SPECTROSCOPIC STUDIES OF COMPLEX COMPOUNDS IN NONAQUEOUS SOLVENTS

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THESIS

This is to certify that the

thesis entitled

SPECTROSCOPIC STUDIES OF COMPLEX
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of the requirements for

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SPECTROSCOPIC STUDIES OF COMPLEX COMPOUNDS IN NONAQUEOUS SOLVENTS

By

William Jan McKinney

AN ABSTRACT OF A THESIS

Submitted to
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ABSTRACT

SPECTROSCOPIC STUDIES OF COMPLEX COMPOUNDS IN NONAQUEOUS SOLVENTS

PART I: PYRIDINE-IODINE COMPLEXES
PART II: ALKALI METAL IONS IN PYRIDINE AND ACETONE SOLUTIONS

By

William Jan McKinney

Spectroscopic techniques have been used in this investigation to study the pyridine-iodine complex as well as the solvation of alkali metal salts in pyridine and acetone.

Pyridine and its homologues are known to form charge-transfer complexes with iodine, the complex formation constant being dependent on several physical and chemical parameters of the system. The effect of substitution on the pyridine ring on the formation constants of the complexes has been determined spectrophotometrically in carbon tetrachloride solutions at 25°. A plot of log K_M (ℓ mole^{-1}) vs. the Hammett σ constants of the pyridines yields a straight line given by the equation log K_M = $-2.25\,\sigma + 2.11$, indicating that the addition of nucleophilic

substituents to the pyridine ring increases the strength of the complex. Likewise a plot of log K_M vs. pK_a of the respective pyridines follows a linear relationship with the exception of cases in which steric hindrance becomes an important factor. If the substituent groups are electron donors themselves (phenyl or nitrile), a simple spectrophotometric technique fails to give the formation constant of the complex, presumably owing to the stepwise formation of two complexes.

Formation constants in mole fraction units of the pyridine-iodine charge-transfer complex have been determined at 25° in twelve solvents with dielectric constants varying from 1.92 to 10.36. The K_X values range from 612 in n-hexadecane to 3248 in o-dichlorobenzene. The enthalpies and entropies of the complex formation have been determined in five solvents. Comparison of the data with the solvent properties indicates that an increase in the dielectric constant of the reaction medium leads to the stabilization of the pyridine-iodine complex. The phenomenon is complicated, in some cases, by specific solute-solvent interactions, such as solvation of pyridine by chloroform or by the formation of the triiodide ion in polar solvents.

The solvation of lithium, sodium, and ammonium salts by pyridine was studied by infrared techniques. A new band was observed in these solutions which was

attributed to a cation-solvent vibration. Studies of the lithium- and ammonium-solvent bands by isotopic substitution techniques tend to confirm the assignment of this band to a cation-solvent vibration. The assignment is also supported by the splittings of several pyridine skeletal vibrations in alkali metal salt solutions. The magnitude of these splittings shows that the strength of the solvation of the above cations by pyridine increases in the order $Na^+ < NH_4^+ < Li^+$. The observed cation-solvent bands show little anion effect, except for the sodium iodide salt. However, a study of the spectra of the perchlorate ion shows that the symmetry of the ion is lowered in pyridine solutions of the lithium, sodium, and ammonium salts.

Some preliminary work in the far-infrared region of the spectrum has been done in acetone solutions. Solvent-cation bands for lithium and sodium salts have been observed in this region. The bands for the lithium salts appear to be anion dependent, especially the lithium chloride and lithium bromide salts. Isotopic studies with the lithium salts and d_6-acetone tend to support the assignment of the bands in the far-infrared to cation-solvent vibrations, although lithium salts in d_6-acetone give ambiguous results.

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I. PYRIDINE-IODINE COMPLEXES

INTRODUCTION

The beginning of interest in molecular complexes probably dates back to 1927 when Pfeiffer published a classic review, "Organische Molekülverbindung."[1] Instances of additive combination between aromatic hydrocarbons and other organic compounds as well as certain inorganic compounds were known at that time but were in apparent violation of the existing rules of chemical bonding. The stability of these additive compounds varied a great deal. Some formed stable solid adducts exhibiting integral stoichiometries while the existence of others could only be inferred from changes in color or other physical properties when the reactants were mixed together in solution. Pfeiffer explained the bonding between the components by postulating the existence of secondary valence forces within aromatic nuclei which were susceptible to saturation through interactions with quinones and various other molecules.

After Pfeiffer's article a basis for understanding these compounds in terms of acid-base theory was given by Lewis.[2] Interest in these compounds (molecular complexes) was stimulated by the discovery by Benesi and Hildebrand of a new absorption band in the ultra-violet region of the

spectrum in solutions of benzene and iodine which was characteristic of a complex.[3] This band provided a new means of studying the benzene-iodine complex and similar complexes, and its interpretation lead Mulliken to an extension of the Lewis acid-base theory in a quantum-theoretical form which provided the basis for the interpretation of a wide variety of phenomena associated with the molecular complexes.[4]

Since that time there has been a large increase in the literature available on the subject of molecular charge-transfer complexes.[5] The interest in charge-transfer complexes has been largely stimulated by the rich variety of possible complexes, their importance in biological systems, their importance as reaction intermediates and, to some extent, by the relative ease of experimental studies. As a result, there has been a large number of studies aimed at gaining an understanding of the factors affecting the stability of these species in solution. These factors can be thought of as belonging to one of four broad categories:

1. acceptor strength
2. donor strength
3. steric considerations
4. solvent effects.

Thus it was of interest to study a homologous series of complexes in order to determine the effect of each of the above factors on the stability of molecular complexes. The pyridine-iodine complex and its homologues were chosen for this purpose.

HISTORICAL PART

The existence of a solid 1:1 molecular addition compound of iodine with pyridine (Py) was first reported by Chatelet in 1933.[6] Chatelet also reported the isolation of two hydrated complexes which he identified as I_2-$Py(H_2O)_6$ and I_2-$Py_4(H_2O)_{24}$.

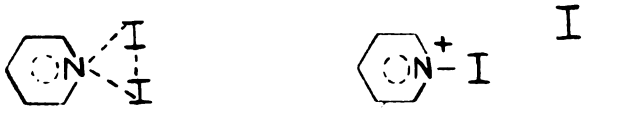
Most of the evidence for the formation of addition compounds of iodine with organic bases comes from spectral studies. Zingaro, et al., have investigated the behavior of iodine in pyridine solutions spectrophotometrically and postulated the reaction to be:

$$2I_2 + Py \rightleftharpoons IPy^+ + I_3^-$$

Infrared studies of iodine with pyridine and 2-picoline in carbon tetrachloride by Glusker, et al.[8] showed a definite shift of the absorption band from those of the individual compounds upon the addition of iodine to the respective organic base. The shift of absorption bands was attributed to the formation of a halogen-amine complex.

Mulliken and Reid,[9] in their study of the pyridine-iodine system in heptane solutions, reported the existence of the 1:1 molecular complex. Upon the addition of pyridine,

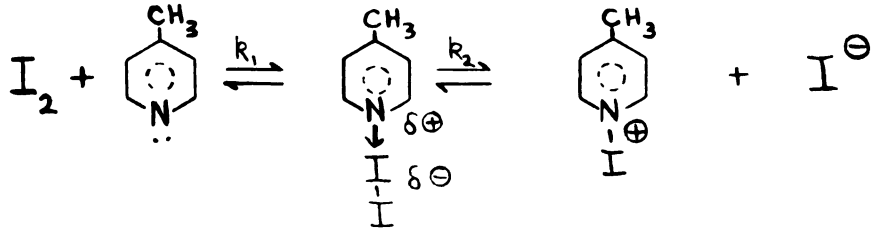
the 520 mμ peak of iodine in heptane was shifted to 422 mμ. This peak was attributed to the absorption by the complex, and the association constant for the complex was calculated to be 290 at 16.7°. Mulliken[9,4b] suggested the existence of two types of complex for the pyridine-iodine system: an "outer complex" (A) and an "inner complex" (B) with the structures

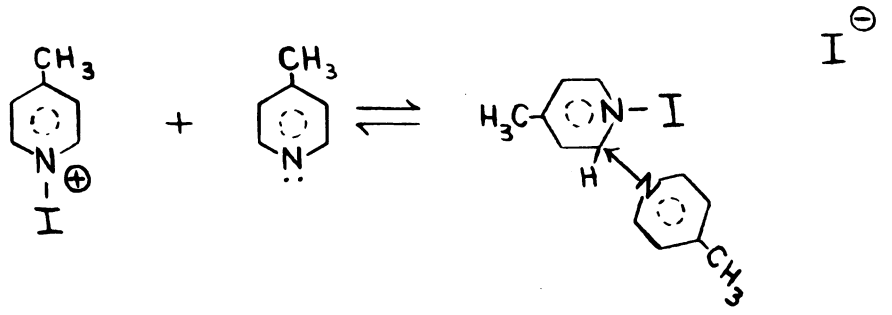


(A) (B)

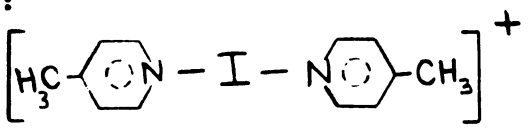
Kortüm and Wilski proposed the same possibility on the basis of conductivity measurements of the pyridine-iodine system.[10]

Glusker and Miller[11] isolated two different addition compounds formed by 4-picoline and iodine: compound II has an ionic structure and compound I is a molecular addition analogous to the addition compound of pyridine and iodine prepared by many workers. Their studies have led to the postulation that compound I is an intermediate in the formation of compound II, and the mechanism of the reaction is as follows:





Crystallographic studies by Hassel, et al.,[12] on the 1:1 addition compound of 4-picoline and iodine showed that the I-I-N arrangement in compound I is linear with the I-I distance of 2.83 A° while the I-N distance is 2.31 A°. Investigation by Hassel and Hope[13] on the reaction product of pyridine and iodine prompted them to postulate that the cation of compound II has a linear structure:



instead of addition next to the N atom on the Py ring as proposed by Glusker and Miller.[11]

Acceptor Strength

A series of complexes between the Lewis bases; pyridine, 2-picoline, and 2,6-lutidine; and the Lewis acids; iodine, iodine monochloride, and iodine monobromide; have been studied by Popov and Rygg.[14] This study shows that the acid strength of the halogens toward the pyridine bases decreased in the order ICl > IBr > I_2. This order agrees with the prediction by Scott[15] based on thermodynamic considerations that the Lewis acid strength of halogens and interhalogens should follow the order ICl >> BrCl > IBr >> I_2 > Br_2 > Cl_2.

Steric Considerations

Popov and Rygg also[14] reported that the stability of the halogen or interhalogen complex with each of the three pyridines decreased in the order 2-picoline > pyridine > 2,6-lutidine. The order of base strength of the pyridine to the aqueous proton is 2,6-lutidine > 2-picoline > pyridine. This reversal of ordering was attributed to steric hindrance.

Chaudhuri and Basu[16] studied the interaction between iodine and a few methyl substituted pyridines in chloroform. They took the pK_a (-log of the dissociation constant of the conjugate acid) values of the pyridines as being proportional to their first ionization potentials and claimed that the pK_a's were related to the formation

constants of the iodine complexes although they had too few experimental points to determine the exact nature of this relationship. They found that the 2,6-lutidine-iodine and the 2,4,6-collidine-iodine systems deviated significantly. This deviation was attributed to steric effects.

Similar results were reported for the 2,6-lutidine-iodine complex by Bhaskar and Singh.[17]

Halleux[18] reported that in the reaction between phenol and pyridine bases

$$C_6H_5OH + B \rightleftharpoons C_6H_5OH---B$$

the strength of the hydrogen bonds formed varies in the following order: 3,5-lutidine > 4-picoline > 2,6-lutidine > 2-picoline > pyridine. The basic strength of the compounds is, 2,6-lutidine > 3,5-lutidine ~ 4-picoline ~ 2-picoline > pyridine.

The above-mentioned investigations showed that steric hindrance is the main factor in the observed discrepancies between the basic strength and strength of the complexes. In the determination of basic strength, the very small proton is involved, and there is little steric effect present. Brown and Mihm reported[19] the absence of any important steric effects in the addition of the proton to pyridine, 2,6-lutidine, and monoalkylpyridines. Sacconi, et al.,[20] studied the heats of neutralization in water of

a series of pyridine bases which include pyridine, picolines and lutidines. They found that for pyridine, picolines, and lutidines a linear relationship between the heats of neutralization and basicity constants is followed, indicating the absence of any steric effect in the reactions. For the large iodine or interhalogen molecules, the presence of substituent groups adjacent to nitrogen atom will invariably hinder the combination of the Lewis acid with the base, and thus weaken the molecular complex formed.

Donor Strength

The work by Chaudhuri and Basu[16] was a step toward evaluating the effect of donor strength on the stability of the complex. Their results were not very meaningful, however, since they evaluated the formation constants of only four pyridine-iodine complexes, three of which involved steric factors. Bhaskar and Singh[17] extended this work by measuring the formation constants of eleven pyridine-iodine complexes. They state that the formation constants of the complexes vary "roughly" in the same order as the pK_a values of the pyridines.

A number of investigators have studied the relationship between the basicity of pyridines and their ability to form various types of complexes. A comprehensive study of the relationship between pK_f (-log of the

formation constant) of silver complexes of amines with their pK_a values by Bruehlman and Verhock[21] has shown that plots of pK_f *vs.* pK_a fall on two straight lines, one for the pyridines and primary aliphatic amines and one for secondary amines. Recently Cattalini and co-workers[22] have shown that the plot of log K *vs.* pK_a for the reaction

$$AuCl_4^- + Py \rightleftharpoons AuPyCl_3 + Cl^-$$

gave three straight lines, one for pyridines without steric hindrance, one for pyridines with one methyl group in the 2-position and a third one for pyridines with methyl groups in the 2 and 6 positions.

Solvent Effects

While numerous authors have studied the influence of the structure of the donor and/or acceptor molecules on the complex-forming reaction, the effect of the properties of the reaction medium has not been carefully scrutinized. Table 1 gives the reported values of the formation constant of the pyridine-iodine complex in M^{-1} in five different solvents. The values for this quantity vary from a low of 44 in chloroform to a high of 185 in *n*-heptane. Obviously some of this variance is due to experimental error as is indicated by the range of values in carbon tetrachloride and in *n*-heptane. Nevertheless, the low value in chloroform does indicate some effect of the solvent on the formation constant of the complex.

Table 1.--Literature Values for the Formation Constant of the Pyridine-Iodine Complex in Several Solvents

Solvent	Formation Constant	
n-Hexane	127	Bhaskar and Singh[17]
"	106	Alosi, et al.[23]
n-Heptane	138	Bist and Person[24]
"	140	Bhaskar and Singh[17]
"	185	Reid and Milliken[9] interpolated from Figure 4
"	108	Mazzucato, et al.[25]
Cyclohexane	126	Bhaskar and Singh[17]
"	107±25	Make and Plyler[26]
"	96	Krishna and Chaudhuri[27]
"	131	Lake and Thompson[28]
Carbon tetrachloride	101	Popov and Rygg[14]
" "	111	Bhaskar and Singh[17]
" "	183	Sobczyk, et al.[29]
Chloroform	63	Bhaskar and Singh[17]
"	44	Chaudhuri and Basu[16]

Merrifield and Phillips [30] studied the complex between tetracyanoethylene (TCNE) and three benzene derivatives. The complexes were examined in three solvents, dichloromethane, diethyl ether, and chloroform.

The difference in the equilibrium constants was explained by invoking a solvent competition for the TCNE. Formation constants for the TCNE-solvent interaction were determined relative to an assumed value of zero for the TCNE-chloroform complex. The values for the benzene and substituted benzene complexes were then corrected for this interaction, and the apparent discrepancy between the equilibrium constants was eliminated within experimental error. Solvent competition for one of the adducts was also used by Foster and Hammick[31] to explain the results they obtained on the N,N-dimethylaniline-s-trinitrobenzene system.

Some studies have also been carried out on complexes which are more polar than the π-π type of interaction in the TCNE complexes. In two of these cases, the Lewis acid used was iodine. The bases in these two studies were N,N-dimethylacetamide[32] and triphenylarsine.[33] Dichloromethane, benzene, dioxane, and 3-methysulfolane were used in the first investigation and dichloromethane, carbon tetrachloride and acetonitrile in the second. In both cases, reactions in solvents with high dielectric constants (3-methylsulfolane and acetonitrile) yielded triiodide ion as a reaction product. While the number of solvents studied was rather small, the results seemed to indicate an increase in the strength of the complex with increasing dielectric constant of the solvent. On the

surface, these results would seem to be contrary to Briegleb's[34] prediction that complex formation constants would have an inverse functional dependence on the dielectric constant of the solvent. However, his prediction was based on the formation of a non-polar complex in which the effect of complexation would be to squeeze out solvent molecules in the solvation sphere of the two reactants. This action should result in a weakening of the complex since the uncomplexed reactants would be more highly solvated than the complex. This effect should increase with increasing dielectric constant of the medium. Bhaskar and Singh[17] previously reported that the formation constant of the pyridine-iodine complex decreased with increasing dielectric constant of the reaction medium. These results cannot be regarded as conclusive for several reasons. In the first place, the authors used n-hexane, n-heptane, cyclohexane, carbon tetrachloride and chloroform as solvents. The range of dielectric constants, therefore, was very narrow with chloroform having the highest dielectric constant of 4.8, and the values for the other solvents hover around 2. Likewise, the differences in the values of the formation constants were very small, and no attempt was made to correct the results obtained in chloroform for the hydrogen-bonding equilibrium between the solvent and pyridine.[35]

EXPERIMENTAL

Chemicals

Pyridine: Fisher "Certified" pyridine was refluxed over granulated barium oxide for 12 hours and fractionally distilled through a 60 cm Vigreaux column. The distillate was then stored in the dark to prevent photo decomposition. One hundred ml portions of this pyridine were then refluxed over BaO for two hours and fractionally distilled through a 20 cm helices packed column and stored over NaOH as they were needed; bp = 115° (lit.[36] bp = 115.58°).

Iodine: The purification of iodine has been described previously.[37]

Carbon Tetrachloride: The purification of carbon tetrachloride has been described previously;[37] bp_{760} = 76.8° (lit.[36] bp_{760} = 76.75°).

3,4-Lutidine: Aldrich Chemical Company (A.C.C.) was refluxed 12 hours over BaO and fractionally distilled through a one meter helices packed column; n_D^{24} = 1.5099 (lit.[38] n_D^{25} = 1.5099).

2,6-Dichloropyridine: A.C.C. 2,6-dichloropyridine was recrystallized twice from a mixture of water and ethanol; mp = 87.0 - 87.2° (lit.[39] mp = 87 - 88°).

