STUDIES ON IODINE COMPLEXES OF SUBSTITUTED PYRIDINES

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ABSTRACT

STUDIES ON IODINE COMPLEXES OF SUBSTITUTED PYRIDINES

by Ming Keong Wong

Halogen and interhalogen compounds can act as Lewis acids and form molecular complexes with electron donors. Aromatic nitrogen-containing organic compounds such as pyridine or substituted pyridines, are stronger electron donors than their carbon analogs, and hence they form stronger molecular complexes with Lewis acids.

Of all the halogens iodine forms relatively weak molecular complexes with organic bases. On the other hand it is not as strong a halogenating agent as the stronger Lewis acids such as iodine monochloride or iodine monobromide. It is, therefore, easier to work with since the probability of side reactions is minimized.

The mole ratio method was used for the determination of formation constants of iodine with 4-picoline, 2,4-lutidine, 3,5-lutidine, 2,3,6-collidine, 4-phenylpyridine, and 3,5-dichloropyridine. Spectrophotometric measurements were made on solutions of iodine and the respective pyridine bases in carbon tetrachloride solutions. From plots of amine/iodine mole ratio, the molar absorptivities of the undissociated complexes were obtained. These values were then used for the calculation of degrees of dissociation and formation constants of the complexes. For very weak complexes (such as the iodine - 3,5-dichloropyridine complex) Ketelaar's modification of Benesi-Hildebrand method was used. In the case of 4-phenylpyridine, neither method gave satisfactory results. This is probably due to the formation of two complexes, $Py \cdot I_2$ and $Py \cdot 2I_2$.

Ming Keong Wong

The strength of the iodine-pyridine base complexes decreases in the order 3,5-lutidine > 2,4-lutidine > 4-picoline > 2,3,6-collidine > 3,5-dichloropyridine. The order of basicity of the compounds is as follows: 2,3,6-collidine > 2,4-lutidine > 3,5-lutidine > 4-picoline > 4-phenylpyridine > 3,5-dichloropyridine.

STUDIES ON IODINE
COMPLEXES OF SUBSTITUTED PYRIDINES

By

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HISTORICAL INTRODUCTION

The Lewis acid character of certain halogen and interhalogen compounds has long been amply illustrated by the large number of complexes which they form with electron donors. Among the halogens, iodine is the strongest Lewis acid, due to the ease of which it expands its octet and accommodates extra electron pairs. The donor strength of Lewis bases as well as the influence of molecular structure on the donor strength can be conveniently illustrated by the relative strength of their halogen complexes. Because of the reactivity of the halogens, such studies must be made in chemically inert solvents.

Since the classic spectrophotometric studies of complexing reaction of iodine with benzene and some other aromatic hydrocarbons by Benesi and Hildebrand[1], a large amount of work on complex formation involving halogens and interhalogens has been reported by many investigators. A large number of organic Lewis bases were investigated and their relative basic strength determined.

Aromatic nitrogen-containing organic compounds are known to be more basic than their carbon analogs. Consequently, they form stronger complexes with halogens and interhalogens. This is evidenced by the fact that relatively stable solid complexes of organic bases with halogens had been reported many years before the work of Benesi and Hildebrand.

The existence of a solid molecular addition compounds of iodine with pyridine was reported in 1933 by Chatelet[2], and the composition $(C_5H_5N)_2$-I_2 was assigned to the crystals obtained. Chatelet also reported 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 come from spectral studies. Zingaro, VanderWerf and Kleinberg[3] have investigated the behavior of iodine in pyridine solutions and postulated the reaction to be:

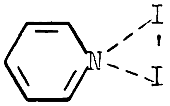
$$2\ I_2 + Py \rightleftharpoons IPy^+ + I_3^-$$

Infrared studies of iodine with pyridine and 2-picoline in carbon tetrachloride by Mulliken, Gluster, and Thompson[4] showed a definite shift of 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 halogen-amine complex.

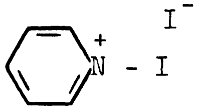
Mulliken and Reid[5], in their study of the pyridine-iodine system in heptane, reported the existence of a 1:1 molecular complex. Upon the addition of pyridine the 520 mμ peak of iodine in heptane was shifted to 422 mμ. This peak was attributed to the absorption by the complex, and the association constant for the complex was calculated to be 290 at 16.7°.

Since iodine is a relatively weak Lewis acid, its molecular complexes with organic bases are likewise weak, and with few exceptions, spectrophotometric studies by mole ratio method and method of continuous variation do not give satisfactory results. The strongest iodine charge-transfer complex reported in literature is the molecular complex between iodine and triethylamine[6], with equilibrium constant of about 4.61×10^3 (liter/mole) at 25°. However, other studies using stronger interhalogen Lewis acids such as iodine monochloride and iodine monobromide, do show the formation of 1:1 molecular complex[7]. Moreover, in determining the equilibrium constants of iodine-organic base molecular complex, consistent values are obtained by calculations at different wavelengths based on the assumption of 1:1 complex.

Mulliken[5,8] 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

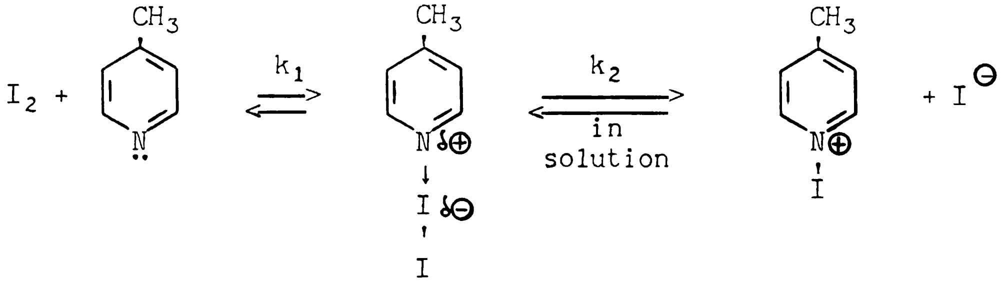


(A)

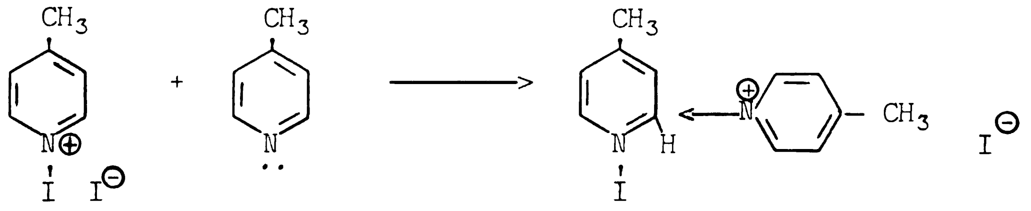


(B)

Glusker and Miller[9] isolated two different addition compounds formed by 4-picoline and iodine: Compound I has an ionic structure and compound II is a molecular addition compound, analogous to the addition compound of pyridine and iodine prepared by many workers. Their studies have led to the postulation that compound II is an intermediate in the formation of compound I, and the mechanism of the reaction is as follows:

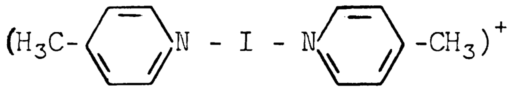


Compound II



Compound I

X-ray studies by Hassel, Roemming and Tufte[10] on the 1:1 addition compound of 4-picoline and iodine showed that the I-I-N arrangement in compound II is linear with the I-I distance of 2.83 Å while the I-N distance is 2.31 Å. Investigations by Hassel and Hope[11] on the reaction product of pyridine and iodine prompted them to postulate the cation of compound I has a similar linear structure as that of compound II:



instead of the α-addition arrangement as proposed by Glusker and Miller[9].

The strength of the molecular complexes formed by iodine and organic bases depends primarily on two factors, the donor strength of the base and on steric effects. Brown, Schlesinger and Cardon[12] studied the reactions of boron trifluoride with pyridine and 2,6-lutidine and reported that pyridine forms a stronger molecular complex than 2,6-lutidine, though the latter is a stronger base than pyridine.

Studies by Popov and Rygg[7] on iodine and interhalogen complexes of substituted pyridines also show the effect of steric hindrance. They reported the order of stability of the complexes in each of the iodine or interhalogen series with the three pyridines as follows: 2-Picoline > pyridine > 2,6-lutidine. The order of basic strength is: 2,6-Lutidine > 2-picoline > pyridine.

S. Basu and J. N. Chandhuri[13] investigated the charge-transfer interaction between iodine and a number of substituted pyridines in chloroform solutions. They found the logarithms of equilibrium constants of the complexes to be approximately proportional to the pKa values of the respective amine. The equilibrium constants for 2,6-lutidine and 2,4,6-collidine were found to be much less than those expected from the corresponding pKa values. They attributed the discrepancies to steric effect of the methyl groups at 2 and 6 positions.

Halleux[14] reported that in the reaction between phenol and pyridine bases

$$C_6H_5OH + B \rightleftharpoons C_6H_5OH \text{ --- } B$$

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 basic strength and strength of the complexes. In the determination of basic strength, very small proton is involved, and there is little steric effect present. Brown and Mihm[15] reported absence of any important steric effects in the addition of the proton to pyridine, 2,6-lutidine and monoalkylpyridines. Sacconi, Paoletti and Ciampolini[16] 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 steric effect in the reactions. For 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 weakening the molecular complex formed.

This present study was intended to determine, by spectrophotometric measurements, the relative strength of the complexes formed in carbon tetrachloride solutions between iodine and the following pyridine bases: 4-Picoline, 2,4-lutidine, 3,5-lutidine, 2,3,6-collidine, 4-phenylpyridine, and 3,5-dichloropyridine. Such studies should yield interesting data on the effects of the basic strength of the organic compounds, and of the steric configuration, on the strength of the molecular complexes formed.

The base ionization constants of some methylpyridines have been investigated by several workers.[12,14-20] Their values are not always in exact agreement, but comparison of available data on some of the methylpyridines show that there is a basic agreement as to the order of basicity. The pK_a values of methylpyridines quoted in Table I are mostly taken from reference 18. The sources of other data are listed immediately after the name of the compound. It should be emphasized that these data do not allow precise comparisons since some of the values have been obtained by different investigators using different methods and different solvents.

The pK_a of 3,5-dichloropyridine is not available in the literature. However, it is reasonable to conclude from the structure that the decrease in pK_a value of pyridine by 3,5-dichloro-substitution will be about twice that caused by 3-chloro-substitution.

Table I. pK_a values of some substituted pyridines

Compound	pK_a
Pyridine	5.30
2-Picoline	5.95
4-Picoline	6.10
3,5-Lutidine	6.34
2,6-Lutidine	6.72
2,4-Lutidine	6.80
2,3,6-Collidine	7.40
4-Phenylpyridine(21)	5.20
2-Chloropyridine(22)	0.72
3-Chloropyridine(22)	2.84
3,5-Dichloropyridine	--

From the pK_a values, it is seen that the substitution of phenyl group in the 4-position of pyridine ring causes a slight decrease in basicity, and according to values given by Favini[21], the decrease in basicity is more pronounced when phenyl group is in positions 2 and 3 of the ring. Favini also attributed the observed bathochromic shift in ultraviolet spectra of 4-phenylpyridine to a quinoid structure contribution. Indeed the substitution of a phenyl group in the para position has changed greatly the nature of the pyridine ring, so that the ultraviolet absorption spectrum of the compound is similar to the spectrum of biphenyl.[23,24]

Since benzene is known to form weak complex with iodine, it is expected that for 4-phenylpyridine, two reaction sites will be available to coordinate with iodine in the phenylpyridine molecule. It has long been regarded that the linearity of the Benesi-Hildebrand plots provides evidence for the presence of only one 1:1 molecular complex[25-28]. Johnson and Bowen[29], by using synthetic data, showed that linearity of the Benesi-Hildebrand plot is not by itself sufficient for asserting the presence or absence of more than one molecular complex in solution. They examined the system tetracyanoethylene-naphthalene-carbon tetrachloride and found a systematic variation of equilibrium constant with wavelength. Thus they emphasized the necessity to examine the variation of equilibrium constant with wavelength before asserting the presence or absence of equilibria other than 1:1 stable charge-transfer complexes. The 4-phenylpyridine-iodine-carbon tetrachloride system will provide interesting data for further examination of the above mentioned relationships.

