	9.256	4.47	7.095	3.426
	30.0	11.856	6.032	9.087	4.624
0.02-N HCl	21.5	15.704	0.312	12.037	0.239
	25.0	15.808	0.416	12.117	0.319
	30.0	20.280	0.52	15.545	0.398
0.2-N HCl	25.0	30.056	0.104	23.038	0.0797
	29.0	43.992	0.312	33.719	0.239
	35.0	66.350	0.208	50.857	0.159

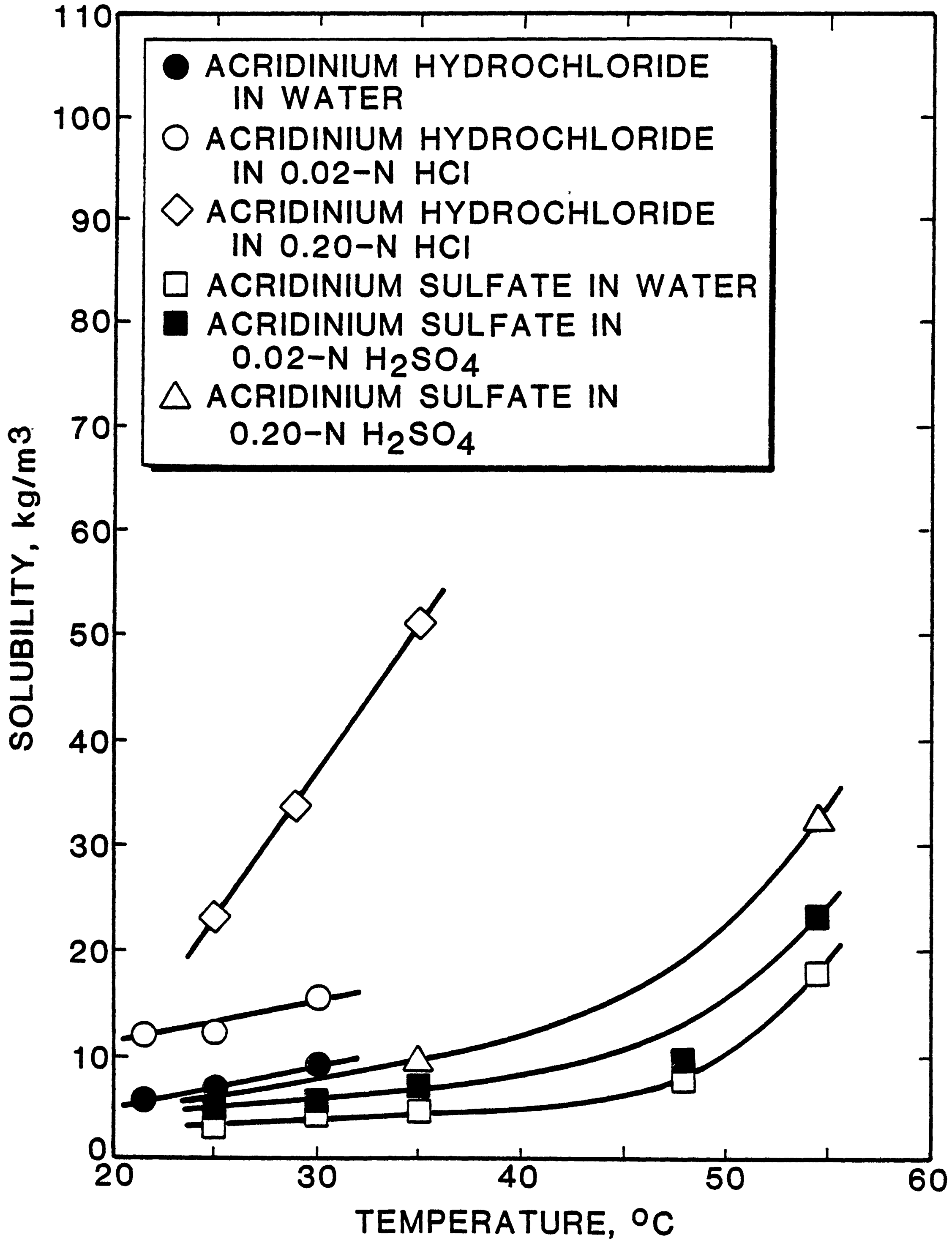


Figure 16. Solubilities of Acridinium Hydrochloride and Acridinium Sulfate (Plotted as kg of acridine in m^3 of solution)

of the acridinium hydrochloride and the calculated corresponding solubilities of pure acridine in the acidic solution.

The solubilities of acridinium sulfate in water, 0.02-N H_2SO_4 and 0.2-N H_2SO_4 have been measured at 25, 35, and 54.4°C. Again the solubility of acridine in these three solvents has been calculated from the solubility of the sulfate and the results are shown in Table XII and Figure 16.

The salts of acridine in both acids HCl and H_2SO_4 have been analyzed in a Perkins-Elmer elemental analyzer and the C-N-H ratio show that these salts are acridinium hydrochloride and acridinium sulfate respectively. The results of these analyses are shown in Appendix E.

The solubility of carbazole in water and in 0.02-N HCl at three temperatures are shown in Table XIII and in Figure 17. Carbazole has also been dissolved in very concentrated H_2SO_4 (96.3%) and then precipitated by diluting with distilled water. The precipitated crystals are then washed four to five times with distilled water and kept to dry. These crystals are not carbazol salts. Our elemental analysis showed that they are pure carbazol crystals precipitated from sulfuric acid solution. The dry crystals of the acid-treated carbazole were then dissolved in three solvents, water, 0.02-N H_2SO_4, and 0.2-N H_2SO_4 at different temperatures. Solubility measurements of this acid-treated carbazole showed an increase in the solubility of pure carbazole in water and in 0.02-N H_2SO_4 acidic solutions. The UV spectra of this acid-treated carbazole showed the same shape as the UV spectra of pure carbazole in water and in 0.02-N HCl confirming that the carbazol in acidic solutions did not form a carbazolium salt but it rather remained

TABLE XII

SOLUBILITY OF ACRIDINIUM SULFATE

Solvent	Temperature, °C	Solubility of Acridinium Sulfate, kg/m^3	Standard Deviation	Solubility of Acridine, kg/m^3	Standard Deviation
Water	25.0	4.609	2.089	3.153	1.429
	30.0	6.251	0.529	4.276	0.362
	35.0	6.781	0.001	4.639	0.000
	48.0	11.549	0.105	7.901	0.072
	54.4	26.488	4.026	18.121	2.754
0.02-N H_2SO_4	25.0	6.728	1.220	4.603	0.834
	30.0	7.946	0.954	5.436	0.653
	35.0	10.277	1.377	7.031	0.942
	48.0	13.562	1.695	9.278	1.159
	54.4	34.328	0.001	23.485	0.000
0.2-N H_2SO_4	25.0	8.582	0.106	5.871	0.072
	35.0	13.879	0.318	9.495	0.217
	54.4	46.778	0.159	32.003	0.109

TABLE XIII

SOLUBILITY OF CARBAZOLE IN WATER AND IN 0.02-N HCl

Temperature, °C	Solubility in water kg/m^3 (pH = 6.9)	Estimated Error (S.D.)	Solubility in 0.02-N HCl, kg/m^3 (pH + 1.9)	Estimated Error (S.D.)
25.0	6.35×10^{-3}	0.050	8.7×10^{-3}	0.300
30.0	6.70×10^{-3}	0.100	8.925×10^{-3}	0.475
46.5	6.975×10^{-3}	0.125	9.175×10^{-3}	0.425

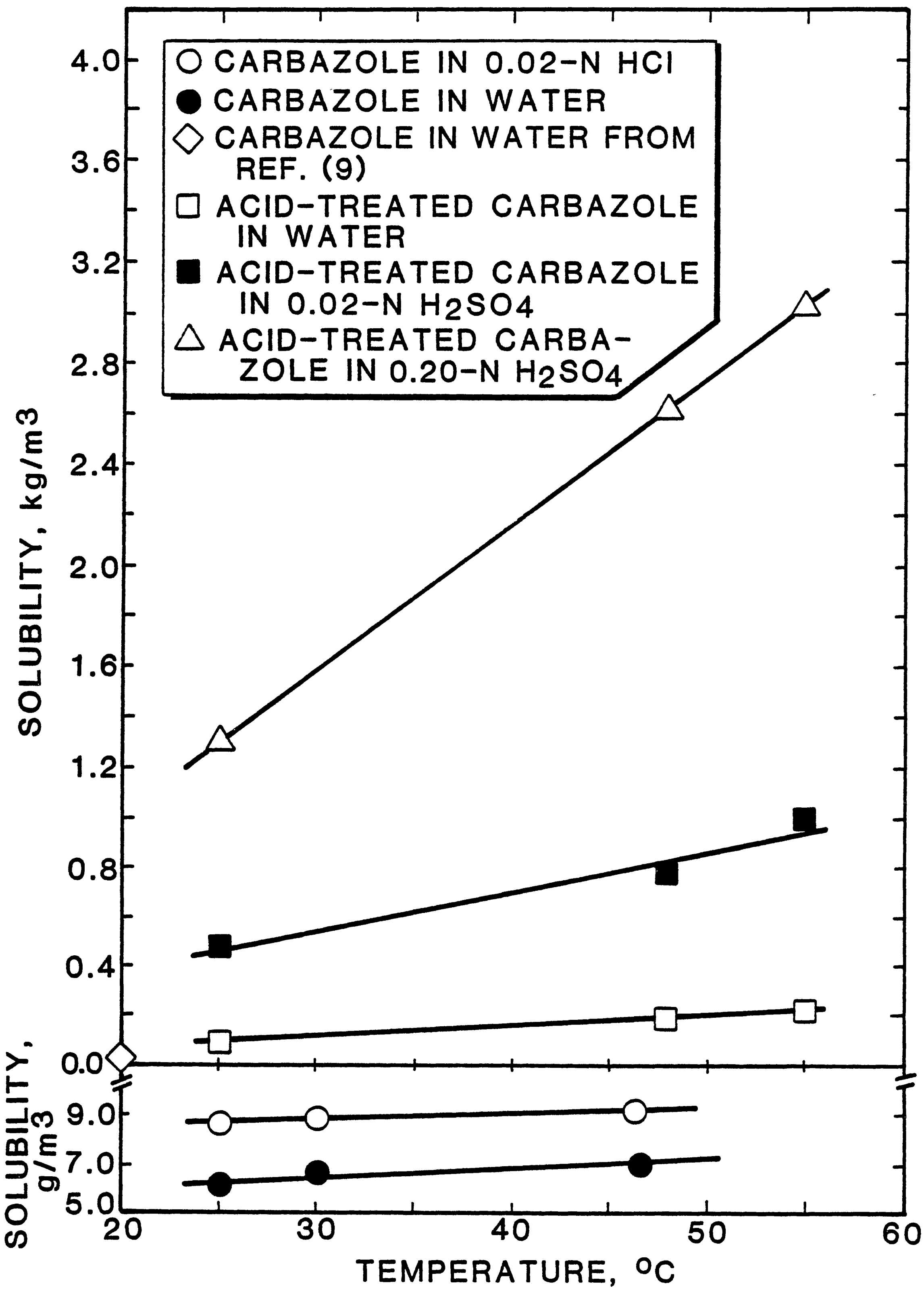


Figure 17. Solubility of Carbazole and Acid-Treated Carbazole

as carbazol. Also the elemental analysis of this acid-treated carbazole showed a total C-H-N percentage of 100% which is the same as the pure carbazole. This indicates that treating carbazole with concentrated H_2SO_4 did not change its structure but it increased its solubility in water and in H_2SO_4 acid solutions. Table XIV and Figure 17 show the solubility of the acid-treated carbazole in three solvents, water, 0.02-N H_2SO_4, and 0.2-N H_2SO_4 at different temperatures.

The solubility of indole in water and in 0.02-N HCl at 23, 35, 55°C are shown in Table XV and Figure 18.

The elemental analysis and the UV spectra of indole in the HCl acid showed that indole also did not form salt when it was dissolved in the acidic solution.

The estimated errors shown in Tables XIV through XV are the standard deviations of these experimental measurements. The formula used to calculate the standard deviation is as follows:

$$\text{Standard Deviation} = \left(\frac{\Sigma(x_i - \bar{x})^2}{n}\right)^{\frac{1}{2}}$$

TABLE XIV

SOLUBILITY OF ACID-TREATED CARBAZOLE

Solvent	Temperature, °C	Solubility, kg/m^3	Standard Deviation
Water	25.0	0.1145	0.018
	48.0	0.1840	0.020
	55.0	0.2200	0.020
0.02-N H_2SO_4	25.0	0.481	0.019
	48.0	0.787	0.087
	55.0	1.012	0.092
0.20-N H_2SO_4	25.0	1.310	0.290
	48.0	2.600	0.400
	55.0	3.020	0.180

TABLE XV

SOLUBILITY OF INDOLE IN WATER AND IN 0.02-N HCl

Temperature, °C	Solubility in Water kg/m^3 (pH =6.5)	Standard Deviation	Solubility in 0.02-N HCl kg/m^3 (pH = 2.1)	Standard Deviation
23.5	1.386	0.014	1.524	0.036
35.0	2.040	0.240	2.620	0.200
55.0	3.240	1.280	4.192	0.200

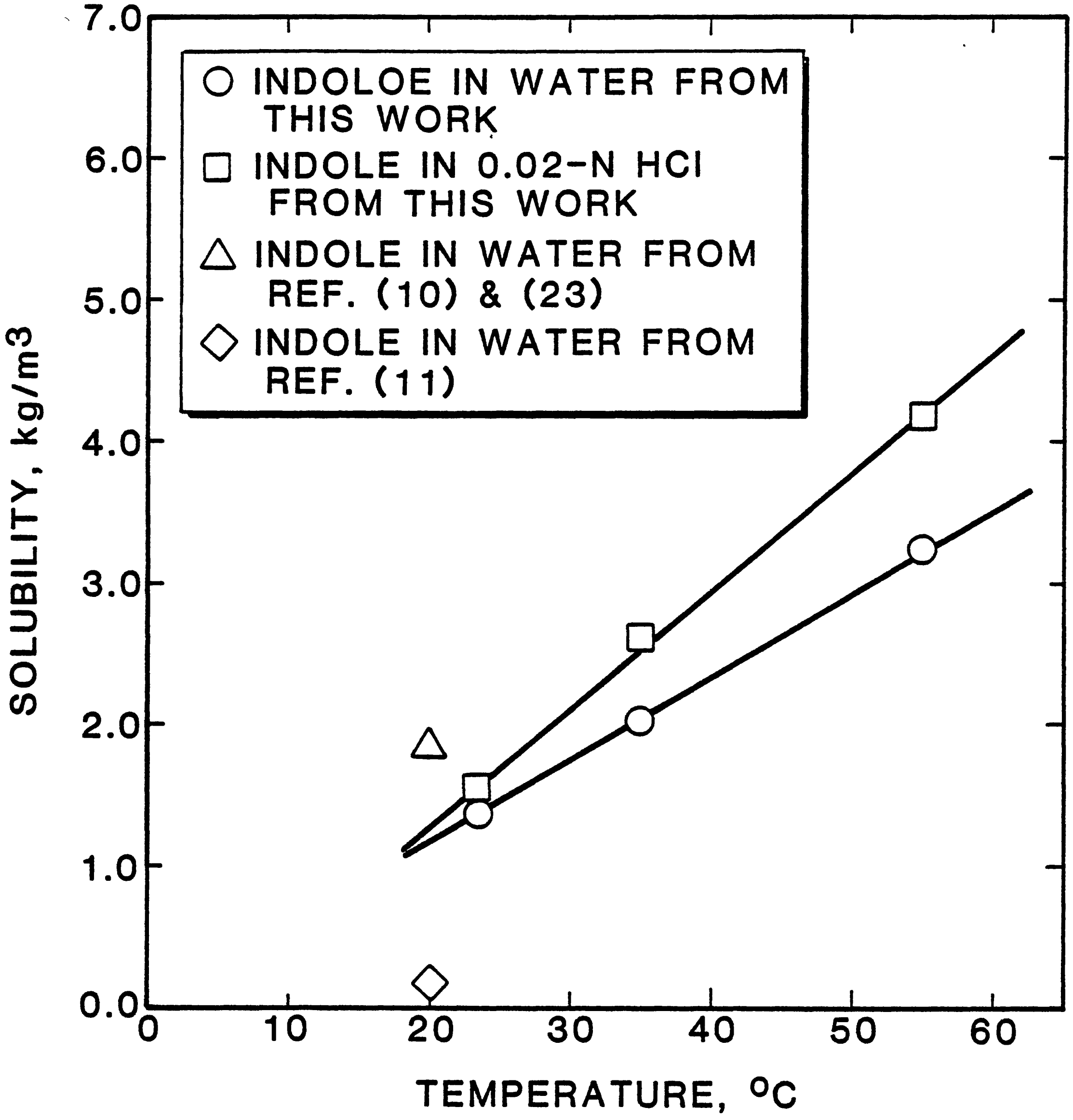


Figure 18. Solubility of Indole

CHAPTER VI

DISCUSSION AND ANALYSIS OF RESULTS

Comparison with Literature Data

The values of the water solubility of quinoline at different temperatures found in references (10, 12, 14, and 15) are compared with the values obtained from this work in Figure 14. However, there are no published values in the literature for the solubilities of quinolinium hydrochloride and quinolinium sulfate in water, 0.02-N HCl, 0.2-N HCl, 0.02-N H_2SO_4, or 0.2-N H_2SO_4. Figure 14 shows that the water solubility of quinoline obtained in this work are in good agreement with those reported in reference (15).