All other pyridines were purchased from A.C.C. except for the 4-t-butyl and 3-ethyl which were gifts of the Reilly Tar and Chemical Company. All of these compounds were purified by refluxing over BaO for at least two hours and fractionally vacuum distilling through a one-half meter, helices packed column. The compounds and their physical constants are given in Table 2.

Dichloromethane: Fisher "Certified" dichloromethane was refluxed for 24 hours over BaO and distilled through a one meter helices packed column; bp_{760} = 39.9° (lit.[36] bp_{760} = 39.95°).

n-Heptane: A.C.C. n-heptane was purified by stirring 3ℓ of the alkane with 300 ml portions of concentrated sulphuric acid until the acid was only slightly colored after two days exposure to the heptane. The alkane was then washed three times with one liter portions of water, dried for several days over anhydrous calcium sulfate, and fractionally distilled through an annular teflon spinning band column at a reflux ration of 6:1; bp_{760} = 98.3 (lit.[36] bp_{760} = 98.427).

Chloroform: Malinkrodt, N. F., chloroform was purified by shaking a portion with 50% of its volume of water sever times. It was then stored in the dark over $CaSO_4$ for at least six hours at which time the water content was less than two millimolar as determined by a Karl Fisher titration. The chloroform was then filtered into a glass stoppered

Table 2.--Physical Constants of Several Substituted Pyridines

Compound	Physical Constant	Literature Value of the Physical Constant	Reference
4-Ethylpyridine	n_D^{24} = 1.4996	n_D^{20} = 1.5010	40
2-Flouropyridine	n_D^{24} = 1.4658	n_D^{20} = 1.4678	41
2-Chloropyridine	bp = 167.6-168.0°	bp = 167-168°	42
2,5-Lutidine	n_D^{24} = 1.4981	n_D^{25} = 1.4982	43
4-Picoline	n_D^{24} = 1.5026	n_D^{25} = 1.5029	44
3-Chloropyridine	bp = 148.5-149.0°	bp = 143.5-148°	45
3-Bromopyridine	n_D^{24} = 1.5686	n_D^{20} = 1.5694	46
2-Bromopyridine	n_D^{24} = 1.5692	n_D^{20} = 1.5713	46
3-Picoline	n_D^{24} = 1.5036	n_D^{24} = 1.5043	47
4-t-Butylpyridine	n_D^{24} = 1.4934	$n_D^{25.5}$ = 1.4934	48
3,5-Lutidine	n_D^{24} = 1.5030	n_D^{25} = 1.5032	49

bottle. The increase in water content due to this operation was determined to be insignificant. The solvent was then used immediately. The entire procedure from the beginning of purification until the final measurement never took more than 24 hours; bp_{760} = 61.1° (lit.[36] bp_{760} = 61.152).

o-Dichlorobenzene: Eastman (99+%) o-dichlorobenzene was agitated for 24 hours with concentrated sulfuric acid, washed three times with 50% of its volume of distilled

water, dried over $CaSO_4$ for 24 hours, refluxed over BaO for 12 hours, and fractionally distilled through a one-half meter Vigereaux column; bp_{760} = 181° (lit.[36] bp_{760} = 180.48°).

m-Dichlorobenzene: A.C.C. m-dichlorobenzene was refluxed over BaO for 24 hours and fractionally distilled through a one meter helices packed column; bp_{760} = 173° (lit.[36] bp_{760} = 173.00°).

n-Hexadecane: A.C.C. n-hexadecane was agitated with concentrated sulfuric acid until a new portion of acid was only slightly colored after six hours of contact. It was then washed three times with 50% of its volume of distilled water and dried over $CaSO_4$ for 12 hours. The solvent was then fractionally vacuum distilled from BaO through a one-half meter Vigreaux column: fp = 18.2° (lit.[50] fp = 18.165°).

1,1,2-Trifluorotrichloroethane: Matheson Coleman and Bell "Spectroquality" 1,1,2-trifluorotrichloroethane was refluxed for 12 hours over BaO and fractionally distilled through a one meter helices packed column at a reflux ratio of 8:1; bp_{743} = 46.8° (lit.[51] bp_{760} = 47.6°).

Benzene and Toluene: Fisher "99% Mole Pure" benzene and Eastman "Sulfur-free" toluene were purified in the following manner. One gallon of the solvent was shaken for five hours with two 500 ml portions of concentrated sulphuric acid. The first portion of acid removed was slightly colored while the second was colorless.

The solvent was then shaken with one liter of water, then with one liter of dilute aqueous potassium hydroxide solution and finally with two, one liter portions of water. The product was then dried over $CaSO_4$ for 12 hours, and fractionally distilled through a one meter helices packed column. The boiling points of the benzene and toluene are respectively; bp_{760} = 80.0° and 110.3° (lit.[36] bp_{760} = 80.103° and 110.623°).

p-Xylene: A.C.C. p-xylene was purified by the method of fractional freezing. Water content was determined to be less than 3 millimolar in the final product; fp = 13.2° (lit.[37] fp = 13.263°).

1,2-Dichloroethane: 1,2-dichloroethane was purified by the method of Vogel;[53] bp_{760} = 83.4° (lit.[36] bp^{760} = 83.483°).

Nitromethane: Nitromethane was purified by the method of Clarke and Sandler;[54] bp_{760} = 101.2° (lit.[36] bp_{760} = 101.25°).

Preparation and Stability of Solutions

For the study of the complexes between fourteen substituted pyridines and iodine in carbon tetrachloride, solutions of iodine in carbon tetrachloride were prepared by the standard techniques. Although their concentration could be determined by iodometric titrations, it was found that equal accuracy was obtained by measuring the absorption

of the solution at 517 mμ and calculating the concentration from the value of the molar absorptivity at this wavelength (ε_{517} = 927). Stock solutions of the respective pyridines were made by weighing the respective compound into a volumetric flask and diluting with purified solvent.

Mixed solutions of iodine and of the respective pyridine were prepared just before each measurement. Contact of solutions with the atmosphere was kept to a minimum but no attempt was made to do all the transfers in a completely inert atmosphere. Preliminary results have indicated that brief contacts of the solution with the atmosphere did not alter the experimental data. Likewise it was found that solutions of iodine and the pyridines were stable for at least one hour after mixing and, in general, spectral measurements were completed within 5-10 minutes of the initial mixing.

For the study of the pyridine-iodine complex in different solvents, stock solutions of pyridine and iodine were prepared by weighing a quantity of the reactant into a clean, dry volumetric flask. They were then diluted to volume with the appropriate solvent in a water-bath thermostated at 25.0°. The proper aliquots of these solutions were then pipetted into another volumetric flask which was brought to volume in a thermostated bath kept at the same

temperature at which the final absorption measurements were made.

Solutions of iodine and pyridine were prepared just prior to each measurement. Again contact of solutions with the atmosphere was kept to a minimum, but no attempt was made to do all of the transfers in an inert atmosphere. The results indicate that the brief contacts of the solutions with air did not alter significantly the experimental data. It was found that pyridine slowly catalyzed the dehydrochlorination of chloroform and 1,2-dichloroethane. In these cases, special care was taken to use solutions as soon as possible after their preparation. A study of absorbance vs. time for a pyridine-iodine solution in the above solvents showed that the decomposition was inconsequential during the time required to complete the measurements. Solutions of pyridine and iodine in nitromethane were also found to be very unstable.

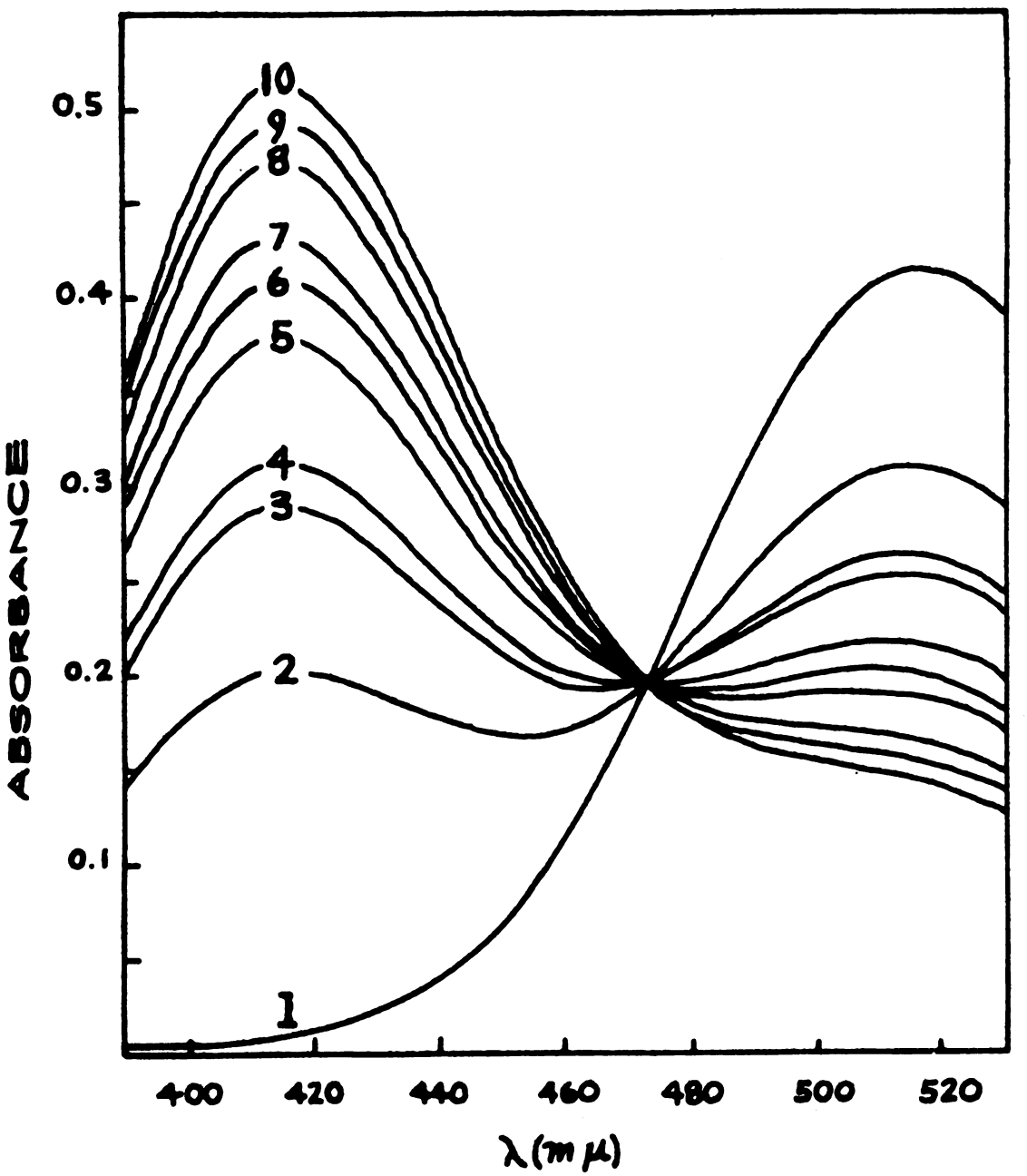
Spectral Measurements

In the study of the substituted pyridine-iodine complexes, absorption spectra were obtained on a Cary Model 14 Spectrophotometer. Either 1 cm or 5 cm pathlength cells were used. All measurements were carried out at room temperature of ≈ 25°. The donor/acceptor ratio was varied within such limits as to give a good spread of experimental points. Spectra of iodine-amine

solutions containing a fixed amount of iodine and a variable amount of the amine were obtained in the 530-390 mμ spectral range. A typical set of absorption curves is illustrated in Figure 1. All pyridine derivatives listed in Table 29 gave essentially ideal isobestic points. In the case of 4-phenylpyridine and of 4-cyanopyridine, a marked shift in the isobestic point was observed with a change in the amine/iodine ratio. It seems quite likely that this behavior may be due to the formation of weak $Py.2I_2$ complexes since second molecule of iodine may form a weak bond with the phenyl or the cyano group, respectively.

In the study of the pyridine-iodine complex in different solvents spectral measurements were made on a Beckman DU spectrophotometer with a thermostated cell compartment. The wavelength scale of the instrument was calibrated using a holmium oxide filter. The accuracy of the absorbance scale was checked by the method of additive absorbances and by the method of G. Haupt[54] using standard alkaline chromate solutions. The temperature of the cell compartment was determined by inserting a calibrated thermometer into the compartment through a styrofoam cover and allowing the system to come to equilibrium. The temperature could be controlled to ± 0.1°.

Figure 1.--Absorption spectra of the pyridine-iodine system in carbon tetrachloride solutions; C_{I_2} = 4.44 x 10^{-4} M; C_{Py} (M): (1) 0.0, (2) 0.00381, (3) 0.00762, (4) 0.00834, (5) 0.01143, (6) 0.01524, (7) 0.01669, (8) 0.02286, (9) 0.02503; (10) 0.03338.


ABSORBANCE
0.5
0.4
0.3
0.2
0.1
10
9
8
7
6
5
4
3
2
1
400
420
440
460
480
500
520
λ(mμ)

Calculations

Spectral data obtained on the donor-iodine mixtures (Tables 3-27) were used to calculate the formation constant of the complex using the method described by Ketelaar, et al.[55] In Ketellar's equation

$$\frac{1}{\varepsilon_t - \varepsilon_{I_2}} = \frac{1}{C_{Py}} \cdot \frac{1}{K_M(\varepsilon_c - \varepsilon_{I_2})} + \frac{1}{\varepsilon_c - \varepsilon_{I_2}} \qquad (1)$$

ε_t is the apparent molar absorptivity of I_2 (i.e., the measured absorbance of the solution divided by the total I_2 concentration), ε_c and ε_{I_2} are the molar absorptivities of the complex and the I_2 respectively, K_M is the formation constant of the complex in ℓ mole^{-1} and C_{Py} is the total concentration of base moles/ℓ. A plot of $1/(\varepsilon_t - \varepsilon_{I_2})$ vs. $1/C_{Py}$ should give a straight line. From the slope and intercept of the line the formation constant and the molar absorptivity of the complex can be determined. It should be noted that this method is likely to give better results than the treatment of Benesi and Hildebrand[3] since measurements had to be made at wavelengths at which both the complex and iodine absorb.

A regression analysis of the data was performed on a CDC 3600 computer with points over three standard deviations off the line being rejected (Appendix I). Large excesses of pyridines were found to cause a shift in the

isobestic point due to an increase in the polarity of the solvent which favors the formation of the triiodide ion. Thus, it was necessary in most cases to use base concentrations such that it was no longer possible to equate the concentration of the free base with the total concentration of the base which is a necessary condition for the use of Ketellar's equation. To overcome this difficulty an iteration was performed on the equation in the following manner. The experimental values of $1/C_{Py}$ and $1/(\varepsilon_t - \varepsilon_{I_2})$ were used in Ketelaar's equation to calculate a value for the concentration of the complex which was then subtracted from the value of C_{Py} to give a new array. The process was then repeated until successive values for K_M agreed within 0.1%.

In performing this type of mathematical analysis a great deal of caution must be exercised since relatively small errors in certain experimental parameters can cause large errors in the evaluation of the formation constant. A good illustration of such an error is the extreme sensitivity of the obtained K_M value to the iodine concentration for complexes where $K_M < 10$. In this study it was found that an error of 2.0% in the iodine concentration caused a 50% change in the value for K_M of the 2-flouropyridine complex. This uncertainty is evident in the large standard deviation for the K_M of the complex.

The iteration procedure for solving Ketelaar's equation offers a distinct advantage in the evaluation of formation constants from experimental data. The values converged rapidly and reproducibly at all wavelengths. This method makes it possible to use lower concentrations of the donors and thus it avoids the possibility of a change in the physical properties of the solvent in solutions with high concentrations of the base. It also makes it unnecessary to use a complex iterative procedure such as the one reported by Conrow, et al.[56]

As in all calculations of this type, we assumed that activity coefficients are equal to unity, i.e., the values of K_M are expressed in concentration units. It should be noted that this assumption may be rather dangerous especially in the case of weak complexes where a large excess of donor (or acceptor) has to be added in order to produce a measurable change in the absorption spectrum.[57] The concentration of the component in excess may be as high as 2 - 4 M, and under these conditions it would be unreasonable to expect that the activity coefficients, even of uncharged species, can be ignored.

Calculations were carried out at least at three different wavelengths over at least a 20 mμ range. It has been previously shown that the linearity of the Benesi-Hildebrand plot by itself is not a sufficient criterion for assuming a simple 1:1 interaction between the donor and the acceptor molecules.[58]

In the study of solvent effects on the formation constants of the pyridine-iodine complex the values of the formation constants were changed from $\underline{M}^{-1}$ to mole fraction units by use of the following relationship:

$$K_X = \frac{K_M}{V_S + X_{Py}(V_{Py} - V_S)} \qquad (2)$$

where K_X and K_M are the mole fraction and the molar equilibrium constants, X_{Py} is the mole fraction of pyridine and V_{Py} and V_S are the molar volumes of pyridine and of the solvents. The above equation is based on the assumption that no volume change occurs on mixing. In the present study the concentration of pyridine was always kept below 0.03 M and the concentration of iodine was ~ 10^{-4} $\underline{M}$. Therefore, $X_{Py} < 0.01$ and under these conditions, equation (1) can be reduced to

$$K_X = K_M S^\circ \qquad (3)$$

where S° is the concentration of pure solvent in moles/ℓ.

Whenever possible, corrections were made for the solvent-solute interaction. It has been shown that chloroform forms a hydrogen-bonded complex with pyridine[35] with $K_X = 0.69$. Likewise, it is well known that aromatic compounds form charge-transfer complexes with iodine. In fact, the formation constants of benzene, toluene, and

xylene complexes with iodine have been reported to be 0.15, 0.16, and 0.31 $\ell.mole^{-1}$ respectively.[59]

In order to allow for the solvent-solute interaction in the case of the four solvents mentioned above, the corrected values of the formation constants were calculated from the expression[32,60] (see Appendix 2)

$$K_{corr} = K_{obs} (1 + K_S S°) \quad (4)$$

where K_S is the equilibrium constant ($\underline{M}^{-1}$) for the solute-solvent interaction, K_{obs} is the experimental value for pyridine-iodine complex in the given solvent and S° is the concentration of the pure solvent in moles/ℓ.

Enthalpy and entropy values for the pyridine-iodine complex were calculated in the usual manner by determining the slope and intercept of a plot of ℓn K_M *vs.* 1/T by a least squares procedure.

Measurements of the absorption maximum of the blue-shifted iodine band of the complex were made in a series of mixed solvents obtained by adding varying amounts of nitromethane to carbon tetrachloride. The dielectric constants of these mixed solvents were calculated by use of the principle of additivity (i.e., $D_{calc} = X_{CCl_4} D_{CCl_4} + X_{CH_3NO_2} D_{CH_3NO_2}$). The value of dielectric constant of nitromethane used in the aforementioned calculations was 35.9. The results of these measurements are contained in Figure 5.