The substitution of electron-withdrawing chlorine atom to the pyridine ring decreases markedly the basicity, the effect being greatest at α-position and smallest at γ-position.

The formation constants of some of the organic base-iodine complexes as reported by Popov and Rygg are listed in Table II. The 2-chloropyridine-iodine system in n-heptane has been investigated by Witmer and Zingaro[30], and the reported K_f for the 1:1 complex is also listed:

Table II. Formation constants of some iodine-substituted pyridine complexes.

Complex	K_f
Pyridine-iodine	101 (25°)
2-Picoline-iodine	150 (25°)
2,6-Lutidine-iodine	50.8(25°)
2-Chloropyridine-iodine	3.3(28°)

EXPERIMENTAL PROCEDURE

Reagents

Carbon Tetrachloride. Carbon tetrachloride used in this study was purified by refluxing it with alkaline potassium permanganate for 24 hours, washing with water, further refluxing with barium oxide for 10 hours, and then distilling two times from fresh barium oxide. The final distillation was done using one meter fractionating column packed with glass beads.

Iodine. Iodine obtained from J. T. Baker Chemical Co. was purified by sublimation from a mixture of twenty grams of iodine, four grams of calcium oxide, and four grams of potassium iodide. The iodine thus obtained was resublimed without adding calcium oxide and potassium iodide.

4-Picoline. Aldrich Chemical Company 95% pure 4-picoline was stored over sodium hydroxide pellets for ten days and then twice distilled from fresh sodium hydroxide, using one meter packed fractionating column. The fraction boiling at 143° at 760 mm was used for subsequent spectrophotometric measurements. Reported boiling point of the liquid is 142-143°.[31] It was also reported that a sample of picoline of 99.88 moles % purity had a boiling point of 145.356° at 760 mm.[32]

2,4-Lutidine. One hundred grams of 2,4-lutidine (Aldrich Chemical Company) was refluxed over barium oxide for three hours, and then fractionally distilled through a one meter fractionating column. The middle fraction, boiling at 156.5° at 755 mm (reported value is 157.1° at 760 mm[32]) was collected and used for subsequent measurements.

3,5-Lutidine. The purification procedure was analogous to that used for 2,4-lutidine. The fraction boiling at 171° at 756 mm was collected and used. The reported boiling point is 171.6° at 760 mm.[32]

2,3,6-Collidine. One hundred grams of collidine (Aldrich Chemical Company) was refluxed with barium oxide for two hours and then distilled through a one meter fractionating column. The fraction boiling at 169° at 733 mm was collected and used. Literature value for the boiling point is 168-170° at 730 mm.[33]

4-Phenylpyridine. This chemical was obtained from L. Light and Co. Ltd., England. Initially recrystallization from n-heptane was used in an attempt to purify the compound.[32] However, after two recrystallizations the crystals obtained were still slightly yellow. The compound was finally purified by recrystallizing it from hot water.[34] After two recrystallizations, the crystals obtained were pure white and their melting point was 74.5° (uncorrected). (Lit. val. 74°[35] and 77-78°[32].)

3,5-Dichloropyridine. This compound (Aldrich Chemical Company) was purified by two recrystallizations from 95% ethanol. The product was dried in a desiccator over calcium chloride for 6-8 hours. The solid compound seemed to have a fairly high vapor pressure at room temperature. The pure white crystals obtained had a melting point of 65° (uncorrected). (Lit. val. 64-65°[36] and 66-67°[37].)

Preparation of Solutions

Stock solutions of iodine of concentrations ranging from 1.0 x 10^{-3} to 2.0 x 10^{-3} mole/liter were prepared by dissolving a known weight of iodine in carbon tetrachloride in volumetric flasks. The exact concentration of the solutions was determined by titration with standard sodium thiosulfate solution.

Stock solutions of 4-picoline, 2,4-lutidine, 3,5-lutidine, 2,3,6-collidine, 4-phenylpyridine and 3,5-dichloropyridine were prepared by dissolving a known weight of the respective substance in an appropriate volume of carbon tetrachloride.

The solutions for spectrophotometric measurement were prepared by mixing proper aliquots of the two desired stock solutions and then diluting to the desired concentration with the solvent.

Spectrophotometric Measurements

All spectrophotometric measurements were made on a Cary recording spectrophotometer, Model 14, using silica cells of 1.00 ± 0.01 cm. path-lengths. The absorption spectra were measured between 300 mμ and 600 mμ. All the measurements were made at room temperature varying between 23-26°C. The absorption of each solution was measured against a reference cell containing the pure solvent.

Applications of Spectrophotometric Data

Since all the pyridine bases studied form relatively weak complex with iodine, the formula of the molecular complex in solution cannot be determined by mole ratio method. However, it is feasible to determine the degree of dissociation and formation constant of the individual molecular complex by the mole ratio method, assuming 1:1 complex is being formed in the solution.

Measurements and Calculations of Equilibrium Constants

It has been fairly well established in a number of previous investigations[1-10], that in reasonably dilute solutions ($\leq 10^{-2}$ M) heterocyclic amines form 1:1 complexes with halogens and interhalogens. Thus, the measurements of the complex formation constant were reduced to the determination of the equilibrium concentrations of the complex, of the free base and of the free halogen in a solution containing known initial amounts of the two reagents.

At a given wavelength the total absorbance (A) of a halogen-amine solution is

$$A = \epsilon_B b[B] + \epsilon_{X_2} b[X_2] + \epsilon_{BX_2} b[BX_2]$$

where b is the pathlength of the cell, ϵ_B, ϵ_{X_2}, and ϵ_{BX_2} are the molar absorptivities of the base (B), the halogen (X_2), and the complex (BX_2) respectively. If

C_B = initial concentration of the base,
C_{X_2} = initial concentration of the halogen, and
C_c = equilibrium concentration of the complex, then

$$A = \epsilon_B b(C_B - C_c) + \epsilon_{X_2} b(C_{X_2} - C_c) + \epsilon_{BX_2} bC_c.$$

If

$$C_B = C_{X_2} = C$$

we can express the concentration of free base and that of free halogen by αC, where α = degree of dissociation of the complex. The equilibrium becomes:

$$A = \epsilon_B b\alpha C + \epsilon_{X_2} b\alpha C + \epsilon_{BX_2} bC(1 - \alpha).$$

Since ϵ_B of the pyridine bases is negligible between 300-600 mμ, the wavelength region selected for this study, the equation reduces further to:

$$A = \epsilon_{X_2} b\alpha C + \epsilon_{BX_2} bC(1 - \alpha).$$

The molar absorptivity for the undissociated complex, ϵ_{BX_2}, is obtained from the mole ratio method plots, the molar absorptivity of the iodine, ϵ_{X_2} , is readily measured, and C is known. Thus, the value of the degree of dissociation, α , can be determined from the above equation. The formation constant was calculated from the equation:

$$K_f = \frac{1 - \alpha}{\alpha^2 C}$$

For extremely weak complex such as 3,5-dichloropyridine-iodine system, the limiting value of molar absorptivity could not be reached even when excess of more than two thousand mole ratio of the base was used. Consequently, the molar absorptivity of the complex, as well as the formation constant, was calculated using Ketelaar's modification of the Benesi-Hildebrand method. For the reaction in this present study:

$$A + B \rightleftharpoons AB$$

Ketelaar, Stolpe, Goudsmit and Dzcubas[38] have shown that if $C_{B(total)} >> C_{I_2(total)}$, then $C_B \sim C_{B(total)}$, the following equation can be derived:

$$\frac{1}{\epsilon_t - \epsilon_X} = \frac{1}{\epsilon_c - \epsilon_X} \times \frac{1}{K_f C_B} + \frac{1}{\epsilon_c - \epsilon_X}$$

where ϵ_t is the apparent molar absorptivity of iodine (i.e. measured absorbance of the solution divided by the total concentration of iodine), ϵ_X is the molar absorptivity of iodine, ϵ_c is the molar absorptivity of the complex, and C_B is the equilibrium concentration of the base. The unknowns are ϵ_c and K_f . A plot of $\frac{1}{\epsilon_t - \epsilon_X}$ vs. $\frac{1}{C_B}$ gives a straight line, of which the intercept yields the value of ϵ_c and the slope, that of K_f .

EXPERIMENTAL RESULTS

Spectrophotometric Measurements on the Individual Components

The absorptions of 4-picoline, 2,4-lutidine, 3,5-lutidine, 2,3,6-collidine and 3,5-dichloropyridine were practically zero between 300 mμ to 600 mμ. At 300 mμ, 4-phenylpyridine had a molar absorptivity of about 70; at 310 mμ, the molar absorptivity decreased to about 7, and above 325 mμ, the absorption was practically zero.

The solution of iodine in carbon tetrachloride showed an absorption maximum at 517 mμ, with a molar absorptivity of 930. The result agrees with the values given by Benesi and Hildebrand (ϵ = 930)[1], and Popov and Rygg (ϵ = 920)[7].

Spectrophotometric Measurement on the Molecular Complexes

In all the runs of the mole ratio method on the iodine-pyridine base systems, the concentration of iodine was held constant and the mole ratio of pyridine base to iodine was increased until the limiting absorbance was obtained. The absorption spectra of all the solutions were obtained during a period of one to eight hours after preparation.

4-Picoline - Iodine Complex. The absorption spectra showed a maximum at 408 mμ and an isosbestic point at 472 mμ. The molar absorptivity of the complex at 408 mμ was 1710. The absorption spectra, with the isosbestic point, are shown in Fig. 1. The absorbance and molar absorptivity values, at four wavelengths, for the different runs are shown in Table 3 and the plots of the molar absorptivity values vs. the mole ratio of 4-pic/I_2 are shown in Fig. 2.