Both curves representing data points obtained from this work and reported in reference (15) are lower than the curve which represents the values reported in reference (12). This indicates that the water solubilities of quinoline given in reference (12) are high.

The solubility of acridine in water is given in some references at only 25°C. References (10) and (20) give a solubility of 1 part acridine in 20,000 parts water by weight at 25°C (which is about 50 g/m^3, and reference (22) gives a solubility of 1 part in 31,250 parts by weight at 25°C (which is 32 g/m^3). The solubility measured in this work for acridine in water at 25°C is 1 part in 4,629 parts by weight (which is 212 g/m^3). Our value is about 4.5 times higher than the values reported in the literature (Figure 15). No solubility values exist in the literature for the solubilities of acridinium hydrochloride and acridinium sulfate in water 0.02-N HCl, 0.2-N HCl, 0.02-N H_2SO_4, or 0.2-N H_2SO_4 solutions. Figures 17 and 18 show the water solubilities of carbazole and indole, respectively, compared with the values found in the literature. No values were found in the literature for the solubilities of the hydrochloride and the sulfate of these compounds in water or acidic solutions.

Thermodynamic Analysis of Solubilities

In this section the solubility correlations discussed in Chapter III will be applied to the experimental data obtained from this work. The correlation between the water solubility and the normal boiling points reported by Almgren et al. (33) was applied to our experimental data. The logarithm of the water solubilities of quinoline, indole, acridine, and carbazole at 25°C were plotted against the normal boiling points of these compounds as shown in Figure 19. From Figure 19 it is obvious that except for the water solubility of acridine at 25°C the other solubilities were in good agreement with this correlation. The solubilities used to plot Figure 19 are molar solubilities (i.e., mole/liter). These molar solubilities of the four N-compounds in water were also plotted against the melting points (in degrees C) of these N-compounds as shown in Figure 20. Again, this figure shows a linear relation between the melting points and the logarithm of the molar solubilities of these N-compounds in water at 25°C.

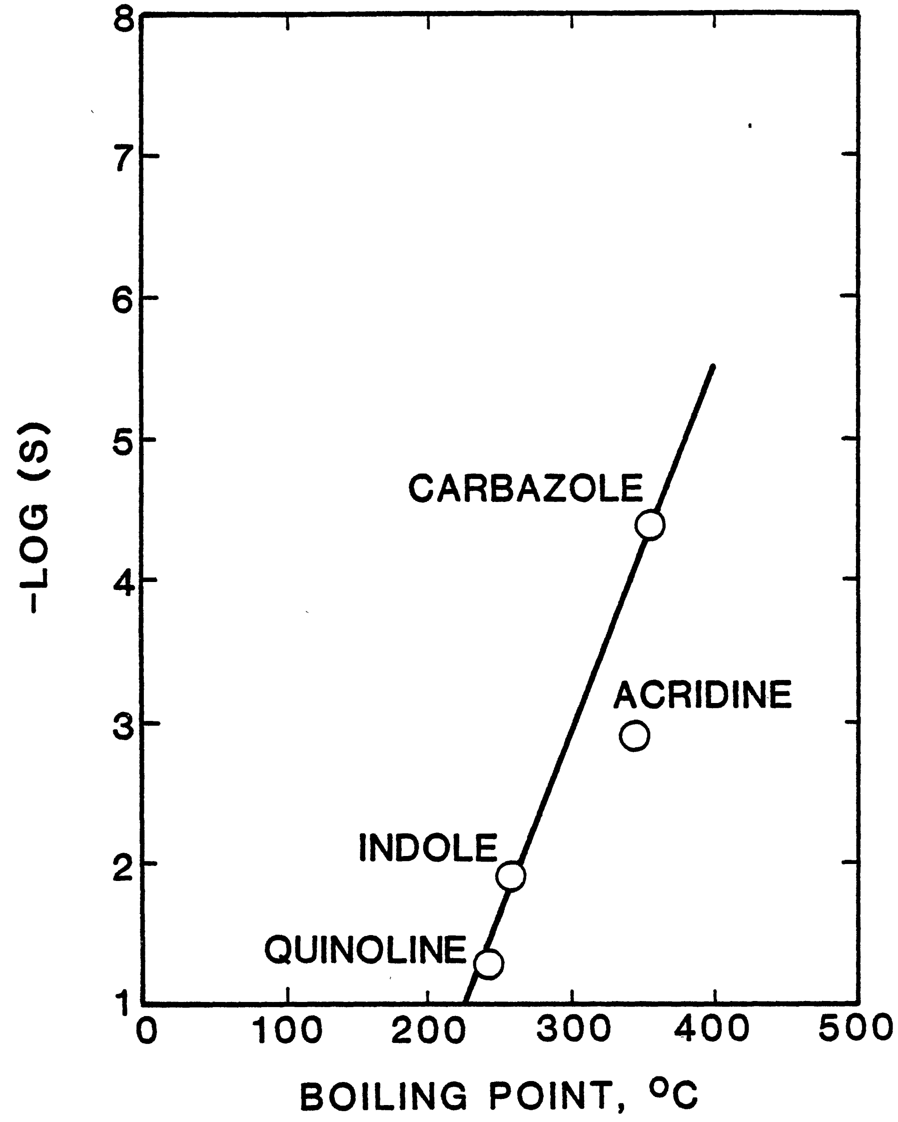


Figure 19. Molar Solubility Versus Boiling Point

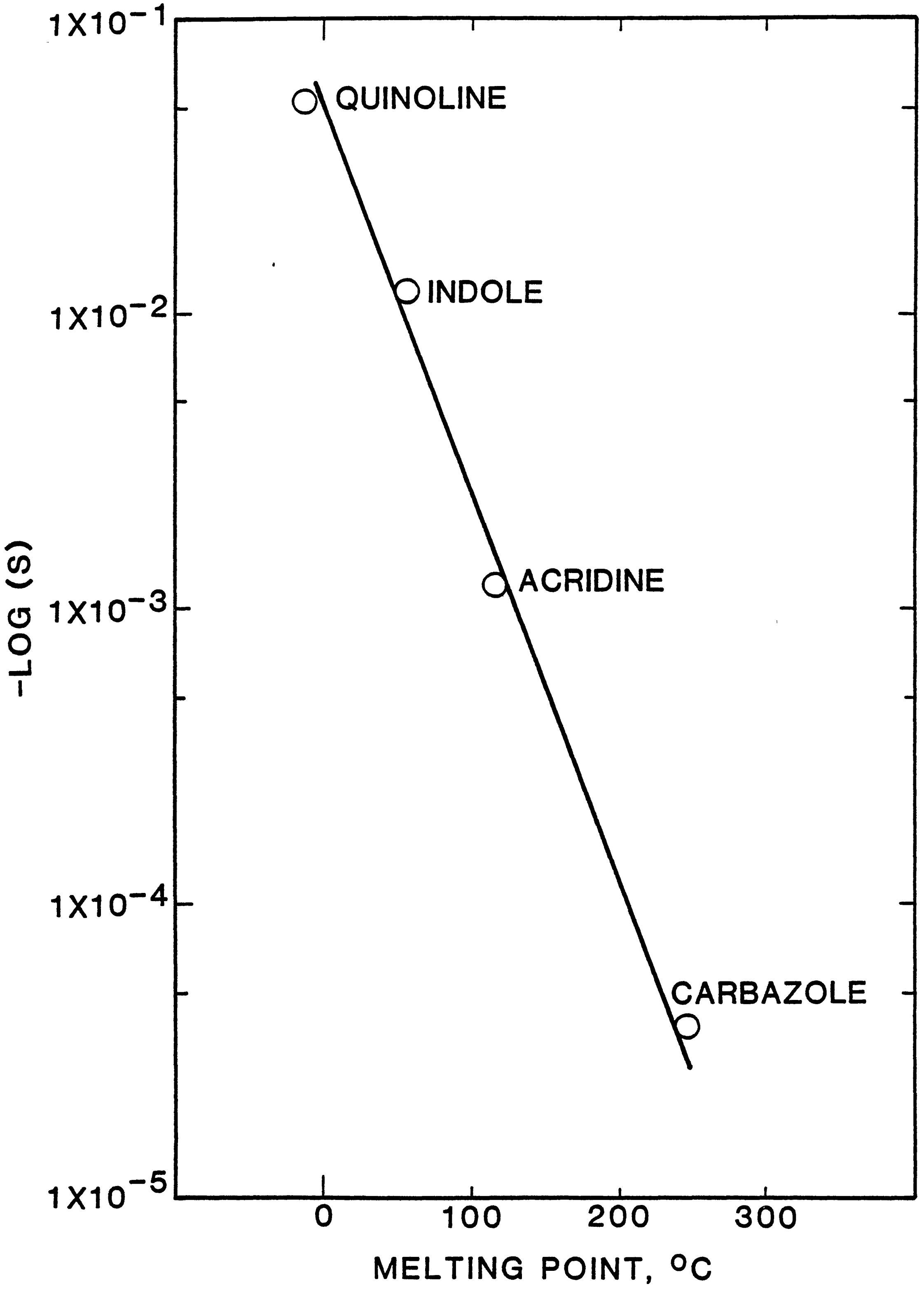


Figure 20. Molar Solubility Versus Melting Point

The empirical formula of May (26) is given here again:

$$\ln S = \frac{-\Delta H_s}{RT} + b \qquad [27]$$

This equation indicates that a plot of ln (S) versus 1/T is a straight line with a slope of $-\Delta H_s/R$. This relation has been applied to the solubilities obtained in this work and the resulting straight lines are shown in Figure 21. These lines represent the following 6 systems:

Line no.	System
1	Quinoline in water
2	Acridine in water
3	Carbazole in water
4	Carbazole in 0.02-N HCl
5	Indole in water
6	Indole in 0.02-N HCl

These graphs indicate that for a set of lines having almost the same slope, a lower line indicates a higher solubility and a higher line indicates a lower solubility. These graphs can be used to estimate the enthalpy of solution, ΔH_s, for the range of temperature shown in these graphs. According to May (26) and Schwarz (34), the enthalpy of solution can be calculated by multiplying the slope of these lines by R (the ideal gas constant).

Values of ΔH_s for the systems in Figure 21 are calculated and tabulated as shown in Table XVI.

Solubility Parameters "δ"

In Chapter III four methods for determining the solubility parameters are described. Two of these methods (Method 1 and Method 4 in

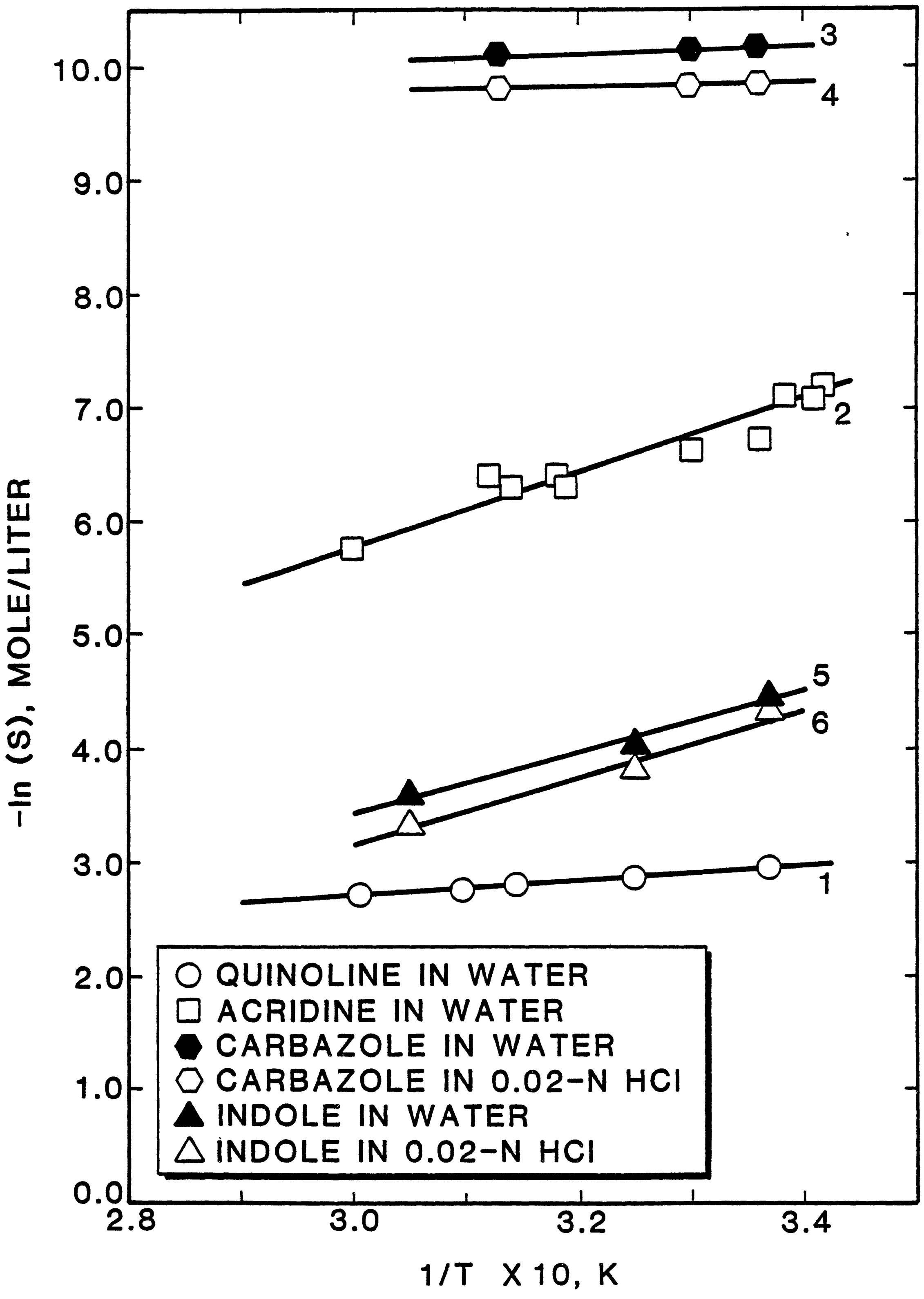


Figure 21. Dependencies of the Solubilities on Temperature

TABLE XVI

ENTHALPIES OF SOLUTIONS OF SOME NITROGEN COMPOUNDS IN DIFFERENT SOLVENTS BETWEEN 20-45°C

Curve No.	N-Compound	Solvent	ΔH_s(kJ/mol)= Slope * 8.314 * 10^{-3}
1	Quinoline	Water	5.618
2	Acridine	Water	27.634
3	Carbazole	Water	2.771
4	Carbazole	0.02-N HCl	1.663
5	Indole	Water	22.572
6	Indole	0.02-N HCl	23.910

Chapter III) will be used here to estimate the solubility parameters of quinoline, indole, acridine, and carbazole in water.