Table 3.--Experimental Data on the 2-Fluoropyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{450m\mu}$	$A_{440m\mu}$	$A_{430m\mu}$
~ 25°, $[I_2]$ = 1.64 · 10^{-4} M, path length = 5.000 cm			
0.1220	0.291	0.240	0.195
0.0697	0.225	0.172	0.130
0.1917	0.359	0.312	0.263
0.1568	0.325	0.276	0.229
0.0666	0.225	0.170	0.129
0.0686	0.224	0.171	0.129
0.0961	0.276	0.223	0.178
0.1163	0.284	0.234	0.189
0.1647	0.332	0.282	0.234
0.2085	0.369	0.322	0.271
0.1099	0.250	0.199	0.153
0.0880	0.260	0.205	0.161
ε_{I_2}	150.0	82.0	44.0
K_M	2.3±.8	2.0±.7	1.7±.8
ε_c	1070	1110	1130

Table 4.--Experimental Data on the 2,5-Lutidine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{420m\mu}$	$A_{410m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2]$ = 6.50 · 10^{-5} M, path length = 5.000 cm			
0.00398	0.290	0.294	0.268
0.00597	0.342	0.350	0.328
0.00796	0.374	0.381	0.347
0.00995	0.399	0.405	0.368
0.01194	0.417	0.421	0.383
0.01593	0.440	0.446	0.407
0.00546	0.331	0.336	0.305
0.00818	0.379	0.384	0.350
0.01091	0.409	0.414	0.371
0.01364	0.428	0.433	0.393
0.01637	0.440	0.446	0.407
0.02182	0.459	0.464	0.422
0.00651	0.350	0.358	0.329
0.00976	0.397	0.404	0.370
0.01301	0.420	0.431	0.398
0.01626	0.439	0.450	0.412
0.01951	0.453	0.463	0.424
0.02602	0.468	0.479	0.440
ε_{I_2}	20.9	10.2	6.41
K_M	301±2.0	304±2.2	308±7.4
ε_c	1630	1660	1510

Table 5.--Experimental Data on the 3-Chloropyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{440m\mu}$	$A_{430m\mu}$	$A_{420m\mu}$
~ 25°, $[I_2] = 2.19 \cdot 10^{-4}$ M, path length = 5.000 cm			
0.03290	0.575	0.577	0.546
0.04935	0.706	0.721	0.689
0.06580	0.800	0.828	0.792
0.08225	0.873	0.910	0.876
0.09870	0.926	0.966	0.930
0.02775	0.520	0.517	0.484
0.04163	0.645	0.654	0.620
0.05551	0.736	0.753	0.719
0.06939	0.809	0.839	0.806
0.08326	0.871	0.905	0.867
0.02126	0.444	0.431	0.401
0.03180	0.560	0.561	0.530
0.04240	0.640	0.647	0.614
0.05301	0.720	0.736	0.702
0.06361	0.779	0.801	0.768
0.03439	0.578	0.580	0.549
ε_{I_2}	82.0	44.0	20.9
K_M	17.2±.25	16.5±.28	16.4±.29
ε_C	1290	1400	1360

Table 6.--Experimental Data on the 2-Chloropyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{440m\mu}$	$A_{430m\mu}$	$A_{420m\mu}$
~ 25°, $[I_2]$ = 2.20 · 10^{-4} M, path length = 5.000 cm			
0.03011	0.224	0.170	0.124
0.04517	0.277	0.220	0.168
0.06022	0.330	0.270	0.209
0.09033	0.427	0.351	0.280
0.02132	0.187	0.137	0.096
0.04265	0.268	0.214	0.160
0.06397	0.340	0.281	0.218
0.08530	0.401	0.340	0.268
0.12790	0.513	0.448	0.359
0.03578	0.243	0.189	0.142
0.05366	0.308	0.249	0.190
0.07155	0.364	0.302	0.239
0.08944	0.418	0.350	0.279
0.03272	0.231	0.177	0.131
0.06543	0.349	0.289	0.226
ε_{I_2}	82.0	44.0	20.9
K_M	3.8±.15	3.5±.13	3.1±.10
ε_c	1240	1200	1110

Table 7.--Experimental Data on the 2-Bromopyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{430m\mu}$	$A_{420m\mu}$	$A_{410m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2] = 2.23 \cdot 10^{-4}$ M, path length = 5.000 cm				
0.03274	0.192	0.144	0.100	0.068
0.04912	0.250	0.191	0.137	0.091
0.06549	0.298	0.230	0.167	0.110
0.08186	0.348	0.272	0.199	0.131
0.09823	0.391	0.303	0.226	0.151
0.02804	0.171	0.126	0.090	0.059
0.04206	0.221	0.166	0.118	0.079
0.05608	0.271	0.210	0.150	0.099
0.07010	0.313	0.242	0.173	0.116
0.08412	0.351	0.274	0.199	0.131
0.03062	0.185	0.137	0.094	0.062
0.06124	0.290	0.223	0.161	0.107
0.07655	0.333	0.261	0.189	0.126
0.09186	0.373	0.292	0.217	0.143
0.02465	0.160	0.113	0.080	0.053
0.04931	0.251	0.190	0.138	0.091
0.09861	0.396	0.312	0.230	0.155
ε_{I_2}	44.0	20.9	10.2	6.41
K_M	4.5±1.8	4.3±.26	4.4±.21	4.4±.24
ε_C	1040	870	640	420

Table 8.--Experimental Data on the 4-Ethylpyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{420m\mu}$	$A_{410m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2] = 6.50 \cdot 10^{-5}$ M, path length = 5.000 cm			
0.03280	0.465	0.487	0.460
0.00570	0.302	0.313	0.293
0.01139	0.390	0.403	0.379
0.00285	0.217	0.224	0.211
0.05110	0.480	0.503	0.473
0.00888	0.359	0.374	0.350
0.01776	0.421	0.439	0.414
0.00222	0.189	0.194	0.181
0.00444	0.273	0.282	0.264
0.00588	0.305	0.318	0.299
0.01178	0.384	0.402	0.375
0.02355	0.443	0.463	0.437
0.02944	0.455	0.477	0.449
0.04122	0.470	0.491	0.462
0.00364	0.248	0.257	0.240
0.00729	0.336	0.349	0.327
0.01459	0.406	0.424	0.398
0.08390	0.491	0.517	0.491
ε_{I_2}	20.9	10.2	6.41
K_M	251±1.9	248±1.5	246±1.7
ε_c	1590	1660	1570

Table 9.--Experimental Data on the 3-Bromopyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{435m\mu}$	$A_{430m\mu}$	$A_{425m\mu}$	$A_{420m\mu}$
~ 25°, $[I_2]$ = 1.096 · 10^{-4} M, path length = 5.000 cm				
0.02286	0.249	0.248	0.191	0.231
0.03428	0.316	0.314	0.309	0.299
0.04571	0.370	0.371	0.367	0.356
0.05714	0.409	0.412	0.409	0.397
0.06857	0.443	0.448	0.444	0.431
0.09142	0.491	0.500	0.497	0.483
0.02058	0.232	0.230	0.173	0.214
0.03086	0.294	0.293	0.289	0.280
0.04115	0.347	0.347	0.342	0.331
0.05144	0.388	0.390	0.386	0.373
0.06172	0.420	0.423	0.420	0.409
0.08230	0.473	0.479	0.475	0.462
0.01615	0.198	0.193	0.188	0.179
0.02422	0.254	0.252	0.247	0.237
0.03230	0.301	0.301	0.296	0.286
0.04037	0.341	0.342	0.339	0.327
0.04845	0.377	0.379	0.373	0.361
0.06460	0.427	0.432	0.428	0.416
ε_{I_2}	62.3	44.0	30.2	20.9
K_M	17.5±.19	17.4±.22	17.1±.18	17.2±.15
ε_C	1430	1460	1470	1430

Table 10.--Experimental Data on the Pyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{430m\mu}$	$A_{420m\mu}$	$A_{415m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2] = 6.50 \cdot 10^{-5}$ M, path length = 5.000 cm				
0.01209	0.267	0.288	0.290	
0.06952	0.403	0.441	0.447	
0.01046	0.248	0.267	0.268	
0.01395	0.279	0.301	0.303	
0.01744	0.300	0.327	0.329	
0.02093	0.319	0.345	0.349	
0.02790	0.347	0.376	0.378	
0,01295	0.270	0.292	0.295	
0.01943	0.308	0.335	0.339	
0.02590	0.338	0.367	0.371	
0.03238	0.355	0.390	0.394	
0.03886	0.368	0.403	0.407	
0.05181	0.387	0.423	0.427	
0.17000	0.425	0.470	0.477	
0.07392	0.401	0.443	0.449	
0.02957	0.349	0.382	0.386	
ε_{I_2}	44.0	20.9	14.4	
K_M	111±1.3	109±1.1	108±1.0	
ε_c	1380	1530	1550	
~ 25°, $[I_2] = 4.44 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.05154		0.579	0.585	0.518
0.02577		0.501	0.508	0.445
0.07732		0.608	0.616	0.541
0.10310		0.622	0.631	0.558
0.15460		0.645	0.653	0.582
0.01016		0.357	0.359	0.312
0.02032		0.469	0.473	0.412
0.03048		0.521	0.527	0.462
0.04064		0.552	0.558	0.489
0.05080		0.574	0.581	0.510
0.06096		0.588	0.594	0.521
0.00381		0.200	0.202	0.179
0.00762		0.287	0.288	0.254
0.01143		0.373	0.380	0.337
0.01524		0.402	0.407	0.360
0.01905		0.459	0.465	0.409

Table 10.--Continued

C_{Py}	$A_{430m\mu}$	$A_{420m\mu}$	$A_{415m\mu}$	$A_{400m\mu}$
0.02286		0.466	0.470	0.414
0.00834		0.309	0.311	0.276
0.01669		0.426	0.430	0.380
0.02503		0.487	0.489	0.431
0.03338		0.503	0.512	0.451
ε_{I_2}		25.0	13.8	6.25
K_M		106±2.3	108±2.6	111±2.7
ε_C		1510	1520	1330

Table 11.--Experimental Data on the 4-t-Butylpyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{420m\mu}$	$A_{415m\mu}$	$A_{410m\mu}$	$A_{405m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2] = 5.86 \cdot 10^{-4}$ M, path length = 5.000 cm					
0.000732	0.157	0.160	0.159	0.156	0.149
0.001464	0.258	0.223	0.276	0.271	0.259
0.002195	0.351	0.361	0.363	0.358	0.342
0.002927	0.416	0.428	0.432	0.427	0.409
0.003659	0.470	0.485	0.489	0.483	0.462
0.004391	0.513	0.531	0.537	0.529	0.505
0.005854	0.579	0.600	0.607	0.599	0.572
0.000947	0.189	0.192	0.192	0.189	0.181
0.001894	0.312	0.323	0.326	0.320	0.306
0.002842	0.406	0.417	0.421	0.413	0.397
0.003789	0.473	0.488	0.492	0.486	0.464
0.004736	0.527	0.542	0.548	0.540	0.517
0.005683	0.569	0.589	0.593	0.584	0.560
0.007578	0.632	0.656	0.662	0.653	0.625
0.001166	0.219	0.222	0.224	0.220	0.209
0.002331	0.355	0.366	0.368	0.362	0.346
0.003497	0.453	0.469	0.473	0.465	0.444
0.004662	0.517	0.536	0.541	0.532	0.510
0.005828	0.568	0.587	0.595	0.585	0.560
0.006993	0.611	0.632	0.639	0.630	0.602
0.009324	0.670	0.695	0.703	0.692	0.662
ε_{I_2}	20.9	14.4	10.2	7.19	6.41
K_M	301±4.6	296±4.7	296±4.6	300±4.1	299±4.0
ε_C	1560	1630	1650	1620	1550

Table 12.--Experimental Data on the 4-Picoline-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{420m\mu}$	$A_{415m\mu}$	$A_{410m\mu}$	$A_{405m\mu}$
~ 25°, $[I_2] = 4.50 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00614	0.419	0.429	0.430	0.421
0.01229	0.529	0.545	0.547	0.534
0.01843	0.587	0.602	0.607	0.594
0.02457	0.614	0.635	0.639	0.627
0.03072	0.638	0.657	0.661	0.650
0.00289	0.278	0.283	0.283	0.276
0.00579	0.399	0.407	0.408	0.399
0.00869	0.470	0.481	0.482	0.471
0.01159	0.512	0.527	0.528	0.517
0.01448	0.546	0.560	0.561	0.549
0.01738	0.569	0.587	0.589	0.576
0.00405	0.328	0.336	0.337	0.328
0.00811	0.451	0.462	0.463	0.452
0.01217	0.517	0.531	0.532	0.520
0.01622	0.552	0.569	0.571	0.558
0.00711	0.431	0.445	0.446	0.433
0.01423	0.541	0.556	0.558	0.548
ε_{I_2}	20.9	14.4	10.2	7.19
K_M	219±3.7	216±3.4	216±3.5	215±3.8
ε_c	1600	1650	1660	1630

Table 13.--Experimental Data on the 3-Picoline-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{420m\mu}$	$A_{415m\mu}$	$A_{410m\mu}$	$A_{405m\mu}$
~ 25°, $[I_2] = 5.83 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00378	0.411	0.419	0.418	0.407
0.00755	0.572	0.585	0.584	0.568
0.01134	0.647	0.671	0.671	0.655
0.01512	0.709	0.727	0.728	0.708
0.01890	0.748	0.766	0.766	0.748
0.02268	0.771	0.791	0.791	0.771
0.00292	0.345	0.351	0.350	0.339
0.00584	0.502	0.512	0.512	0.498
0.00877	0.598	0.608	0.608	0.591
0.01169	0.659	0.673	0.673	0.657
0.01462	0.692	0.709	0.710	0.689
0.01754	0.731	0.747	0.747	0.728
0.00203	0.268	0.270	0.269	0.261
0.00407	0.412	0.420	0.419	0.408
0.00610	0.511	0.520	0.517	0.500
0.00814	0.570	0.582	0.580	0.561
0.01018	0.618	0.631	0.630	0.611
0.01221	0.657	0.670	0.668	0.649
0.00461	0.438	0.447	0.445	0.430
0.00923	0.600	0.610	0.609	0.591
ε_{I_2}	20.9	14.4	10.2	7.19
K_M	207±2.8	206±2.9	207±3.0	207±3.4
ε_c	1600	1640	1640	1590

Table 14.--Experimental Data on the 3,5-Lutidine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{415m\mu}$	$A_{410m\mu}$	$A_{405m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2] = 5.81 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00279	0.505	0.511	0.505	0.483
0.00559	0.675	0.685	0.679	0.651
0.00838	0.773	0.788	0.782	0.754
0.01118	0.823	0.837	0.831	0.803
0.01397	0.862	0.886	0.880	0.854
0.01677	0.899	0.920	0.919	0.894
0.02235	0.942	0.969	0.972	0.952
0.00081	0.222	0.223	0.221	0.211
0.00163	0.363	0.368	0.362	0.349
0.00102	0.264	0.267	0.262	0.251
0.00204	0.421	0.426	0.421	0.402
0.00306	0.533	0.542	0.536	0.515
0.00408	0.606	0.615	0.609	0.586
0.00510	0.661	0.672	0.665	0.640
0.00612	0.707	0.717	0.711	0.685
0.00816	0.767	0.779	0.772	0.743
0.00293	0.517	0.523	0.519	0.499
0.00586	0.690	0.701	0.697	0.670
0.00880	0.785	0.799	0.792	0.767
ε_{I_2}	14.4	10.2	7.19	6.41
K_M	382±2.3	378±2.8	377±3.3	369±3.6
ε_c	1760	1800	1790	1740

Table 15.--Experimental Data on the 3,4-Lutidine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{415m\mu}$	$A_{410m\mu}$	$A_{405m\mu}$	$A_{400m\mu}$
~ 25°, $[I_2]$ = 6.54 · 10^{-4} M, path length = 1.000 cm				
0.00223	0.517	0.526	0.523	0.504
0.00335	0.637	0.648	0.645	0.624
0.00446	0.716	0.726	0.724	0.701
0.00558	0.763	0.779	0.774	0.744
0.00669	0.815	0.831	0.827	0.800
0.00186	0.458	0.466	0.464	0.446
0.00279	0.576	0.585	0.582	0.560
0.00372	0.654	0.665	0.663	0.641
0.00465	0.717	0.728	0.726	0.702
0.00558	0.771	0.787	0.783	0.754
0.00162	0.413	0.416	0.412	0.395
0.00243	0.525	0.532	0.528	0.509
0.00323	0.605	0.614	0.609	0.591
0.00404	0.673	0.681	0.675	0.653
0.00485	0.717	0.730	0.727	0.797
0.00253	0.530	0.536	0.532	0.511
0.00379	0.645	0.655	0.652	0.625
0.00506	0.728	0.740	0.734	0.709
ε_{I_2}	14.4	10.2	7.19	6.41
K_M	427±10.2	421±11.4	420±12.3	386±17.9
ε_C	1700	1740	1730	1740

Table 16.--Experimental Data on the 3-Ethylpyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{420m\mu}$	$A_{415m\mu}$	$A_{410m\mu}$	$A_{405m\mu}$
~ 25°, $[I_2] = 6.59 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00908	0.711	0.731	0.732	0.716
0.01816	0.849	0.872	0.875	0.854
0.00208	0.337	0.342	0.342	0.334
0.00415	0.505	0.521	0.522	0.507
0.00623	0.617	0.631	0.633	0.617
0.00831	0.688	0.707	0.708	0.689
0.01038	0.739	0.758	0.759	0.738
0.01246	0.740	0.759	0.760	0.740
0.01661	0.831	0.855	0.857	0.835
0.00449	0.528	0.538	0.538	0.526
0.00898	0.704	0.723	0.723	0.706
0.01348	0.792	0.812	0.814	0.795
0.01797	0.842	0.866	0.869	0.848
0.02246	0.878	0.902	0.905	0.881
0.00118	0.221	0.224	0.223	0.217
0.00236	0.364	0.370	0.370	0.360
0.00354	0.462	0.474	0.474	0.461
0.00471	0.537	0.549	0.549	0.532
0.00707	0.647	0.660	0.661	0.644
0.00943	0.712	0.731	0.731	0.715
ε_{I_2}	20.9	14.4	10.2	7.19
K_M	243±1.0	243±0.9	245±1.0	247±1.4
ε_c	1580	1620	1620	1580

Table 17.--Experimental Data on the Pyridine-Iodine Complex in Carbon Tetrachloride