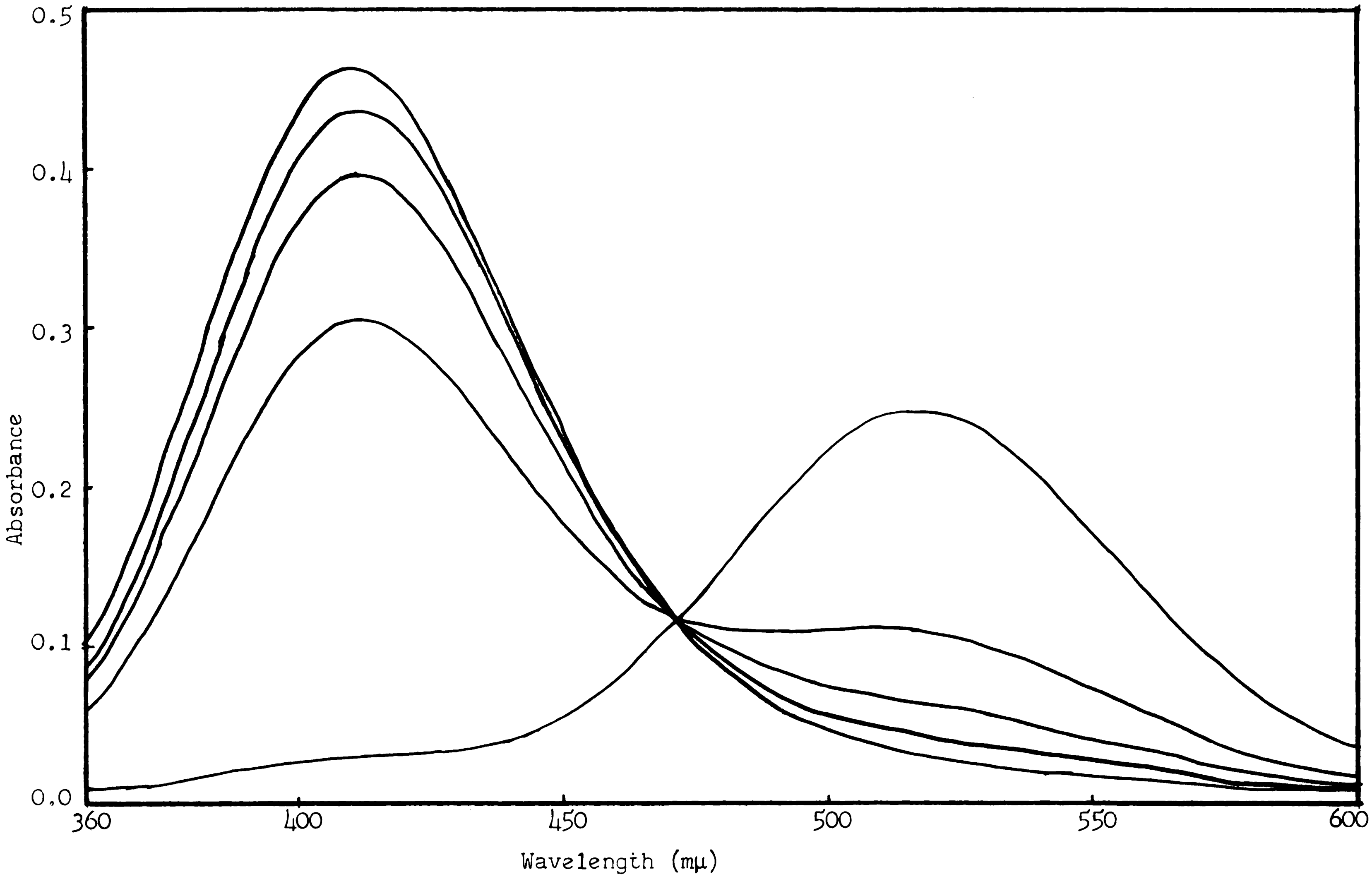


Fig. 1. Absorption spectra of 4-Picoline - I_2 system in Carbon tetrachloride (Run III).

Table 3. Spectrophotometric data of mole ratio method on the 4-picoline - I_2 system in CCl_4

Conc. of I_2	M.R. of 4-Pic/I_2	408 mμ		420 mμ		450 mμ		517 mμ	
		As	ε	As	ε	As	ε	As	ε
Run I	0.0	0.007	14	0.016	31	0.086	165	0.482	923
	1.0	.092	177	.095	182	.118	227	.437	836
.0005215 M	5.1	.309	593	.304	583	.215	413	.331	635
	20.3	.610	1170	.591	1133	.345	662	.176	337
	50.7	.734	1410	.712	1365	.396	760	.110	211
	96.0	.790	1515	.770	1477	.425	815	.083	159
	192	.833	1598	.800	1535	.435	835	.065	125
	287	.834	1600	.797	1530	.425	815	.057	109
	383	.854	1640	.811	1556	.425	815	.053	102
	480	.869	1668	.820	1572	.432	826	.053	102
	752	.863	1657	.810	1553	.425	815	.053	102
	1028	.878	1686	.820	1572	.425	815	.053	102
	1648	.892	1711	.810	1553	.390	747	.047	90
Run II	0.0	.009	17	.014	27	.081	156	.483	930
	1.0	.089	171	.091	175	.118	228	.440	846
.0005196 M	34.0	.685	1320	.667	1283	.372	716	.140	270
	85.0	.776	1492	.750	1442	.410	788	.090	173
	200	.831	1600	.795	1530	.423	815	.065	125
	500	.868	1672	.816	1571	.428	824	.054	104
	800	.872	1678	.811	1561	.413	794	.050	96
	1000	.887	1706	.823	1585	.415	798	.049	94
	1200	.896	1723	.820	1578	.400	770	.047	90
	1400	.904	1740	.822	1583	.400	770	.047	90
Run III	0.0	.004	14	.008	29	.047	169	.260	935
	1.0	.030	108	.032	115	.057	205	.247	887
.0002781 M	31.8	.302	1085	.293	1052	.175	628	.110	395
	95.4	.395	1420	.382	1374	.216	776	.065	234
	223	.434	1562	.419	1508	.225	809	.045	162
	353	.443	1595	.426	1531	.231	830	.038	137
	705	.460	1655	.438	1578	.233	837	.034	122
	1058	.466	1675	.440	1581	.230	826	.032	115
	1410	.471	1695	.443	1595	.230	826	.030	108
	1765	.477	1715	.442	1588	.230	826	.030	108
	2115	.478	1723	.438	1578	.219	787	.025	90
	2820	.477	1715	.431	1550	.205	737	.022	79
Run IV	0.0	.010	14	.018	26	.113	163	.646	930
	1.0	.144	207	.146	210	.170	244	.578	832
.0006951 M	38.2	.978	1407	.950	1367	.527	758	.169	243
	149	1.119	1610	1.078	1550	.578	832	.088	127
	447	1.170	1683	1.113	1603	.585	841	.072	104
	746	1.195	1720	1.108	1595	.550	792	.064	92
	882	1.200	1727	1.108	1595	.540	777	.064	92
	1100	1.215	1748	1.113	1603	.545	784	.058	83

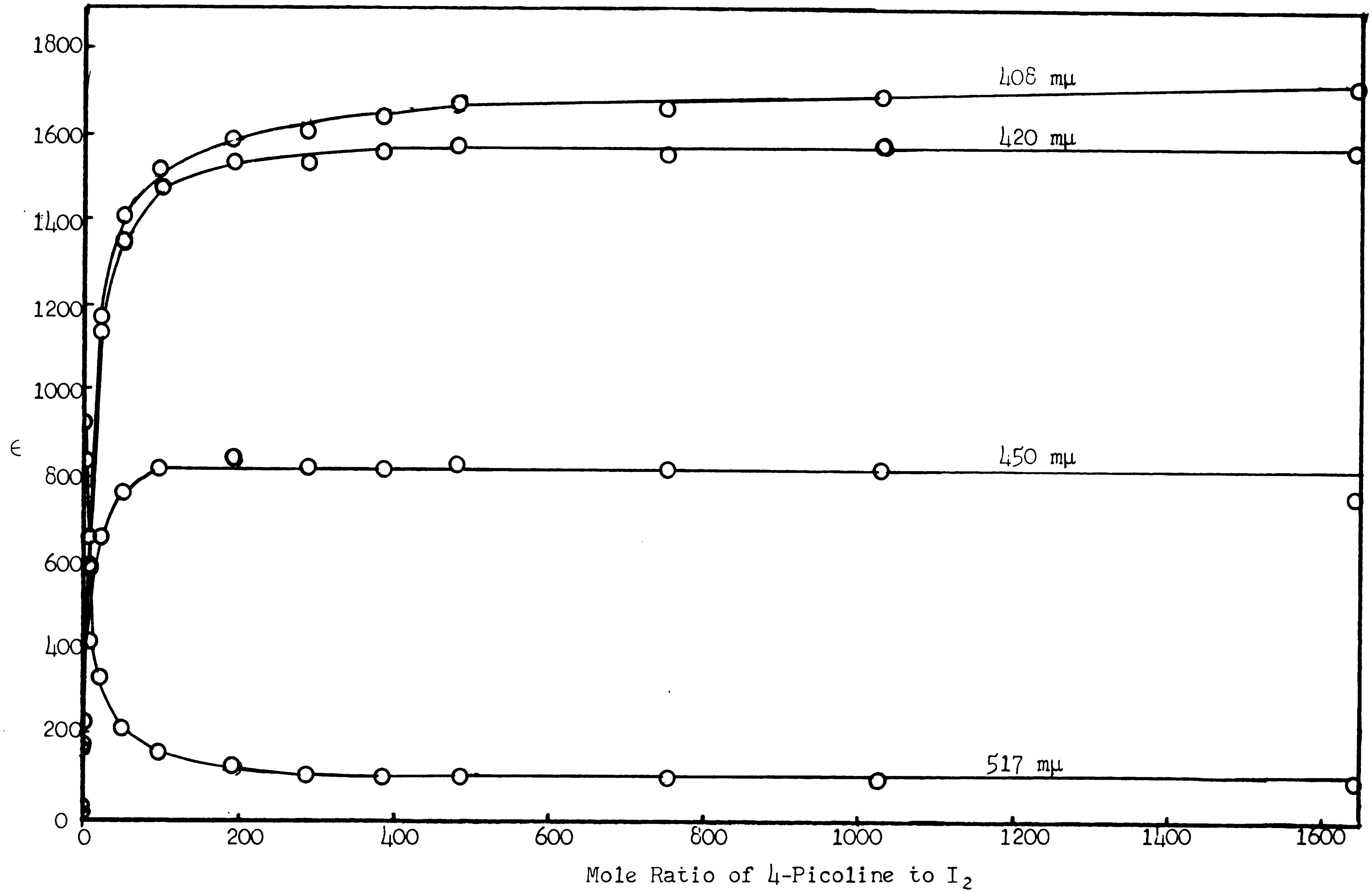


Fig. 2. Mole Ratio Method on the 4-Picoline - I_2 system in carbon tetrachloride.

2,4-Lutidine - Iodine Complex. The absorption spectra showed a maximum at 412 mμ, and the molar absorptivity of the complex at this wavelength was 1680. The isosbestic point showed by all the runs was at about 473 mμ. The absorption spectra, with the isosbestic point, are shown in Fig. 3. The absorbance and molar absorptivity values, at four wavelengths, for the different runs are given in Table 4 and the plots of the molar absorptivity values vs. the mole ratio of 2,4-lut/I_2 are shown in Fig. 4.

3,5-Lutidine - Iodine Complex. The maximum absorption wavelength of the complex was at 409 mμ, and the molar absorptivity at that wavelength was 1690. The isosbestic point was at about 472 mμ. The absorption spectra, with the isosbestic point, are shown in Fig. 5. The absorbance and molar absorptivity values, at four wavelengths, for the different runs are given in Table 5 and the plots of the molar absorptivity values vs. the mole ratio of 3,5-lut/I_2 are shown in Fig. 6.

2,3,6-Collidine - Iodine Complex. The absorption spectra of the complex showed a maximum at 422 mμ, and the isosbestic point was at about 479 mμ. The molar absorptivity at 422 mμ was 1600. The absorption spectra, with the isosbestic point, are shown in Fig. 7. The absorbance and molar absorptivity values, at four wavelengths, for the different runs are given in Table 6 and the plots of the molar absorptivity values vs. the mole ratio of 2,3,6-coll/I_2 are shown in Fig. 8.