Method 1: Evaluation of the Solubility Parameter from the Heat of Vaporization

In order to calculate the solubility either equation [13] given by Hildebrand and Scott (27) or equation [28] given by Schwarz (34) can be used:

$$\delta = \left(\frac{\Delta H^{V} - RT}{V} \right)^{\frac{1}{2}} \qquad [13]$$

or

$$\delta = \left(\frac{D(\Delta H^{V} - RT)}{M} \right)^{\frac{1}{2}} \qquad [28]$$

where D = Density of the solute
M = Molecular weight of solute
R = Ideal gas constant
T = Absolute temperature
δ = Solubility parameter

Equation [28] is used and the solubility parameters obtained are shown in Table XVII.

Method 4: Evaluation of the Solubility Parameters From the Solubility Data

The solubility data obtained in this work will be used to calculate solubility parameters for quinoline, acridine, indole, and carbazole. The solubility parameter for indole will not be estimated by this method because no values of the relative activity or the enthalpy of

TABLE XVII

SOLUBILITY PARAMETERS FROM ENTHALPY OF VAPORIZATION FOR THE FOUR NITROGEN COMPOUNDS

Compound	Density (g/cm^3) (Ref.)	ΔH^v ($\frac{cal}{gmole}$) (Ref.)	T, ^oC	δ $(kJ/m^3)^{1/2}$
Quinoline	1.625 (15)	12575.4 (30)	25.0	794.2
			35.0	793.5
Acridine	1.278 (22)	15174.6 (30)	25.0	659.6
			35.0	659.1
Carbazole	1.159 (22)	15421.6 (30)	25.0	655.8
			35.0	655.4
Indole	1.220 (23)	11900.0 (30)	25.0	701.9
			35.0	701.3

fusion (which are essential parameters in this estimation procedure) were found in the literature for indole. In order to estimate the solubility parameters from the water solubility of these compounds, equation [2] for liquid solute (quinoline) and equation [8] for solid solute will be used.

$$\ln x_2 = -\frac{V_2\phi_1^2(\delta_1 - \delta_2)^2}{RT} \qquad [2]$$

$$\ln x_2 = \ln a_2 - \frac{V_2\phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad [8]$$

Equations [2] and [8] can be rearranged and the following equations are obtained:

$$\delta_2 = \delta_1 - \left(-\ln x_2 \frac{RT}{V_2\phi_1^2}\right)^{\frac{1}{2}} \qquad [29]$$

and

$$\delta_2 = \delta_1 - \left(\frac{\ln a_2 - \ln x_2}{V_2\phi_1^2} RT\right)^{\frac{1}{2}} \qquad [30]$$

where:

$\delta_2 \equiv$ Solubility parameter of solute

$\delta_1 \equiv$ Solubility parameter of solvent

$V_2 \equiv$ Molar volume of solute

$\phi_1 \equiv$ Volume fraction of solvent

$x_2 \equiv$ Mole fraction of solute

$a_2 \equiv$ Relative activity of solute

Equation [29] can be used to evaluate a solubility parameter for quinoline (liquid). But, in order to use equation [30] for the solid solutes, values of the relative activity (a_2) of these solid solute need to be known. Since, the relative activities of acridine and carbazole are not reported in the literature, then they need to be estimated. The relative activity can be estimated, as discussed in Chapter III, by using equation [18] which is:

$$\ln a_2^s = -\frac{\Delta H_2^f}{R} \left(\frac{T_m - T}{T_m \; T}\right) \qquad [18]$$

Equation [18] was used to calculate the relative activities of acridine and carbazole and they were found to be 0.2074, and $9.8 * 10^{-3}$ respectively.

The solubility data of quinoline, acridine, and carbazole in water were used to calculate solubility parameters for these compounds at different temperatures. The results are shown in Table XVIII.

The last column in Table XVIII shows that the variation of the solubility parameters of the three compounds with temperature is not large, which according to Hildebrand and Scott (27) is a good indication for the accuracy of this measured values of solubilities.

Determination of Liquids and Solids Solubilities in Liquid Solvents by Theoretical Equations

A theoretical and a semiempirical equation will be used to estimate the solubilities of the N-Compounds in water. The results of these

TABLE XVIII

SOLUBILITY PARAMETERS FOR SOME N-COMPOUNDS FROM THEIR WATER SOLUBILITIES DATA

Compound	T, ^{o}C	V cm^{3}/mole	x_2 (mole fraction)	δ^* (kJ/m^{3})$^{1/2}$
Quinoline	23.5	79.49	9.36×10^{-4}	1074.4
	35.0		1.02×10^{-3}	1068.6
	45.0		1.08×10^{-3}	1062.8
	50.0		1.30×10^{-3}	1060.2
	61.0		1.20×10^{-3}	1050.4
Acridine	19.0	140.1	1.36×10^{-5}	1130.7
	20.0		3.79×10^{-5}	1152.7
	30.0		2.44×10^{-5}	1135.9
	40.0		3.07×10^{-5}	1134.6
	61.0		5.57×10^{-5}	1135.9
Carbazole	25.0	127.8	6.80×10^{-7}	1108.7
	35.0		7.24×10^{-7}	1102.9
	46.5		7.61×10^{-7}	1095.8

* The solubility parameter for water used to calculate these δ's is 23.8 (cal/cm^{3})$^{1/2}$ (Ref. 33).

theoretical methods will be compared with the experimental values in this work.

Theoretical Equation

The same equations given by Hildebrand and Scott (27) and Shinoda (28) for liquid and solid solute will be used. Equation [2] for liquid solutes will be used to calculate the solubility of quinoline in water.

$$\ln x_2 = -\frac{V_2\phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad [2]$$

Equation [8] for solid solutes will be used to calculate the solubilities of the other compounds in water.

(see Chapter III for definitions of terms)

Estimation of Water Solubility of Quinoline. Equation [2] can be used to calculate the solubility of quinoline in water at different temperatures.

$$\ln x_2 = -\frac{V_2\phi_1^2}{RT}(\delta_1 - \delta_2)^2 \qquad [2]$$

The molal volume of quinoline (V_2) is reported in reference (15) as 118.5 cm^3/mole. The volume fraction of water (ϕ_1) will be assumed to be 1.0 since we have a dilute solution. If we use the solubility parameter of quinoline calculated from the heat of vaporization (Method 1 in the previous section) then the water solubility of quinoline can be calculated for each temperature T. The calculated solubility expressed in mole fraction are tabulated in Table XIX along with the experimental solubility of quinoline.

Table XIX shows that the calculated solubility, compared with the measured values, are very small. These low values (calculated from equation [2]) indicate that the solubility parameter obtained from the heat of vaporization are not good values to use in this equation.

Estimation of the Water Solubilities of Acridine and Carbazole. Equation [8] will be used to estimate the water solubilities (in mole fractions) of acridine and carbazole.

$$\ln x_2 = \ln a_2 - \frac{V_2\phi_1^2\,(\delta_1 - \delta_2)^2}{RT} \qquad [8]$$

The relative activities of acridine and carbazole calculated in the previous section will be used here. Again the volume fraction of water ϕ_1 will be assumed to be 1.0. The solubility parameters obtained from the heat of vaporization will be used in equation [8] to calculate the mole fractions of acridine and carbazole. Only two temperatures will be considered at which the solubility of acridine and carbazole will be calculated and compared with the measured values as shown in Table XIX.

Again, as can be seen from Table XX, the use of the solubility parameters obtained from the heat of vaporization to calculate the solubilities gives very low values of these solubilities.

Semiempirical Equation

The semiempirical estimation procedure, discussed in Chapter III, can be used to estimate the water solubilities of the solid solutes in water. The values obtained from this procedure will not be accurate

TABLE XIX

ESTIMATED WATER SOLUBILITIES OF QUINOLINE COMPARED WITH EXPERIMENTAL VALUES

T,°C	Estimated Value of x_2	Measured Value Value of x_2
20.0	$1.84 * 10^{-12}$	---
23.5	$2.53 * 10^{-12}$	$9.36 * 10^{-4}$
35.0	$6.56 * 10^{-12}$	$1.02 * 10^{-3}$
45.0	$1.47 * 10^{-11}$	$1.08 * 10^{-3}$
50.0	$2.17 * 10^{-11}$	$1.13 * 10^{-3}$
61.0	$4.87 * 10^{-11}$	$1.21 * 10^{-3}$

TABLE XX

ESTIMATED WATER SOLUBILITIES OF ACRIDINE AND CARBAZOLE COMPARED WITH EXPERIMENTAL VALUES

T,°C	Acridine		Carbazole	
	x_2* Estimated	x_2 Measured	x_2* Estimated	x_2 Measured
25.0	$1.97 * 10^{-20}$	$2.14 * 10^{-5}$	$3.07 * 10^{-20}$	$6.8 * 10^{-7}$
35.0	$8.16 * 10^{-20}$	$2.85 * 10^{-5}$	$1.14 * 10^{-19}$	$7.24 * 10^{-7}$

* The solubility parameters used for acridine and carbazole are 10.19 and 10.13 $(cal/cm^3)^{\frac{1}{2}}$ respectively

because the infinite dilution activity coefficient (γ^∞) will be calculated from the form given for the n-alkylbenzenes in water. However this approximation of using this formula for the nitrogen compounds is made only to give a comparison with the experimental values. Recalling the simplified form of the solubility equation of solids in liquids given by equation [11]

$$\ln x_1 = \frac{\Delta H_F}{RT} \left(\frac{T}{T_m} - 1\right) - \ln \gamma_1^\infty \qquad [11]$$

and the equation used to calculate the infinite dilution activity coefficient at 25°C which is given by equation [13]

$$\log \gamma_1^\infty = A_{1,2} + B_2 (N_1 - 6) + C_1 \left(\frac{1}{N_1 - 4}\right) \qquad [13]$$

These two equations can be used to calculate the water solubilities of acridine and carbazole at 25°C as follows:

1. Acridine in water at 25°C

Equation [13] can be used to find the γ_1^∞ for acridine. Substituting the values of the constants $A_{1,2}$, B_2 and C_1, then equation [13] would be:

$$\log \gamma_1^\infty = 3.554 + 0.622 (N_1 - 6) - 0.466 \left(\frac{1}{N_1 - 4}\right)$$

For acridine N = 13, therefore

$$\log \gamma_1^\infty = 3.554 + 0.622 (13 - 6) - 0.466 \left(\frac{1}{13 - 4}\right) = 7.856$$

From the correction table, given in reference (30), the correction factor is -1.11 per each additional ring. Thus for two additional rings in acridine the correction is -2.22.

Therefore, $\log \gamma_1^{\infty} = 7.856 - 2.22 = 5.636$

or, $\ln \gamma_1^{\infty} = 12.98$

Using this value in equation [11] we get:

$$\ln x_1 = \frac{4110.89}{1.987 * 298} \left(\frac{298}{385.3} - 1\right) - 12.98 = -14.55$$

and hence x_1 = mole fraction of acridine in water at 25°C = $4.79 * 10^{-7}$

Note: Values of ΔH^F = 4110.89 cal/g mole, and T_m = 385.3 K are from reference (22).

2. For Carbazole in Water at 25°C

In the same way we can calculate $\ln \gamma_1^{\infty}$ for carbazole and use it in equation [11] to calculate x_1 (mole fraction of carbazole in water).

Doing this we get:

$\log \gamma_1^{\infty} = 7.228$

Corrected $\log \gamma_1^{\infty} = 5.008$

or $\ln \gamma_1^{\infty} = 11.53$

Therefore,

$$\ln x_1 = -16.155$$

or, x_1 = mole fraction of carbazole in water at 25°C = $9.64 * 10^{-8}$

Note: Values of ΔH^F = 6429.25 cal/g mole, and T_m = 519 K are from reference (22).

The water solubilities of acridine and carbazole at 25°C obtained from this method are compared with the experimental values and values from the literature in Table XXI.

Table XXII shows that the experimental solubility of acridine in water at 25°C is higher than both the estimated value (using the semi-empirical equation) and the literature value. While the experimental solubility of carbazole at 25°C is lower than the literature value and higher than the estimate value. In both cases the experimental values are closer to the literature values than the estimated values. For example, the experimental water solubility of acridine is 4.5 times higher than the literature value, while the estimated value is 10 times lower than the literature value. Also the experimental solubility of carbazole is 2.5 times lower than the literature value, while the estimated value is 18.5 times lower than the literature value. This would give more confidence to the experimental solubilities determined in this work.

It was obvious that the estimation procedures used in this section require a knowledge of different constants and parameters which are not reported in the literature for the hydrochloride or sulfate of these compounds. Also information about the other solvents (HCl, and H_2SO_4 acidic solution) such as the solubility parameters are not available. Therefore our calculations were limited to the pure compounds in water.

TABLE XXI

COMPARISON OF WATER SOLUBILITIES OF ACRIDINE AND CARBAZOLE AT 25°C

Compound	X_2 Estimated	x_2 Measured	x_2 from Literature	Ref.
Acridine	$4.79 * 10^{-7}$	$2.14 * 10^{-5}$	$4.94 * 10^{-6}$	21
Carbazole	$9.64 * 10^{-8}$	$6.8 * 10^{-7}$	$1.80 * 10^{-6}$	21

TABLE XXII

ESTIMATED WATER SOLUBILITIES OF ACRIDINE AND CARBAZOLE COMPARED WITH EXPERIMENTAL VALUES

T., °C	X_2* Acridine	x_2	x_2* Carbazole	x_2
	Estimated	Measured	Estimated	Measured
25.0	$1.97 * 10^{-20}$	$2.14 * 10^{-5}$	$3.07 * 10^{-20}$	$6.8 * 10^{-7}$
35.0	$8.16 * 10^{-20}$	$2.85 * 10^{-5}$	$1.14 * 10^{-19}$	$7.24 * 10^{-7}$

* The solubility parameters used for acridine and carbazole are 10.19 and 10.13 $(cal/cm^3)^{1/2}$ respectively.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

From the results of this work, the following conclusions can be drawn:

1. The solubilities of quinoline in water at different temperatures compare very well with the values reported in the literature.

2. The water solubility of acridine obtained in this work is 4 to 5 times higher than the values reported in the literature. However, the water solubilities of carbazole and indole are about 2.5 times lower than the literature values.

3. In all cases studied the solubility increases with temperature and with the acidity of the solvent.

4. As the acidity of the solvent increases the depency of the solubility on temperature increases.

5. The solubility parameters evaluated from the heat of vaporization are not accurate, and when used to estimate the solubility give very low values.

6. UV spectra and elemental analysis show that the reaction of concentrated H_2SO_4 with carbazole did not change the structure of the latter, however, it increased its solubility in water and in H_2SO_4 acidic solutions.

Recommendations

The following recommendations are offered for future investigators in this field:

1. To reduce the error in the dilution process, a glasswool plug in the pipette is recommended before drawing samples from the saturated solutions. This might prevent the presence of any impurities which may interfer with the UV spectra of the compounds. Also it would prevent drawing any undissolved compounds from the saturated solution and hence the exact concentration needed can be achieved.