C_{Py}	$A_{410m\mu}$	$A_{416m\mu}$	$A_{420m\mu}$	$A_{428m\mu}$
8.5°, $[I_2] = 4.362 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00528	0.369	0.371	0.368	0.346
0.00793	0.440	0.443	0.438	0.408
0.01057	0.486	0.487	0.483	0.448
0.01322	0.515	0.519	0.511	0.472
0.01586	0.543	0.549	0.539	0.498
0.02115	0.575	0.581	0.569	0.527
0.00619	0.398	0.402	0.398	0.370
0.00928	0.466	0.470	0.464	0.432
0.01238	0.511	0.515	0.507	0.468
0.01548	0.539	0.542	0.534	0.492
0.01857	0.566	0.569	0.561	0.517
ε_{I_2}	9.2	16.0	18.3	36.7
K_M	216±1.5	213±1.9	220±1.9	226±2.1
ε_c	1610	1630	1600	1450
25.0°, $[I_2] = 5.383 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.01522		0.498	0.496	0.480
0.03043		0.621	0.616	0.597
0.04565		0.675	0.671	0.648
0.06087		0.702	0.697	0.672
0.07609			0.717	0.691
0.01447		0.488	0.486	0.470
0.02171		0.564	0.560	0.539
0.02895		0.611	0.606	0.586
0.00724		0.347	0.348	0.336
0.03618		0.643	0.638	0.613
0.04342		0.662	0.662	0.636
ε_{I_2}		11.1	18.6	30.0
K_M		104±0.4	105±0.2	103±0.5
ε_c		1510	1500	1450

Table 17.--Continued

C_{Py}	$A_{410m\mu}$	$A_{416m\mu}$	$A_{420m\mu}$	$A_{428m\mu}$
16.3°, $[I_2] = 4.362 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00663	0.342	0.346	0.346	
0.00996	0.409	0.414	0.413	
0.01326	0.459	0.463	0.458	
0.01989	0.512	0.515	0.511	
0.02652	0.553	0.555	0.546	
0.00874	0.389	0.395	0.391	
0.01312	0.453	0.457	0.452	
0.01749	0.503	0.509	0.503	
0.02186	0.528	0.532	0.527	
0.01658	0.490	0.493	0.489	
0.02623	0.549	0.553	0.546	
ε_{I_2}	11.5	16.0	18.3	
K_M	151±1.5	153±1.8	159±1.8	
ε_C	1580	1580	1550	
34.5°, $[I_2] = 5.084 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.01854	0.430	0.442	0.442	0.426
0.02781	0.503	0.519	0.519	0.495
0.03708	0.553	0.566	0.565	0.538
0.04635	0.587	0.589	0.598	0.571
0.05562	0.610	0.621	0.620	0.593
0.01414	0.379	0.391	0.392	0.378
0.02827	0.503	0.520	0.520	0.496
0.04241	0.573	0.388	0.588	0.563
0.02121	0.457	0.466	0.467	0.450
0.03534	0.545	0.556	0.557	0.531
0.05655	0.611	0.620	0.620	0.594
ε_{I_2}	11.8	17.7	23.6	39.3
K_M	68.8±0.48	70.8±0.48	70.8±0.46	71.4±0.48
ε_C	1510	1530	1530	1450

Table 17.--Continued

C_{Py}	$A_{410m\mu}$	$A_{416m\mu}$	$A_{420m\mu}$	$A_{428m\mu}$
25.0°, $[I_2]$ = 5.383 · 10^{-4} M, path length = 1.000 cm				
0.00617	0.317	0.327	0.327	0.310
0.01234	0.452	0.462	0.459	0.433
0.01851	0.529	0.541	0.538	0.512
0.02468	0.583	0.595	0.591	0.563
0.03085	0.613	0.624	0.619	0.589
0.01767	0.523	0.533	0.530	0.504
0.00532	0.279	0.296	0.296	0.286
0.01065	0.425	0.435	0.433	0.404
0.01597	0.501	0.514	0.511	0.485
0.02130	0.562	0.571	0.569	0.539
0.02662	0.596	0.606	0.603	0.571
0.00776	0.360	0.369	0.368	0.354
0.01551	0.500	0.513	0.511	0.485
0.02327	0.574	0.588	0.585	0.556
ε_{I_2}	13.0	20.4	22.3	42.7
K_M	100±1.2	107±0.6	108±0.7	105±1.0
ε_c	1520	1520	1500	1430

Table 18.--Experimental Data on the Pyridine-Iodine Complex in Dichloromethane

C_{Py}	$A_{390m\mu}$	$A_{395m\mu}$	$A_{400m\mu}$	$A_{410m\mu}$
25.0°, $[I_2]$ = 5.390 · 10^{-4} M, path length = 1.000 cm				
0.001265	0.150	0.155	0.155	0.149
0.002530	0.257	0.266	0.267	0.249
0.003796	0.343	0.352	0.352	0.325
0.005061	0.407	0.420	0.419	0.383
0.006326	0.460	0.472	0.472	0.432
0.004505	0.382	0.393	0.392	0.364
0.006070	0.452	0.463	0.462	0.430
0.007509	0.507	0.520	0.519	0.479
0.009011	0.550	0.565	0.562	0.517
0.003325	0.320	0.327	0.327	0.302
0.004988	0.412	0.422	0.422	0.388
0.006650	0.476	0.487	0.486	0.451
0.008313	0.530	0.544	0.542	0.499
ε_{I_2}	9.3	9.3	11.1	27.8
K_M	149±0.8	153±0.5	152±0.6	151±0.6
ε_c	1800	1820	1820	1670
16.4°, $[I_2]$ = 3.640 · 10^{-4} M, path length = 1.000 cm				
0.00494	0.344	0.349	0.343	0.307
0.00741	0.411	0.415	0.408	0.364
0.00989	0.455	0.459	0.449	0.401
0.01236	0.488	0.492	0.482	0.428
0.01484	0.514	0.518	0.506	0.447
0.01978	0.553	0.555	0.542	0.485
0.00640	0.382	0.386	0.382	0.348
0.00960	0.445	0.450	0.442	0.399
0.01281	0.487	0.492	0.485	0.437
0.01921	0.537	0.543	0.532	0.476
ε_{I_2}	13.7	13.7	16.5	33.0
K_M	213±4.1	217±3.9	222±3.0	223±3.6
ε_c	1850	1860	1810	1610

Table 18.--Continued

C_{Py}	$A_{390m\mu}$	$A_{395m\mu}$	$A_{400m\mu}$	$A_{410m\mu}$
8.7°, $[I_2] = 4.059 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00394	0.426	0.431	0.425	
0.00591	0.497	0.505	0.496	
0.00789	0.550	0.557	0.546	
0.00986	0.579	0.587	0.576	
0.01184	0.608	0.613	0.601	
0.00318	0.384	0.388	0.380	
0.00635	0.514	0.519	0.507	
0.00953	0.580	0.584	0.571	
0.00476	0.464	0.469	0.463	
0.00794	0.550	0.558	0.548	
0.01272	0.618	0.620	0.612	
ε_{I_2}	7.4	9.9	14.8	
K_M	339±2.8	340±1.8	339±3.5	
ε_c	1880	1890	1860	
32.6°, $[I_2] = 5.100 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00503	0.310	0.322	0.323	0.301
0.00754	0.400	0.411	0.411	0.384
0.01006	0.464	0.476	0.475	0.444
0.01258	0.520	0.530	0.530	0.491
0.01510	0.562	0.575	0.572	0.530
0.02013	0.629	0.641	0.638	0.591
0.00601	0.333	0.345	0.346	0.325
0.00901	0.436	0.447	0.447	0.418
0.01202	0.502	0.516	0.516	0.476
0.01202	0.503	0.517	0.517	0.477
0.01803	0.580	0.594	0.595	0.545
ε_{I_2}	13.7	15.7	21.6	33.3
K_M	96±2.4	101±2.4	102±2.3	103±2.3
ε_c	1850	1850	1840	1690

Table 19.--Experimental Data on the Pyridine-Iodine Complex in 1,2-Dichloroethane

C_{Py}	$A_{385m\mu}$	$A_{390m\mu}$	$A_{395m\mu}$	$A_{404m\mu}$
25.2°, $[I_2] = 4.585 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00370	0.351	0.358	0.358	0.339
0.00555	0.430	0.441	0.441	0.419
0.00740	0.498	0.511	0.511	0.480
0.00925	0.545	0.559	0.559	0.525
0.01110	0.581	0.596	0.596	0.561
0.01481	0.646	0.657	0.656	0.606
0.00430	0.387	0.394	0.394	0.368
0.00645	0.471	0.480	0.480	0.448
0.00860	0.535	0.548	0.547	0.509
0.01076	0.582	0.596	0.595	0.552
0.01291	0.616	0.628	0.626	0.584
ε_{I_2}	10.9	13.1	15.3	26.2
K_M	190±3.0	187±2.3	187±2.2	192±1.2
ε_c	1890	1940	1940	1790
C_{Py}	$A_{390m\mu}$	$A_{395m\mu}$	$A_{400m\mu}$	$A_{410m\mu}$
8.4°, $[I_2] = 3.624 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00358	0.401	0.406	0.394	0.352
0.00537	0.464	0.469	0.456	0.407
0.00716	0.507	0.512	0.500	0.443
0.00895	0.536	0.540	0.529	0.466
0.01075	0.559	0.562	0.550	0.483
0.00295	0.367	0.372	0.365	0.326
0.00590	0.483	0.487	0.477	0.424
0.00885	0.537	0.542	0.529	0.467
0.00443	0.439	0.441	0.431	0.383
0.00738	0.515	0.518	0.506	0.447
0.01181	0.570	0.575	0.562	0.492
ε_{I_2}	13.8	16.6	22.1	44.2
K_M	409±3.5	416±2.8	412±4.8	424±3.6
ε_c	1900	1900	1860	1630

Table 19.--Continued

C_{Py}	$A_{390m\mu}$	$A_{395m\mu}$	$A_{400m\mu}$	$A_{410m\mu}$
16.3°, $[I_2]$ = 3.851 · 10^{-4} M, path length = 1.000 cm				
0.00491	0.405	0.410	0.407	0.366
0.00736	0.471	0.479	0.472	0.427
0.00982	0.525	0.529	0.522	0.467
0.01473	0.577	0.584	0.571	0.515
0.00608	0.429	0.437	0.431	0.390
0.01217	0.523	0.531	0.525	0.470
0.01826	0.586	0.594	0.585	0.525
0.00913	0.510	0.517	0.507	0.449
0.01522	0.579	0.587	0.574	0.508
0.02435	0.628	0.635	0.618	0.546
ε_{I_2}	13.0	15.6	18.2	41.5
K_M	266±12.6	268±11.4	280±11.1	285±11.0
ε_c	1860	1880	1830	1620
33.3°, $[I_2]$ = 4.440 · 10^{-4} M, path length = 1.000 cm				
0.00547	0.357	0.357	0.349	0.321
0.00821	0.438	0.439	0.429	0.392
0.01095	0.505	0.508	0.496	0.449
0.01369	0.548	0.550	0.538	0.485
0.01643	0.581	0.585	0.571	0.517
0.00626	0.387	0.387	0.379	0.345
0.01253	0.528	0.529	0.519	0.468
0.01879	0.607	0.607	0.595	0.536
0.00939	0.474	0.474	0.461	0.420
0.01253	0.532	0.531	0.522	0.470
0.02506	0.667	0.666	0.648	0.583
ε_{I_2}	11.3	13.5	18.0	38.3
K_M	134±1.6	133±1.4	132±1.2	134±1.0
ε_c	1920	1930	1890	1680

Table 20.--Experimental Data on the Pyridine-Iodine Complex in Chloroform

C_{Py}	$A_{414m\mu}$	$A_{404m\mu}$	$A_{400m\mu}$	$A_{395m\mu}$
25.1°, $[I_2] = 5.355 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00504	0.238	0.251	0.249	0.242
0.00756	0.313	0.326	0.326	0.322
0.01009	0.368	0.393	0.393	0.382
0.01261	0.416	0.411	0.441	0.429
0.01513	0.451	0.482	0.482	0.469
0.02017	0.512	0.548	0.547	0.530
0.00814	0.328	0.349	0.348	0.337
0.01221	0.412	0.439	0.438	0.426
0.01628	0.461	0.492	0.490	0.480
0.02035	0.511	0.548	0.546	0.531
0.02442	0.545	0.583	0.582	0.569
ε_{I_2}	20.5	11.2	9.3	9.3
K_M	79.0±0.6	77.7±0.7	77.0±0.7	77.0±0.5
ε_c	1550	1670	1680	1640
33.3°, $[I_2] = 5.730 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00760	0.271	0.282	0.280	0.271
0.01140	0.354	0.369	0.366	0.356
0.01520	0.414	0.435	0.431	0.419
0.01900	0.461	0.486	0.483	0.468
0.02280	0.500	0.528	0.524	0.508
0.03041	0.565	0.595	0.592	0.570
0.01078	0.339	0.355	0.354	0.341
0.01616	0.427	0.449	0.448	0.430
0.02155	0.488	0.516	0.512	0.496
0.02694	0.538	0.568	0.565	0.546
0.03233	0.577	0.607	0.603	0.586
ε_{I_2}	19.2	8.7	8.7	7.0
K_M	57.0±0.3	56.6±0.1	56.6±0.2	56.8±0.2
ε_c	1540	1640	1630	1580

Table 20.--Continued

C_{Py}	$A_{414m\mu}$	$A_{404m\mu}$	$A_{400m\mu}$	$A_{395m\mu}$
16.4°, $[I_2]$ = 5.064 · 10^{-4} M, path length = 1.000 cm				
0.00566	0.313	0.335	0.341	0.332
0.00849	0.394	0.427	0.430	0.421
0.01132	0.447	0.484	0.487	0.479
0.01415	0.488	0.529	0.531	0.525
0.01698	0.523	0.570	0.571	0.563
0.02265	0.569	0.616	0.622	0.615
0.00748	0.365	0.394	0.400	0.394
0.01123	0.447	0.481	0.488	0.481
0.01497	0.487	0.539	0.545	0.536
0.01872	0.531	0.586	0.591	0.582
0.02246	0.560	0.615	0.620	0.612
ε_{I_2}	21.7	11.8	9.9	7.9
K_M	122±1.6	116±1.0	121±0.7	117±0.8
ε_c	1520	1690	1680	1680
8.7°, $[I_2]$ = 4.551 · 10^{-4} M, path length = 1.000 cm				
0.00698	0.375	0.414	0.420	0.416
0.01048	0.442	0.489	0.496	0.491
0.01397	0.477	0.537	0.543	0.541
0.01746	0.510	0.575	0.581	0.580
0.02095	0.533	0.602	0.609	0.607
0.02794	0.567	0.638	0.645	0.640
0.00923	0.413	0.463	0.469	0.465
0.01384	0.477	0.537	0.543	0.538
0.01864	0.521	0.580	0.587	0.579
0.02307	0.551	0.610	0.618	0.611
0.02769	0.569	0.632	0.640	0.633
ε_{I_2}	19.8	11.0	8.8	6.6
K_M	174±3.6	169±1.5	172±1.6	171±2.3
ε_c	1500	1690	1710	1690

Table 21.--Experimental Data on the Pyridine-Iodine Complex in n-Heptane

C_{Py}	$A_{430m\mu}$	$A_{424m\mu}$	$A_{420m\mu}$	$A_{410m\mu}$
26.2°, $[I_2] = 4.699 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00563	0.301	0.304	0.301	0.275
0.00844	0.366	0.371	0.368	0.336
0.01126	0.408	0.415	0.410	0.377
0.01409	0.443	0.450	0.447	0.412
0.01689	0.469	0.478	0.473	0.437
0.02252	0.503	0.511	0.509	0.467
0.00617	0.315	0.320	0.316	0.291
0.00925	0.383	0.386	0.385	0.353
0.01234	0.426	0.427	0.425	0.395
0.01543	0.455	0.463	0.461	0.429
0.01851	0.481	0.488	0.487	0.452
ε_{I_2}	29.8	17.0	12.8	6.4
K_M	152±1.0	155±1.0	153±1.2	149±1.7
ε_c	1380	1400	1400	1300
32.3°, $[I_2] = 4.699 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00916	0.335	0.337	0.333	0.303
0.01374	0.398	0.395	0.397	0.362
0.01832	0.440	0.446	0.440	0.404
0.02290	0.469	0.476	0.471	0.431
0.02784	0.489	0.498	0.494	0.453
0.03664	0.525	0.532	0.528	0.489
0.01059	0.357	0.360	0.357	0.330
0.01589	0.419	0.424	0.420	0.388
0.02118	0.463	0.469	0.465	0.427
0.02648	0.490	0.497	0.492	0.452
0.03177	0.509	0.519	0.513	0.466
ε_{I_2}	40.4	29.8	23.4	17.0
K_M	114±1.0	110±1.6	112±0.8	112±1.8
ε_c	1380	1410	1390	1280

Table 21.--Continued

C_{Py}	$A_{430m\mu}$	$A_{424m\mu}$	$A_{420m\mu}$	$A_{410m\mu}$
16.5°, $[I_2]$ = 4.002 · 10^{-4} M, path length = 1.000 cm				
0.00980	0.392	0.404	0.401	0.373
0.01470	0.434	0.445	0.444	0.414
0.01960	0.464	0.477	0.476	0.444
0.02450	0.480	0.492	0.491	0.460
0.02940	0.487	0.504	0.504	0.468
0.03920	0.511	0.526	0.526	0.488
0.01027	0.398	0.408	0.408	0.380
0.01540	0.438	0.450	0.449	0.422
0.02053	0.466	0.480	0.479	0.446
0.02566	0.486	0.500	0.500	0.465
0.03080	0.492	0.508	0.507	0.472
ε_{I_2}	40.0	27.5	22.5	15.0
K_M	231±4.3	231±4.2	228±4.1	231±3.5
ε_c	1410	1450	1450	1350
7.9°, $[I_2]$ = 4.002 · 10^{-4} M, path length = 1.000 cm				
0.00528	0.372	0.384	0.384	0.361
0.00792	0.422	0.434	0.434	0.408
0.01057	0.454	0.466	0.466	0.442
0.01321	0.470	0.487	0.487	0.460
0.01585	0.483	0.498	0.498	0.471
0.02113	0.502	0.520	0.520	0.488
0.00674	0.403	0.418	0.418	0.392
0.01011	0.446	0.458	0.458	0.434
0.01348	0.475	0.488	0.488	0.458
0.01685	0.490	0.508	0.509	0.477
0.02022	0.501	0.518	0.518	0.485
ε_{I_2}	40.0	27.5	22.5	17.5
K_M	362±3.8	366±4.8	468±5.2	369±4.7
ε_c	1420	1470	1470	1380

Table 22.--Experimental Data on the Pyridine-Iodine Complex in 1,1,2-Trifluorotrichloroethane