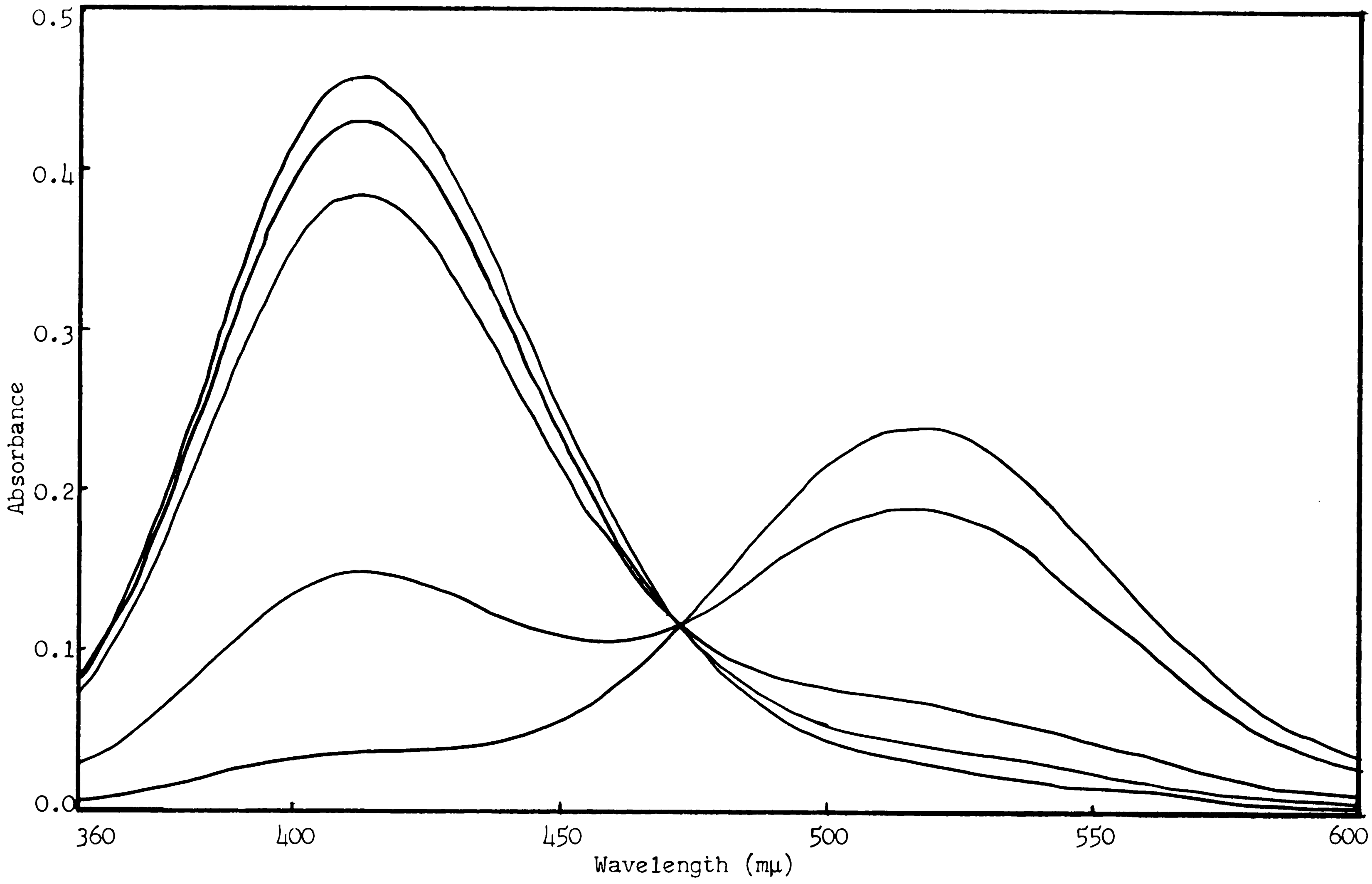


Fig. 3. Absorption spectra of 2,4-Lutidine - I_2 system in carbon tetrachloride (Run I).

Table 4. Spectrophotometric data of mole ratio method on the 2,4-lutidine - I_2 system in CCl_4

Conc. of I_2	M.R. of 2,4-Lut/I_2	400 mμ		412 mμ		440 mμ		517 mμ	
		As	ε	As	ε	As	ε	As	ε
Run I	0.0	0.000	0	0.001	4	0.024	86	0.256	920
	1.0	.033	119	.037	133	.046	165	.240	862
.0002781 M	5.7	.137	492	.150	540	.120	432	.189	680
	53.8	.352	1265	.385	1384	.274	985	.070	252
	144	.395	1420	.430	1545	.302	1085	.044	158
	370	.420	1510	.457	1644	.314	1128	.034	122
	555	.419	1508	.458	1650	.321	1154	.030	108
	740	.427	1537	.459	1654	.320	1150	.027	97
Run II	0.0	.008	8	.013	13	.091	88	.950	915
	1.0	.310	298	.350	337	.307	295	.766	737
.001039 M	49.5	1.505	1450	1.627	1565	1.146	1104	.149	144
	148	1.578	1520	1.705	1640	1.185	1140	.114	110
	248	1.627	1565	1.738	1673	1.200	1155	.105	101
	308	1.632	1571	1.737	1672	1.177	1133	.100	96
	410	1.655	1592	1.767	1700	1.175	1130	.098	94
	513	1.683	1620	1.770	1705	1.180	1135	.095	92
Run III	0.0	.006	11	.010	19	.049	94	.488	933
	1.0	.111	212	.122	233	.121	231	.431	826
.0005230 M	47.7	.733	1401	.790	1510	.554	1058	.088	168
	209	.808	1545	.868	1610	.595	1137	.060	115
	314	.815	1558	.874	1670	.596	1139	.055	105
	418	.819	1565	.879	1679	.596	1139	.053	101
	523	.835	1595	.886	1693	.595	1137	.050	96
Run IV	0.0	.004	6	.008	13	.054	87	.575	922
	1.0	.149	239	.163	261	.157	252	.494	793
.0006236 M	40.0	.850	1362	.925	1482	.650	1042	.120	192
	175	.950	1522	1.024	1642	.713	1145	.070	112
	263	.960	1538	1.035	1660	.710	1138	.067	107
	342	.970	1555	1.044	1675	.708	1135	.063	101
	512	1.000	1602	1.067	1710	.704	1130	.058	93
	577	.992	1590	1.066	1709	.710	1138	.057	91

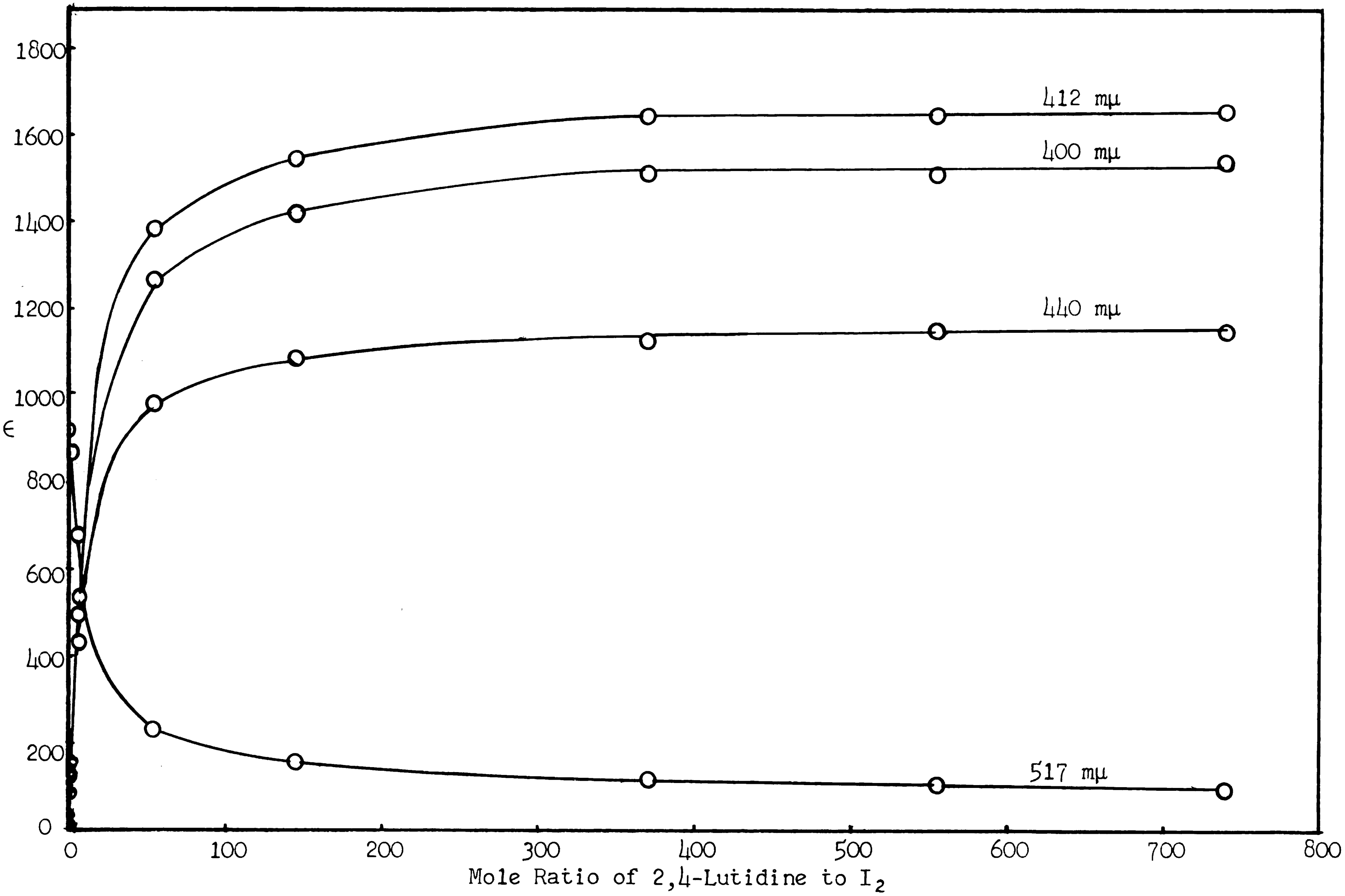


Fig. 4. Mole Ratio Method on the 2,4-Lutidine - I_2 system in carbon tetrachloride