2. The purity of the compounds might be checked by a gas chromatograph. Compounds which may have some impurities, recrystallization can be used for the purification of these compounds.

3. The solubility of quinoline salts (hydrochloride and sulfate) may be determined at temperatures below the room temperature.

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APPENDIX A

PHYSICAL PROPERTIES OF QUINOLINE, ACRIDINE, CARBAZOLE, AND INDOLE

TABLE XXIII

SIMPLE PHYSICAL PROPERTIES OF QUINOLINE

Physical Property	Value	Ref.
Molecular Weight	129.161	14
Melting Point, °C	-14.900	14
Normal boiling point, °C	237.900	14
Enthalpy of fusion, ΔH_m, $\frac{kJ}{mol}$	10.800	14
Enthalpy of vaporization, ΔH_m, $\frac{kJ}{mol}$	46.500	14
Critical temperature, °C	509.000	17
Critical pressure, bar	46.600	17
Critical density, $kg.m^{-3} \times 10^{-3}$	0.321	17
Critical volume, $m^3.mol^{-1} \times 10^6$	403.000	17
Critical compression factor, Z_c	0.296	17
Acentric factor, ω	0.330	17
pka	4.940	4, 18
Dipole moment	2.160	8
Viscosity at 20°C (c.g.s.) $\times 10^4$	361.800	8

TABLE XXIV

PHYSICAL PROPERTIES OF ACRIDINE (Ref. 21)

Physical Property	Value
Molecular Weight	179.2210
Freezing Point, °C	112.3000
Normal boiling point, °C	346.0000
Enthalpy of: (kJ/mol)	
sublimation, ΔH_s	84.0000
fusion, ΔH_F	17.2000
vaporization, ΔH_v	61.2000
Critical temperature, °C	632.0000
Critical pressure, bar	36.0000
Critical density, $kg.m^{-3} \times 10^{-3}$	0.3300
Critical volume, $m^3.mol^{-1} \times 10^6$	543.0000
Critical compression factor, Z_c	0.2600
Acentric factor, ω	0.4300
Cryoscopic constant, A, k^{-1}	0.0139
Molar volume $m^3\ mol^{-1} \times 10^6$ at 25°C	140.1000

TABLE XXV

PHYSICAL PROPERTIES OF CARBAZOLE
(Ref. 21)

Physical Property	Value
Molecular Weight	167.199
Transition Point, T_r, °C	147.000
Freezing Point, T_m, °C	246.100
Normal boiling point, °C	354.760
Enthalpy of: (kJ/mol)	
sublimation, ΔH_s	94.300
fusion, ΔH_m	26.900
vaporization, ΔH_v	61.100
Critical temperature, °C	626.900
Critical pressure, bar	32.400
Critical density, $kg.m^{-3} \times 10^{-3}$	0.268
Critical volume, $m^3.mol^{-1} \times 10^6$	624.000
Critical compression factor, Z_c	0.270
Acentric factor, ω	0.488
Cryoscopic constant, A, K^{-1}	0.012
Molar volume, m^3 $mol^{-1} \times 10^6$ at 25°C	127.800

Safety and Health Hazards

For Quinoline:

According to Clayton [35] quinoline is moderately toxic by most routes of exposure. Inhalation of saturated vapor (room temperature) for 6 or 8 hours caused no death (calculated concentration - 17 ppm)

The fire and disaster hazards of quinoline as given by Sax [36] are as follows:

Fire Hazard: Slight, when exposed to heat.

Disaster Hazard: Dangerous: when heated to decomposition, it emits toxic fumes of nitrogen oxides.

Caution: Quinoline may produce retinitis similar to that caused by naphthalene but without causing opacity to the lens.

For Acridine:

According to Sax [36] acridine has the following hazardous properties: It is a strong irritant to skin, eyes and mucous membranes of the body. It causes Lachrymation and irritation of the conjuntive.

Treatment and Antidotes:

Parts of the body which have been exposed to this material should be washed copiously with luke-warm water and soap. If eyes become irritated by it, they should be washed. Consult a physician.

Storage and Handling:

Personnel exposed to this material should wear chemical safety goggles; also respiratory protection is indicated. It should be kept from eyes, skin, or mucous membranes of the body. Impermeable clothing should be worn to keep material from coming in contact with the skin.

Acridine is not considered excessively dangerous.

Carbazole:

Sax [36] stated that carbazole has been known to cause allergic symptoms in humans. Exposed personnel who are sensitive to it should wear protective clothing, if necessary, to avoid bodily contact.

Indole:

Limited animal experiments suggest low toxicity of indole [37].