C_{Py}	$A_{420m\mu}$	$A_{414m\mu}$	$A_{410m\mu}$
25.0°, $[I_2]$ = 5.566 · 10^{-4} M, path length = 1.000 cm			
0.00939	0.486	0.486	0.476
0.01409	0.568	0.568	0.556
0.01879	0.610	0.610	0.599
0.02348	0.642	0.644	0.631
0.00469	0.345	0.344	0.336
0.00733	0.435	0.433	0.426
0.01467	0.570	0.571	0.561
0.02201	0.632	0.633	0.621
0.01101	0.519	0.519	0.508
0.01834	0.608	0.608	0.599
0.02935	0.676	0.678	0.669
ε_{I_2}	14.4	9.0	5.4
K_M	159±0.08	159±1.0	158±0.9
ε_C	1470	1470	1450

Table 23.--Experimental Data on the Pyridine-Iodine Complex in m-Dichlorobenzene

C_{Py}	$A_{420m\mu}$	$A_{410m\mu}$	$A_{404m\mu}$	$A_{400m\mu}$
25.0°, $[I_2] = 4.208 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00494	0.365	0.370	0.368	0.338
0.00741	0.430	0.437	0.435	0.394
0.00989	0.480	0.486	0.482	0.444
0.01236	0.515	0.520	0.518	0.473
0.01484	0.539	0.548	0.544	0.497
0.01978	0.567	0.577	0.573	0.517
0.00587	0.392	0.400	0.396	0.361
0.00881	0.459	0.468	0.465	0.424
0.01176	0.507	0.514	0.507	0.467
0.01470	0.531	0.538	0.530	0.489
0.01763	0.560	0.566	0.559	0.514
ε_{I_2}	14.3	14.3	16.6	40.4
K_M	224±2.7	227±2.2	230±2.9	220±3.9
ε_c	1660	1680	1660	1530

Table 24.--Experimental Data on the Pyridine-Iodine Complex in n-Hexadecane

C_{Py}	$A_{426m\mu}$	$A_{420m\mu}$	$A_{416m\mu}$	$A_{410m\mu}$
25.0°, $[I_2]$ = 4.119 · 10^{-4} M, path length = 1.000 cm				
0.00426	0.277	0.277	0.272	0.241
0.00639	0.334	0.335	0.330	0.293
0.00852	0.372	0.372	0.367	0.328
0.01065	0.407	0.408	0.401	0.357
0.01278	0.430	0.431	0.425	0.380
0.01704	0.458	0.460	0.455	0.406
0.00527	0.309	0.310	0.305	0.271
0.00790	0.365	0.366	0.361	0.323
0.01054	0.405	0.406	0.399	0.356
0.01318	0.432	0.434	0.428	0.382
0.01581	0.451	0.453	0.449	0.400
ε_{I_2}	26.7	17.0	14.6	12.1
K_M	211±2.0	214±2.3	211±2.1	206±1.9
ε_c	1420	1430	1410	1270

Table 25.--Experimental Data on the Pyridine-Iodine Complex in o-Dichlorobenzene

C_{Py}	$A_{520m\mu}$	$A_{510m\mu}$	$A_{506m\mu}$	$A_{500m\mu}$
25.0°, $[I_2] = 5.988 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.002186	0.338	0.354	0.353	0.347
0.004371	0.244	0.260	0.262	0.261
0.006577	0.195	0.210	0.212	0.214
0.008742	0.166	0.180	0.182	0.187
0.010930	0.143	0.156	0.161	0.166
0.001232	0.404	0.421	0.419	0.409
0.002464	0.322	0.336	0.338	0.332
0.003695	0.267	0.282	0.284	0.282
0.004927	0.230	0.245	0.246	0.247
0.002603	0.316	0.331	0.331	0.327
0.005206	0.222	0.231	0.239	0.239
ε_{I_2}	912	945	937	937
K_M	368±2.2	367±2.5	370±1.9	363±1.7
ε_C	69	86	101	116

Table 26.--Experimental Data on the Pyridine-Iodine Complex in p-Xylene

C_{Py}	$A_{510m\mu}$	$A_{500m\mu}$	$A_{496m\mu}$	$A_{490m\mu}$
25.0°, $[I_2]$ = 5.292 · 10^{-4} M, path length = 1.000 cm				
0.00608	0.398	0.428	0.430	0.430
0.00913	0.352	0.377	0.384	0.386
0.01218	0.316	0.338	0.348	0.352
0.01522	0.287	0.308	0.319	0.326
0.01827	0.266	0.286	0.295	0.304
0.00304	0.461	0.490	0.492	0.489
0.00384	0.443	0.471	0.475	0.471
0.00768	0.371	0.398	0.402	0.404
0.01152	0.323	0.349	0.354	0.358
0.01536	0.285	0.308	0.316	0.323
0.01920	0.256	0.282	0.290	0.296
ε_{I_2}	1062	1120	1124	1104
K_M	91.3±0.7	89.2±1.0	94.3±1.1	91.6±0.7
ε_c	167	192	238	261

Table 27.--Experimental Data on the Pyridine-Iodine Complex in Benzene

C_{Py}	$A_{420m\mu}$	$A_{410m\mu}$	$A_{404m\mu}$	$A_{400m\mu}$
25.1°, $[I_2] = 4.942 \cdot 10^{-4}$ M, path length = 1.000 cm				
0.00626	0.300	0.316	0.315	0.308
0.00940	0.376	0.398	0.398	0.391
0.01235	0.430	0.459	0.459	0.451
0.01567	0.473	0.509	0.509	0.498
0.01880	0.509	0.546	0.546	0.537
0.02507	0.567	0.607	0.608	0.598
0.00720	0.327	0.344	0.345	0.338
0.01080	0.401	0.428	0.429	0.420
0.01440	0.456	0.486	0.487	0.479
0.01800	0.498	0.534	0.535	0.525
0.02160	0.530	0.572	0.572	0.563
ε_{I_2}	87.0	60.7	54.6	54.6
K_M	82.4±0.6	83.0±0.5	83.8±0.5	82.2±0.5
ε_c	1650	1780	1780	1770

Table 28.--Experimental Data on the Pyridine-Iodine Complex in Toluene

C_{Py}	$A_{490m\mu}$	$A_{496m\mu}$	$A_{500m\mu}$	$A_{510m\mu}$
25.0°, $[I_2]$ = 5.449 · 10^{-4} M, path length = 1.000 cm				
0.00398	0.447	0.453	0.451	0.430
0.00598	0.413	0.420	0.417	0.391
0.00797	0.384	0.385	0.382	0.359
0.01197	0.335	0.333	0.329	0.307
0.00997	0.362	0.361	0.358	0.336
0.01596	0.303	0.298	0.293	0.271
0.00523	0.428	0.431	0.429	0.407
0.00784	0.384	0.385	0.382	0.360
0.01047	0.353	0.352	0.348	0.327
0.01308	0.324	0.321	0.315	0.294
0.01570	0.306	0.303	0.297	0.276
ε_{I_2}	1028	1055	1055	1013
K_M	87.9±1.7	88.9±1.8	87.9±1.9	86.4±1.2
ε_c	223	195	174	127

RESULTS AND DISCUSSION

Donor Strength and Steric Considerations

The results of our measurements are shown in Table 29. The values of the formation constants vary from << 1 for the 2,6-dichloropyridine · I_2 complex to 421 for the strongest complex 3,4-dimethylpyridine · I_2. An attempt to measure the formation constants of complexes in which the substituent groups on the pyridine were themselves electron donors (phenyl or nitrile) failed, presumably due to stepwise formation of two complexes. A comparison of our values for the formation constant of the pyridine-iodine complex with those reported by Popov and Rygg,[14] Make and Plyler[26] and of Alosi, et al.[23] shows a satisfactory agreement (109 ± 1.3 vs. 101, 107 and 106, respectively). The higher value of Mulliken and Reid[9] is due to the difference in solvent as is shown in Table 30. The values of 43.74 of Chaudhuri and Basu[16] or 183 reported by Sobczyk, et al.[29] seem to be less reliable as well as their value of 358 for the formation constant of the 4-methylpyridine-iodine complex. On the other hand, Alosi and co-workers[23] report formation constants of 223 and 230 for 3-methyl and 4-methylpyridine, respectively, which are in good agreement with our data.

Table 29.--Formation Constants ($\ell mole^{-1}$) of Iodine Complexes with Pyridine and Substituted Pyridines in Carbon Tetrachloride Solutions at ≈ 25°

Base	Conc. of $I_2 \times 10^4$	K_M	Acidity Constant[a] pKa	Range of Base Conc.	λ_{max}
2,6-Dichloropyridine	7.99	<<1	?		
2-Fluoropyridine	1.64	2.0±0.8	-0.44	0.0274-0.2085	b
2-Chloropyridine	2.20	3.4±0.15	0.72	0.02132-0.1279	b
2-Bromopyridine	2.23	4.4±0.22	0.90	0.02465-0.09861	b
3-Chloropyridine	2.19	16.6±0.30	2.84	0.02126-0.09870	430
3-Bromopyridine	1.10	17.2±0.20	2.84	0.01615-0.09142	428
Pyridine	0.650	109±1.3	5.21	0.0105-0.1700	415
3-Methylpyridine	5.83	207±3.0	5.63	0.00378-0.01890	412
4-Methylpyridine	4.50	216±3.5	5.98	0.00289-0.03072	411
4-t-Butylpyridine	5.86	300±4.3	5.99	0.001464-0.009324	410
2,5-Dimethylpyridine	0.650	304±2.2	6.40	0.00398-0.02602	413
4-Ethylpyridine	0.650	248±1.7	5.99	0.00364-0.08390	410
3,5-Dimethylpyridine	5.81	377±3.3	6.15	0.000817-0.01677	408
3,4-Dimethylpyridine	6.54	421±12.0	6.46	0.00162-0.00669	408
3-Ethylpyridine	6.59	244±1.0	5.56	0.00208-0.02246	412

[a]Dissociation Constants of Organic Bases in Aqueous Solutions. D. D. Perrin, editor. International Union of Pure and Applied Chemistry, 1965.

Best values were selected (25°) whenever possible.

[b]An absorption maxima was not discernable at the concentrations used.

Table 30.--Formation Constants of the Pyridine-Iodine Complex in Different Solvents

Solvent	K_M[a]	K_X	K_S	$K_{X_{corr}}$	D	λ_{max}
p-Xylene	91.6±0.9	739±7.3	0.31[b]	2588	2.27	402
Toluene	87.8±1.8	822±17	0.16[b]	2053	2.38	405
Benzene	82.9±0.5	928±5.6	0.15[b]	2486	2.28	404
Chloroform	77.7±0.6	963±7.4	0.69[c,d]	1627	4.81	400
n-Heptane	157±1.2	1064±8.1			1.92	424
Carbon tetrachloride	105±0.7	1082±7.2			2.24	416
1,1,2-Trifluorotrichloroethane	159±0.9	1328±7.5			2.41	414
Dichloromethane	151±0.6	2341±9.3			9.08	395
1,2-Dichloroethane	189±2.2	2351±27			10.36	395
m-Dichlorobenzene	225±2.9	1964±25			5.04	404
o-Dichlorobenzene	367±2.1	3248±19			9.93	400
n-Hexadecane	211±2.1	612±6.1			2.05	419

[a]All values at 25.0°.

[b]L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc., 74, 4500 (1952).

[c]P. J. Berkeley, Jr., and M. W. Hanna, J. Phys. Chem., 67, 846 (1963).

[d]The value of K_S is given in mole fraction units. The value of K_S in moles is approximately equal to K_S in molar units times the concentration of pure solvent.

There is a considerable amount of disagreement between our data and those of Bhaskar and Singh.[17] In general, their values of the formation constants are about 50% smaller than the values listed in Table 1. It should be noted that Bhaskar and Singh carried out their measurements in chloroform solutions. Chloroform, besides being more polar than carbon tetrachloride, is known to hydrogen bond to pyridine.[35] The specific effects of these two factors are discussed in the following section. Chloroform is also a notoriously poor solvent for the study of halogen complexes due to the ease with which it is oxidized by air to give HCl as one of the products. Hydrochloric acid easily reacts with halogens to give polyhalide ions, and this reaction, obviously, can introduce a large error in the spectrophotometric study of iodine complexes. Chloroform can only be used as a solvent for such studies if it is very carefully purified just prior to use. It also appears that the spectral measurements of Bhaskar and Singh[17] were carried out only at a single wavelength.

It has been shown by Person and co-workers that it is possible to correlate the formation constants of halogen complexes with acetonitrile and chlorinated acetonitrile with the Taft σ^* constant,[61] where σ^* is a measure of only the inductive effect in a rigid aliphatic compound. Since in the case of substituted pyridines the

resonance effects would likewise be important, it seemed more reasonable to investigate the possible correlation between the Hammett σ function and the log of the formation constant of the respective complexes. A plot of log K_M *vs.* σ is shown in Figure 2. It is seen that a reasonably straight line is obtained. The equation of the line is given by

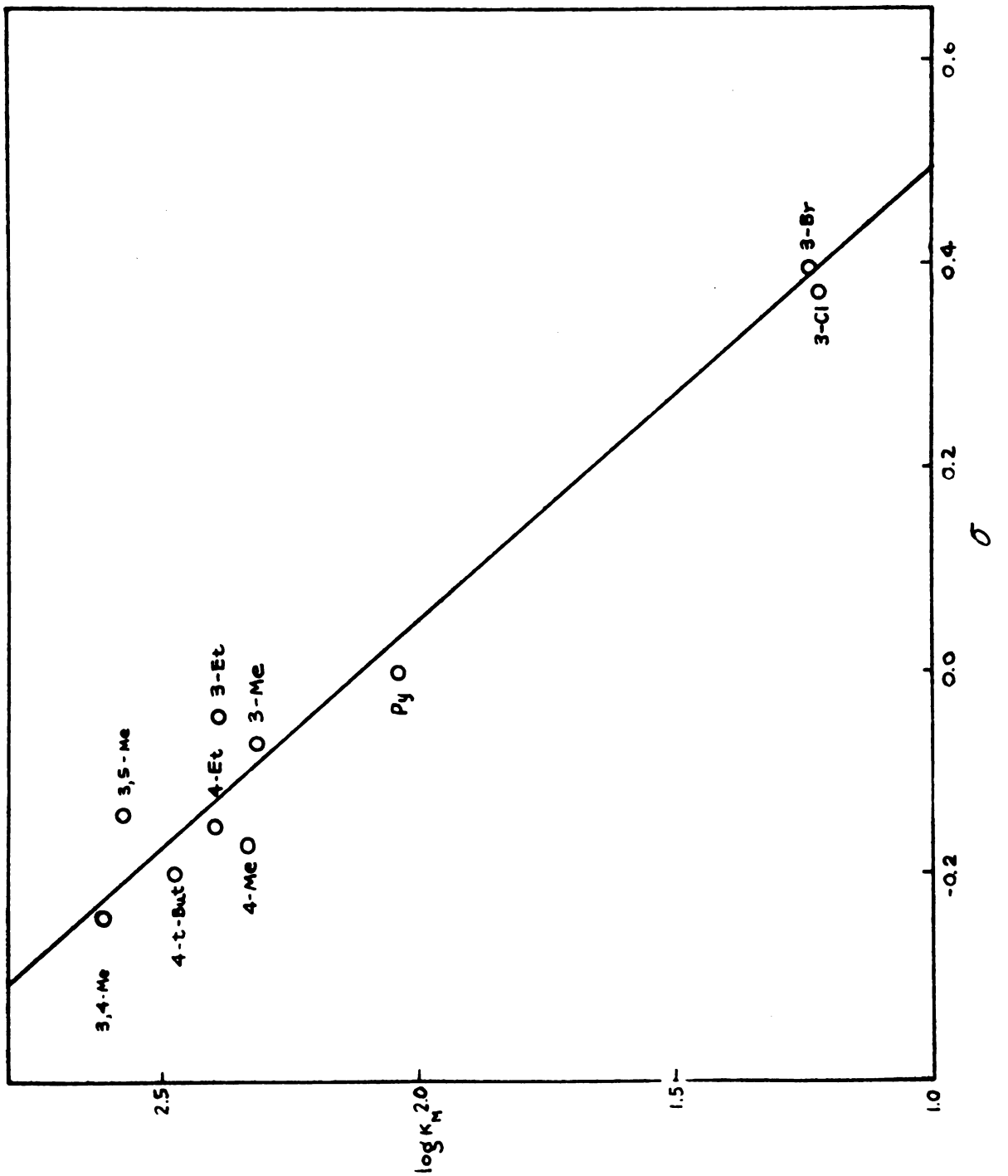
$$\log K_M = -2.25\sigma + 2.11$$

The standard deviation of the slope is 0.16 and the value of r, Jaffe's correlation coefficient,[62] is 0.98.

According to Jaffe's criteria[62] for the magnitude of the correlation coefficient, the value of r indicates good agreement with the Hammett equation. A similar study of iodine complexes of substituted styrylpyridines by Mazzucato, *et al.*,[63] gave values of ρ = -2.1 with r = 0.93 (values for pyridine, 4-methylpyridine and 3-methylpyridine were also included in the calculation). Rather poor correlation as shown by the low value of r may be due to the interaction of the halogen with the delocalized electrons of the stilbene ring (c.f. our results with the 4-phenylpyridine and 4-cyanopyridine described above).

There are some rather minor discrepancies which illustrate the limitations of the theory. For example, one would expect the value of σ for 3-chloropyridine to be greater than that of 3-bromopyridine which would imply that

Figure 2.--Relationship between log K_M and Hammett σ function for the pyridine-iodine complexes in carbon tetrachloride solutions.