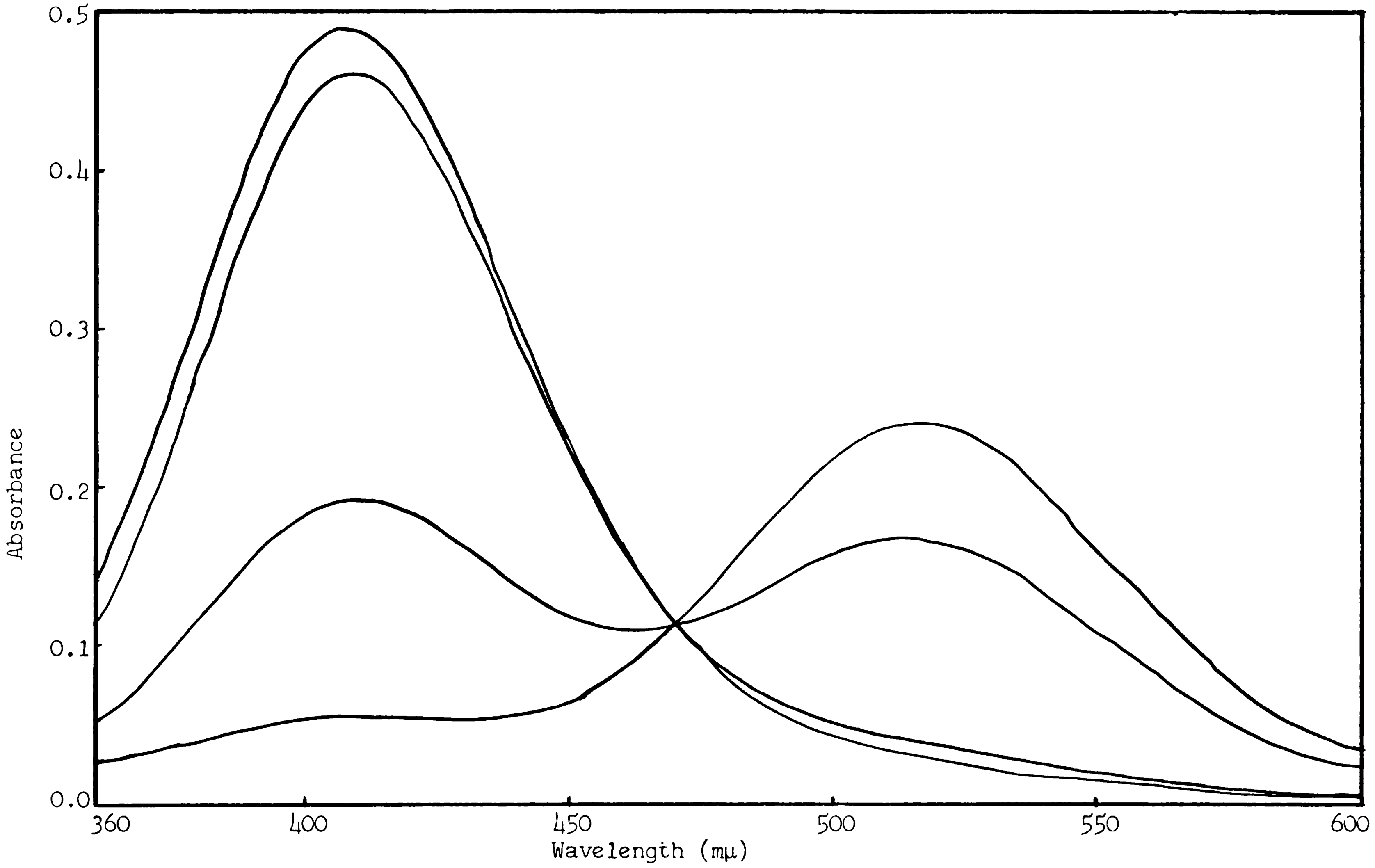


Fig. 5. Absorption spectra of 3,5-Lutidine - I_2 system in carbon tetrachloride (Run IV).

Table 5. Spectrophotometric data of mole ratio method on the 3,5-lutidine - I_2 system in CCl_4.

Conc. of I_2	M.R. of 3,5-Lut/I_2	409 mμ		430 mμ		460 mμ		517 mμ	
		As	ε	As	ε	As	ε	As	ε
Run I	0.0	0.006	12	0.022	44	0.134	268	0.470	927
	1.0	.137	273	.125	249	.158	316	.401	800
.0005014 M	5.0	.419	838	.350	698	.212	423	.263	525
	20.0	.672	1340	.552	1100	.257	513	.125	250
	50.0	.779	1555	.635	1267	.283	564	.080	160
	101	.815	1627	.660	1316	.288	575	.064	128
	201	.844	1685	.675	1346	.285	568	.052	104
	302	.842	1680	.670	1338	.275	548	.046	92
	402	.836	1670	.660	1316	.275	548	.045	90
Run II	0.0	.005	10	.021	42	.128	256	.466	932
	1.0	.130	260	.120	240	.153	306	.401	802
.0005005 M	5.1	.414	828	.350	700	.214	428	.271	542
	20.5	.693	1386	.565	1130	.270	540	.134	268
	101	.820	1640	.665	1330	.288	576	.065	130
	202	.835	1670	.677	1354	.291	582	.054	108
	303	.846	1692	.676	1352	.289	578	.051	102
	404	.842	1684	.667	1334	.278	556	.046	92
	505	.846	1692	.667	1334	.280	560	.046	92
Run III	0.0	.012	14	.040	48	.214	258	.773	930
	1.0	.300	361	.270	325	.273	328	.625	752
.0008314 M	25.6	1.275	1535	1.038	1249	.460	553	.148	178
	156	1.407	1692	1.118	1345	.468	564	.084	101
	312	1.426	1715	1.113	1340	.451	542	.077	93
	390	1.438	1730	1.123	1352	.454	546	.075	90
	468	1.467	1763	1.130	1360	.460	553	.075	90
Run IV	0.0	.009	32	.017	61	.076	275	.260	935
	1.0	.056	201	.054	194	.085	305	.240	862
.0002781 M	6.1	.193	693	.163	585	.111	400	.168	604
	153	.460	1652	.370	1330	.161	578	.040	144
	257	.465	1670	.378	1358	.163	585	.034	122
	350	.467	1678	.372	1338	.159	572	.031	112
	467	.476	1711	.378	1358	.160	575	.030	108
	583	.488	1755	.384	1381	.163	585	.030	108

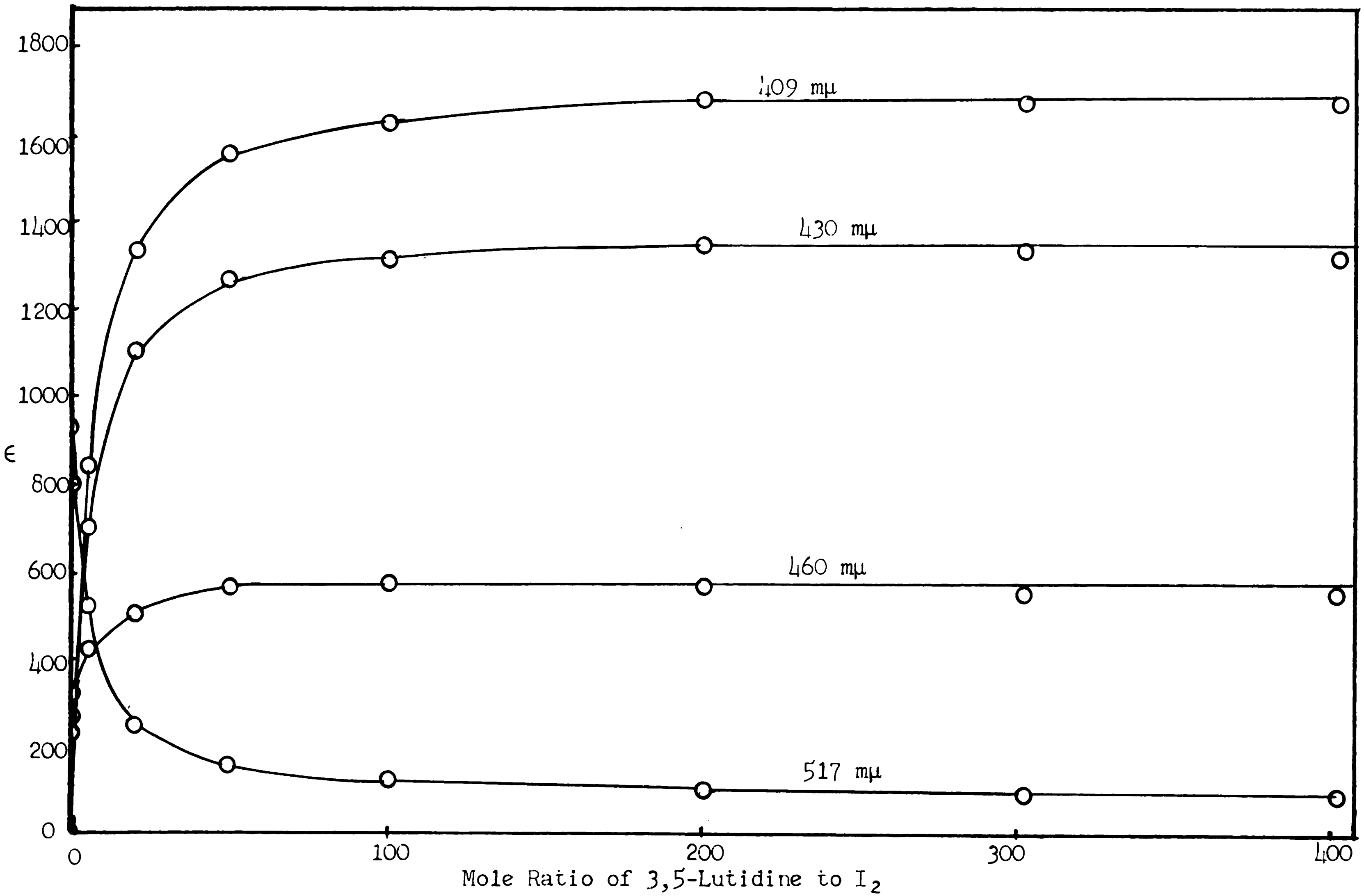


Fig. 6. Mole Ratio Method on the 3,5-Lutidine - I_2 system in carbon tetrachloride.

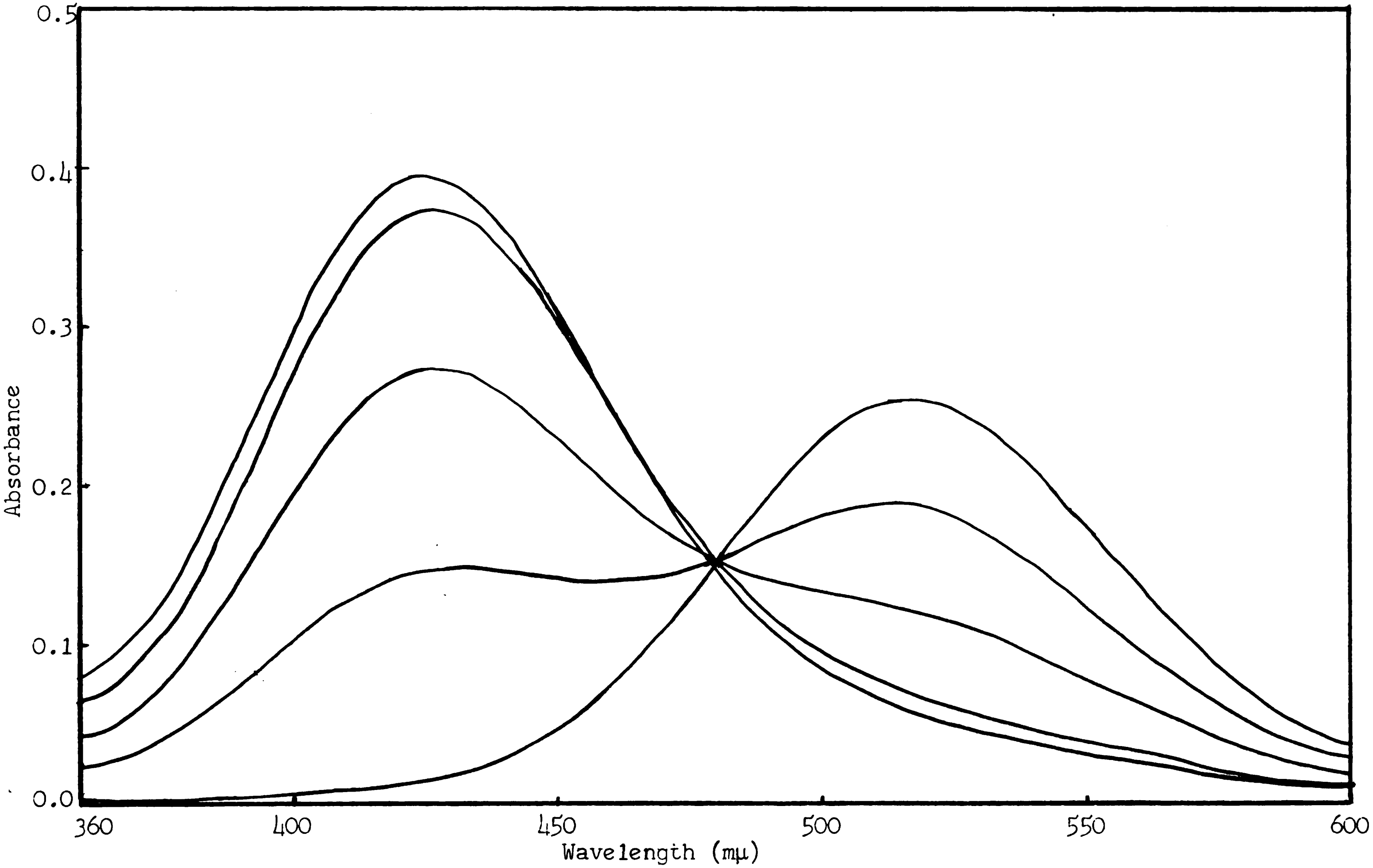


Fig. 7. Absorption spectra of 2,3,6-Collidine - I_2 system in carbon tetrachloride (Run III).