APPENDIX B

CALIBRATION CURVES

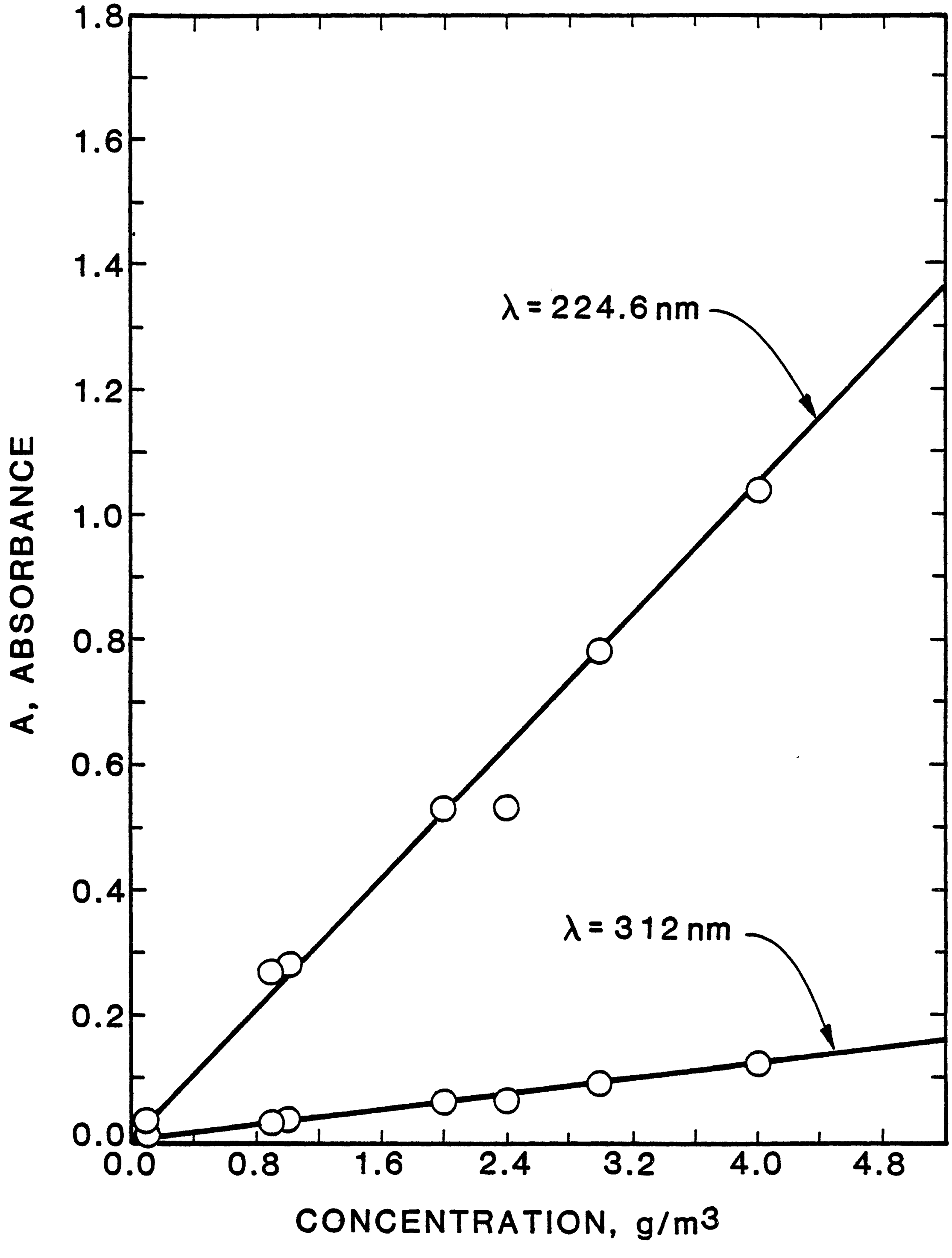

Figure 22. Calibration Curve for Quinoline in Water

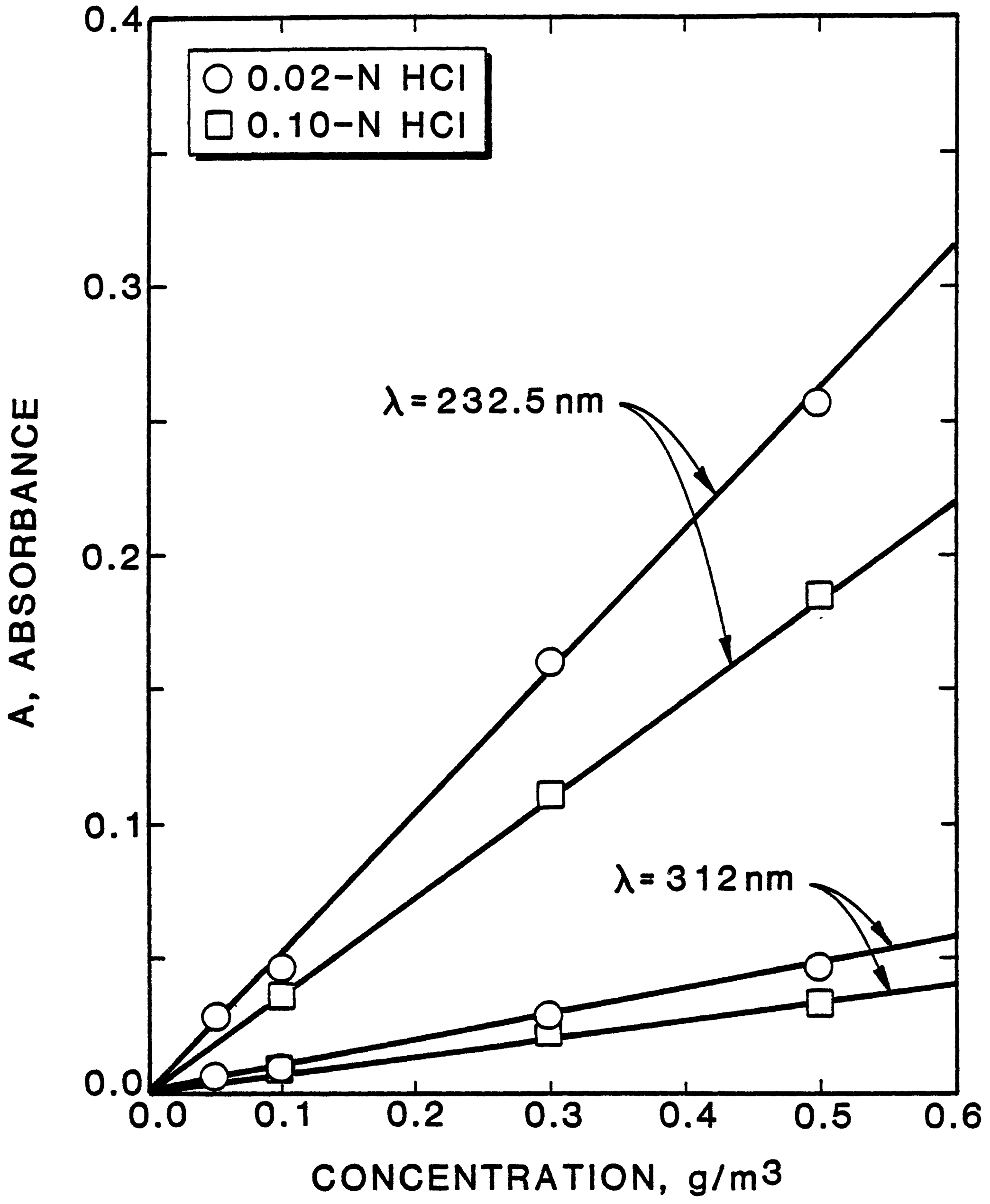

Figure 23. Calibration Curves for Quinoline in 0.02-N and 0.10-N HCl

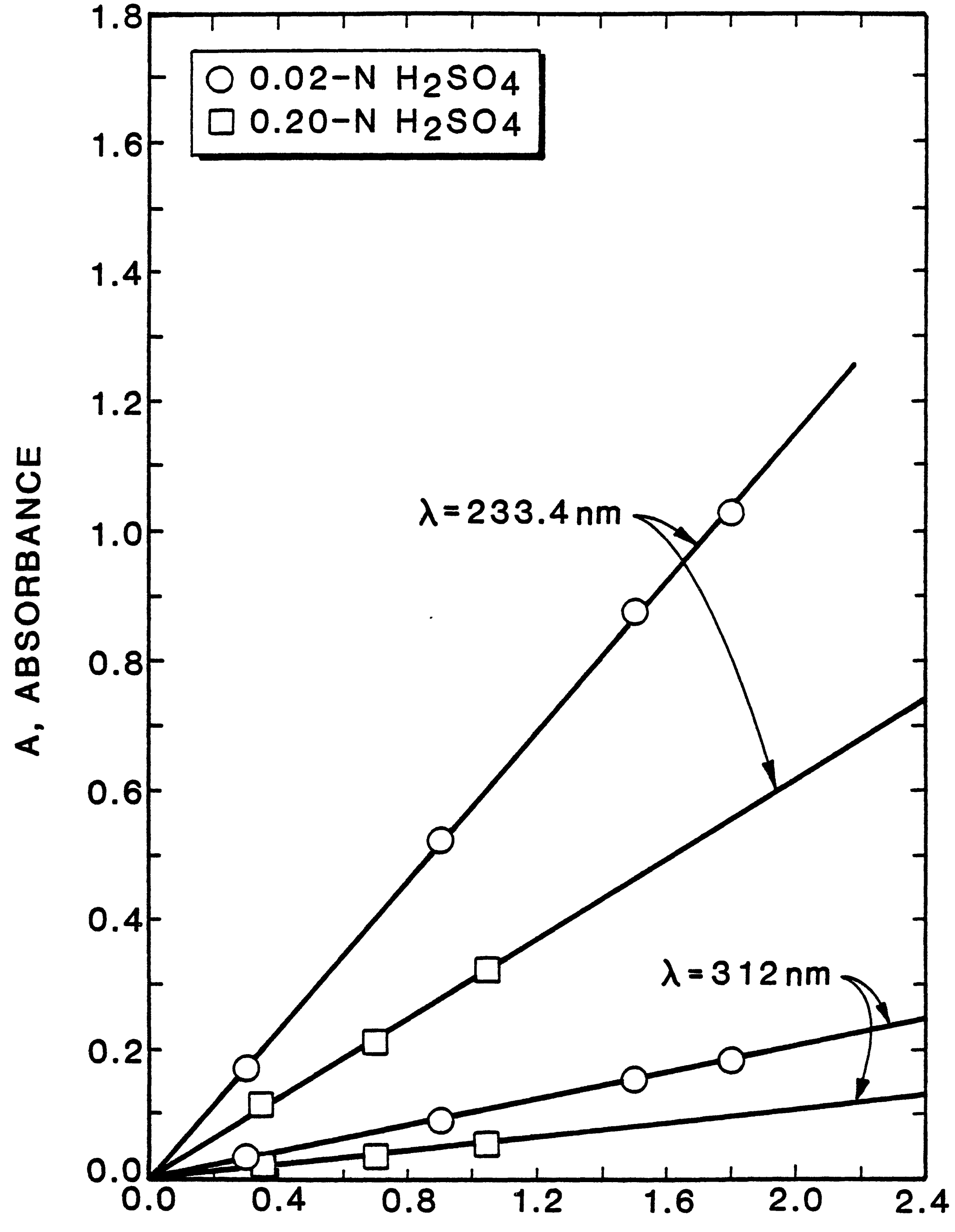

Figure 24. Calibration Curves for Quinoline in 0.02-N and 0.20-N H_2SO_4

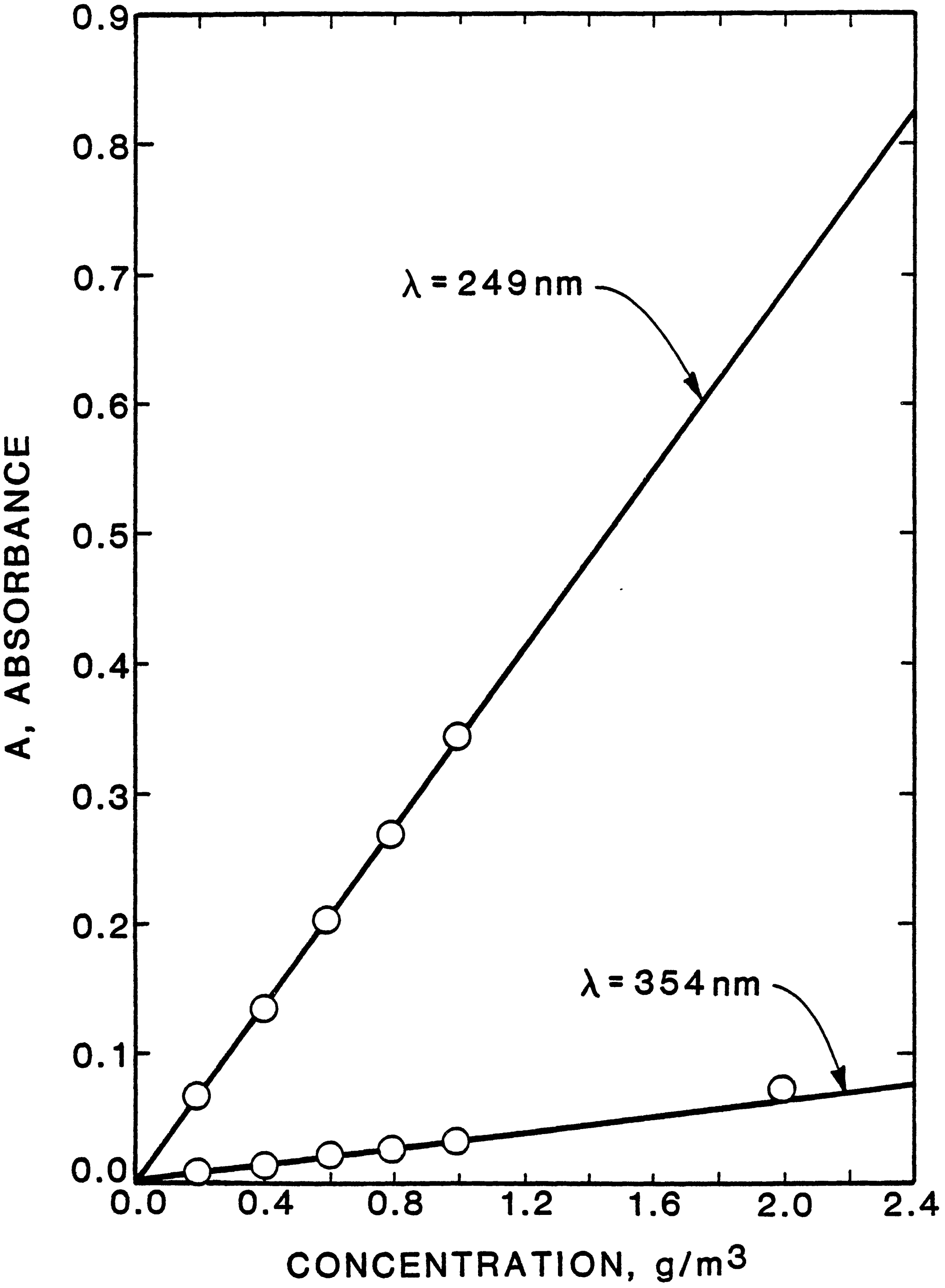

Figure 25. Calibration Curve for Acridine in Water

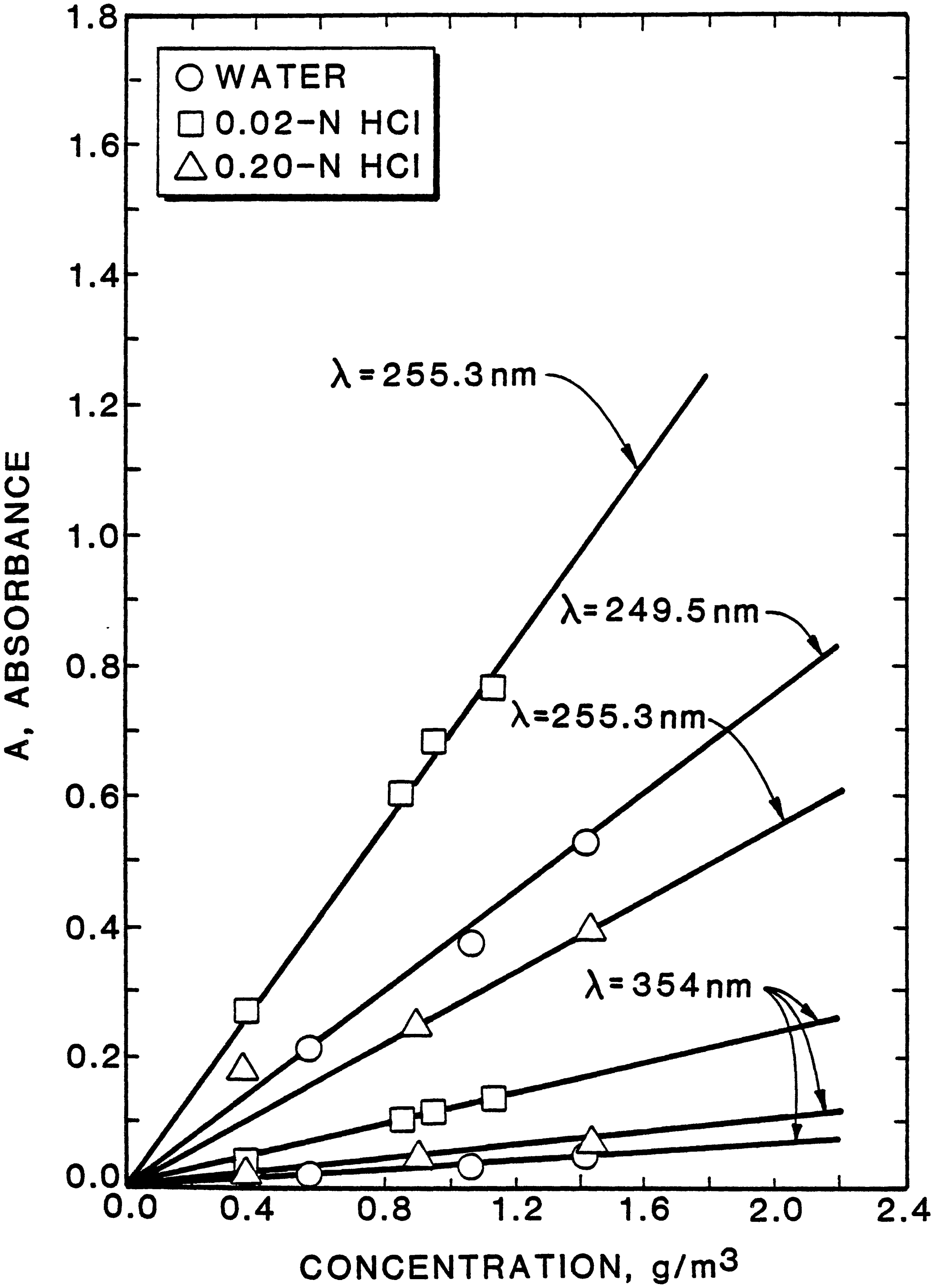

Figure 26. Calibration Curves for Acridinium Hydrochloride (Corrected for the water content)

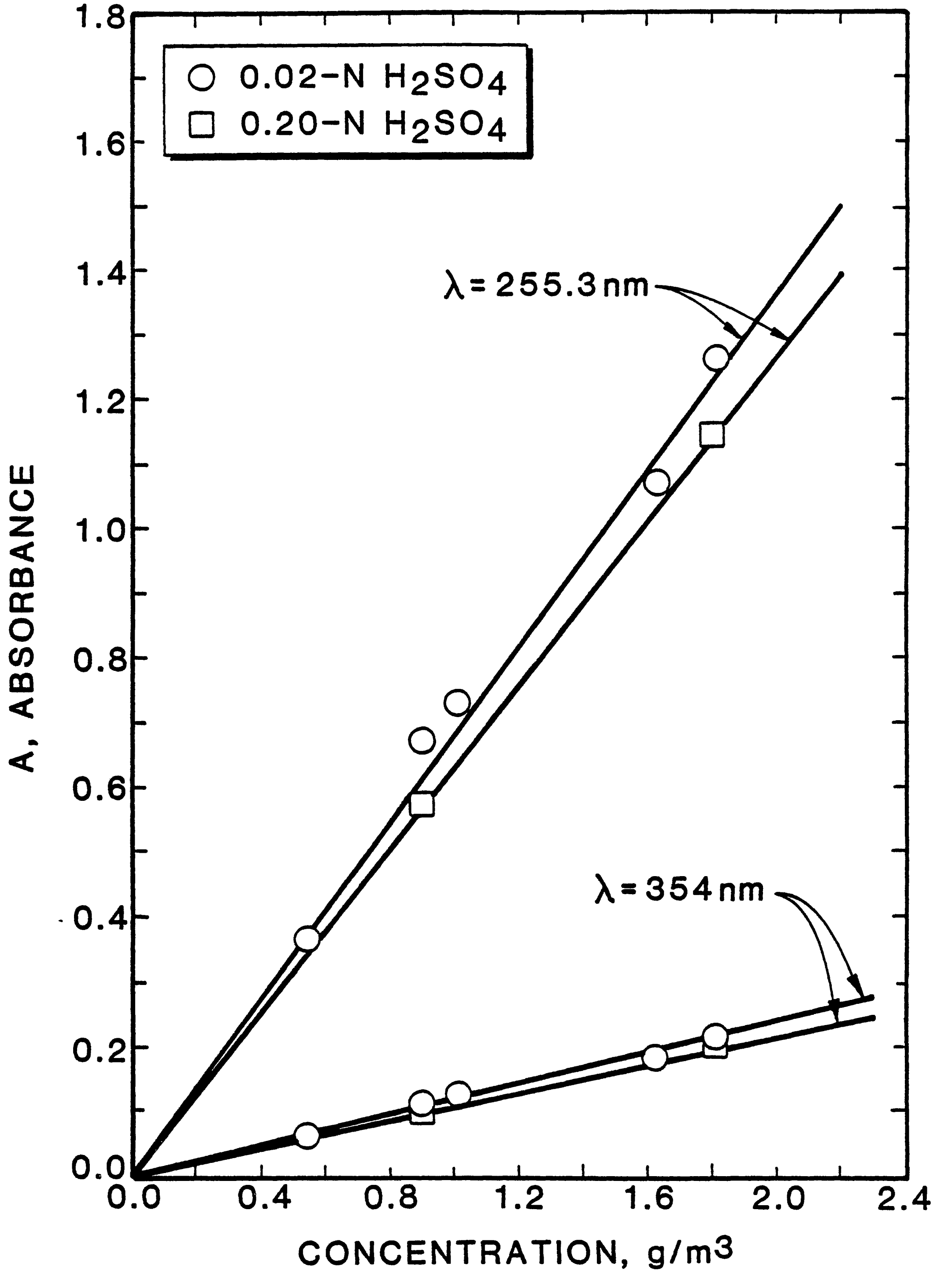

Figure 27. Calibration Curves for Acridinium Sulfate
(Corrected for the water content)