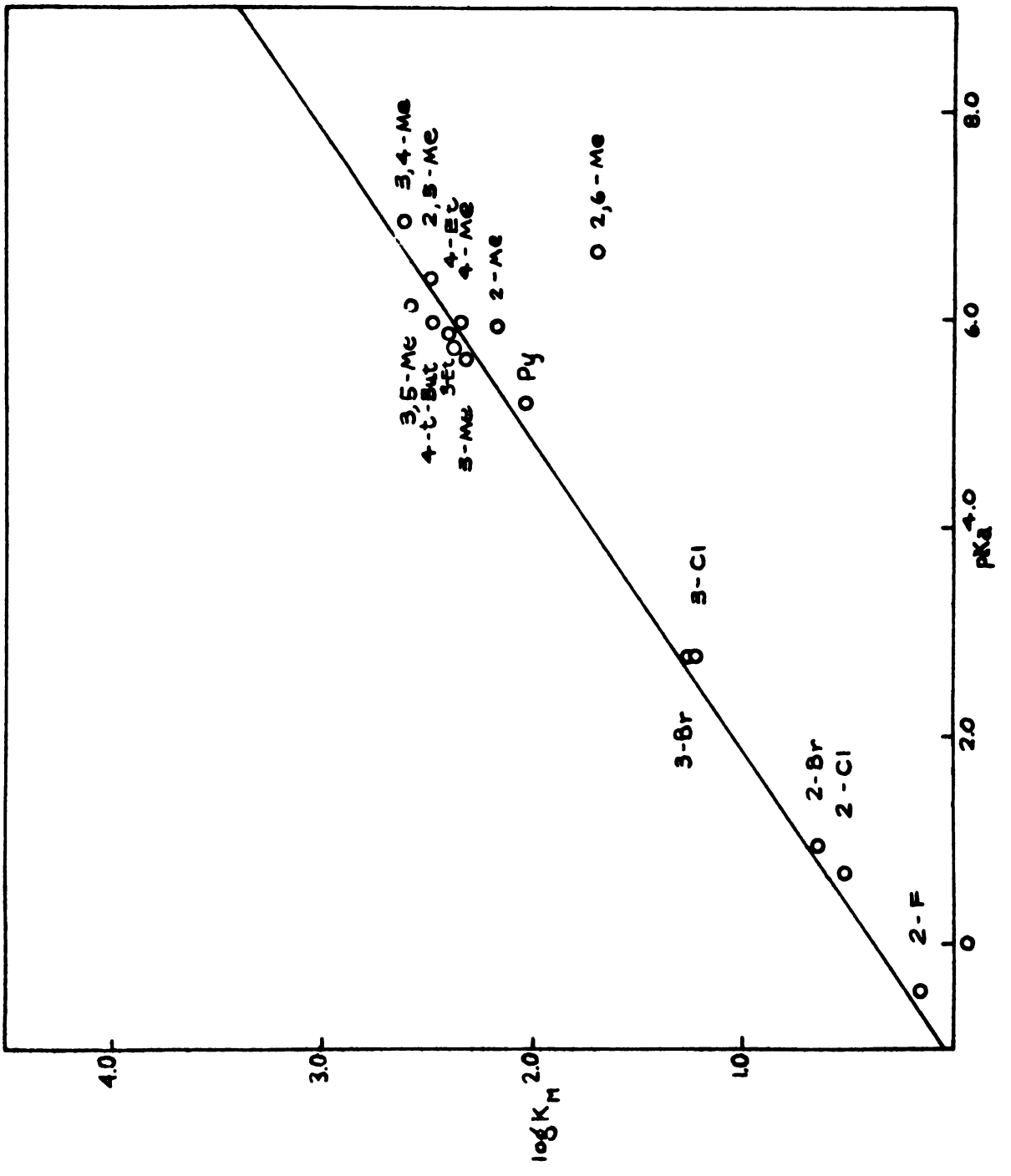

3,4-Me
3,5-Me
4-t-But
4-Et
3-Et
4-Me
3-Me
Py
3-Cl
3-Br
2.5
2.0
1.5
1.0
log K_M
-0.2
0.0
0.2
0.4
0.6
σ

the K_M value for the corresponding 3-bromopyridine complex would be the larger of the two. Experimentally the values for K_M follow the expected order, while the σ values do not.

It was also of interest to us to determine if there is a correlation between the acid dissociation constants of the pyridines and the iodine complex formation constant. As seen from Figure 3, a plot of $\log K_M$ *vs.* pK_a does indeed yield a fairly straight line although there is some scatter of the experimental points. This is implied from the combination of our results in Figure 3 and those of Jaffé and Doak[64] in which they obtained a linear plot between the pK_a's of several substituted pyridines and the Hammett σ constant. The advantage of plotting the log of the formation constant of the complex *vs.* pK_a for the pyridines is that the values for sterically hindered pyridines can be compared. From this comparison one can gain an understanding of the relative importance of steric factors. As can be seen in Figure 3 there is very little difference between the steric hindrance for the proton and the iodine molecule for pyridines substituted in the two positions. The effect of steric factors on the 2,6-lutidine-iodine complex is quite pronounced.

It can be concluded, therefore, that in pyridine and in substituted pyridines, in the absence of steric effects, there is a definite parallelism between the complexing abilities of the amines and their basicities.

Figure 3.--Relationship between the acidity constant of the pyridines in aqueous solutions and the formation constants of the pyridine-iodine complexes in carbon tetrachloride solutions.


4.0
3.0
2.0
1.0
log K_H
0
2.0
4.0
6.0
8.0
pKa
3,4-Me
2,5-Me
4-Et
4-Me
2-Me
Py
2,6-Me
3,5-Me
4-t-But
3-Et
3-Me
3-Cl
3-Br
2-Br
2-Cl
2-F

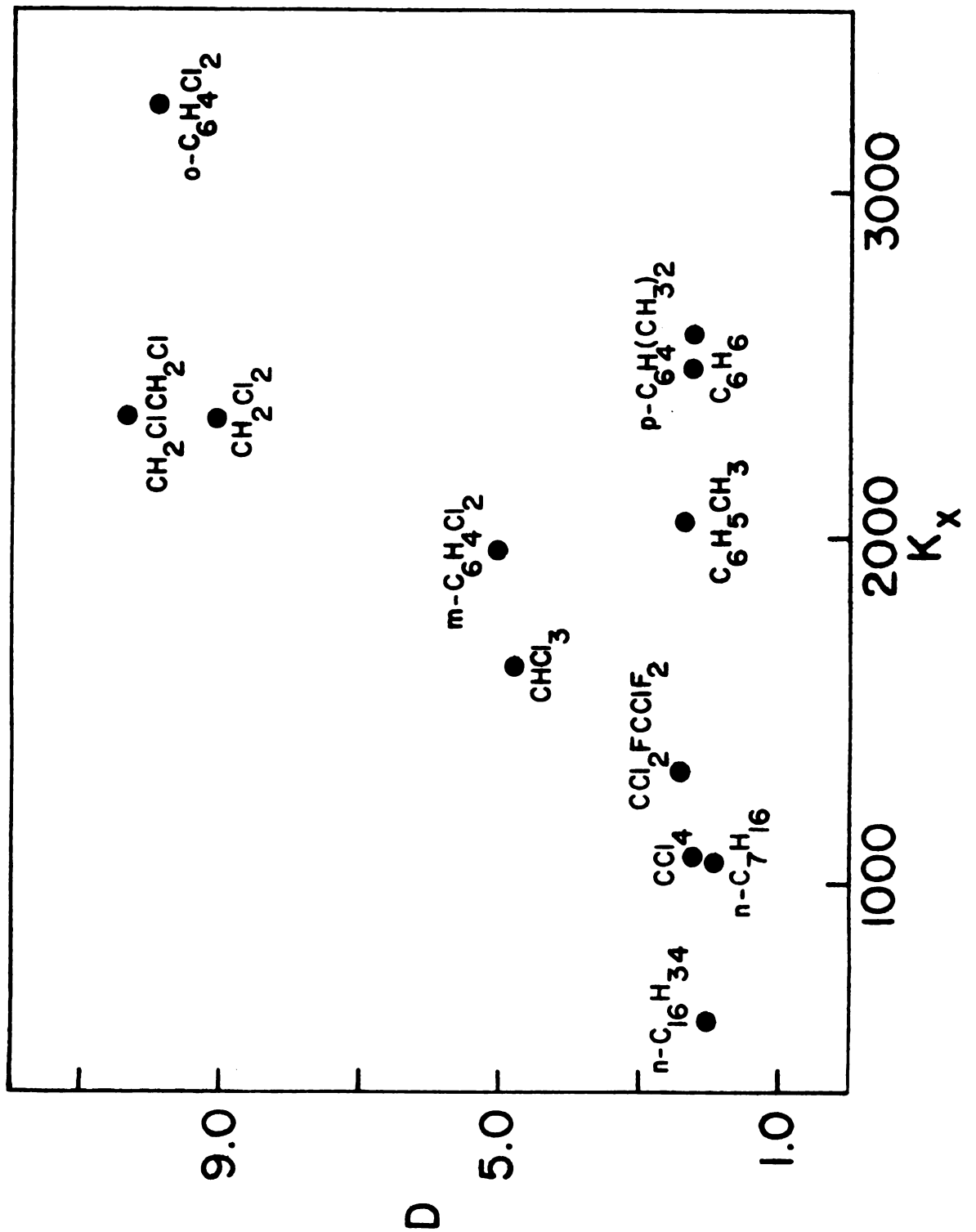
Such correlation, of course, would be expected if one adopts Lewis' definition of acids and bases since both H^+ and I_2 are Lewis acids. It should be noted, however, that such generalizations are only applicable to cases where the reference bases do not differ appreciably in structure.

Solvent Effects

Formation constants of the pyridine-iodine complex in twelve different solvents are presented in Table 30. Comparison of these values with various physical properties of the respective solvents indicates a possible correlation only with the dielectric constant of the medium. A plot of D *vs.* K_x is shown in Figure 4. While the points do not fall on a smooth curve, there seems to be little doubt that, other factors being equal, an increase in the dielectric constant of the solvent results in an increase in the stability of the complex. The observed scatter, in all likelihood, is the result of specific solvent-solute interactions.

It seems reasonable to expect that the increase in the bulk dielectric constant of the reaction medium will result in greater stability of the pyridine-iodine complex. The dipole moments of iodine, pyridine, and of the complex are 0.0, 2.20, and 4.90 Debyes respectively.[65] It appears, therefore, that with increasing polarity, the solvents will

Figure 4.--Relationship between the formation constant expressed in mole fraction units of the pyridine-iodine complex and the dielectric constant of the solvent in which it was measured.

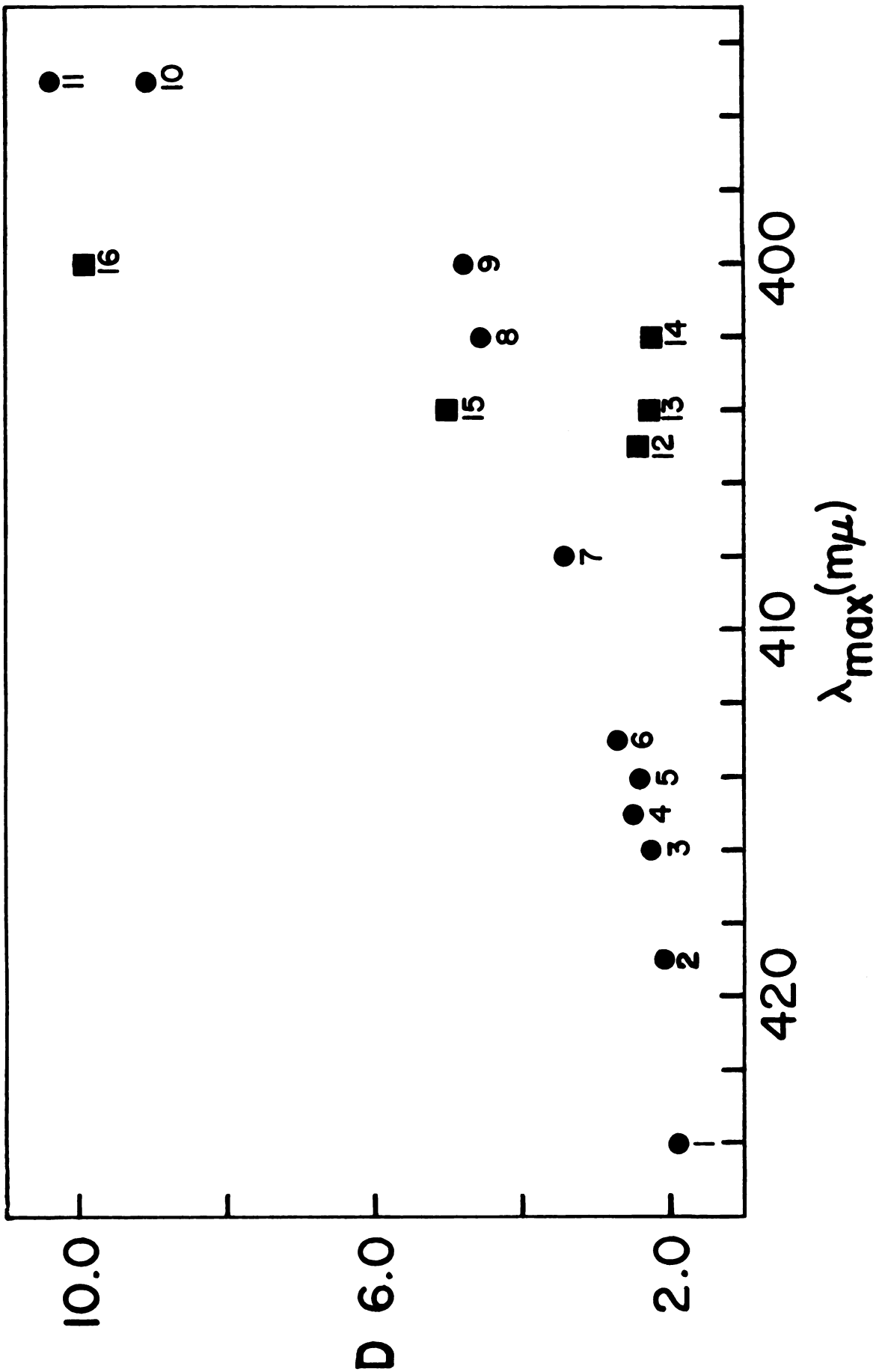

9.0
5.0
1.0
D
1000
2000
3000
K_x
$o\text{-}C_6H_4Cl_2$
CH_2ClCH_2Cl
CH_2Cl_2
$m\text{-}C_6H_4Cl_2$
$CHCl_3$
CCl_2FCClF_2
CCl_4
$n\text{-}C_7H_{16}$
$n\text{-}C_{16}H_{34}$
$p\text{-}C_6H_4(CH_3)_2$
C_6H_6
$C_6H_5CH_3$

tend to solvate more strongly the highly polar complex and thus contribute to its stability. Kobinata and Nagakura,[66] as well as Boule,[67] recently reported a study of the dipole moments of iodine complexes with aliphatic amines in benzene and in dioxane solutions. All of the values obtained were in the 6.0 - 7.2 Debye range. Kobinata and Nagakura noted that the dipole moments of the complexes increased with increasing concentration of the amines in the solvent mixtures. Since the dielectric constant of the medium likewise increased with the amine concentration, the authors interpreted the results by postulating an increase in the stabilization of the charge-transfer. These results agree with our observation that in solvents with $D > 15$, the charge separation in the complex increases to the extent that clear cut separation of the charges occurs with the resulting formation of the triiodide ion.

The above phenomena would be expected from an examination of the theoretical behavior of polarizable dipoles in a changing dielectric medium.[68] Indeed, other ramifications of this behavior would be expected. According to Mulliken's theory[9] of charge-transfer complexes, the spectrum of the complex would be altered by the dielectric constant of the medium. In particular, the energy of the charge-transfer band would be shifted. The direction of this shift would depend upon the relative importance of two factors, if one assumes that the energy

of the no bond wave function remains constant. One effect would be due to the increase in energy of the dative wave function as a result of the increased charge separation, and the other effect would be due to the decrease in energy of the dative wave function as a result of the solvation of the polar species. Due to the absorption of pyridine and of the solvents in the ultraviolet region, the charge-transfer band cannot be observed. Lacking this information it is nevertheless informative to examine the relationship between the dielectric constant of the solvent and the wavelength of maximum absorption of the blue shifted iodine band of the complex as shown in Figure 5. The blue shifted iodine band has been explained by Mulliken.[4] This explanation is based on the assumption that in the excited state of the complex an electron has been transferred from the donor to the iodine molecule. This electron goes into an antibonding orbital of the iodine which is diffuse and increases the effective size of the iodine molecule. When light is absorbed by the complexed iodine molecule, the excitation energy is supplemented by an energy of repulsion between the donor and the abnormally large iodine molecule. The blue shift should become larger with increasingly close contact between the donor and iodine which is related to the bond strength of the complex. Thus the fact that the frequency shift of the iodine band is related to the dielectric

Figure 5.--Relationship between the wavelength of maximum absorption of the blue-shifted iodine band of the complex and the dielectric constant of the solvent in which it was measured. Solvents: (1) n-heptane; (2) n-hexadecane; (3) carbon tetrachloride; (4) X_{CCl_4} = 0.99284 and $X_{CH_3NO_2}$ = 0.00716, D_{calc} = 2.48; (5) 1,1,2-trifluorotrichloroethane; (6) X_{CCl_4} = 0.9857 and $X_{CH_3NO_2}$ = 0.0143, D_{calc} = 2.72; (7) X_{CCl_4} = 0.9646 and $X_{CH_3NO_2}$ = 0.0345, D_{calc} = 3.43; (8) X_{CCl_4} = 0.9304 and $X_{CH_3NO_2}$ = 0.0696, D_{calc} = 4.58; (9) chloroform; (10) dichloromethane; (11) 1,2-dichloroethane; (12) toluene; (13) benzene; (14) p-xylene; (15) m-dichlorobenzene; (16) o-dichlorobenzene.


10.0
D 6.0
2.0
420
410
400
λmax(mμ)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

constant of the medium is another indication of the influence of the dielectric constant on the complexation reaction. It is also interesting to note the deviation of the points (12-16) in cases where aromatic solvents were used. This can easily be understood in terms of the known specific solute-solvent interactions which have already been mentioned.

Thermodynamic data obtained by measuring the formation constant of the complex as a function of temperature are given in Table 31. As can be seen by examining the values, the differences are not significant within experimental error and, therefore, do not, at this time, contribute to our understanding of the role of the solvent in the complexation reaction.

On the basis of the above results it seems reasonable to conclude that the reports on the <u>decrease</u> in the stability of iodine complexes with increasing dielectric constant of the medium[17] cannot be correct.

It is clear, however, that it would be naive to expect a monotonic correlation between a given physical property of a series of solvents and the stability of the pyridine-iodine complex since this approach neglects specific solvent-solute interactions. While we endeavored to correct in the case of aromatic solvents and chloroform, this correction is tenuous at best, and it only takes into account the interaction of iodine with the solvent in the first three cases and of pyridine with the solvent in the

Table 31.--Enthalpy and Entropy Values for the Pyridine-Iodine Complexation in Different Solvents

Solvent	$-\Delta H$(kcal/mole)	$-\Delta S$(e.u.)
n-Heptane	8.16±0.22	17.3±0.8
Carbon tetrachloride	7.47±0.06	15.8±0.2
Dichloromethane	8.59±0.31	18.9±1.1
1,2-Dichloroethane	7.77±0.16	15.6±0.6
Chloroform	7.82±0.19	17.5±0.6

last. There is little doubt that weak interactions exist between other solvents and pyridine as well as iodine and that these interactions influence overall stability of the complex. In fact it has been shown recently that there is a significant interaction between pyridine and carbon tetrachloride (as well as other aromatic compounds).[69] In the calculation of formation constants, however, it is a common practice to arbitrarily treat the solvent as an inert dispersing medium regardless of the magnitude of the concentrations of the solutes. In certain cases it may be possible to find systems where such assumptions may be justifiable,[70] but such cases must be rather exceptional. In general, it seems safe to conclude that if we wish to understand the role of the solvent in molecular complex formation, we should know the nature and the extent of solute-solvent interactions with both reactants and products to the maximum accuracy attainable. See Addendum (p. 104).