Table 6. Spectrophotometric data of mole ratio method on the 2,3,6-collidine - I_2 system in CCl_4

Conc. of I_2	M.R. of Collidine/I_2	400 mμ As	400 mμ ε	422 mμ As	422 mμ ε	450 mμ As	450 mμ ε	517 mμ As	517 mμ ε
Run I	0.0	0.005	10	0.014	27	0.086	165	0.482	923
	1.0	.022	42	.037	73	.100	192	.471	903
.0005215 M	5.0	.070	134	.105	201	.148	284	.440	844
	9.9	.121	232	.176	337	.198	380	.403	777
	50.0	.340	652	.457	875	.385	738	.250	478
	96.3	.418	803	.570	1092	.470	900	.187	359
	289	.525	1008	.706	1355	.555	1063	.118	226
	483	.560	1075	.747	1433	.581	1115	.104	200
	701	.590	1131	.767	1472	.592	1135	.095	182
	1000	.614	1176	.786	1510	.595	1140	.088	169
	1450	.663	1271	.809	1552	.598	1148	.083	159
	1942	.653	1252	.805	1542	.592	1135	.081	155
	3820	.776	1490	.858	1646	.592	1135	.073	140
Run II	0.0	.008	8	.027	26	.170	164	.970	933
	1.0	.062	60	.103	99	.218	210	.919	885
.0010393 M	24.9	.670	645	.916	882	.772	742	.486	468
	96.8	1.010	972	1.337	1287	1.060	1020	.330	318
	402	1.210	1165	1.548	1490	1.180	1135	.180	173
	810	1.370	1320	1.613	1552	1.185	1140	.160	154
	1215	1.485	1430	1.685	1620	1.200	1155	.157	151
	1620	1.627	1565	1.730	1665	1.180	1135	.146	141
	2025	1.828	1780	1.785	1718	1.182	1137	.144	139
Run III	0.0	.001	4	.008	28	.046	165	.262	941
	1.0	.006	22	.013	47	.049	176	.254	913
.0002781 M	37.2	.104	374	.145	521	.140	503	.187	672
	130	.187	672	.272	977	.230	827	.122	438
	543	.270	970	.371	1335	.302	1085	.078	282
	905	.299	1075	.395	1420	.308	1108	.057	205
	1510	.340	1221	.417	1500	.315	1133	.050	180
	1880	.360	1293	.430	1545	.322	1157	.049	176
	2255	.359	1290	.429	1542	.320	1150	.047	169
	2570	.348	1251	.425	1530	.320	1150	.047	169
Run IV	0.0	.006	11	.015	27	.090	162	.514	924
	1.0	.028	50	.042	76	.106	191	.503	903
.0005561 M	43.3	.343	617	.475	853	.410	736	.278	500
	130	.500	900	.678	1220	.550	988	.172	309
	260	.571	1028	.755	1358	.600	1078	.132	237
	758	.663	1194	.838	1508	.644	1158	.100	180
	1138	.800	1440	.890	1598	.652	1171	.094	169
	1520	.828	1490	.900	1618	.650	1168	.087	156
	2085	.832	1496	.907	1630	.647	1162	.086	144

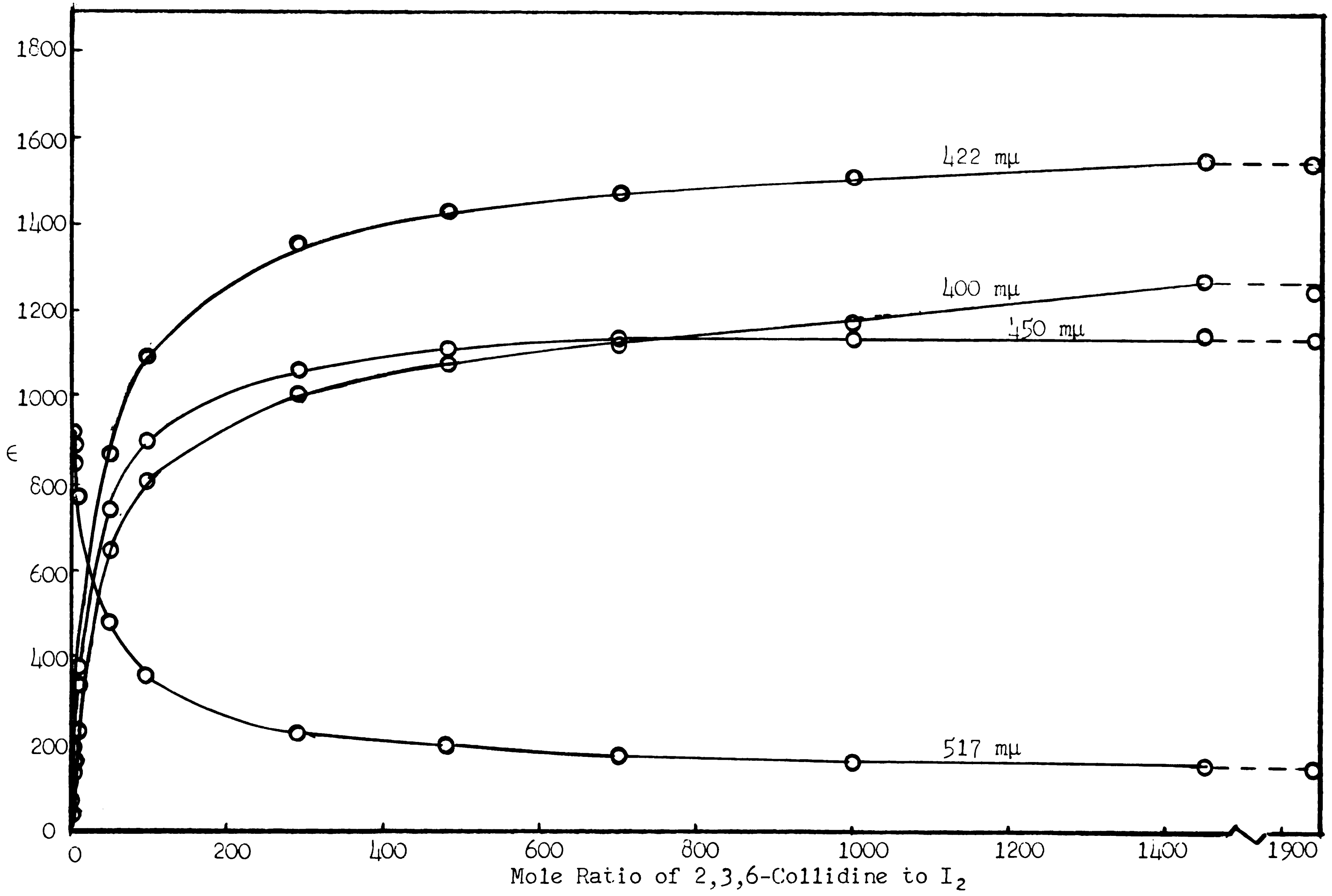


Fig. 8. Mole Ratic method on the 2,3,6-Collidine - I_2 system in carbon tetrachloride.

4-Phenylpyridine - Iodine Complex. The absorption spectra of the complex seemed to depend markedly on the concentrations of iodine and 4-phenylpyridine. From Runs II to V, the maximum absorption peak was at about 410 mμ, and the isosbestic point at 473 mμ. The Ketelaar's plots showed that a straight line generally could not be obtained. In the wavelength region between 410 mμ and 430 mμ, a fairly straight line might be drawn through the points. However, the formation constants calculated at 410 to 430 mμ differ widely, ranging from about 80 to 200 (liter/mole), and the values were reproducible for runs (IV and V) with approximately equal iodine concentration. The absorption spectra, with the isosbestic point, are shown in Fig. 9. The data for the Ketelaar's plots, at six wavelengths, are given in Table 7 and the Ketelaar's plots are shown in Fig. 10.

3,5-Dichloropyridine - Iodine Complex. The absorption spectra of the complex showed a maximum at 440 mμ, and the isosbestic point was at 485 mμ. The molar absorptivity at 440 mμ was 1320. The absorption spectra of the complex are shown in Fig. 11. The data for Ketelaar's plots, at four wavelengths, for the different runs are shown in Table 8 and the Ketelaar's plots of $\frac{1}{\epsilon_t - \epsilon_x}$ vs. $\frac{1}{C_B}$ are shown in Fig. 12.

Detailed study of change in absorbance of the solutions with time was not carried out. About half of the solutions of every complex were rerun after a period of twenty-four to thirty hours. With the exception of 4-picoline and 4-phenylpyridine, only slight changes (from 0.3 to 4 per cent) in absorbance were observed. For 4-picoline and 4-phenylpyridine, greater changes in absorbance (from 5 to 8 per cent) were observed for several solutions. No correlation of change in