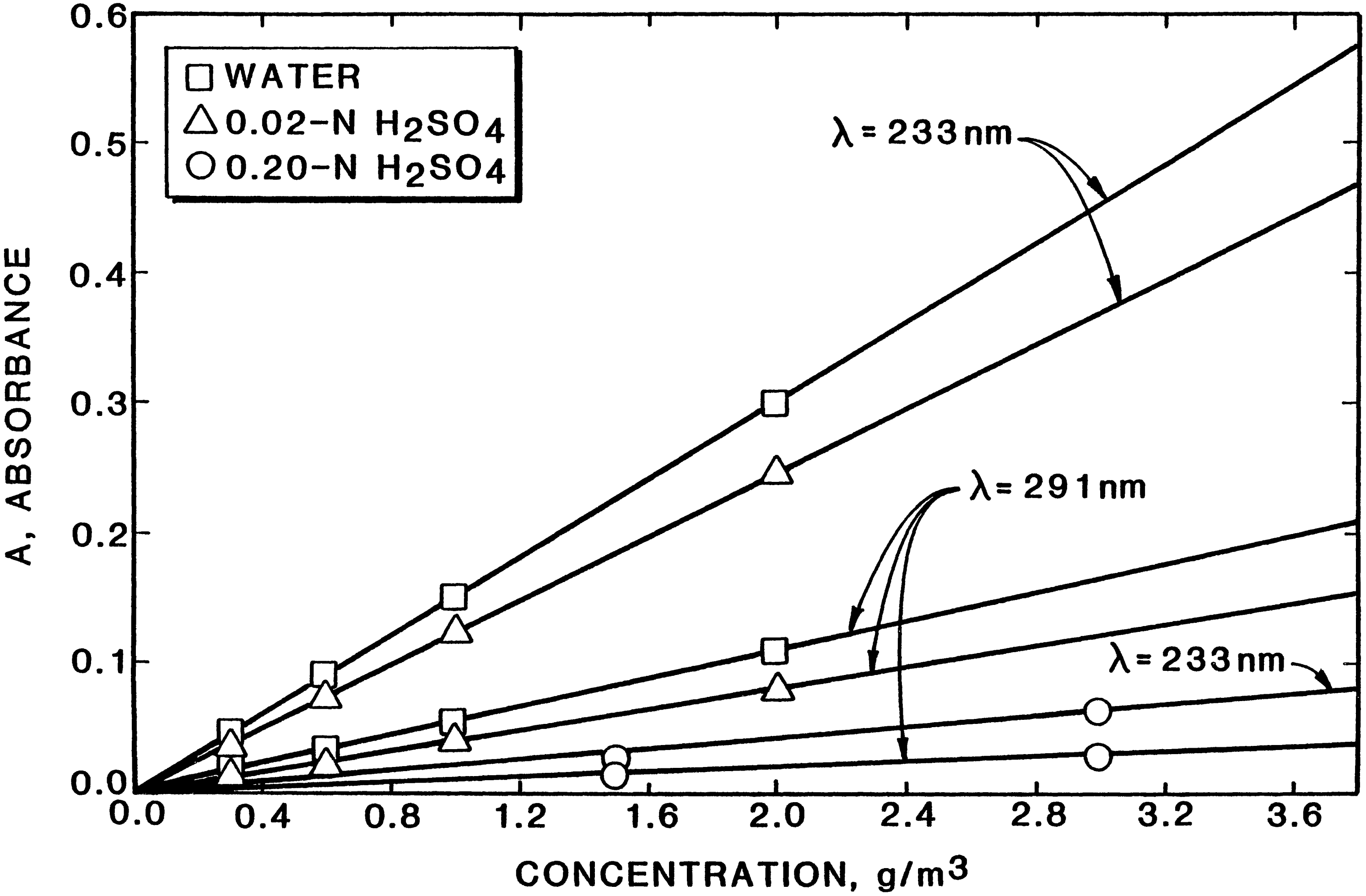

Figure 28. Calibration Curves for Acid-Treated Carbazole

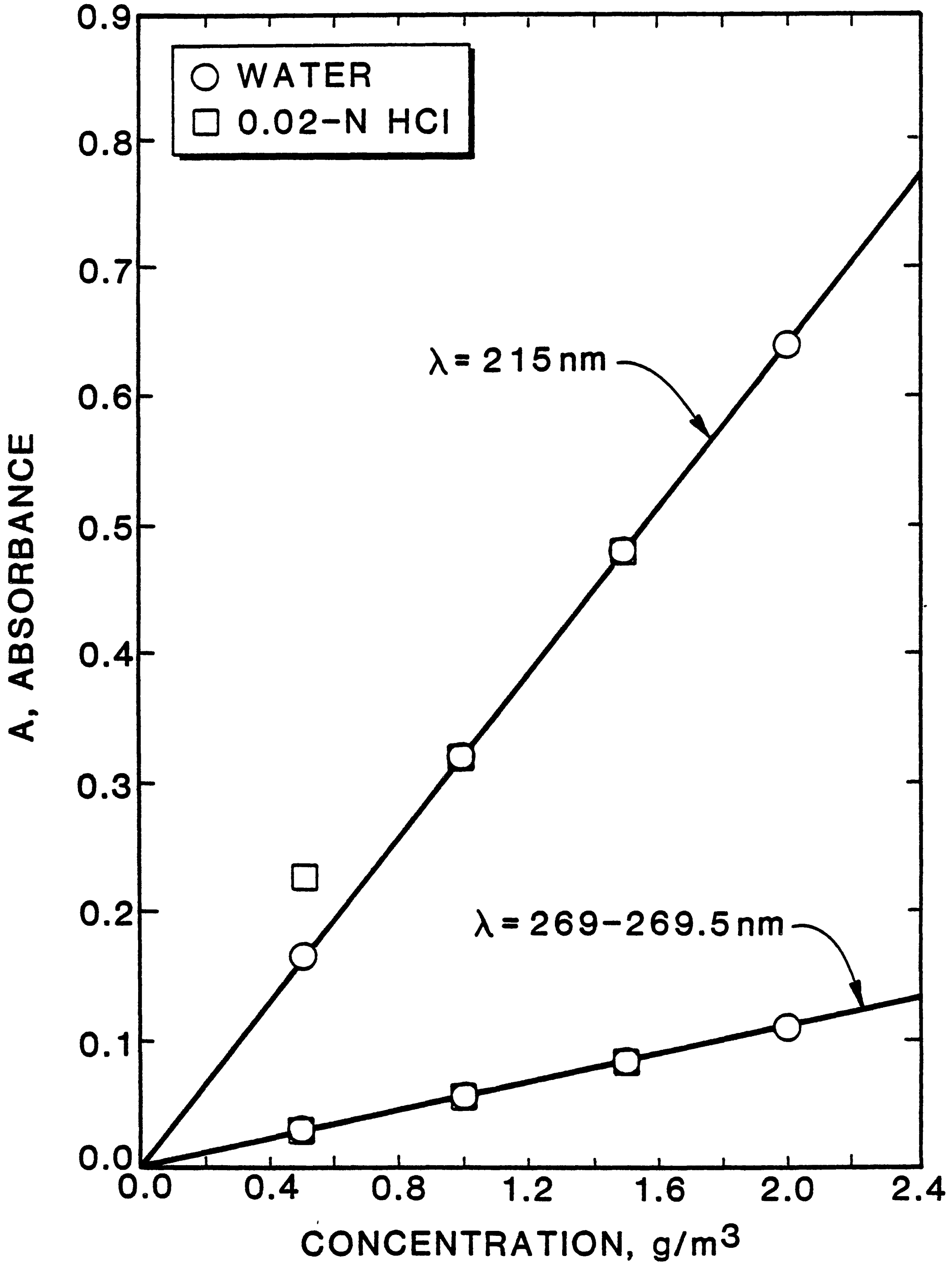

Figure 29. Calibration Curve for Indole in Water and in 0.02-N HCl

APPENDIX C

UV SPECTRA OF EACH COMPOUND IN DIFFERENT SOLVENTS

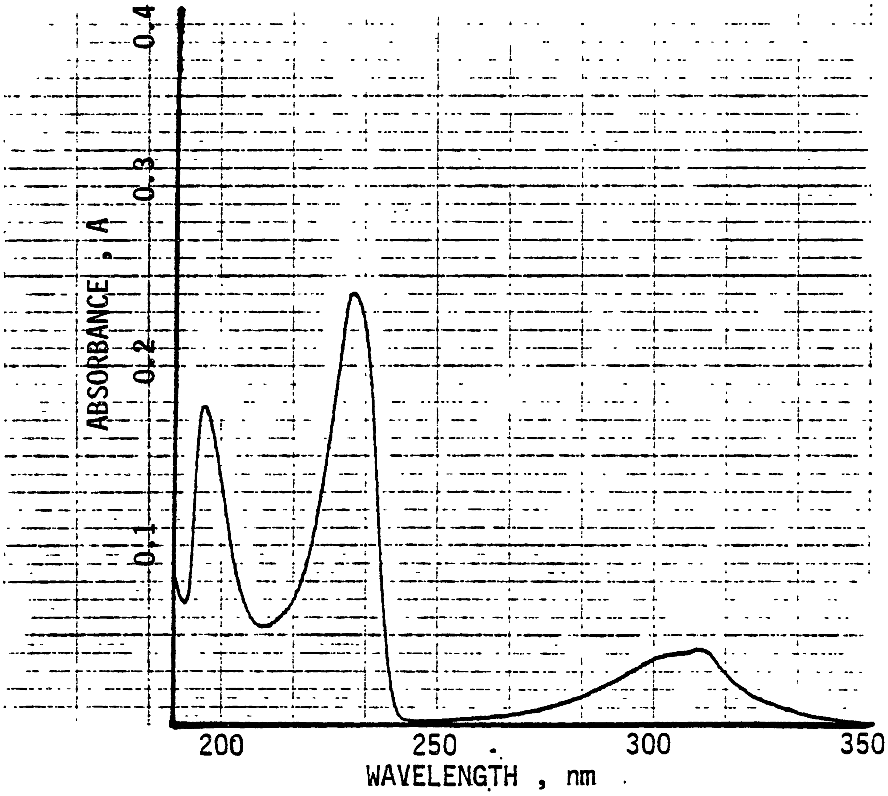

Figure 30. UV Spectrum of Quinolinium Hydrochloride in Water pH = 1.9

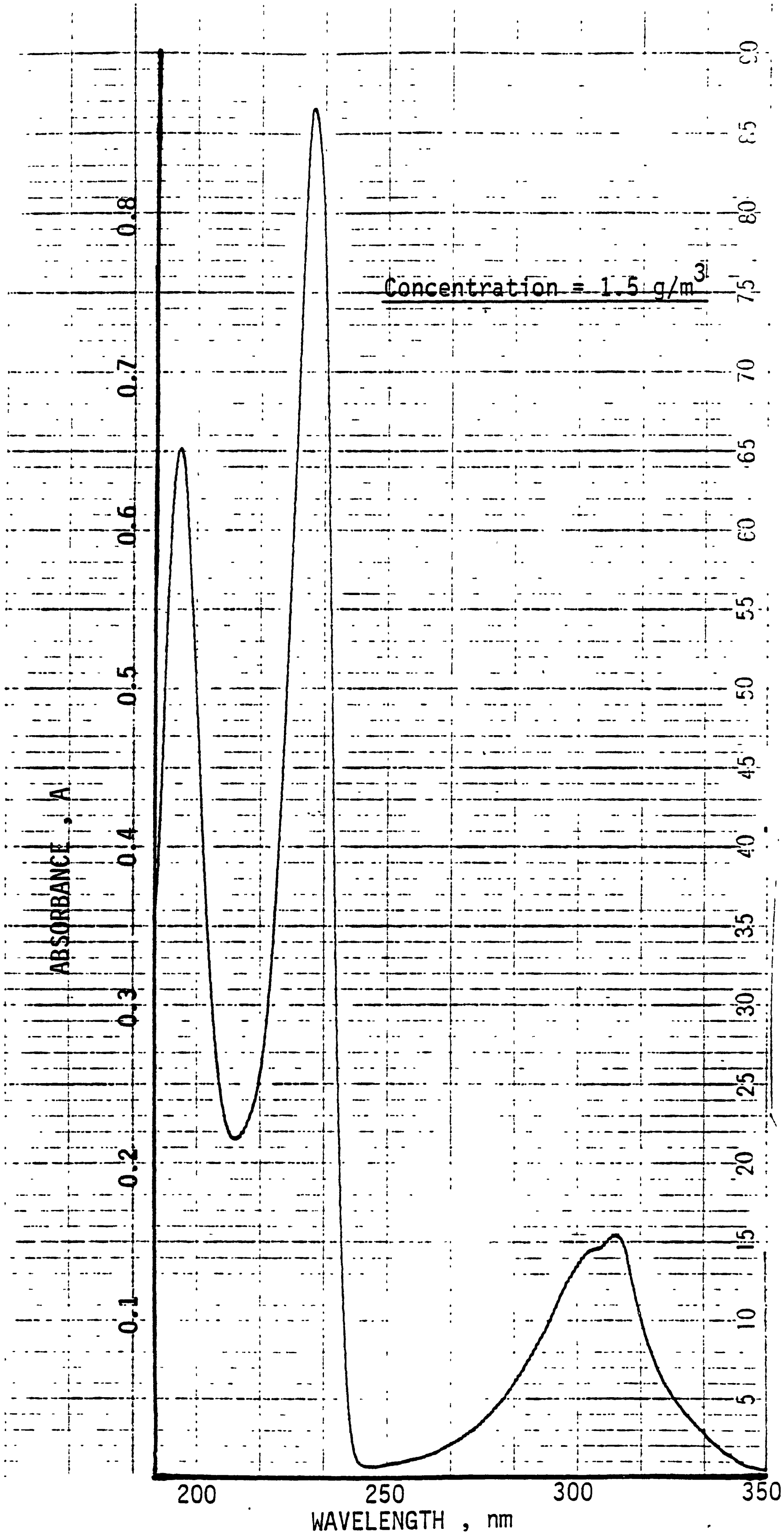

Figure 31. UV Spectrum of Quinoline in 0.02-n H_2SO_4

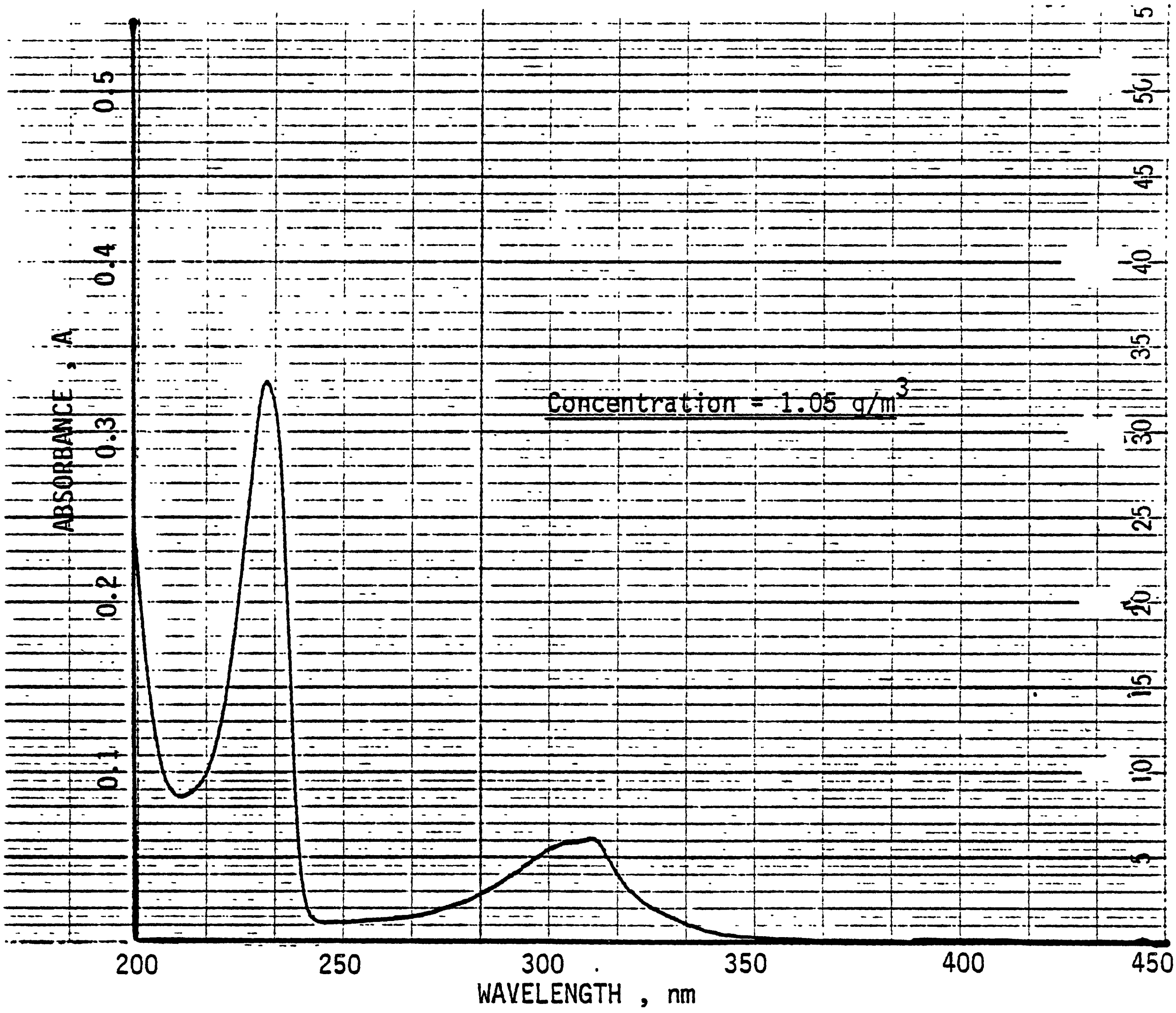

Figure 32. UV Spectrum of Quinoline in 0.20-N H_2SO_4

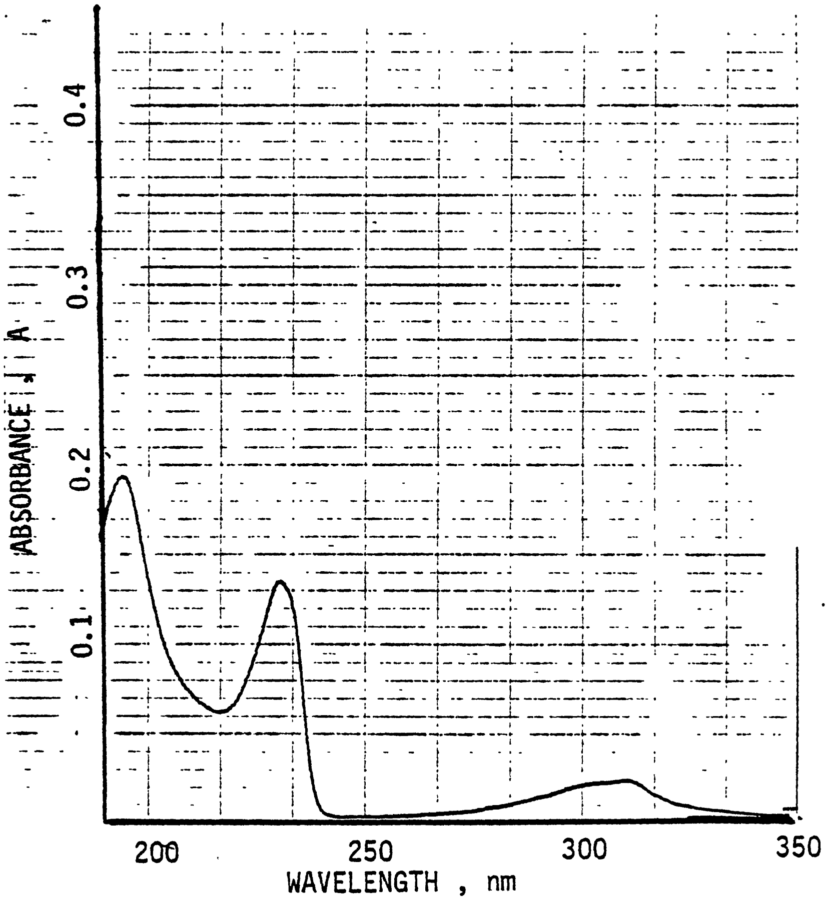

Figure 33. UV Spectra of Quinolinium sulfate in Water pH = 1.8

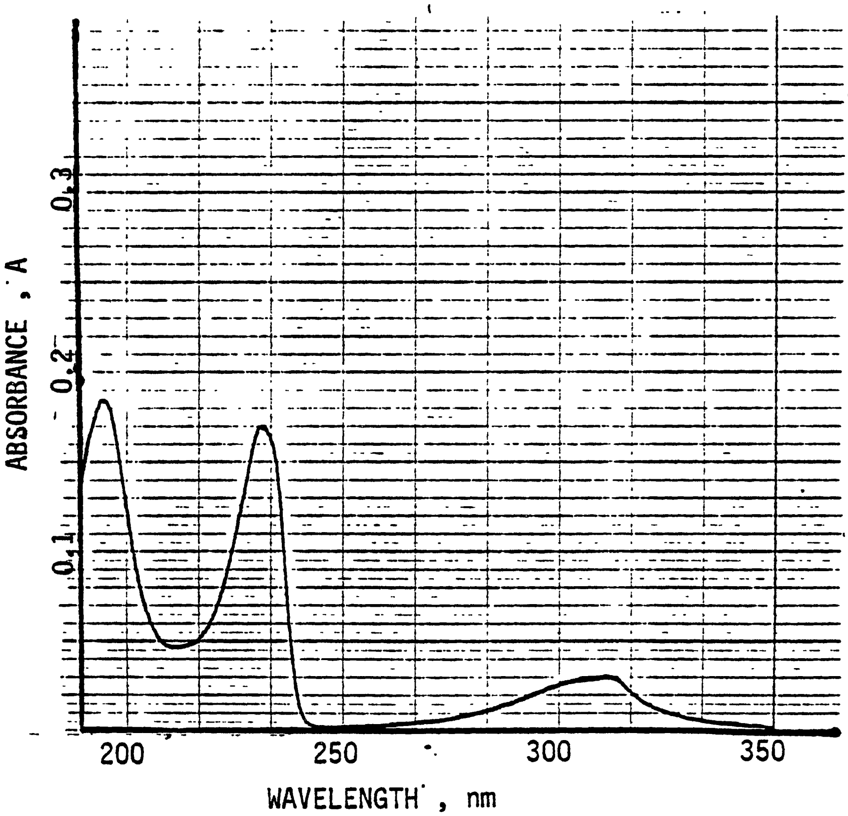

Figure 34. UV Spectra of Quinolinium sulfate in Water pH = 2.04

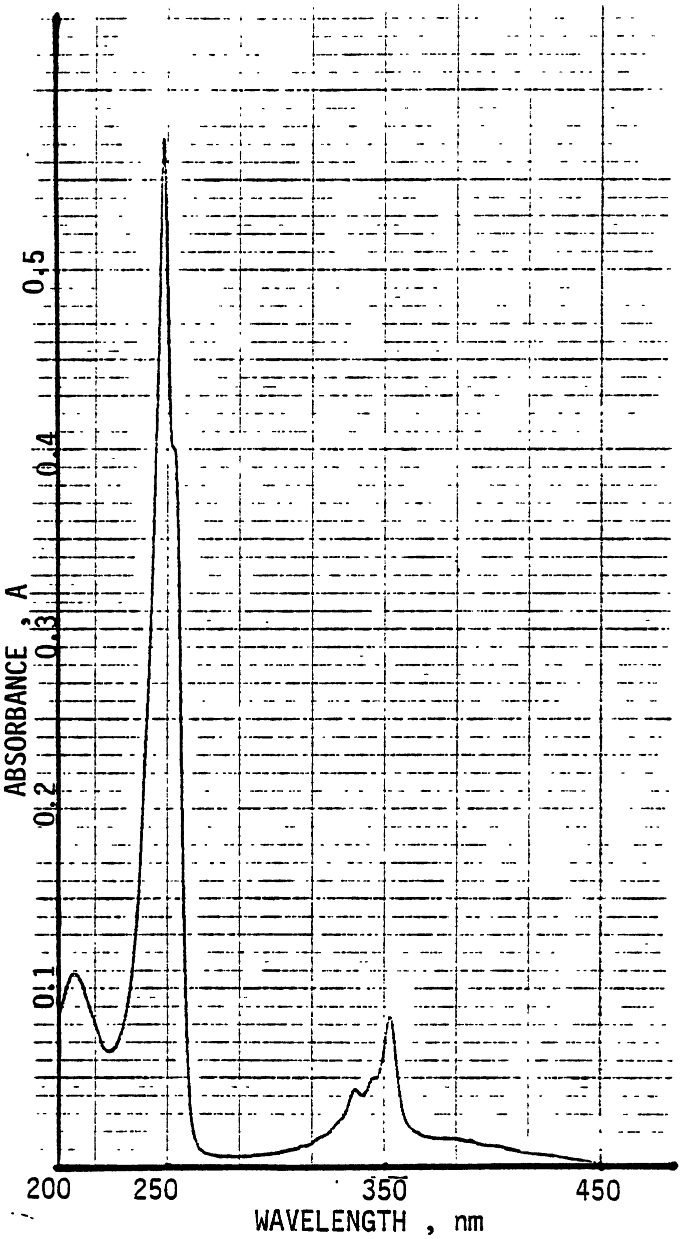

Figure 35. UV Spectrum of Acridinium Hydrochloride in water

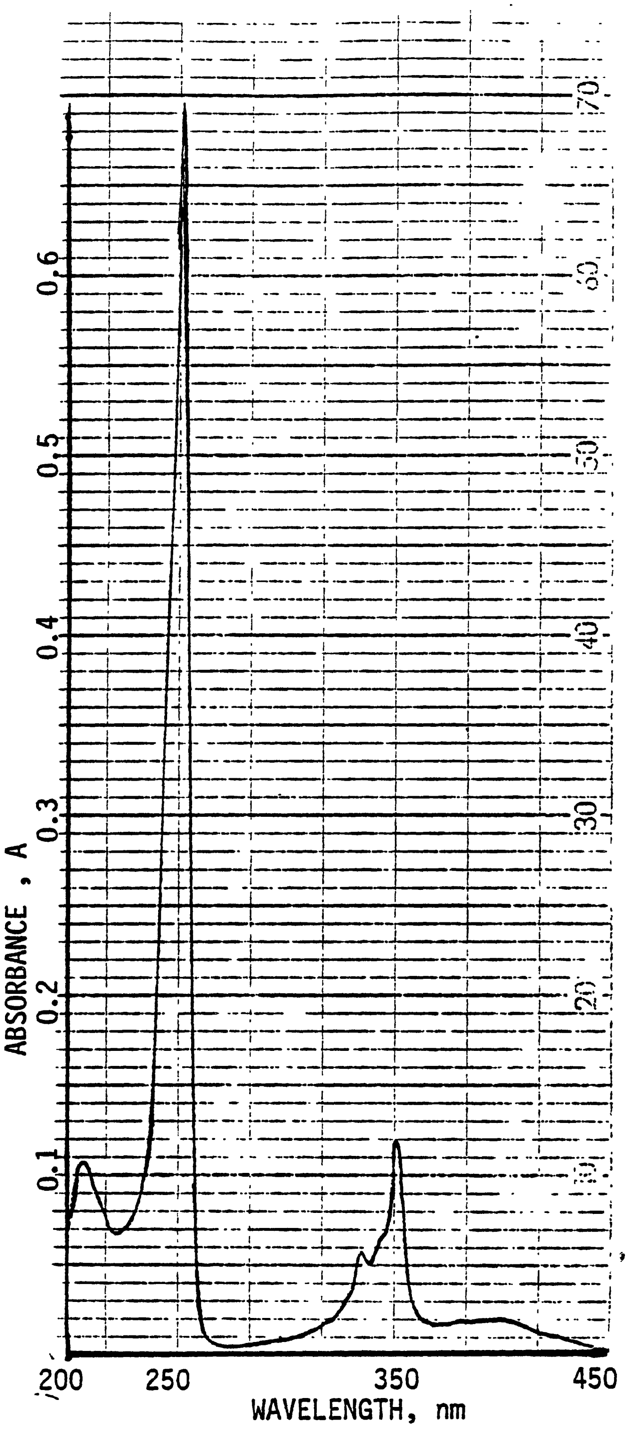

Figure 36. UV Spectrum of Acridinium Hydrochloride in 0.02-N HCl

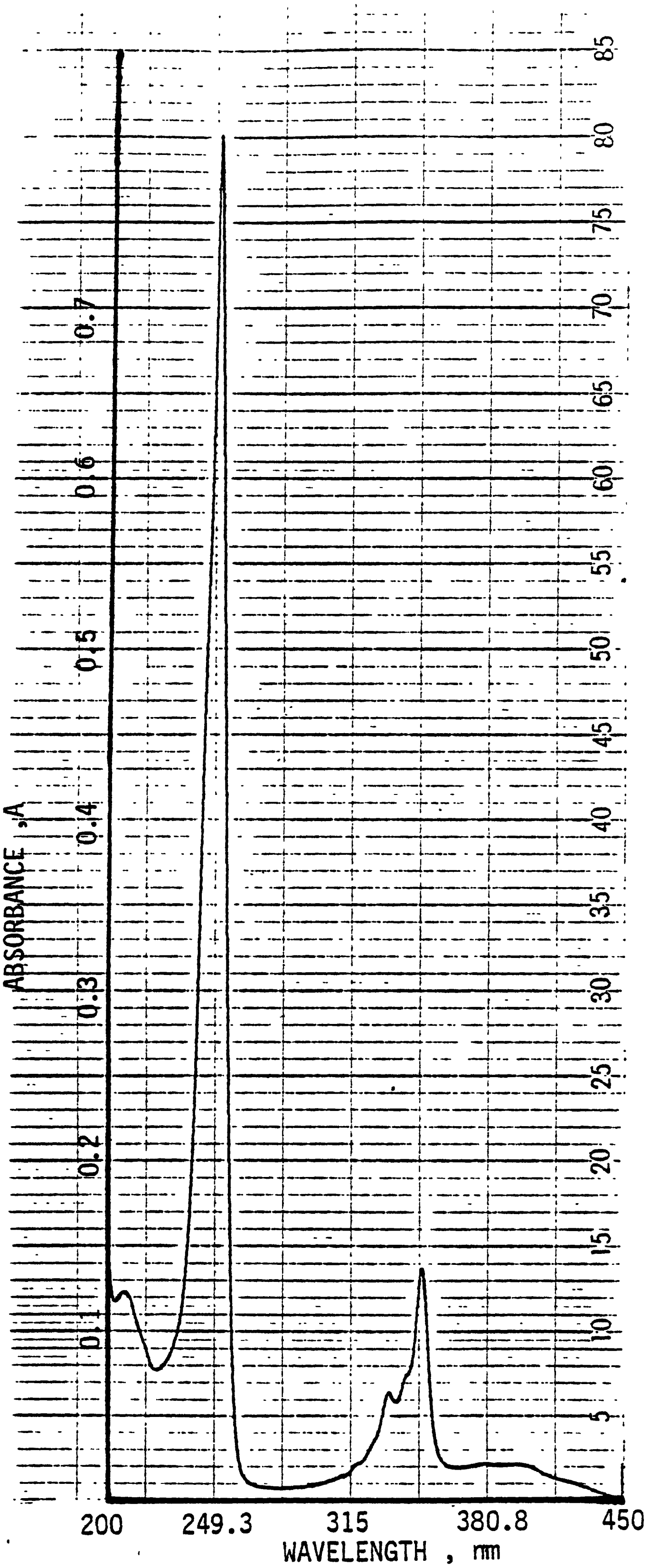

Figure 37. UV Spectrum of Acridinium Hydrochloride in 0.20-N HCl

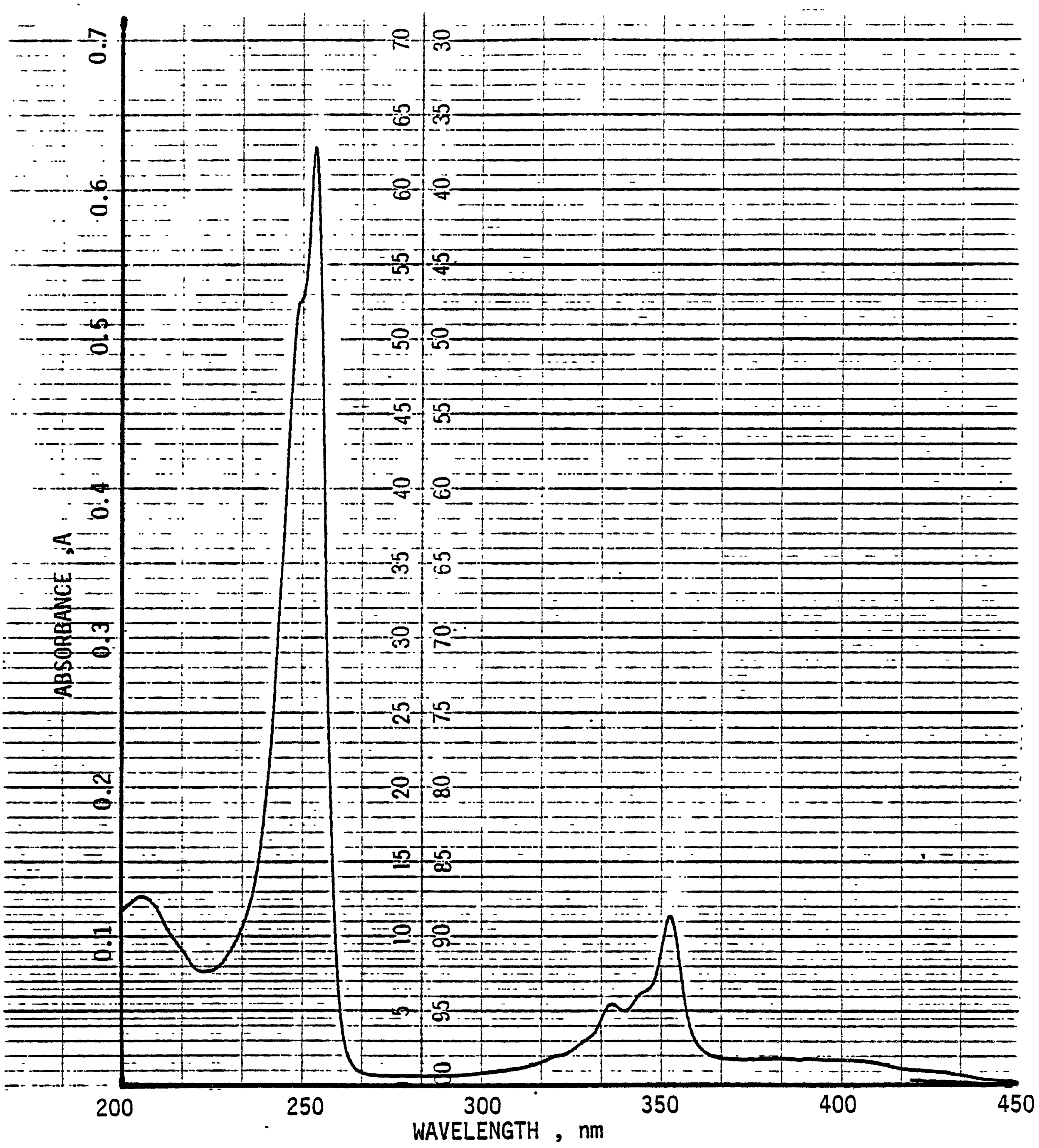

Figure 38. UV Spectrum of Acridinium sulfate in Water

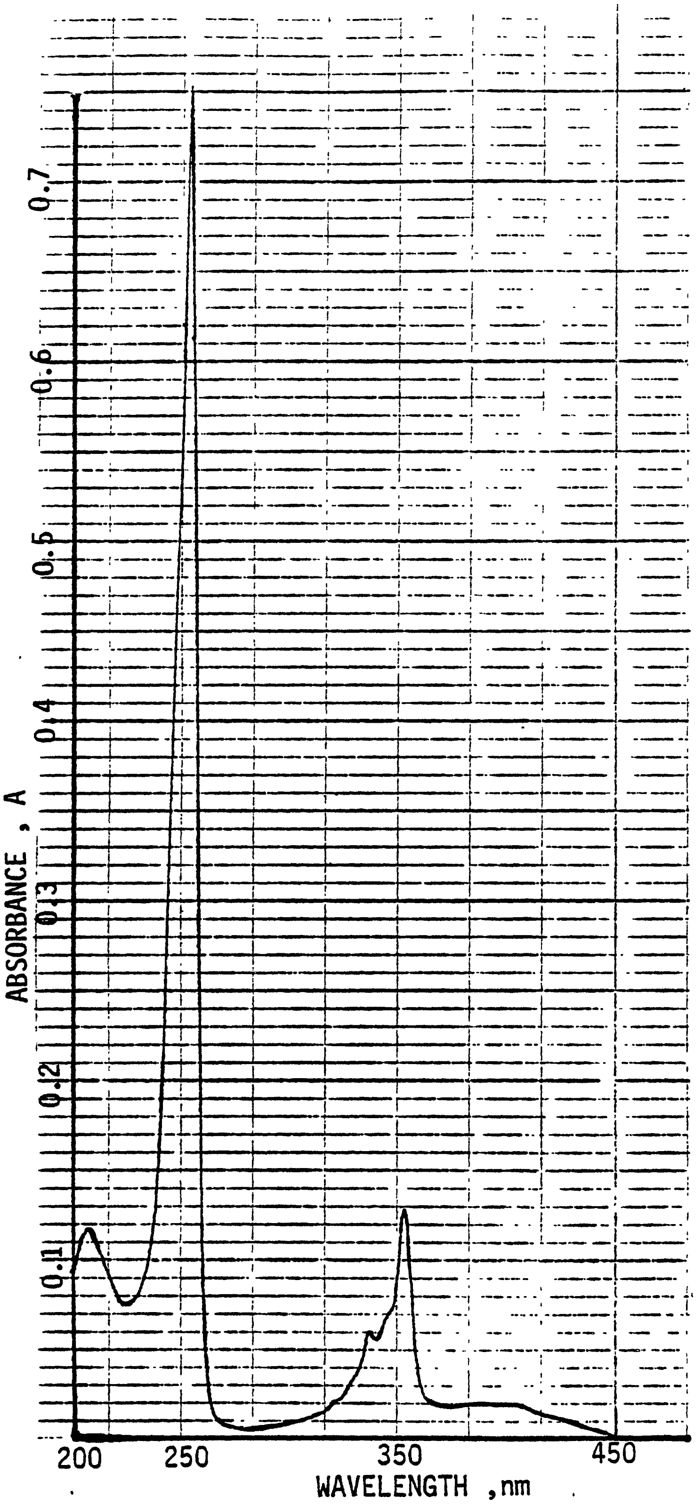

Figure 39. UV Spectrum of Acridinium sulfate in 0.02-N H_2SO_4

APPENDIX D

SAMPLE CALCULATIONS

I. CALCULATION OF THE CONCENTRATION

The calculation method used to obtain the solubility values is shown by the following example:

Consider the solution of quinoline in water at 23.5°C, the saturated solution of this system has been diluted by 8000 fold. When this diluted solution was read in UV spectrophotometer it showed two peaks at γ= 317 nm and at γ= 224.6 nm with absorption values of 0.027 A, and 0.202 A respectively (UV spectrum of this sample is in Appendix B).

The concentrations corresponding to these absorption values can be read from the calibration curve of quinoline in water (see Appendix B). These concentrations were found to be 0.84 and 0.80 gm^3 for γ= 312 nm and γ= 224.6 nm respectively. Now to get the solubility of the sample, the concentration value is multiplied by the number of dilution.

i.e., Solubility of sample = number of dilution times X concentration from calibration curve.

Therefore:

a. At γ= 312 nm

Solubility = 8000 * 0.84

b. At γ= 224.6 nm

Solubility = 8000 * 0.80

The same procedure is followed for any other samples or duplicate runs at this temperature (23.5°C). Then the average over the two wavelengths (γ= 312 and γ= 224.6nm) for all these runs is reported as the solubility of quinoline in water at 23.5°C.

Similarly all the experimental solubility values reported in Chapter IV are average values. These average solubilities were obtained from the two significant peaks in the spectra of all measurements made at a specific temperature.

II. Calculation of Acridine Solubility from the Solubility of its Hydrochloride and Sulfate

The solubilities of acridine in H_2O, 0.02-N, and 0.2-N HC were calculated from the measured solubilities of its hydrochloride in these solutions. Also the solubilities of acridine in H_2O, 0.02-N, and 0.2-N H_2SO_4 were calculated from the measured solubilities of acridinium sulfate in these solutions. The calculation procedure used to estimate the solubilities of acridine in these acidic solutions from its salts can be illustrated by the following example:

Consider the solubility of the acridinium sulfate in 0.02-N H SO at 25°C which was 6.728 kg/m^3. The pure acridine $C_{13}H_9N$ (MW = 179) contains 7.82%N, 87.15%C, and 5.03%H; While the elemental analysis of acridinium sulfate $(C_{13}H_9N)\cdot H_2O$ showed the following percentages: 5.35%N, 63.12%C, and 3.593%H. Therefore the amount of pure acridine contained in the sulfate can be estimated using the % of Nitrogen as a basis:

i.e. % of acridine in the sulfate $= \frac{5.35}{7.82} \times 100 = 68.44\%$

Using this correction factor the solubility of acridine in 0.02-N H_2SO_4 25°C can be calculated as follows:

$$\text{Solubility of acridine in } 0.02N\ H_2SO_4 = .6844 * 6.728$$
$$= 4.603\ kg/m^3$$

Similarly all the corrected solubilities of acridine in the HCl and H_2SO_4 acidic solutions were obtained using the elemental analysis of the acridinium hydrochloride and sulfate. The elemental analysis of all nitrogen compounds and their salts studied in this project are shown in Appendix E. This elemental analysis was also used to identify the hydrochloride and sulfate of all the nitrogen compounds in this study.

APPENDIX E

EXPERIMENTAL RAW DATA

I. Raw Data for the Calibration Curves

QUINOLINE IN WATER

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 312 nm	λ_2 = 224.6 nm
0.1	0.006	0.030
2.4	0.064	0.532
0.9	0.031	0.270
1.0	0.035	0.286
2.0	0.063	0.532
3.0	0.092	0.783
4.0	0.121	1.040

QUINOLINE IN 0.02-N HCl

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 312 nm	λ_2 = 232.5 nm
0.05	0.007	0.029
0.10	0.010	0.046
0.30	0.026	0.146
0.50	0.044	0.249
0.80	0.249	0.393

QUINOLINE IN 0.10-N HCl

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 312 nm	λ_2 = 232.5 nm
0.10	0.008	0.037
0.30	0.023	0.111
0.50	0.033	0.185
0.80	0.053	0.292

QUINOLINE IN 0.02-N H_2SO_4

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 312 nm	Absorbance λ_2 = 233.4 nm
0.30	0.032	0.171
0.90	0.095	0.521
1.50	0.158	0.877
1.80	0.187	1.032

QUINOLINE IN 0.20-N H_2SO_4

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 312 nm	Absorbance λ_2 = 233.4 nm
0.35	0.023	0.119
0.70	0.039	0.212
1.05	0.060	0.325

ACRIDINE IN WATER

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 249 nm	Absorbance λ_2 = 354 nm
0.40	0.142	0.012
0.60	0.213	0.018
0.80	0.283	0.024
0.60	0.274	0.047
1.20	0.177	0.019
1.80	0.127	0.015
2.40	0.174	0.019
2.00	1.162	0.080
3.00	0.214	0.022
1.00	1.897	0.344
1.00	0.677	0.117
1.20	0.763	0.132

ACRIDINIUM HYDROCHLORIDE* IN WATER

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 249.5 nm	 λ_2 = 354 nm
0.60	0.206	0.017
1.02	0.375	0.030
1.50	0.528	0.045

ACRIDINIUM HYDROCHLORIDE IN WATER
(Corrected for the H_2O Content)

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 249.5 nm	 λ_2 = 354 nm
0.564	0.206	0.017
0.959	0.375	0.030
1.411	0.528	0.045

ACRIDINIUM HYDROCHLORIDE* IN 0.02-N HCl

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 255.3 nm	 λ_2 = 354 nm
0.40	0.274	0.047
0.90	0.601	0.103
1.00	0.683	0.118
1.00	0.677	0.117
1.20	0.763	0.132

* This salt contains some water molecules

ACRIDINIUM HYDROCHLORIDE IN 0.02-N HCl

(Corrected for the H_2O Content)

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 255.3 nm	λ_2 =354 nm
0.376	0.274	0.047
0.846	0.601	0.103
0.941	0.683	0.118
0.941	0.677	0.117
1.129	0.763	0.132

ACRIDINIUM HYDROCHLORIDE* IN 0.20-N HCl

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 255.3 nm	λ_2 = 354 nm
0.380	0.177	0.018
0.950	0.247	0.042
1.520	0.393	0.067

ACRIDINIUM HYDROCHLORIDE IN 0.20-N HCl

(Corrected for the H_2O Content)

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 255.3 nm	λ_2 = 354 nm
0.357	0.177	0.018
0.894	0.247	0.042
1.430	0.393	0.067

---

* This salt contains some water molecules

ACRIDINIUM SULFATE* IN 0.02-N H_2SO_4