PART II

ALKALI METAL IONS IN PYRIDINE AND ACETONE SOLUTIONS

HISTORICAL INTRODUCTION

Solvation

The importance of ion-solvent interactions in solutions of electrolytes cannot be overemphasized. Yet at this time these interactions are understood only in rather crude qualitative terms. Recent developments in the use of far-infrared spectroscopy in the study of solutions of alkali metal salts (ammonium salts are considered to be part of this group) in several nonaqueous solvents have added a new perspective from which these interactions can be examined. Several authors have reported the appearance of new bands in this region of the spectrum which have been described primarily in terms of cation-solvent vibrations although some anion effects on these bands have been noted. The work presented in this portion of the thesis is an extension of the aforementioned studies in two other solvents, pyridine and acetone. A more extensive historical discussion of solvation studies can be found in the Ph.D. theses of Brian W. Maxey[71] and John L. Wuepper.[72]

Pyridine

The donor properties of pyridine toward a wide variety of Lewis acids have been well established; however, its usefulness as a solvent has not been studied extensively. Pyridine is characterized by a wide liquid range (-41.8° to 115.6°), a low dielectric constant of 12.3, a moderate dipole moment of 2.20 Debyes, and a Trouton constant of 21.8, indicating that it is relatively unassociated in the liquid phase. The donor properties of pyridine and its moderate dipole moment should make pyridine a good solvating agent for alkali metal ions although the solubility of these salts may not be particularly high due to the low dielectric constant of the solvent.

Two solid complexes between pyridine and lithium chloride have been found by Brussed and Halut-Desportes in their study of the solubility of lithium chloride in pyridine.[73] They found that a solid complex corresponding to the formula $LiCl \cdot C_5H_5N$ existed in contact with a saturated solution of the salt in pyridine above a temperature of 19.3°. Below this temperature the solid corresponded to the trisolvate, $LiCl \cdot 3C_5H_5N$. The latter compound melts incongruently at 19.3 ± 0.1°. Slow evaporation of a solution of LiCl in pyridine open to the laboratory atmosphere produced a solid with a composition of $LiCl \cdot H_2O \cdot 2C_5H_5N$.

The existence of interactions between alkai metal ions and pyridine was used by Burgess and Kraus[74] as an explanation

for the low conductances of these ions in pyridine. This study also gave the ion pair dissociation constants for lithium, sodium, potassium, and ammonium picrates as 0.83×10^{-4}, 0.43×10^{-4}, 1.00×10^{-4}, and 2.8×10^{-4}, respectively, and the ion pair dissociation constants for sodium, potassium, and ammonium iodides as 3.7×10^{-4}, 2.1×10^{-4}, and 2.4×10^{-4}, respectively. The values of these constants indicate a high degree of ion pairing as would be expected for a solvent with a low dielectric constant. The ion pair dissociation constant was found to be relatively unchanged upon addition of water to the pyridine. Good agreement is found between the results obtained by Burgess and Kraus and the more recent conductance work of Mandel and co-workers.[75]

The infrared and Raman spectra of pyridine have been studies by numerous workers. From infrared and Raman data Corrsin, et al.,[76] made a complete assignment of all the pyridine fundamentals. This assignment has been slightly modified by McCullough, et al.,[77] so that the values of thermodynamic functions statistically calculated from the observed vibrational frequencies would agree with experimental values. The change in assignment made by McCullough has since been criticized and modified by Wilmshurst and Bernstein[78] on the basis of an infrared and Raman study of pyridine and three partially deuterated pyridines.

The effect of the pyridine interaction with hydrogen bonding solvents on the infrared spectrum of pyridine has been studied by Takahaski and co-workers.[79] They found that there were relatively large shifts to higher energies for several of the skeletal vibrational bands of the pyridine molecule. If there were no changes in the electron distribution in the pyridine molecule upon hydrogen bonding, the skeltal vibrations would shift to lower frequencies due to the increased mass. The increase in frequency of these vibrations indicates a considerable change in the electron distribution which strengthen the chemical bonds of the ring system. Upon comparing the spectra of the hydrogen bonded pyridine molecule to the spectra of the pyridinium ion, the authors conclude that the electron distribution of the hydrogen bonded pyridine is close to that of the pyridinium ion.

French and Wood[80] recently reported a study of ammonium, d_4-ammonium, sodium, and potassium tetraphenylborates in pyridine solutions by far-infrared techniques. The sodium salt was also examined in three other solvents, 1,4-dioxane, piperidine, and tetrahydrofuran. From the data obtained in this study, the authors claim that sodium tetraphenylborate exists in pyridine solutions as an unsolvated ion pair. This hypothesis seems to be contrary to previous work done in this laboratory and a further investigation of pyridine solutions of alkali metal salts was thought to be worthwhile.

Acetone

Acetone had been used extensively as a solvent for organic materials. It also has the ability to solvate some inorganic salts as is indicated by the high solubility of 0.427 mole fraction units of lithium perchlorate.[81] The solvent is characterized by a wide liquid range (-95.4 to 56.2°), a moderate dielectric constant of 20.70, a relatively high dipole moment of 2.72 Debyes, and a Trouton constant of 21.5 indicating that it is a relatively unassociated liquid. Solubilities of electrolytes are enhanced by the dipole moment and the low Trouton constant of acetone.

The solid diacetonate of lithium bromide has been prepared by Bell, et al.[82] It was found to decompose into the unsolvated salt at 35.5°. On the other hand, the authors found that lithium chloride did not form a solid solvate. The acetonates of sodium iodide and bisulfite are well known due to their use in a method for the purification of acetone.[36] In this method a solution of one of the sodium salts in acetone is cooled causing the acetonate to precipitate. The precipitate is then filtered from the mother liquor. Upon heating the precipitate melts and the acetone is fractionally distilled from the solution.

A conductance study of lithium bromide solutions in acetone by Olson and Konecny[83] gave a value of

2.56×10^{-4} for the ion pair dissociation constant for the salt. The ion pair dissociation constant for potassium iodide in acetone was determined to be approximately 9×10^{-3} by Dippy.[84] These dissociation constants illustrate that, in acetone, as would be expected for a solvent with a dielectric constant of 20, dissolved salts of alkali metals exist primarily as ion pairs.

The infrared spectra of sodium iodide,[85] sodium perchlorate,[86] and lithium perchlorate[81] solutions in acetone have been studied previously from 4000 to 400 cm^{-1}. The primary emphasis in these studies has been on the changes in the infrared spectrum of acetone upon addition of the above salts. The results obtained by these authors are interpreted in terms of complex formation between the cation and the carbonyl group of acetone. The shifts in the acetone bands have also been found to be independent of the anion present. The appearance of a band in the 420-430 cm^{-1} region of lithium perchlorate-acetone solutions is mentioned by Pullin and Pollock[81] and is attributed to a higher frequency component of the 380 cm^{-1} acetone band.

Yamada[86] has also studied the effect of lithium and sodium perchlorate on the $\eta \rightarrow \pi^*$ transition of acetone in the ultraviolet spectral region, and found that the absorption band for this transition is shifted to higher energy upon addition of the two salts. The effect is more

pronounced in the case of the lithium prechlorate. These results are interpreted in terms of charge transfer complex formation between the alkali metal ion and the acetone. Assuming this type of interaction, the author calculates the percent covalent character of the oxygen-lithium and oxygen-sodium bonds using Pauling's "bond length" relationship.[87] The percent covalent character of the bonds is found to be 13% and 8% respectively.

EXPERIMENTAL

Chemicals

Pyridine: Fisher "certified" pyridine was fractionally distilled from granulated barium oxide through a one meter, helicies packed column. It was then stored over molecular sieves (Fisher type 4A). The water content of the pyridine was determined to be approximately three millimolar by a Karl Fisher titration.

Acetone: Baker, N. F., acetone was dried over calcium sulphate. The water content as determined by a Karl Fisher titration was approximately seven millimolar.

d_6-Acetone: Diaprep, Inc., d_6-acetone with a minimum isotopic purity of 99.5 percent was dried over molecular sieves (Fisher type 4A) and decanted.

Piperidine: Fisher "certified" piperidine was refluxed over granulated barium oxide for two hours and fractionally distilled.

Tetrahydrofuran: Fisher "certified" tetrahydrofuran was dried over calcium sulphate and decanted. The water content of the solvent was approximately one millimolar as determined by a Karl Fisher titration.

1,4-Dioxane: Fisher "certified" 1,4-dioxane was dried over calcium sulphate and decanted. The water

content of the solvent was approximately one millimolar as determined by a Karl Fisher titration.

Alkali Metal Salts: All of the alkali metal salts, with the exceptions of LiI, $KBPh_4$, NH_4BPh_4, ND_4I, and the Li^6 salts, were reagent grade chemicals and were used after drying without further purification.

Lithium iodide, 98% pure, was obtained from K & K Laboratories and was used without purification. The tetraphenylborates were prepared by adding a stoichiometric amount of sodium tetraphenylborate to an aqueous chloride solution of the desired cation. The precipitate was then washed with water and vacuum dried. The d_4-ammonium iodide was purchased as the 98% isotopically pure salt from Diaprep, Inc., and was used without further purification. The separated isotope, Li^6, was purchased as the metal from Union Carbide Oak Ridge Laboratory, Oak Ridge, Tennessee. The assay furnished with the metal showed that it was 95.6% Li^6 and 4.4% Li^7. In order to prepare the Li^6 salts, the metal was first added to water. The resulting basic solution was then neutralized with the reagent grade acid of the desired anion. The titration was followed potentiometrically. The water was then removed from the solution of the Li^6 salt by evaporation. All the salts except the Li^6I were then dried at 230°. The Li^6I was dissolved in acetone and precipitated as the acetonate by cooling in dry ice slush. The acetonate was then decomposed to the

pure salt by placing it in a vacuum oven 80° and 0.1 mm pressure for two days.

Preparation of Solutions

Both of the solvents and most of the salts used in this study were hygroscopic and care was taken to prepare them in as nearly anhydrous conditions as possible. Exposure of the solvents and solutions to the atmosphere during preparation or transfer was minimized by performing these operations with syringes. All solutions were prepared at room temperature of approximately 22°.

Instrumentation

Infrared spectra were obtained on two instruments, a Perkin-Elmer Model 225 Spectrometer with a range of 4000-200 cm^{-1} and Perkin-Elmer Model 301 Spectrometer with a range of 666-14 cm^{-1}. Normally the Model 225 instrument was used for spectra from 4000 to 600 cm^{-1} and the Model 301 was used in the 666 to 50 cm^{-1} region. In cases where duplicate measurements were made, they always agreed within experimental error.

The frequency scale of the 301 spectrometer was calibrated using the rotational spectrum of water vapor.

The construction, optical layout, and electronics of both spectrophotometers are described very well in the operational manual supplied by the manufacturer.

Some suggestions for special instrument procedures on the 301 are given by B. W. Maxey.[71]

Experimental Techniques

Spectra on the 225 Spectrometer were obtained using conventional solution cells with sodium chloride windows in the 4000-600 cm^{-1} region. Polyethylene spacers were used to obtain pathlengths of 0.015 mm to 0.1 mm. For spectra below 600 cm^{-1} polyethylene cells with 0.10 mm pathlengths purchased from Barnes Engineering were used. The 225 Spectrometer was operated in the double beam mode with air as a reference. Spectra on the Model 301 were obtained using polyethylene cells purchased from Barnes Engineering with pathlengths of 0.10 or 0.20 mm. The 301 Spectrometer was usually operated in the double beam mode with an equal thickness of solvent in the reference beam. In cases in which this procedure was inconvenient or impossible, an empty polyethylene cell was placed in the reference beam and corrections were made for solvent absorption. Concentrations of salts in the solvents varied between 0.05 and 1.5 M.

RESULTS AND DISCUSSION

Infrared Spectra of Alkali Metal Salt Solutions in Pyridine

The infrared spectra of alkali metal salt solutions in pyridine have been examined for three effects:

1. shifts in skeletal vibrations of pyridine
2. appearance of a solvent-cation band
3. splitting of perchlorate bands and the appearance of Raman active bands of this anion due to symmetry lowering by solution structure

An examination of the effect of the alkali metal salts on three skeletal vibrations of pyridine yielded results which were completely analogous to the work of Takahashi, et al.,[79] mentioned previously. The results are given in Table 32. The skeletal vibrations of pyridine at 1581, 991.5 and 603 cm^{-1} all shift to higher energies upon addition of the alkali salts. The magnitude of this shift is $Na^{+}<NH^{+}_{4}<Li^{+}$ and should give an indication of the relative bond strengths of the three ions with the pyridine molecule. At least four salts of each cation were examined with no anion effect being observed. The 1438 cm^{-1} band of pyridine was found to shift to 1443 cm^{-1} by Takahashi, et al., when large concentrations of

Table 32.--Splitting of Three Pyridine Skeletal Vibrations by Li^+, Na^+, and NH_4^+ Ions

	ν_{max}, cm^{-1}						
Py	1598		1581		991.5		603
Na^+	1598	1590	1581	996	991.5	611	603
NH_4^+	1598	1592	1581	999	991.5	614	603
Li^+	1597*		1581	1003	991.5	620	603

*The shifted 1581 cm^{-1} band lies too close to the 1598 cm^{-1} pyridine band to be resolved, and as a result a single band at 1597 cm^{-1} is observed.

hydrogen donor solutes were used. Due to the limited solubility of the alkali metal salts in pyridine, this shift was not observed although some broadening and asymmetry of the band was noted.

Sodium tetraphenylborate was one of the salts used in the above study which definitely shows that the sodium ion in pyridine solutions of this salt is solvated by one or more pyridine molecules. These results are not consistent with the report by French and Wood[80] that sodium tetraphenylborate exists in pyridine solutions as a completely unsolvated ion pair. Their assumption was based on the fact that a band at 175 ± cm^{-1}, which they ascribed to an ion pair vibration, was in the same position in four solvents, pyridine, piperidine, 1,4-dioxane

and tetrahydrofuran. An attempt to duplicate their results was unsuccessful. No band was observed in this region in 1,4-dioxane due to the low solubility of the salt, and the band in tetrahydrofuran was located at 194 ± 4 cm^{-1}. Edgell, et al.,[88] have also examined the sodium tetraphenylborate-tetrahydrofuran system and found this band to be at 198 ± 3 cm^{-1}. This band has been found at 179 ± 3 cm^{-1} and 176 ± 4 cm^{-1} in pyridine and piperidine, respectively.

As has been noted, the results obtained in this laboratory point to a pyridine-cation interaction. This would be expected on the basis of previous work by Maxey and Popov,[89] Wuepper and Popov,[90] and Edgell, et al.,[88] who found this type of interaction with alkali metal salts in dimethylsulfoxide and several of its homologues, 2-methylpyrolidone and several homologues, and tetrahydrofuran, respectively. Investigations of pyridine-alkali metal salt solutions in the far-infrared region yielded bands similar in most respects to the ones reported by the above authors. These results are summarized in Table 33.

The lithium solvent band is at 419 ± 4 cm^{-1}. There appears to be little effect on the band positions due to different anions as all the values for lithium salts lie within four wavenumbers. Substitution of the Li^6 cation for the Li^7 cation produces a small effect on

Table 33.--Absorption Bands of Alkali Metal Salts in Pyridine

Compound	ν_{max}, cm^{-1}
Li^7ClO_4	420 ± 4
Li^7Br	418 ± 4
Li^7I	419 ± 4
Li^7NO_3	419 ± 4
Li^7Cl	416 ± 4
Li^6ClO_4	426 ± 4
Li^6Br	422 ± 4
Li^6I	423 ± 4
Li^6NO_3	424 ± 4
Li^6Cl	421 ± 4
NH_4I	196 ± 3
NH_4ClO_4	197 ± 3
NH_4BF_4	198 ± 3
NH_4SCN	199 ± 3
NH_4NO_3	201 ± 3
NH_4BPh_4	199 ± 3
ND_4I	182 ± 3
$NaClO_4$	182 ± 3
$NaBPh_4$	179 ± 3
NaSCN	180 ± 3
NaI	170 ± 3

the band, shifting it to 423 ± 4 cm^{-1}. As can be seen, this is easily within experimental error; however, the shift is felt to be real. A Hook's Law calculation of the effect of Li^6 substitution assuming a psuedo-diatomic model gives an expected value of 450 cm^{-1}. No satisfactory explanations for the small observed shift can be given at this time.

The ammonium solvent and sodium-solvent bands were found at 199 ± 3 cm^{-1} and 180 ± 3 cm^{-1}, respectively, with the exception of the sodium iodide-pyridine system which gives a band at 170 ± 3 cm^{-1}. The ammonium iodide solutions do give bands slightly lower (196 cm^{-1}) than the average for all ammonium-solvent bands (199 cm^{-1}), but the difference is easily within the experimental error. Solutions of LiI in pyridine give a broad band in the 470-510 cm^{-1} region which preliminary examinations have shown to be time dependent. Specific interactions between the iodide ion and the solvent are possible. These interactions may take the form of complex formation and/or a reaction between the components of the system.

Examination of the d_4-ammonium iodide showed an ammonium-solvent vibration at 182 ± 3 cm^{-1}. A Hook's Law calculation of the effect of the increased mass predicts that the 199 ± 3 cm^{-1} band should shift to 184 ± 3 cm^{-1}. The good agreement between theory and experiment can be used as proof that a cation-solvent vibration is

involved in the appearance of these bands; however, it must be noted that in a calculation of this type where molecules and ions are being treated as point masses, the predicted shift is a result of the change of mass of the ammonium ion. It is not sensitive to the mass of the solvent or anion as can be seen in the following equation:

$$\bar{\nu}_{ND_4^+} = \bar{\nu}_{NH_4^+} \sqrt{\frac{18xS}{18+S} \times \frac{22+S}{22xS}}$$

In this equation $\bar{\nu}_{ND_4^+}$ and $\bar{\nu}_{NH_4^+}$ are the frequencies of the vibration with the interacting species, 18 is the mass of the ammonium ion, 22 is the mass of the d_4- ammonium ion, and S is the mass of the solvent molecule or anion interacting with the ammonium ions. For most values of S the term under the radical reduces to 18/22. It is significantly different from this value for very small values of S. French and Wood[80] also carried out measurements of band shifts upon substitution of the ND_4^+ cation for the NH_4^+ cation. Their value of 183 ± 3 cm^{-1} for the d_4-ammonium tetraphenylborate band in pyridine agrees with the value obtained in this investigation for the d_4-ammonium iodide. The above authors, however, interpreted their results as an added evidence for their assignment of the band to an inner ion pair vibration. It is seen, however, that if the study of the splitting of the

pyridine skeletal vibrations is considered along with the above information, an equally plausible explanation is the assignment of the band to a cation-solvent interaction.