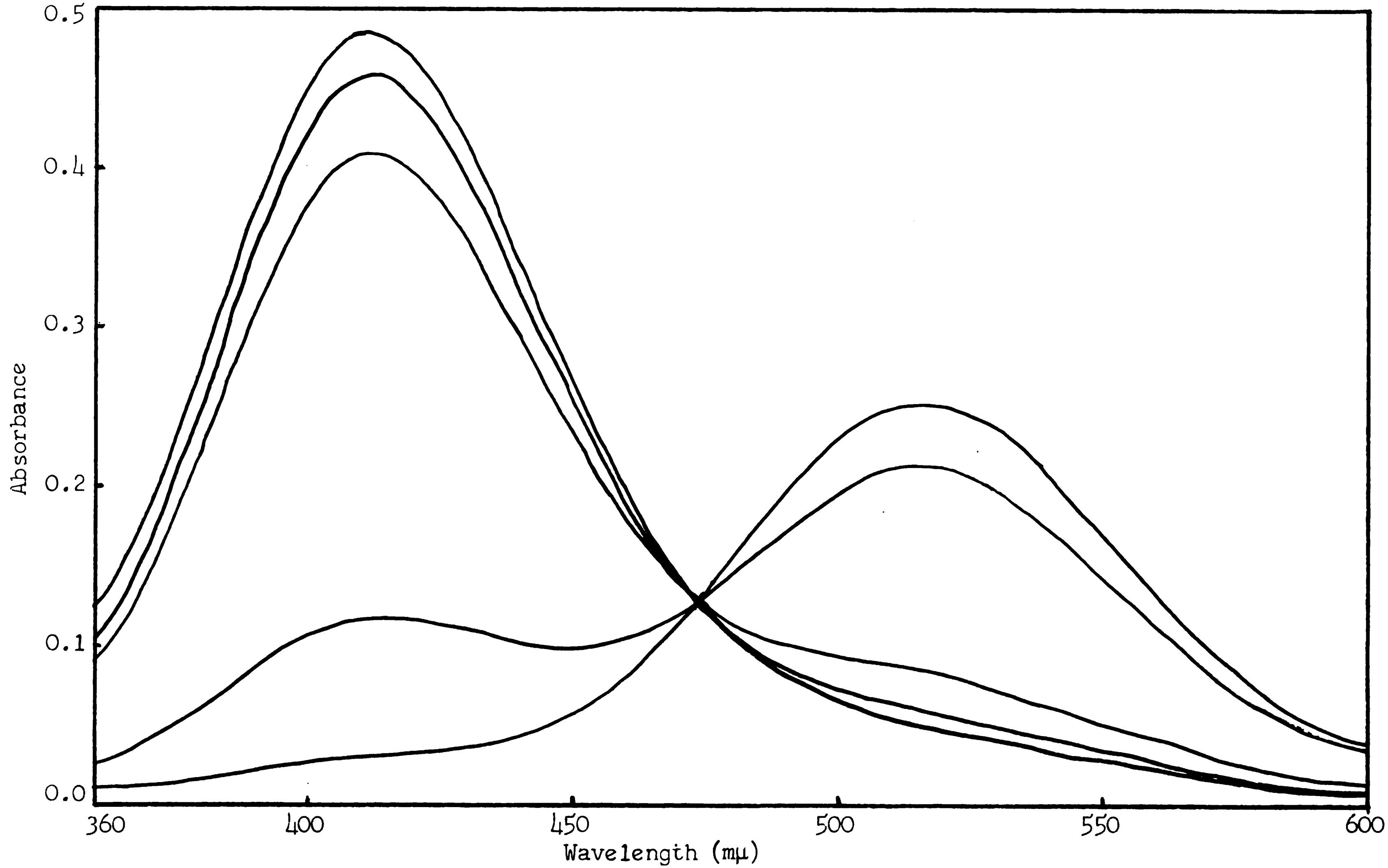


Fig. 9. Absorption spectra of 4-Phenylpyridine-I_2 system in carbon tetrachloride (Run II).

Table 7. Spectrophotometric data for Ketelaar's plots on 4-phenylpyridine - I_2 system in CCl_4

Conc. of I_2	M.R. of B/I_2	$\frac{1}{C_B}$	$\frac{1}{\epsilon_t - \epsilon_x} \times 10^4$					
			390 mμ	400 mμ	410 mμ	420 mμ	430 mμ	450 mμ
Run I	20	100	9.65	8.30	7.92	8.36	9.76	17.60
	50	40	6.72	5.99	5.82	6.19	7.15	12.99
.0005010 M	200	10	5.03	4.83	4.75	5.09	5.90	10.10
	399	5	3.48	3.61	3.98	4.37	5.22	9.20
	498	4	3,08	3.28	3.61	4.12	4.93	8.77
Run II	73	49.5	9.44	7.43	6.84	7.13	8.12	15.15
	145	24.8	8.04	6.61	6.11	6.42	7.36	13.65
.0002781 M	294	12.2	7.48	6.23	5.79	6.04	6.95	12.82
	442	8.1	7.19	5.97	5.60	5.89	6.79	12,67
	735	4.9	6.85	5.82	5.50	5.78	6.73	12.67
Run III	194	24.7	8.04	6.60	6.11	6.34	7.20	13.30
	587	8.16	6.98	5.85	5.48	5.70	6.52	12.02
.0002086 M	980	4.88	6.12	5.26	5.04	5.31	6.14	11.15
	1372	3.49	5.63	4.92	4.73	5.02	5.79	10.48
Run IV	192	15.1	7.46	6.32	5.78	6.01	6.95	12,75
	319	9.02	7.02	5.88	5.52	5.76	6.63	12.09
.0003480 M	447	6.45	6.88	5.76	5.44	5.70	6.58	12.09
	574	5.02	6.47	5.53	5.16	5.52	6.42	11.78
Run V	171	16.9	7.67	6.34	5.90	6.17	7.07	13.03
	256	11.3	7.30	6.12	5.74	5.98	6.92	12.68
.0003465 M	341	8.45	6.98	5.82	5.48	5.74	6.64	12.05
	512	5.64	6.55	5.56	5.30	5.50	6.48	11.75
	683	4.23	6.12	5.23	5.10	5.42	6.35	11.52

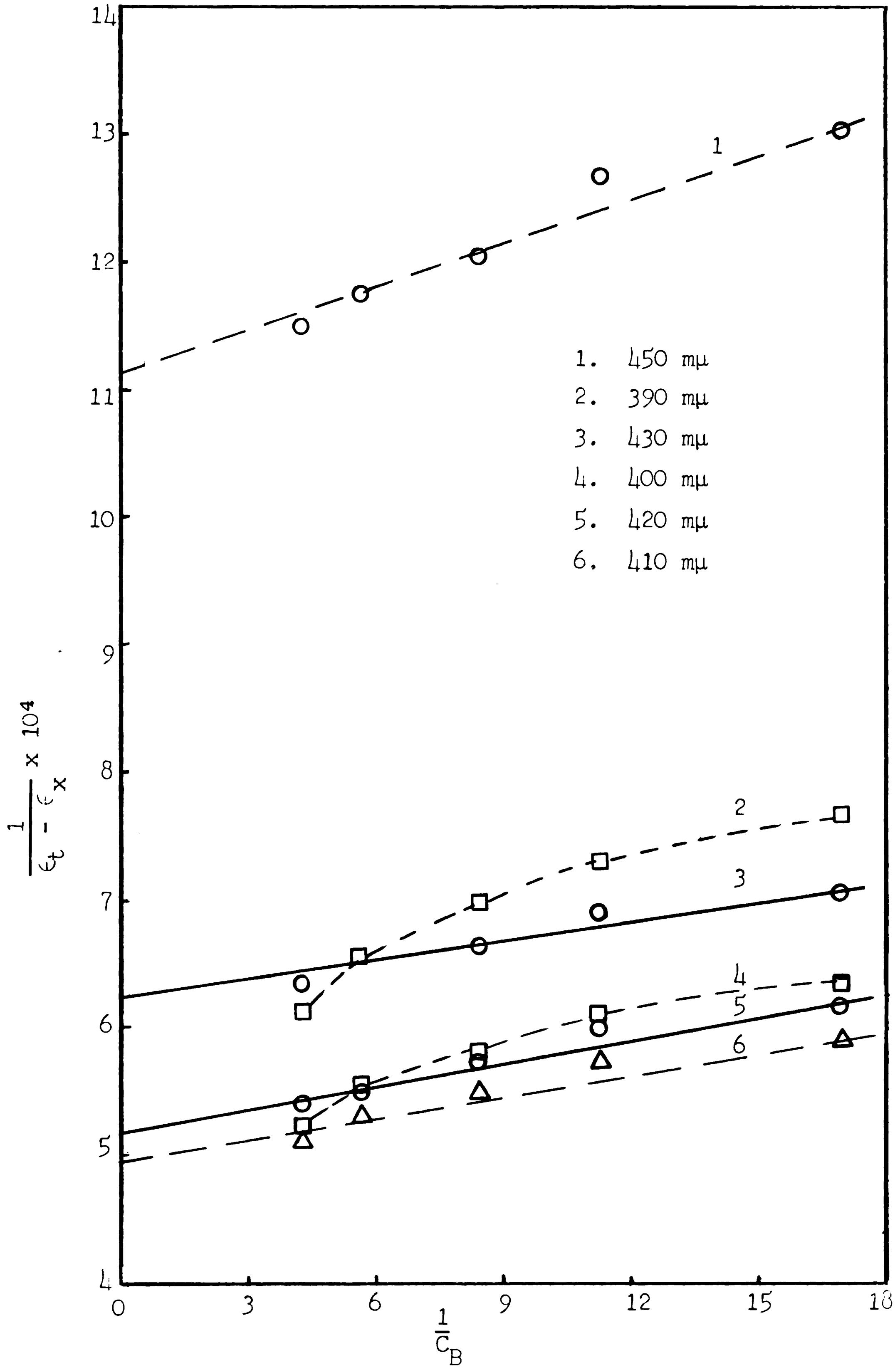


Fig. 10. Ketelaar's Plots for 4-Phenylpyridine-I_2 system in carbon tetrachloride (Run V).

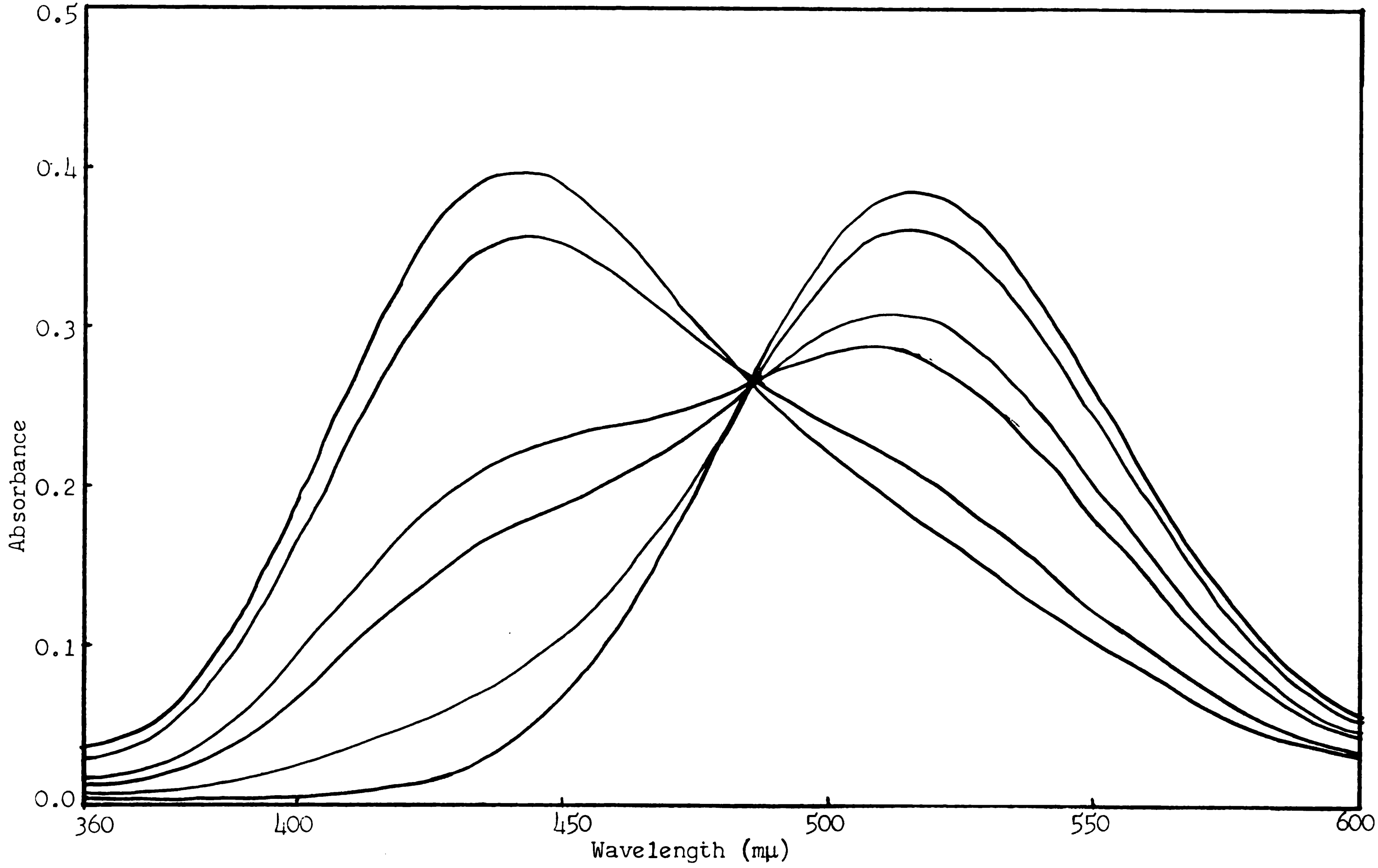


Fig. 11. Absorption spectra of 3,5-Dichlorophyridine-I_2 system in carbon tetrachloride (Run I).