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 255.3 nm	Absorbance λ_2 = 354 nm
0.600	0.368	0.065
1.200	0.734	0.128
1.800	1.077	0.188
2.400	1.417	0.250
3.000	1.740	0.313
1.000	0.678	0.117
2.000	1.264	0.220
3.000	1.835	0.332

ACRIDINIUM SULFATE IN 0.02-N H_2SO_4
(Corrected for the H_2O Content)

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 255.3 nm	Absorbance λ_2 = 354 nm
0.545	0.368	0.065
1.089	0.734	0.128
1.634	1.077	0.188
2.179	1.417	0.250
2.723	1.740	0.313
0.908	0.678	0.117
1.815	1.264	0.220
2.723	1.835	0.332

ACRIDINIUM SULFATE* IN 0.20-N H_2SO_4

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 255.3 nm	Absorbance λ_2 = 354 nm
1.000	0.580	0.100
2.000	1.150	0.200
3.000	1.640	0.290

* This salt contains some water molecules

ACRIDINIUM SULFATE IN 0.20-N H_2SO_4
(Corrected for the H_2O Content)

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 255.3 nm	λ_2 = 354 nm
0.908	0.580	0.100
1.815	1.150	0.200
2.723	1.640	0.290

ACID-TREATED CARBAZOLE IN WATER

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 291 nm	λ_2 = 233 nm
0.300	0.018	0.046
0.600	0.034	0.091
1.000	0.055	0.152
2.000	0.110	0.290

ACID-TREATED CARBAZOLE IN 0.02-N H_2SO_4

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 291 nm	λ_2 = 233 nm
0.300	0.013	0.036
0.600	0.024	0.072
1.000	0.040	0.123

ACID-TREATED CARBAZOLE IN 0.20-N H_2SO_4

Concentration x 10^3 kg/m^3	Absorbance	
	λ_1 = 291 nm	λ_2 = 233 nm
1.500	0.014	0.027
3.000	0.026	0.063

INDOLE IN WATER

Concentration x 10^3 kg/m^3	Absorbance λ_1 = 269-269.5 nm	λ_2 = 215 nm
0.500	0.030	0.165
1.000	0.055	0.318
1.500	0.082	0.478
2.000	0.109	0.638

INDOLE IN 0.02-N HCl

Concentration x 10^3 kg/m^3	Absorbance λ_2 = 269-269.5 nm	λ_2 = 215 nm
0.500	0.037	0.217
1.000	0.054	0.318
1.500	0.078	0.462

II. Raw Data of Elemental Analysis

Sample No.	Compound Name	N%	C%	H%	CHN%
A1	Quinoline	10.27	84.36	5.40	100.03
A2		10.23	82.12	5.58	97.93
A3		10.30	82.14	5.57	98.01
Average		10.267	82.87	5.517	98.66
B1	Quinolinium	7.97	62.45	4.98	75.40
B2	Hydrochloride	7.81	60.18	5.01	73.0
B3		7.86	60.98	5.04	73.88
B4		8.05	59.72	5.12	72.89
B5		7.80	59.34	5.11	72.25
B6		7.75	58.25	4.97	70.97
Average		7.87	60.153	5.04	73.063
C1	Acridine	7.49	88.40	5.01	100.90
C2		7.28	90.14	4.90	102.32
C3		7.24	88.30	4.70	100.24
Average		7.337	88.95	4.87	101.15
D1	Acridinium	5.52	66.52	5.01	77.05
D2	Hydrochloride	6.16	70.21	4.48	80.85
D3	"Before Drying"	6.07	67.51	5.05	78.63
E1		6.14	67.07	4.93	78.14
E2		6.08	66.79	5.28	78.15
Average		5.994	67.62	4.95	78.564
1	Acridinium	6.064	75.46	4.88	86.407
2	Hydrochloride	5.967	71.818	5.179	82.964
3	"Dried at 210°F"	5.951	70.257	5.163	81.371
Average		5.994	72.511	5.074	83.581
F1	Acridinium	5.39	63.86	3.59	72.84
F2	Sulfate	5.32	62.42	3.62	71.36
F3	"Before Drying"	0.57*	63.08	3.57	67.22
Average		5.355	63.12	3.593	70.47
1	Acridinium	6.15	67.3	4.24	77.69
2	Sulfate	5.3	68.43	3.85	77.58
Average	"Dried at 210°F	5.725	67.865	4.045	77.635
G1	Carbazole	8.22	85.69	5.52	99.43
G2		8.15	84.93	5.56	98.64
G3		8.13	85.30	5.57	99.00

Sample No.	Compound Name	N%	C%	H%	CHN%
4		8.02	88.73	4.77	101.52
5		7.79	88.80	4.78	101.37
6		9.38	1.03	5.49	15.9*
Average		8.2838	87.04	5.282	100.234
H1	H_2SO_4 Acid-	8.04	81.81	5.68	95.53
H2	Treated	8.05	80.71	5.55	84.31
H3	Carbazole	7.71	88.79	4.57	101.07
H4		7.95	90.65	4.69	103.29
H5	7.85	89.24	4.58	101.67	
Average		7.943	85.41	5.114	98.465
I1	Indole	11.97	92.85	6.06	110.88
I2		11.90	79.28	6.11	97.29
I3		12.03	79.05	6.18	97.26

VITA 2

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Master of Science

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