Addition of small amounts of water to pyridine solutions of the lithium, sodium, and ammonium salts did not have any effect on the position of the cation-solvent bands, but they were broadened.

Attempts to locate solvent-cation bands for potassium, rubidium, and cesium salts were unsuccessful due to their low solubility in pyridine.

The question of the degree of anion involvement in the solution structure is of major importance. A preliminary study of the perchlorate bands in pyridine solutions of the lithium, ammonium, and sodium salts gave some indication of the role of the anion in these solutions. The results of this study are contained in Table 34. As can be seen in this table, the triply degenerate ν_3 vibration of the perchlorate, which appears at 1097 cm^{-1} in pyridine solutions of the tetrabutylammonium perchlorate, is split by 29 cm^{-1} in pyridine solutions of the lithium salt. These results indicate a lowering of the symmetry of the perchlorate ion from T_d to C_{3v}. Although solutions of the sodium and ammonion salt show no splitting, the above band appears to be somewhat asymmetric on the high energy side. Another indication of the symmetry lowering of the perchlorate anion is in the appearance of the

Table 34.--Position of Several Perchlorate Bands in Pyridine Solutions of the Tetrabutylammonium, Lithium, Ammonium, and Sodium Salts

Salt	ν_{max}, cm^{-1}			
NBu_4ClO_4		1097		624
$LiClO_4$	1127	1098	936	624
NH_4ClO_4		1099	936	624
$NaClO_4$		1100		623

963 cm^{-1} ν_1 band in solutions of the lithium and ammonium salt. This band is infrared forbidden for T_d symmetry but is allowed for lower symmetries. The absence of this band in solutions of the sodium salt is not understood. The triply degenerate ν_4 band at 624 cm^{-1} does not appear to split as might be expected. The presence of shifted pyridine band in this region might obscure a small splitting of this band in solutions of the lithium salt, and if the splitting is small, one would not expect to observe it in solutions of the other salts.

These results indicate that in solutions of alkali metal salts in pyridine, the cation is solvated by one or very probably several pyridine molecules. The strength of this interaction increases $Na^+ < NH_4^+ < Li^+$. The far infrared bands observed in these solutions are probably due to the vibration of the cations in a solvent cage.

Preliminary results on the spectra of the perchlorate ion seem to indicate that in certain cases the anions may be included in the solvation shell. The evidence, however, is not very clear and more work will have to be done before the role of the anion is clarified.

Infrared Spectra of Alkali Metal Salt Solutions in Acetone and d_6-Acetone

Some preliminary work has been done in acetone and d_6-acetone solutions of alkali metal salts. Spectral measurements on alkali metal salt solutions in these solvents were carried out in the 666 cm^{-1} spectral region on the 301 Spectrometer. A summary of the data obtained is given in Table 35.

Examination of lithium salts in acetone showed a lithium-solvent band which appears to be anion dependent in the 423 cm^{-1} region. The anion dependence of the band is shown primarily by the bromide and chloride salts which give bands at 412 ± 4 cm^{-1} and 409 ± 6 cm^{-1}, respectively. The relatively large uncertainty for the latter band is due to the low solubility of lithium chloride in acetone and the presence of an intense acetone fundamental band at 386 cm^{-1}. Spectra of lithium salts in d_6-acetone show bands in the 388 cm^{-1} region. Anion dependence of the band is shown by LiBr solutions which give a band at 372 ± 5 cm^{-1}. The chloride salt was not run. The large shift of 35-40 cm^{-1} is unexpected since a Hook's Law calculation, based on a pseudo-diatomic situation in which the d_6-acetone and acetone molecules are considered

Table 35.--Absorption Bands of Alkali Metal Salts in Acetone and d_6-Acetone

Salt	ν_{max}, cm^{-1}
Acetone	
$LiClO_4$	425 ± 4
LiBr	412 ± 4
$LiNO_3$	420 ± 4
LiI	424 ± 4
LiCl	409 ± 6
Li^6ClO_4	434 ± 5
Li^6NO_3	434 ± 5
Li^6Br	423 ± 5
Li^6I	436 ± 5
Li^6Cl	412 ± 5
NaSCN	192 ± 5
$NaClO_4$	192 ± 5
$NaBPh_4$	192 ± 5
NaI	187 ± 5
d_6-Acetone	
LiI	389 ± 5
$LiNO_3$	389 ± 5
LiBr	372 ± 5
$LiClO_4$	387 ± 5
$NaClO_4$	191 ± 5
$NaBPh_4$	189 ± 5
NaI	188 ± 5
NaSCN	194 ± 6

point masses in the same manner as the lithium atoms, predicts a shift of only two cm^{-1}. A similar Hook's Law calculation of the effect of substitution of Li^6 salts in place of the naturally occurring Li^7 salts predicts a shift of thirty cm^{-1}. Experimentally the shift is found to be approximately twelve cm^{-1} except in the case of the lithium chloride salts where the shift is only 3 cm^{-1}. No explanation can be given for this discrepancy at this time.

Ammonium salts were found to be insoluble in acetone and their spectra could not be obtained. The sodium salts were found to give two bands in acetone. The first is at 313 ± 3 cm^{-1} and is of low intensity. The origin of this band is unknown at this time. The second band has the shape of the usual solvent-cation band and is located at 192 ± 5 cm^{-1}. The sodium salts in d_6-acetone give a band at 190 ± 6 cm^{-1}. The expected value for sodium salts in d_6-acetone would be 189 cm^{-1}, based on a Hook's Law calculation.

The above results along with the previous work of Yamada[85,86] and Pullin and Pollock[81] on the changes in the infrared and ultraviolet spectrum of acetone, when used as a solvent for some lithium and sodium salts, indicate that we are looking at solvent-cation vibrations in this case. The anion dependence of the lithium band is similar to that reported by Edgell, et al.,[88]

for lithium salts in tetrahydrofuran. Since the anion dependence of the solvation band does not follow the mass dependence which would be expected if an ion pair vibration (such as was observed by Evans and Lo[91] for some tetraalkylammonium salts in benzene) was being detected, it can be assumed that the anion is acting only as a perturbing influence on the cation-solvent vibration. It is quite possible that the observed anion dependence is due to contact ion pairs as has been suggested by Edgell, et al.[88] The above explanation fits the data insofar as the chloride and bromide ions would be the most likely to form ion pairs.

ADDENDUM

During the time this thesis was being typed, there appeared in the literature a paper by Huong, et al.,[92] reporting the formation constant of the pyridine-iodine complex in eight non-polar solvents with dielectric constants less than 2.64. A plot of log K_M vs. δ_S, the Hildebrand solubility parameter,[93] is approximately linear as would be expected from the theory of Buchowski, et al.,[94] which is based on Hildebrand's theory of regular solutions.[93] Such a solution, while not ideal, does not exhibit high chemical reactivity or large solvent effects. When a plot of log K_M vs. δ_S is made for both their data and the data in this thesis, it is found that the latter points give a considerable amount of scatter. The scatter exists because the assumption of regular solutions inherent in Buchowski's theory would not be valid for the polar solvents used in the present work. Our value for K_M in n-hexadecane is also much larger than would be expected on the basis of their theory.

The data presented in the paper by Huong, et al.,[92] were plotted as in Figures 4 and 5 in this thesis, except for the points corresponding to squalane and i-octane for which dielectric constants were not readily available. Their data were found to correlate well with the data

presented herein, but their points are closely spaced due to the small range of dielectric constants of their solvents, 1.89 to 2.64.

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APPENDICES

APPENDIX 1

COMPUTER PROGRAM OF THE KETELAAR EQUATION FOR THE CALCULATION OF FORMATION CONSTANTS

The numerical calculations of the formation constants of the pyridine-iodine complexes were performed on a Control Data 3600 digital computer using the program contained in this appendix. The program was written with the aid of Dr. J. A. Caruso.

The following data are read in for the Ketelaar equation computer program. The first data card is the identification card, ID, and uses columns 1 through 56. The second data card contains in columns 1 through 10 the absorbance of iodine, AI, at the wavelength of interest, the molar concentration of iodine, CI, in columns 11 through 20, and the number of data sets read in, N, in columns 21 and 22. The third through N data cards contain in columns 1 through 10 the absorbance, A(I), at the wavelength of interest and the molar concentration, CB, of the pyridine or substituted pyridine in colums 11 through 20. The last data card contains the END of D statement in colums 21 through 28.

For the case in which an absorbance cell with a pathlength other than 1 cm is used, the statement A(I) = A(I)/b, where b is the numerical value of the pathlength, is inserted after statement number 22.

```
    PROGRAM KETTLAR
    TYPE REAL M
    DIMENSION X(50), Y(50), A(50), CB(50), YCALC(50), DEV(50), T(50),
   1ID(7), CC(50), CB2(50), CB3(50)
    CALLQ8Q ERSET(0)
 99 READ 1, ID
  1 FORMAT(7A8)
    PRINT 2, ID
  2 FORMAT (1H1,10X,7A8)
    IF (ID,EQ,8HEND OF R) STOP
    READ 3, AI, CI, N
  3 FORMAT (2F10, I2)
    PRINT 4,CI, N, AI
  4 FORMAT(/10X*IODINE CONC =*F12.10,5X*NUMBER OF DATA PAIRS =*12,5X
   1*IODINE ABS =*F5.3)
    PRINT 5
  5 FORMAT(/10X*ABSORBANC            CONC BASE*/)
    IL = 1
    I=1
101 READ 6, A(I), CB(I), IJ
  6 FORMAT(2F10, A8)
    PRINT 7, A(I), CB(I)
  7 FORMAT(12X,F6,4,10X,F12,10)
    CB3(I) = CB(I)
    IF(IJ.EQ,8HEND OF D) 22, 21
 21 I = I+1 R GO TO 101
 22 DO 201 I = 1,N
201 Y(I) =1,0/(A(I)-AI)
111 SUMX = XUMY = SUMXY = SUMX2 = SUMY2 = 0.0
    DO 301 I = 1, N
    X(I) = 1.0/CB(I)
    SUMX = SUMX + X(I)
    SUMY = SUMY + Y(I)
    SUMXY = SUMXY + X(I)*Y(I)
    SUMX2 = SUMX2 + X(I)**2
301 SUMY2 = SUMY2 + Y(I)**2
    PRINT 700, SUMX, SUMY, SUMX2, SUMY2, SUMXY
700 FORMAT(/10X*SUMX =*F20,4,10X*SUMY =*F15,10,/10X*SUMX2 =*F20,4,10X*
   1SUMY2 =*F15,10,/10X*SUMXY =*F20.10)
    FN = N
    M = (FN*SUMXY - SUMX*SUMY)/(FN*SUMX2 - SUMX**2)
    B = (SUMY*SUMX2 - SUMXY*SUMX)/(FN*SUMX2 - SUMX**2)
    PRINT 10, M, B
 10 FORMAT(/10X*SLOPE = F20.10, 5X*INTERCEPT = *F20.10)
    EPSC = (1,0/B+AI)/CI
    IF (IL,EQ,1)302,303
302 CONST = B/M      $ GO TO 305
303 CONST2 = B/M
    DIFF = ABSF(CONST2 - CONST)
    IF(DIFF,LE, ,001*CONST)99,304
```

```
304 CONST =CONST2
305 PRINT 11, EPSC, CONST
 11 FORMAT(/10X*MOLAR ABSORPTIVITY = *F8.3, 5X*FORMATION CONSTANT = *F
   110,3)
    FRACT = ((SUMXY - SUMX*SUMY/FN)**2)/(SUMX2 -SUMX**2/FN)
    E = SUMY2 - (SUMY**2/FN) - FRACT
    S2 = E/(FN -2.0)
    S = SQRTF(S2)
    SA2 = S2/(SUMX2 - (SUMX**2/FN))
    SA = SQRTF(SA2)
    SB2 = S2*SUMX2/(FN*SUMX2 - SUMX**2)
    SB= SQRTF(SB2)
    SKE = CONST*SA/M
    PRINT 12, S, SA, SB, SKF
 12 FORMAT(/10X* STD, OF A SINGLE Y = *F14.11,5X*STD, DEV. OF SLOPE =*
   1F14.11,/10X*STD. DEV. OF INTERCEPT =*F14.11,10X*STD. DEV. OF KF =*
   2F10.4)
    PRINT 15
 15 FORMAT(/19X*X              Y          YCALC          T          DE
   1VIATION*/)
 14 FORMAT(10X, 5F14.8)
    DO 231 I = 1, N
    YCALC(I) = M*X(I) +B
    T(I) = ABSF(Y(I) - YCALC(I))
    DEV(I) = T(I) - 3.0*S
    PRINT 14, X(I), Y(I), YCALC(I), T(I), DEV(I)
    IF(DEV(I)) 231, 241, 241
231 CONTINUE
    GO TO 251
241 PRINT 13, Y(I)
 13 FORMAT(1H),2X,14HREJECTED POINT,5X,E14.8)
    J = I
    DO 261 I = J, N
    CB(I) = CB(I + 1)
    CB3(I) = CB3(I + 1)
261 Y(T) = Y(I + 1)
    N = N -1
    GO TO 111
251 CONTINUE
    DO 888 I = 1,N
    CC(I) + (CONST*CB(I)*CI)/(1+ CONST*CB(I))
    CB2(I) = CB3(I) - CC(I)
888 CB(I) = CB2(I)
    IL = 2
    GO TO 111
    END
```

APPENDIX 2

CALCULATION OF THE EFFECT OF A COMPETING EQUILIBRIUM WITH THE SOLVENT ON THE FORMATION CONSTANT OF A PYRIDINE-IODINE COMPLEX

For the situation in which there are competing equilibria between the solvent and one of the components of a complex, the Ketelaar equation can be modified to account for this equilibrium in the calculation of the formation constant. There are two cases for this type of interference. Case 1 is for the situation in which the solvent interacts with the specie in excess, in this instance the pyridine. For the equilibria

$$Py + I_2 \rightleftharpoons Py \cdot I_2 \tag{1}$$

$$Py + S \rightleftharpoons Py \cdot S \tag{2}$$

and assuming that $C^{\circ}_{Py} >> C_{Py \cdot I_2}$ and $C^{\circ}_{S} >> C_{PyS}$ where the superscript zero denotes the analytical concentration of the specie, we can write the following equilibrium expressions.

$$K_{corr} = \frac{C_{Py \cdot I_2}}{(C^{\circ}_{I_2} - C_{Py \cdot I_2})(C^{\circ}_{Py} - C_{PyS})} \tag{3}$$

$$K_S = \frac{C_{Py \cdot S}}{(C^{\circ}_{Py} - C_{Py \cdot S})\ C^{\circ}_{S}} \tag{4}$$

An expression for the total absorbance of a solution at a particular wavelength, A_t, can also be written, assuming a 1 cm pathlength.

$$A_t = \varepsilon_{Py\cdot I_2} C_{Py\cdot I_2} + \varepsilon_{I_2} (C^{\circ}_{I_2} - C_{Py\cdot I_2}) \qquad (5)$$

Inherent in the above equation is the assumption that the pyridine-solvent complex and the pyridine do not absorb light at the wavelength at which the measurements have been made. Substituting in equations (3), (4), and (5) so as to eliminate the concentration of the two complexes we arrive at equation (6).

$$\frac{1}{\varepsilon_t - \varepsilon_{I_2}} = \frac{1 + K_S C^{\circ}_S}{K_{corr} C^{\circ}_{Py} (\varepsilon_{Py\cdot I_2} - \varepsilon_{I_2})} + \frac{1}{\varepsilon_{Py\cdot I_2} - \varepsilon_{I_2}} \qquad (6)$$

This equation is identical to the Ketelaar Equation except for the term $1 + K_S C^{\circ}_S$, which is a constant for low concentrations of pyridine and iodine. Thus, if we equate $1/K_{obs}$ from the slope of the Ketelaar plot with the term in equation (6)

$$1/K_{obs} = \frac{1 + K_S C^{\circ}_S}{K_{corr}} \qquad (7)$$

and rearrange we obtain

$$K_{corr} = (1 + K_S C^{\circ}_S) K_{obs} \qquad (8)$$

where K_{corr} is the formation constant of the pyridine-iodine complex corrected for the competing equilibrium.

For Case 2, the situation in which the solvent interacts with the specie in limiting concentration, in

this instance the iodine, we can follow an entirely analogous development. The equilibria involved are given as follows.

$$Py + I_2 \rightleftharpoons Py \cdot I_2 \tag{9}$$

$$I_2 + S \rightleftharpoons I_2 \cdot S \tag{10}$$

Making the assumptions that $C^{\circ}_{Py} >> C_{Py \cdot I_2}$ and $C^{\circ}_{S} >> C_{I_2 \cdot S}$ we can write the equilibrium expressions given below.

$$K_{corr} = \frac{C_{Py \cdot I_2}}{(C^{\circ}_{I_2} - C_{Py \cdot I_2} - C_{I_2 \cdot S})\, C^{\circ}_{Py}} \tag{11}$$

$$K_{S} = \frac{C_{I_2 \cdot S}}{(C^{\circ}_{I_2} - C_{Py \cdot I_2} - C_{I_2 \cdot S})\, C^{\circ}_{S}} \tag{12}$$

A similar equation for the total absorbance of a solution which includes the previous assumptions can be written as before.

$$A_t = \varepsilon_{Py \cdot I_2} C_{Py \cdot I_2} + \varepsilon_{I_2} (C^{\circ}_{I_2} - C_{Py \cdot I_2} - C_{I_2 \cdot S}) \tag{13}$$

Eliminating the concentration of the two complexes in equations (11), (12), and (13) we arrive at an equation which is identical to equation (6). Thus corrections for solvent competition can be made in the same manner as in Case 1.

APPENDIX 3

SUGGESTIONS FOR FUTURE WORK

1. Studies of the infrared spectra of polynuclear anions, e.g., ClO_4^-, SCN^-, and NO_3^-, should be extended in both acetone and pyridine solutions. These studies might give some indication of the degree of anion participation in the solvation shell of the alkali metal ions.

2. An examination of the far-infrared spectra of solutions of alkali metal salts in several substituted pyridines should give some idea of the effect of donor strength and steric effects on the solvation of the alkali metal ions.

3. The ultraviolet spectrum of solutions of alkali metal salts in pyridine should be examined. The shifts of the skeletal vibrations of pyridine in these solutions suggests that the electron distribution in the pyridine molecule has been altered significantly.

4. A mole ratio study of alkali metal salt solutions in pyridine and acetone by nmr techinques should be undertaken to determine the solvation numbers of the alkali metal ions in solution.

5. Vapor pressure studies, or studies of some other colligative property, should be undertaken in pyridine and acetone to determine if there are any polymeric species in solution.

6. A study of Li^7 and Na^{23} salts in solution by magnetic resonance techniques might provide some evidence for the existence of polymeric species in solution.