Table 8. Spectrophotometric data for Ketelaar's plots on 3,5-dichloropyridine - I_2 system in CCl_4

Conc. of I_2	M.R. of B/I_2	$\frac{1}{C_B}$	$\frac{1}{\epsilon_t - \epsilon_x} \times 10^3$			
			400 mμ	420 mμ	440 mμ	460 mμ
Run I	242	9.97	6.62	3.60	3.11	4.43
	362	6.65	4.67	2.63	2.34	3.32
.0004157 M	483	4.97	3.85	2.22	1.96	2.77
	1078	2.23	2.62	1.49	1.33	1.89
	1615	1.49	2.27	1.30	1.17	1.68
Run II	1.0	--	--	--	--	--
	361	10	5.67	3.16	2.88	4.03
.0002781 M	722	4.97	3.71	2.08	1.85	2.67
	1070	3.36	3.03	1.70	1.54	2.21
	1775	2.03	2.38	1.39	1.25	1.79
	2420	1.49	2.16	1.25	1.14	1.65
	2840	1.27	2.14	1.22	1.11	1.62
Run III	154	15.60	7.58	4.29	3.80	5.44
	231	10.40	5.56	3.16	2.80	3.98
.0004171 M	308	7.80	4.45	2.53	2.28	3.22
	384	6.24	3.88	2.19	1.97	2.81
	615	3.90	3.00	1.73	1.57	2.22

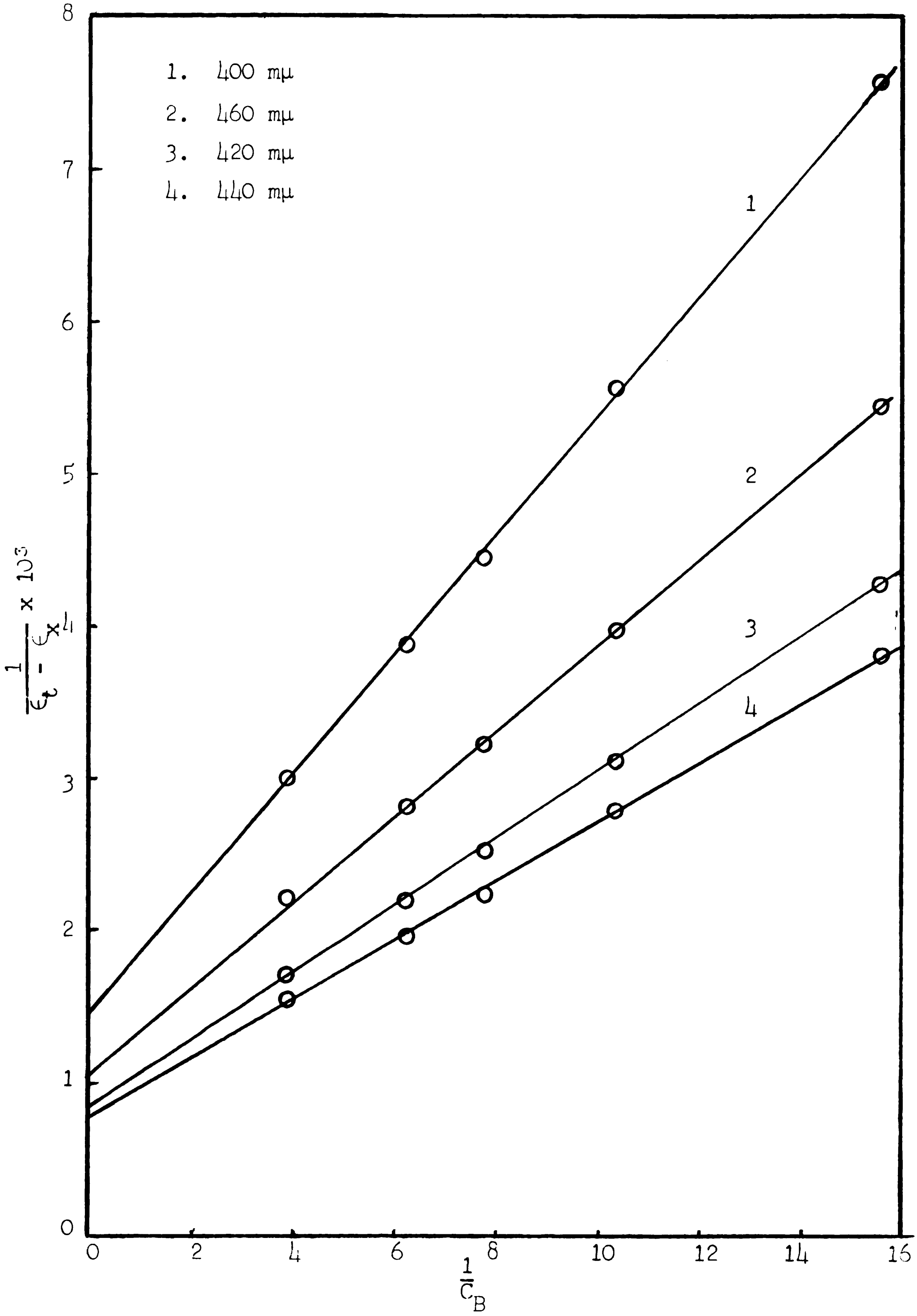


Fig. 12. Ketelaar's Plotsfor 3,5-Dichloropyridine - I_2 system in carbon tetrachloride (Run III).

absorbance with concentrations of iodine and pyridine bases could be observed. However, there was a tendency that greater changes were observed for solutions of high concentration of pyridine base (high pyridine-base/I_2 mole ratio).

The degree of dissociation and formation constant values for the five complexes are listed in Table 9. For 4-phenylpyridine-iodine system, because of non-linearity of Ketelaar's plots and variation of formation constant value with wavelength, no meaningful values of formation constant can be given.

Table 9. Degree of dissociation, formation constants of Iodine - substituted pyridine complexes in carbon tetrachloride.

Complex	Run	Conc. of I_2 (M)	α	K_f	K_f Average
4-Picoline - I_2	I	.0005215	0.904	225	223
	II	.0005196	.904	226	
	III	.0002781	.945	222	
	IV	.0006951	.882	218	
2,4-Lutidine - I_2	I	.0002781	.923	325	317
	II	.0010390	.813	290	
	III	.0005230	.871	325	
	IV	.0006236	.852	327	
3,5-Lutidine - I_2	I	.0005014	.843	441	438
	II	.0005005	.848	422	
	III	.0008314	.780	435	
	IV	.0002781	.898	455	
2,3,6-Collidine - I_2	I	.0005215	.974	52.4	50.9
	II	.0010390	.953	49.7	
	III	.0002781	.987	48.1	
	IV	.0005561	.972	53.2	
3,5-Dichloropyridine - I_2	I	.0004157	--	3.63	3.77
	II	.0002781	--	3.89	
	III	.0004171	--	3.78	

DISCUSSION OF RESULTS

The complex formation of iodine with certain substituted pyridines have been studied in carbon tetrachloride solutions. In each case a 1:1 complex between the amine and the halogen was expected[7-10]. As will be shown below, in the case of 4-phenylpyridine some evidence was obtained for the formation of higher complexes.

In most cases the molar absorptivity of the complex was obtained by the extrapolation of the mole-ratio plots.[7] It should be noted that in the case of very weak complexes, such as 2,3,6-collidine-iodine complex, very large excess of the base had to be added (up to 2000 fold excess) before the absorbance became reasonably constant. Under these conditions the solutions were quite concentrated in the base and small deviations in the molar absorptivity were observed, which could be due to the change of the refractive index of the solution[7,34]. In any case the change in the extrapolated molar absorptivity was quite small and should not affect the calculated value of the complex formation constant.

The data obtained in this investigation indicated that the positions of the absorption maximum as well as those of the isosbestic point are somewhat related to the strength of the complex. Thus for 3,5-lutidine-iodine complex, which is the strongest complex in the series, both maximum absorption peak and isosbestic point are at shorter wavelengths than that of the other complexes, while 3,5-dichloropyridine has the longest wavelengths for its maximum absorption peak and its isosbestic point.

The 4-phenylpyridine-iodine complex offers an interesting example of a case where more than one complex can be expected to form in solution. It has long been regarded that the presence of only one absorbing complex was evidenced by a straight line resulting from the Benesi-Hildebrand plot.[25-28] Recently, however, Johnson and Bowen[29], using synthetic data, showed that a straight line could be obtained from the Benesi-Hildebrand plot even though two different complexes might be present in solution. They concluded that constancy of formation constant calculated at different wavelengths was a better criterion for asserting the presence of only one complex. This present study of 4-phenylpyridine-iodine complex showed that at low iodine concentration a fairly straight line could be obtained between 410 mμ to 430 mμ, using Ketelaar's modification of Benesi-Hildebrand plots. At other wavelength regions studied, reasonably straight lines generally could not be obtained. However, even in the region that gave fairly straight lines, the resulting formation constant calculated at different wavelengths differed widely, ranging from 80 to 200 (1/m). From Runs IV and V, with approximately equal concentration of iodine and excess 4-phenylpyridine, the results were reproducible. The values varied with iodine concentration and also were affected by the concentration of the base. In Run I, at higher iodine concentration, the maximum absorption peak shifted from 410 mμ at 4-phenylpyridine/iodine mole ratio of 20 to about 375 mμ at mole ratio of 500. This drastic shift of maximum absorption was not observed in the other compounds studied. The presence of more than one absorbing complex was further affirmed by the high molar absorptivities obtained from Ketelaar's plots. It is likely that at relatively low iodine/base mole ratios, the complexation occurs primarily through the nitrogen of the pyridine ring. At higher concentration of iodine, the complexation of phenyl group with iodine becomes more extensive and thus causes a change in molar absorptivity and shift of maximum absorption peak to lower wavelength. Due to lack of time the study of the two 4-phenylpyridine-iodine complexes were not pursued further.

From Table I, it is seen that 2,4-lutidine is slightly more basic than 3,5-lutidine. However, due to the presence of one methyl group adjacent to the complexing nitrogen atom, the complex formation is slightly hindered. Thus 2,4-lutidine forms a weaker complex than 3,5-lutidine. The effect of steric hindrance is more pronounced for 2,3,6-collidine, in which two methyl groups are adjacent to the complexing nitrogen atom. Thus though 2,3,6-collidine is the strongest base, it forms the weakest complex among the four methyl pyridines studied. Comparison between the formation constants of iodine with 3,5-dichloropyridine and 2-chloropyridine also reveal the steric effect of the chlorine atom adjacent to complexing nitrogen atom. Although 2-chloropyridine is more basic than 3,5-dichloropyridine, steric hindrance again renders the 2-chloropyridine-iodine complex to be slightly weaker than that of the 3,5-dichloropyridine.

The strength of the iodine-pyridine base complexes follows the order 3,5-lutidine > 2,4-lutidine > 4-picoline > 2,3,6-collidine > 3,5-dichloropyridine. The order of basic strength is as follows: 2,3,6-collidine > 2,4-lutidine > 3,5-lutidine > 4-picoline > 4-phenylpyridine > 3,5-dichloropyridine.

In summary, the investigations of the interaction of iodine with some substituted pyridines have shown the following: (1) The Lewis acid-base interaction of pyridines with iodine does not parallel their basic strength. This is probably due to steric effects. (2) Iodine-4-phenylpyridine system cannot be explained on the basis of a simple 1:1 complex formation. It is possible that the results are indicative of the presence of more than one complex.

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